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by

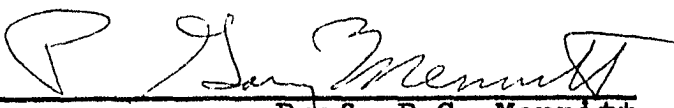
RICHARD E. ZADJURA

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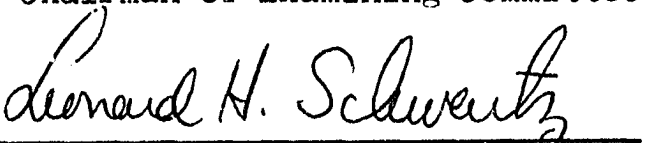
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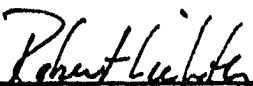
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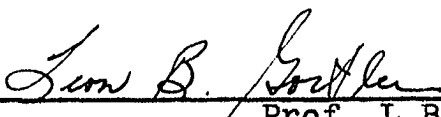
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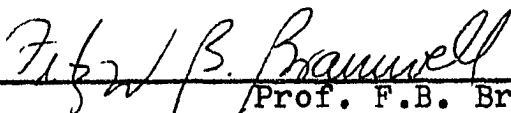

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Abstract

CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION DURING THE THERMAL DECOMPOSITION OF PEROXYESTERS

by

RICHARD E. ZADJURA

The nuclear polarization generated during the thermal decomposition of t-butyl peroxyesters has been studied and explained using the Radical Pair Model for CIDNP. In every case, the CIDNP observed was independent of the initial alkyl-t-butoxy radical pair. This indicates that there is no nuclear polarization developed by radical pairs which contain the t-butoxy radical. Because of this, no mechanistic information, regarding the initial decomposition of peroxyesters, has been found or should be expected from CIDNP studies.

CIDNP obtained during the decompositions of peresters has been found to be due to free radical interaction of perester and solvent derived radicals. In non-aromatic solvents, CIDNP is generated from the interaction in alkyl-solvent derived (or radical trap derived) radical pairs giving only net CIDNP effects. In aromatic solvents, CIDNP is generated from alkyl-cyclohexadienyl and alkyl-alkyl radical pairs giving both net and multiplet phase CIDNP.

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I would like to thank all those who have made my stay at the City University a pleasant and memorable experience.

Special thanks are due to my mentor Professor P. Gary Mennitt who has provided guidance and encouragement throughout all phases of my graduate career. Additional thanks are owed to my committee members who provided helpful suggestions on many areas of this work.

The final acknowledgment is to my wife, Barbara, who has offered her support and understanding throughout the research and preparation required for this manuscript.

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INTRODUCTION

Chemically Induced Dynamic Nuclear Polarization (CIDNP) is a recently discovered phenomenon which can give valuable information of the course of radical reactions. The early researchers in this field focused their attention on the origin of CIDNP rather than trying to discover new mechanistic information. Initial research on radical initiators involved detailed studies of diacyl peroxides and azo compounds, both systems where the chemical reactions are well documented. Further work in recent years has applied CIDNP to a large variety of radical reactions, however, an important class of radical initiators, peroxyesters, has been left largely unexplored. We have studied the decomposition of peroxyesters and have explained the CIDNP spectra obtained from them.

Since this work lies at an interface between free radical chemistry and nuclear magnetic resonance, the reader will need a background in two largely independent areas of chemistry. To provide a clear introduction to this work, I have divided the historical background into three logical sections.

Section I will deal with the phenomenon of CIDNP, its discovery, an explanation of the effect and some simple examples from the literature. Section II will review the basic chemistry of peroxyesters and the reactions of the

radicals produced upon their decomposition. Section III will present the few applications of CIDNP to peroxyester decompositions and the extensive CIDNP studies of the structurally similar diacyl peroxides.

HISTORICAL BACKGROUND

SECTION I

Chemically Induced Dynamic Nuclear Polarization (CIDNP) is the occurrence of emission and enhanced absorption in the NMR spectra of systems undergoing radical reactions. This phenomenon was first reported by Fischer, Bargon and Johnson¹ in 1967 after they observed a strong emission signal for the protons of benzene during the decomposition of benzoyl peroxide. (see Figure I) Their initial (but incorrect) explanation² for this distortion of NMR intensities involved forming the radicals at an infinite electron spin temperature (both α and β spins equally populated). As the spins relaxed toward their equilibrium distribution, a small nuclear polarization developed by electron nuclear cross relaxation. This nuclear polarization could be observed in the NMR spectrum of the diamagnetic products formed. This mechanism was referred to as Dynamic Nuclear Polarization or the Overhauser Effect.

Although the Overhauser Effect was sufficient to explain Fischer's results new data soon demonstrated that it could not be correct. The nuclear polarization was thought to result from electron nuclear relaxation but this process was known to be inefficient from ESR studies³. The maximum enhancement factor which could be calculated as 128 was lower than some observed data⁴. This maximum



Fig. I. Net polarization
observed during the thermal
decomposition of benzoyl peroxide.

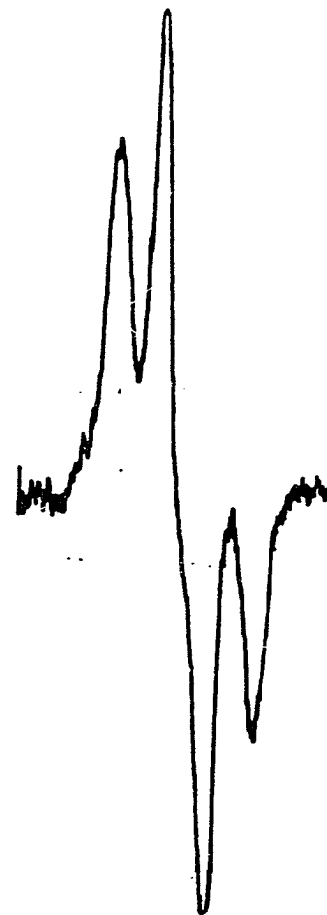


Fig. II. Multiplet effect
observed in the exchange reaction:
between ethyllithium and ethyl iodide.

calculated value was only obtained for a radical with a specific lifetime, any distribution of lifetimes would make the observed values lower yet. The most important evidence demonstrating the limitations of the Overhauser Effect appeared in 1967^{5,6}. This was the observation of the "multiplet effect", which is the appearance of both emission and enhanced absorption in the same multiplet (see Fig. II).

The first correct explanations for the multiplet effect came independently from Closs⁷ and from Kaptein and Oosterhoff⁸⁻¹⁰. They assumed that the origin of the nuclear polarization was the interaction of radical pairs within their solvent cage. This model was quickly termed the Radical Pair theory of CIDNP.

The Radical Pair Theory (Vector Model)

The immediate cause of the observed effects in NMR spectra is the distortion of the nuclear Boltzman distributions of the polarized products. This can be explained if the rates of product formation are nuclear spin dependent.

Before dealing with radical pairs, I would like to review the properties of a single spin in a magnetic field. Figure III is a schematic representation of this spin(R_1).

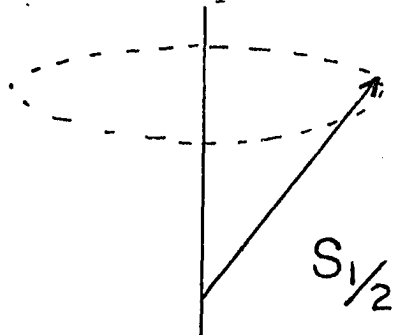


Fig. III

in one of its energy levels. The total spin along the Z axis will be 1/2. The dotted line represents a circle about which this spin will precess at a rate (ω) which is given by;

$$\omega = \beta \hbar^{-1} (g H_0 + \sum a_i m_i) \quad (1)$$

where $\beta \hbar$ is a constant and H_0 is the applied field¹¹. The g term is a property of the radical which corresponds to the g -factor of ESR spectroscopy. This is dependent on the shielding from the field of nearby orbitals to the odd spin. The $a_i m_i$ term includes any coupling of magnetically active nuclei to the unpaired electron. The a_i is termed the hyperfine coupling constant and the m_i is the nuclear spin state of the coupling nucleus.

A radical pair which is subject to an external field will have two distinct energy levels; a singlet S_0 and a degenerate triplet T_0, T_+, T_- as shown in figure IV where the subscripts denote the Z component of the net spin. In this diagram, the spins R_i and R_j are weakly coupled to each other but strongly coupled to the external field. Each spin will precess at a rate given by equation 1. If the rates of precession of the two radicals are different, there will be an interconversion from S_0 to T_0 . This crossing of the S_0 and T_0 states is the true origin of CIDNP and is termed singlet-triplet mixing. All that is required to go from the singlet to T_0 (or vice versa) is that the dihedral angle between the two vectors change from π to 0. The rate at which this will happen is related to

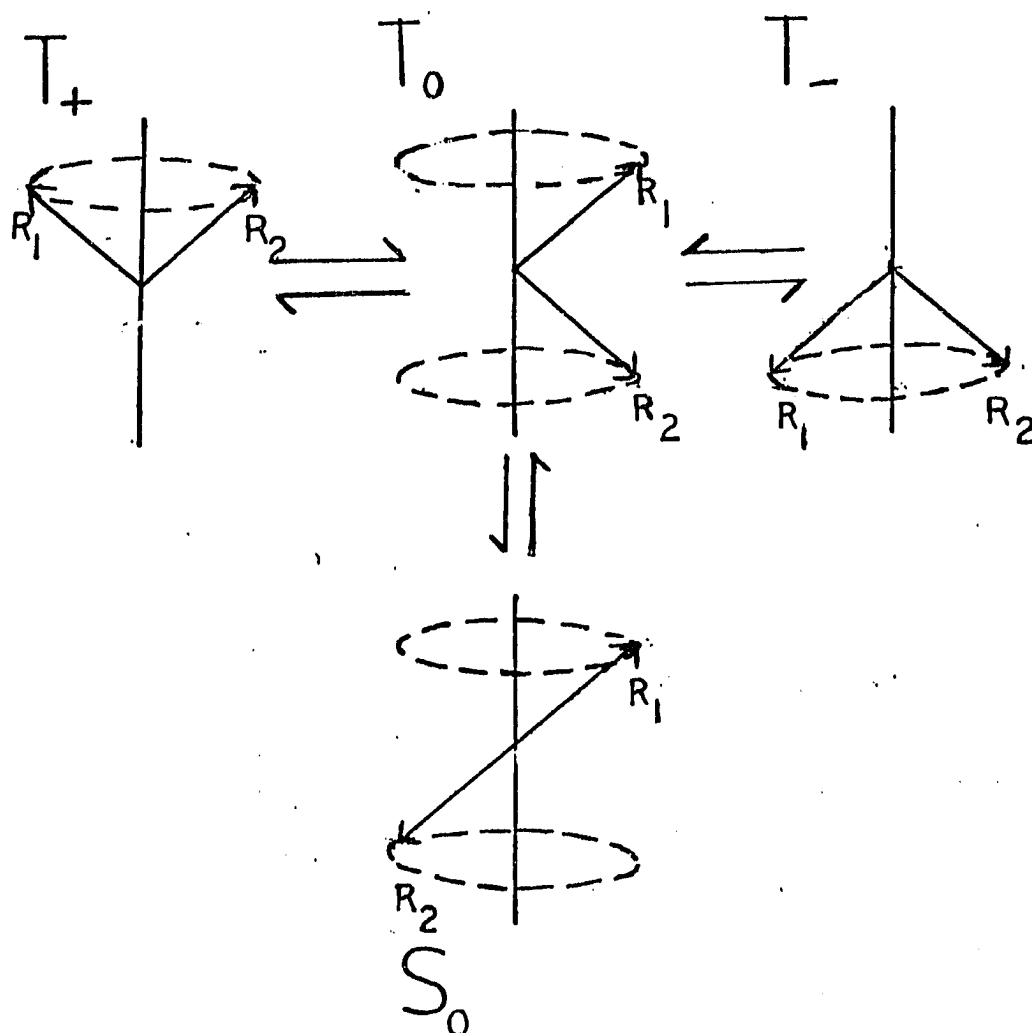


Fig. IV. Schematic diagram of the two possible energy levels in a radical pair.

the difference between ω_1 and ω_2 .

$$\omega_i = \beta \hbar^{-1} (g_i H_0 + \sum a_i m_i) \quad (2)$$

$$\omega_j = \beta \hbar^{-1} (g_j H_0 + \sum a_j m_j) \quad (3)$$

$$\omega_i - \omega_j = \beta \hbar^{-1} ((g_i - g_j) H_0 + \sum a_i m_i - \sum a_j m_j) \quad (4)$$

Equation 4 demonstrates that a radical pair in the singlet state will develop triplet character at a rate dependent on 1) the difference in the g factors of the radicals ($g_i - g_j$) or Δg 2) the applied field and 3) the signs and magnitudes of all the nuclear electron hyperfine couplings. The rate of this intersystem crossing is estimated at about 10^7 to 10^8 per second¹¹.

Since all radical reactions yield products in the singlet state, it is reasonable to assume that only singlet state S_0 radical pairs may form product. This assumption leads us to the conclusion that the rate of product formation is dependent upon the singlet state probability of the precursor radical pair which in turn is dependent on the magnetic properties of the radical pair.

It has been estimated that typical singlet triplet crossing rates of 10^7 - 10^8 per second will result in 1% of mixing during the lifetime of a radical pair (10^{-9} - 10^{-10} sec.). This 1% change will result in an enhancement factor of several thousand¹².

The explanation of CIDNP presented here is largely qualitative, however, a more rigorous derivation can result in reasonably quantitative agreement with experiment. By incorporating this "derivation" with the laws of quantum

mechanics, one could set up the appropriate Hamiltonian operator and via the time dependent Schrodinger equation, calculate the populations of each nuclear spin state. The resulting values would provide accurate simulation of the observed spectra. Computer programs which treat CIDNP spectra are available.

Kaptein's Empirical Rules

While a sound theoretical framework is important to the application of CIDNP, most of the mechanistic information can be extracted from the spectra using a set of empirical rules which were derived by Kaptein. These rules have been extensively applied throughout the literature to infer pathways of radical reactions and properties of radicals, and allow prediction of the phase (emission E, enhanced absorption A, or either multiplet effect E/A or A/E) of the polarized resonance¹².

There are two rules, the first (equation 5) for the net effect and the other (equation 6) for the multiplet effect.

$$\Gamma_{\text{net effect}} = \mu \epsilon \Delta g a_i \quad (5)$$

$$\Gamma_{\text{mult. effect}} = \mu \epsilon a_i a_j J_{ij} \sigma_{ij} \quad (6)$$

If one assigns values (± 1) to each of these parameters, the product will indicate the phase of the polarized resonance.

$\mu = +1$ for triplet or free radical precursor pairs

$\mu = -1$ for singlet precursor pairs

$\epsilon = +1$ for recombination (cage) products

$= -1$ for escape products

$\Delta g = (g_1 - g_2)$ where the observed nucleus is on R_1

a_i or $a_j =$ the signs of the nuclear-electron hyperfine coupling constant

$J_{ij} =$ the sign of the nuclear-nuclear coupling constant

$\sigma_{ij} = +1$ if i and j reside on the same radical

$= -1$ if i and j reside on different radicals

$\Gamma_{\text{net effect}} = +1$ enhanced absorption (A)

$= -1$ emission (E)

$\Gamma_{\text{mult. effect}} = +1$ E/A multiplet effect

$= -1$ A/E multiplet effect

It is a necessary condition for the observation of the multiplet effect that Δg be very small. This is the result of equation 4

$$\omega_i - \omega_j = \beta \hbar^{-1} \left[(g_i - g_j) H_0 + \sum a_i m_i - \sum a_j m_j \right] \quad (4)$$

Since the Δg term is multiplied by the external field, its effect will dominate the expression if Δg is not very small. By careful selection of the radical pair so that Δg is almost but not quite zero, both the net effect and the multiplet effect can be observed in the same resonance pattern.

Origin of the sign reversals in Kaptain's Rules

Although the values assigned to the various parameters are largely empirical, their sign reversals can be easily understood from the radical pair model.

The first term in either equation 5 or 6, μ , refers to the origin of the radical pair. A pair initially in the singlet state will undergo singlet triplet mixing to introduce triplet character into the pair. The exact opposite will be expected of a triplet radical pair which will develop singlet character via the mixing process. A free radical pair will initially be found as an equal mixture of both singlet and triplet pairs. A fraction of the singlet pairs will be expected to react immediately upon collision before nuclear polarization can be developed. This process will deplete the singlet state leaving an excess number of spin pairs in the triplet state. The free radical pairs should then behave as a pair from a triplet precursor.

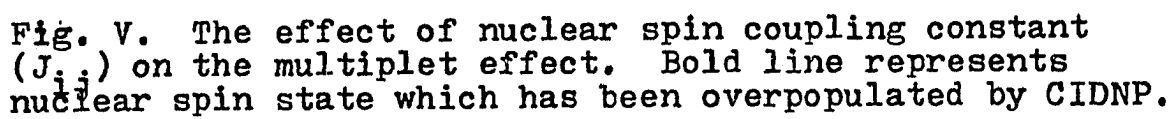
The next term, ϵ , which appears in both equations 5 and 6, refers to the dependence of the type of product formed on the various spin states. If one nuclear spin state,

e.g., α , favors product formation (there is more singlet character in the pair), the cage product will have an excess of molecules with an α nuclear spin. The escaping radicals will contain an excess of the β spin state and the opposite phase will be observed in the NMR spectrum. This will be true only if the escaping radicals are scavenged before nuclear spin relaxation (in the radical) destroys any polarization which had been present. This relaxation effect in escaping radicals, leads to the expectation that the intensity of the polarization will be higher in the cage product than in the escape product.

The hyperfine coupling constant, a_i , appears in both equations 5 and 6. The physical implication of this sign involves the orientation of the nuclear spin of atom i to the unpaired spin in the lowest energy configuration. If the nuclear spin is parallel to the spin of the odd electron, the value of a_i is positive; if in the lowest energy conformation the spins are opposed, the value of a_i is negative. For a given electronic spin state of a radical in a pair, the orientation of the coupling nuclei will be determined by the sign of the hyperfine coupling constant.

The Δg term is only found in the equation describing the net effect. The dependence of the phase of CIDNP on Δg is a direct result of the first term in equation 4.

The remaining terms (J_{ij} and σ_{ij}) in Kaptein's rules appear only in the equation for the multiplet effect. The J_{ij} term is the sign of the nuclear spin-spin coupling constant. The sign of this parameter indicates the relative energy of the transitions in the NMR spectrum. This is best explained with the aid of figure V for two coupled protons on neighboring carbon atoms. In this diagram, arrows represent the possible nuclear transitions and the schematic NMR spectrum indicates their relative energies. A change in the sign of the spin-spin coupling constant will change the ordering of the resonance lines and, therefore, change the phase of the multiplet effect which will be observed.



The final term σ_{ij} is the result of equation 4.

$$\omega_i - \omega_j = \beta \hbar^{-1} \left[(g_i - g_j) H_0 + \sum a_i m_i - \sum a_j m_j \right]$$

If Δg is very small then this equation will become

$$\omega_i - \omega_j = \beta \hbar^{-1} \left[\sum a_i m_i - \sum a_j m_j \right]$$

Since the sign of the contribution of "a" will change depending upon which radical it resides, i or j, Kaptein's rules must contain a parameter to express this.

Application of Kaptein's Rules

An early example designed to test the Radical Pair Theory was provided by Closs and his co-workers¹³. They studied the reactions of a benzyl-benzhydryl radical pair produced by the thermal decomposition of benzyl azodiphenylmethane $(C_6H_5)CH_2N=NCH(C_6H_5)_2$. Closs observed an E/A multiplet for the coupling product, 1,1,2-triphenylethane. (See figure VIb). This product is an obvious result of the recombination of a singlet benzyl-benzhydryl pair. It is known that the g factor of the benzyl and benzhydryl radicals are equal (both 2.0025) therefore, only the multiplet effect will be observed. The hyperfine coupling constant for the α protons on both partners are negative (the α protons of any π type radical have a negative value for a_H) and the J_{H-H} is positive for the vicinal protons of ethanes. Using Kaptein's Rule,

$$\begin{aligned} \Gamma_{\text{mult. effect}} &= \mu_B a_i a_j J_{ij} \sigma_{ij} \\ &= (-)(+)(-)(-)(+)(-) = + E/A \end{aligned}$$

we find that this agrees with the observed spectrum.

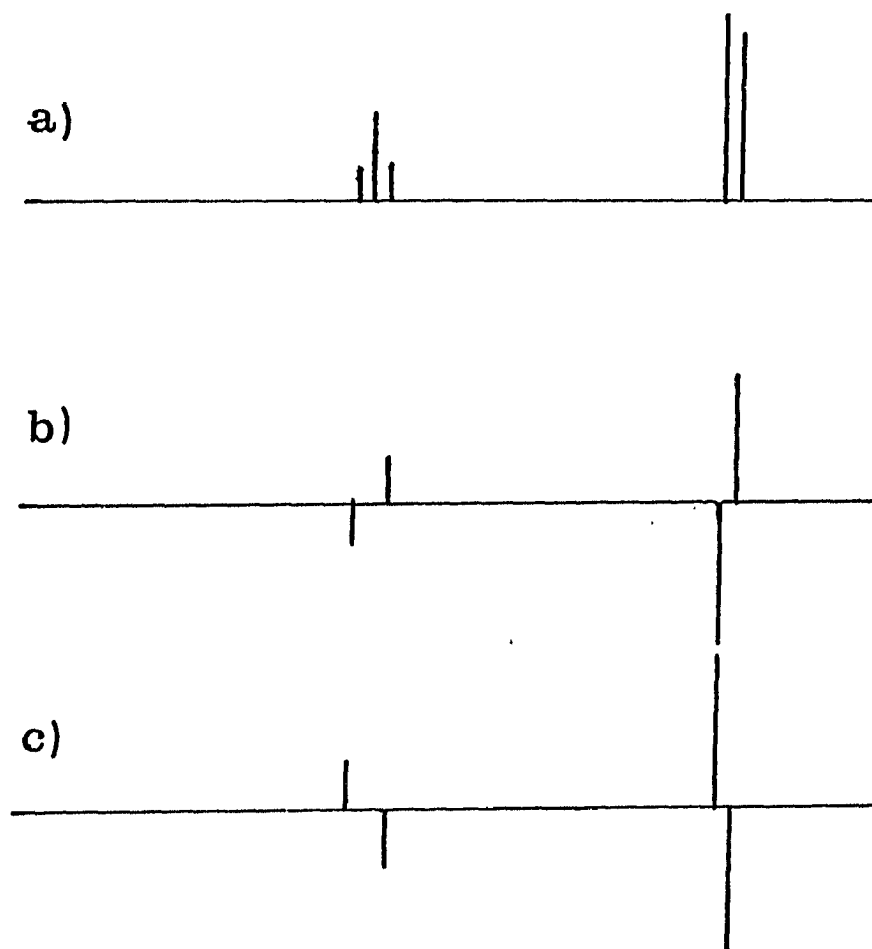


Fig. VI. NMR spectra observed for 1,1,2-triphenylethane
a) normal spectrum, b) spectrum observed during the
thermal decomposition of benzylazodiphenylmethane
c) spectrum observed during the photo-chemical
decomposition of benzylazodiphenylmethane.

The same radical pair may be produced in the triplet state by the photolysis of diphenyl diazomethane in toluene. (See figure VIc). Initial decomposition of this compound leads to the formation of diphenyl methylene which exists as a ground state triplet. This carbene abstracts a hydrogen atom from toluene to give a triplet benzyl-benzhydryl radical pair. Kaptein's rule will predict an A/E multiplet for the 1,1,2-triphenylethane formed from this pair:

$$\Gamma_{\text{mult. effect}} = \mu_e a_i a_j J_{ij} \sigma_{ij} \\ = (+)(+)(-)(-)(+)(-) = - A/E$$

which is in agreement with the experimental result.

A free radical pair containing the partners may be generated by abstracting hydrogen atoms from a mixture of diphenylmethane and toluene using phenyl radicals (from the decomposition of benzoyl peroxide). The CIDNP observed for 1,1,2-triphenylethane is identical in phase to that produced from the triplet radical pair.

In all of the above reactions, no polarization was observed for the products corresponding to escape from the radical pair. These compounds, toluene, diphenylmethane, bibenzyl and sym. tetraphenylethane, exhibit single lines for the α protons in the NMR spectrum and the multiplet effect cannot be observed.

It is possible to modify the benzyl or the benzhydryl radical to produce a Δg term in the radical pair. The photolysis of bis (p-bromophenyl) diazomethane in toluene will produce a benzyl-bis (p-bromophenyl) methyl radical

pair in the triplet state upon decomposition. The g factors of both these radicals are known from ESR studies to be 2.0025 for the benzyl radical and 2.0050 for this benzhydryl radical. Using Kaptein's rule, we predict:

$$\Gamma_{\text{net effect}} = u \cdot \epsilon \cdot \Delta g \cdot a_i$$

$$= (+)(+)(+)(-) = - E$$

emission for the protons on the diphenylmethyl radical in the 1,1,2-triphenylethane formed,

$$\Gamma_{\text{net effect}} = (+)(+)(-)(-) = + A$$

enhanced absorption for both protons in the tetraphenylethane formed,

$$\Gamma_{\text{net effect}} = (+)(-)(-)(-) = - E$$

emission for the protons of bibenzyl.

The observed spectrum is in agreement with that predicted with Kaptein's rules for all the products except the tetraphenylethane. The formation of this product from the coupling of two diphenylmethyl radicals must be much slower than the nuclear relaxation in the radicals¹⁴.

Closs studied a variety of halogen substituted benzyl and benzhydryl radical pairs from several precursors and found that in each case there was excellent agreement with the radical pair model for CIDNP.

The Information Derived from CIDNP

After publication of the radical pair theory, it was quickly realized that CIDNP can provide information

unobtainable by other techniques. Kaptein's initial investigations served to experimentally confirm the signs of hyperfine coupling constants in alkyl radicals¹². These values were previously only obtained from molecular orbital calculations. CIDNP was easily used to provide signs of this coupling in alkyl¹², cycloalkyl¹², and aryl radicals¹⁵.

The multiplet was found to be very sensitive to small changes in Δg . Closs used this property to estimate the g-factor in various substituted benzyl and benzhydryl radicals^{13,14}. In this work, he found excellent agreement with published values from ESR studies.

Nuclear polarization is developed during interactions of radicals in a solvent cage. Since the lifetime of this cage is extremely short (10^{-9} - 10^{-10} sec.) CIDNP is capable of giving information on extremely short lived radicals. CIDNP has been used to study radicals which rapidly decompose, such as acyloxy radicals ($\text{RCO}_2\cdot$)¹², diazenyl radicals ($\text{RN}=\text{N}\cdot$)¹⁶ and cyclohexadienyl radicals¹⁷⁻¹⁹. Kaptein demonstrated that the technique could be applied to the observation of radical rearrangements¹². This has led the studies reporting the structure of β -bromoethyl radicals²⁰.

The application of CIDNP to the observation of short-lived products from radical reactions has been particularly fruitful. Closs observed that phenyl azocumene produced the unfavorable cis isomer upon photolysis¹³. This cis isomer then decomposed to give additional CIDNP spectra.

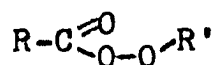
A variety of groups have studied the formation of enolic alcohols during radical reactions. Blank and Fischer observed the formation of vinyl alcohol during the photolysis of either acetaldehyde or acetoin (2-hydroxybutan-3-one)²¹. The enolic forms of acetone²² and acetophenone²³ have both been observed by similar methods. In all these cases, the enhancement due to CIDNP made it possible to observe low concentrations of thermally unstable products.

Reversible radical reactions have also been demonstrated using CIDNP. Closs reported that phenyl azocumene is reformed during its photolysis¹³. The photolysis of ketones has been shown to involve a reversible cleavage of the bond α to the carbonyl function²⁴. These reactions are easily observed via their CIDNP studies. Conventional observation of these reactions would require isotope labeling or stereochemical studies.

SECTION II

Chemistry of Peresters

Peroxyesters (peresters) are a group of organic compounds which are commonly used as sources of free radicals. The structure of peresters (I) can be varied.



(I)

R can be almost any alkyl or aryl group. The alkoxy half, O-R', may also have a variety of structures, although the tertiary alkyl peresters are most suitable as radical precursors. Primary, secondary alkyl or aryl structures for R' accelerate decomposition by ionic mechanisms. For the purposes of this study, only the tertiary alkyl peresters will be considered²⁵.

While the first syntheses of peresters were reported in 1901²⁶, little additional work was done in this area until the mid-1940's. During their study of organic peroxides, Milas and Surgenor²⁷ reported the first general synthesis of tertiary alkyl peresters. Their method involved the simultaneous addition of an acyl chloride and aqueous potassium hydroxide to t-butyl hydroperoxide at low temperatures. Using this procedure, they were able to prepare and characterize five new t-butyl peresters and three di-t-butyl peresters. Milas and Surgenor realized the utility of these compounds as polymerization catalysts.

Structure Reactivity Relationships

It was not until the late 1950's that an interest in the mechanism of the decomposition of peroxyesters developed. A systematic survey of many t-butyl peresters was carried out and the effect of the structure of R (the acyl fragment) on the decomposition was determined. Bartlett and his co-workers^{28,29} found that two different homolytic paths were available for the decomposition. Using both product studies and kinetic data from the thermal decomposition in chlorobenzene, they were able to divide the peresters studied into two groups. The first group where R is CH_3- , C_6H_5- , or $\text{C}_6\text{H}_5\text{CH}=\text{CH}-$ decomposed relatively slowly. Product analysis after the decomposition indicated considerable formation of the corresponding carboxylic acids.

These compounds decomposed by initial cleavage of the O-O bond followed by loss of carbon dioxide from the acyloxy radical to give an alkyl radical and a t-butoxy radical. The isolation of the carboxylic acids indicated that the acyloxy radical formed had a considerable lifetime.

The second group of peresters included $\text{R}=(\text{CH}_3)_3\text{C}-$, $\text{C}_6\text{H}_5\text{CH}_2-$ and $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2-$. These compounds decomposed many times faster than the previous group and product analysis indicated that no carboxylic acid was formed. In this case, the decomposition involved a simultaneous cleavage of the O-O bond and loss of carbon dioxide from the acyloxy fragment to give alkyl and alkoxy radicals as the initial radicals formed. Attempts to trap the acyloxy

radical using Hammond's reagent ($\text{CCl}_4 + \text{I}_2 + \text{H}_2\text{O}$) gave only small yields of the acids indicating an extremely short or non-existent lifetime for the acyloxy radical.

Product analysis of group II peresters indicated the formation of t-butyl ethers during the decomposition. This ether formation was attributed to a cage reaction where the alkyl and alkoxy radicals couple in the initial solvent cage before they are able to diffuse apart. Other products were isolated resulting from the free radical coupling and disproportionation of the alkyl radicals. The t-butoxy radical reacted by hydrogen atom abstraction to give t-butyl alcohol or by a unimolecular decomposition to give acetone and methyl radical.

The difference between the two mechanisms was rationalized by comparing the relative stability of the resulting alkyl radicals. When loss of carbon dioxide from the acyloxy radical results in the formation of an unstable radical such as methyl or phenyl, the decomposition is step-wise (group I). When R is a more stable radical, the stabilization of the radical will contribute to the lowering of the activation energy of the decomposition if a concerted mechanism is followed (group II). The two available pathways are summarized in figures VII and VIII.

In addition to the homolytic pathways, it was found that t-butyl trifluoroperacetate decomposed by an ionic mechanism. The trifluoroperacetate is an unusual case but ionic mechanisms have been shown to operate in polar solvents

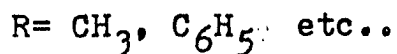
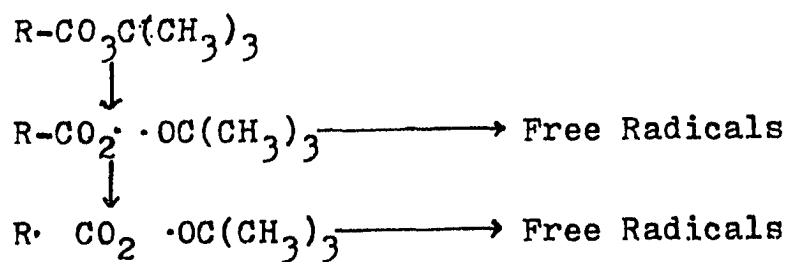


Fig. VII. Decomposition of Group I peresters (two step decomposition).

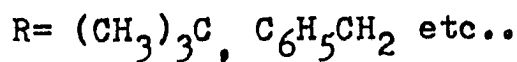
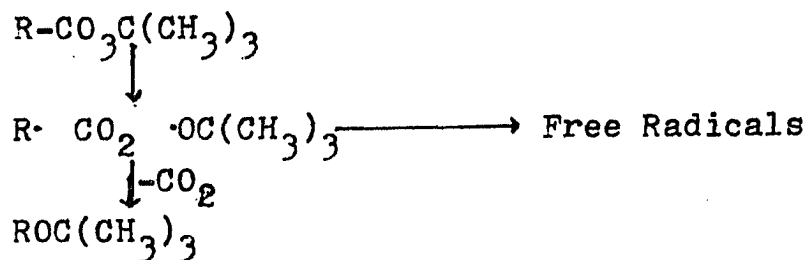


Fig. VIII. Decomposition of Group II peresters (concerted or one step decomposition).

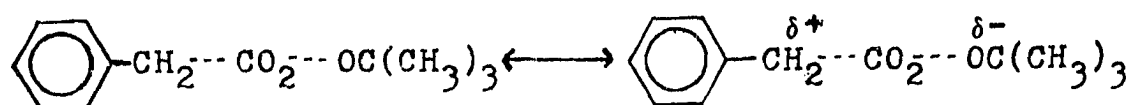
for other peresters. Further information on the ionic decomposition of peresters can be found in recent reviews of perester chemistry²⁵.

Further confirmation of these homolytic mechanisms was found by Koenig and his co-workers who studied the primary deuterium isotope effect during the decomposition. They found the k_H/k_D values for *t*-butyl phenylperacetate and 2-phenyl perpropionate were 1.17 and 1.14 respectively³⁰. This large effect indicated that there was considerable change in the hybridization of the benzylic carbon. These results are consistent with the loss of carbon dioxide during the rate determining step. They were in agreement with other well defined radical forming reactions such as the decomposition of the corresponding azo compound³¹. These values of the isotope effect were considerably higher than the isotope effect observed for the decomposition of acetyl peroxide which is known to decompose by a multistep process³².

Polar Effects in Perester Decompositions.

The rate of decomposition of a perester may be influenced by the addition of substituents. This influence may appear in two different fashions, it may alter the bond energy of the O-O bond in the perester or it may change the energy of the transition state leading to the decomposition. Bartlett and Rüchardt³³ demonstrated that the rates of thermal decomposition of a series of *t*-butyl phenyl peracetates can be correlated with Hammett's σ values. Their correlation

with σ^+ (rather than with σ) values indicate that the aromatic ring is stabilizing considerable positive charge. Viewing the transition state as a hybrid between structure II and III, we can rationalize this effect during the transition state.



Had the substituent effect been due to a perturbation of the ground state of the perester, a better correlation would have been expected using σ values.

Similar correlations with σ^+ observed for the chlorination of toluenes had been rationalized in a similar manner³⁴. A comparison of the ρ values (-1.20 for the perester to -0.66 for the chlorination) indicate that more positive charge is stabilized by the ring in the perester decomposition.

It is important to realize that although the transition state does develop considerable charge, the radicals produced are neutral. The addition of substituents on the ring still allows for the decomposition to occur via a homolytic mechanism.

Reactions of the Alkyl-Alkoxy Radical Pair

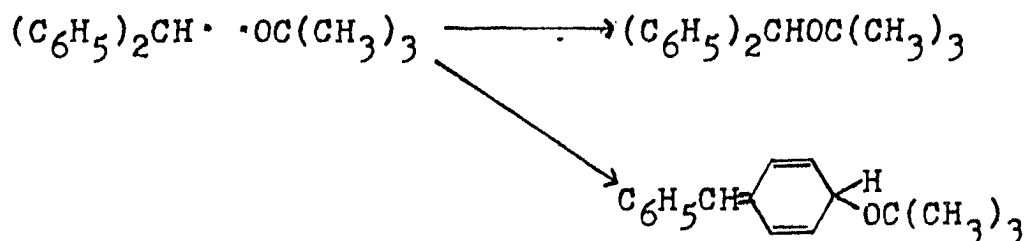
The decomposition of a perester (group II) can give initially an alkyl and alkoxy radical separated by one molecule of carbon dioxide and surrounded by a shell of solvent molecules. During this time, there is a relatively

high probability these radicals will react by coupling or disproportionation. These reactions, termed "cage reactions", occur between two radical partners before they can be separated by diffusion. The time scale for the cage reaction is on the order of 10^{-9} to 10^{-10} seconds³⁵ and is dependent upon the initiator, the radicals produced and the solvent.

The nature of cage reactions in perester decompositions has been studied by several groups. Sheldon and Kochi³⁶ first demonstrated that ethers are formed only by cage reactions. This is based on their failure to find crossover ethers in the photolysis of a t-butyl peracetate-t-amyl perpropionate mixture. Peresters which produce extremely stable alkyl radicals will violate this rule since the alkyl radicals will scavenge the t-alkoxy radicals in bulk solution.

A survey of cage reactions in a variety of t-butyl peresters was recently published by Lorand³⁷. He found that t-butoxy radicals show a preference for hydrogen atom abstraction rather than coupling to alkyl radicals when possible. This is clearly demonstrated by the decomposition of t-butyl perpivalate where the cage products obtained in cumene are isobutylene and t-butyl alcohol (50%) with little di-t-butyl ether formed (about 2%). Similar results were obtained with other peresters. Lorand found that coupling of the t-butoxy alkyl pair decreases in going from primary to tertiary radicals. The explanation for these effects is based on both steric and orientation restrictions in the

t-butoxy radicals. The methyl groups of a t-butoxy radical provide increasing steric hindrance to coupling reactions as the alkyl radical goes from primary to tertiary. Lorand compares the t-butoxy radical to a neopentyl fragment to describe the orientation restrictions in coupling reactions. The occurrence of aromatic ring attack by t-butoxy radicals upon diphenylmethyl or triphenylmethyl radicals is suggested as an alternative reaction involving less steric hindrance than simple coupling.

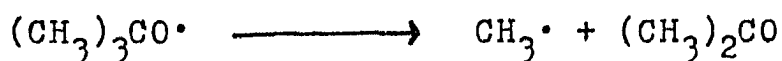


The effect of viscosity³⁷⁻³⁸ on cage reactions of peresters has been studied by several groups. Since the viscosity of the solution affects the rate of diffusion from the initial cage, increasing the viscosity of the solution increases the fraction of cage coupling. High yields of cage products were found when the solvent is extremely viscous (90% cage coupling for t-butyl diphenyl peracetate in mineral oil vs. 17% in cumene)³⁷.

Reactions of the t-Butoxy Radicals

The eventual fate of t-butoxy radicals is of importance in all perester decompositions. The t-butoxy radicals which

escape from the solvent cage, readily abstract hydrogen atoms from various solvents (cyclohexane, cumene and slowly from benzene)³⁹ giving t-butyl alcohol. In solvents where proton abstraction is difficult, the t-butoxy radical undergoes scission giving acetone and methyl radicals.



This decomposition has been shown to occur only in bulk solution and is unimportant in the initial solvent cage⁴⁰.

Electron Spin Resonance of the Radicals Derived from Peresters

The alkyl radicals derived from peresters have been extensively studied using E.S.R. spectroscopy. Photolyses of several t-butyl peresters have given well resolved E.S.R. spectra of alkyl radicals in solution³⁶. In a detailed study of substituted alkyl radicals, Kochi employed peresters to generate several alkyl radicals; in each case these spectra were identical to that obtained using other sources of these radicals⁴¹.

The E.S.R. spectrum of the t-butoxy radical, however, is the subject of some controversy. The first reported observation⁴² of the t-butoxy radical generated by the photolysis of t-butyl hydroperoxide was later shown to be due to the t-butyl peroxy radical⁴³. Hammond and Wiemer reported⁴³ that a single line spectrum ($g=2.004 \pm 0.004$) appearing during the photolysis of di-t-butyl peroxide was due to t-butoxy radicals. Their reported range, $g=2.000 - g=2.008$, almost covers the entire range in which organic radicals appear.

Bartlett and Guaraldi⁴⁴ have reported that the spectrum of this radical is a single line with $g=2.009$. They believe that the results of Hammond were due to the t-butyl peroxy radical. All these results are reported to be incorrect by Symons⁴⁵ who feels that the t-butoxy radical like the hydroxy radical, will not give a well defined spectrum in solution. This belief is based on the fact that the free electron is held in an orbital which is triply degenerate (an oxygen 2p orbital). The symmetrical field allows the electron to exist in a rapidly changing environment which provides an efficient mechanism for electron spin relaxation. The combination of the rapidly changing environment and short lifetime of the excited state causes severe line broadening. Symons assigns the structure of a peroxy radical to the line at 2.004 and the structure of an ozonide radical $(CH_3)_3COO\cdot$ to the signal at 2.009.

There were no E.S.R. spectra attributed to the t-butoxy radical reported by Kochi who used this radical extensively during his studies of bridged radicals. . In the study of photolysis of peresters, there was again no spectrum due to the t-butoxy radical but instead its decomposition product, the methyl radical was observed.³⁶ .

SECTION III

CIDNP of Peroxides and Peresters

Because of the structural and mechanistic similarities between diacyl peroxides and t-butyl peresters, there are many parallel features in their decomposition. The decomposition of peroxides has been the most intensely studied area of CIDNP. Since many of the CIDNP features of peroxide decomposition will be expected in peroxyester decomposition, a review of the peroxide studies may be helpful in understanding this work.

The original report of CIDNP during the thermal decomposition of benzoyl peroxide has led the way for extensive CIDNP studies involving this compound¹⁵. The radical-pair theory is capable of fully explaining the CIDNP observed from this reaction. The decomposition of benzoyl peroxide involves initial cleavage of the O-O bond to give two benzoyloxy radicals. Rapid loss of one carbon dioxide gives a phenyl-benzoyloxy radical pair, in which the nuclear polarization is generated. In this pair the g factor of the benzoyloxy radical is larger than that of the phenyl. The hyperfine coupling constants of the phenyl radical are all positive ($a_{Ho}=+17.4G$, $a_{Hm}=+5.9G$ and $a_{Hp}=+1.9G$) while the hyperfine couplings of the protons on the benzoyloxy radical are zero. Using Kaptein's Rules, we would expect enhanced absorption for the cage product, phenyl benzoate, and emission for the escape product benzene. The predicted emission for benzene is observed, however,

the ester polarization is difficult to observe because of the complexity of the NMR spectrum of the phenoxy protons. In the decomposition of bis-4-chlorobenzoyl peroxide, an enhanced absorption of 4-chlorophenyl-4-chlorobenzoate is observed⁴⁶.

The photolysis of benzoyl peroxide has been shown to exhibit interesting spectra^{47,48}. Irradiation with the unfiltered light from a high pressure mercury lamp yields

spectra similar to those produced by thermal decomposition. These results indicate that the decomposition is occurring from the singlet state. Addition of a singlet sensitizer (anthracene, pyrene, phenanthrene or triphenylene) results in an increased emission. Irradiation using only light of $\lambda \geq 300$ nm. changes the phase of the CIDNP indicating that the decomposition is now occurring from the triplet state.

¹³C polarization has been observed during the thermolysis of the peroxide⁴⁹. These results confirm that the polarization is developed in the phenyl-benzoyloxy pair. CIDNP effects were observed for carbon dioxide, benzene, phenyl benzoate and biphenyl.

The decompositions of benzoyl peroxide¹⁷⁻¹⁹ and bis-pentafluorobenzoyl peroxide in aromatic solvents have been shown to involve the intermediacy of cyclohexadienyl radicals. These radicals are formed by the addition of either phenyl or pentafluorobenzoyloxy radicals to the solvent. Nuclear polarization is developed in the benzoyloxy

(or phenyl) cyclohexadienyl radical pair. Upon escape from this pair, the cyclohexadienyl radical decomposes to give the benzoyloxy (or phenyl) radical and polarized solvent.

A detailed systematic survey of the decomposition of aliphatic acyl peroxides has been reported by Kaptein.¹² In this work, he found that peroxides can be divided into two groups (similar to the two groups that peresters were divided into by Bartlett). The first group gives net polarization due to an acyloxy-alkyl radical pair (similar to benzoyl peroxide). These peroxides decompose to give an acyloxy radical with a relatively long lifetime. Acetyl, benzoyl, cyclopropane carbonyl and acrylyl peroxides were found to fit into this class. When decomposed in hexachloroacetone (HCA), each of these peroxides exhibited nuclear polarization in the cage product (an ester) and escape products (an alkyl chloride). The second group gave only multiplet effect polarization from an alkyl-alkyl radical pair. Net polarization found in these peroxides was attributed to a solvent derived radical being involved in a second polarizing cage. Peroxides in this group included all saturated acyl peroxides except acetyl peroxide. The difference between these two groups is rationalized by the rate of loss of carbon dioxide from the acyloxy radicals. If this is sufficiently slow, net polarization will be developed by the alkyl acyloxy radical pair.

The important features of group I peroxides may be demonstrated by the thermal decomposition of acetyl peroxide.

This peroxide when decomposed in HCA gave intense nuclear polarization (the asterisk designates the protons which displayed nuclear polarization) for methyl acetate ($\text{CH}_3\text{COCH}_3^*$), ethane (CH_3CH_3^*), methyl chloride (CH_3^*Cl), methane (CH_4^*) and pentachlorobutanone ($\text{CH}_3^*\text{CCl}_2\text{COCCL}_3$). The CIDNP observed is rather straight forward but may require some comments. In the formation of methyl acetate from a geminate acetoxy-methyl radical pair, only the protons on the methyl radical are polarized. This indicates that there is no hyperfine coupling from the protons of the acetoxy radical to the unpaired electron. The escape products, methyl chloride and methane, exhibit nuclear polarization which is opposite in phase to the cage products. This is a generally observed effect in all CIDNP spectra. The production of pentachlorobutanone is the result of interaction with solvent derived pentachloroacetyl radicals trapping free methyl radicals¹². The most interesting effect in this spectrum is observed in ethane. In this reaction, the ethane has the same phase polarization as does the methyl acetate. The origin of the polarized ethane is the same acetoxy-methyl radical pair. This compound indicates that the acetoxy radical may decarboxylate forming a methyl-methyl radical pair but retaining the polarization of the acetoxy-methyl pair. This process is known as the "memory effect" and leads to cage polarization of ethane. The proposed mechanism was confirmed by ^{13}C enriched samples which were studied using both proton and carbon NMR.

The decomposition of propionyl peroxide is an example of a group II peroxide. CIDNP is observed during the decomposition of this compound in HCA for ethyl chloride and butane. The main polarization appears as a multiplet effect which is due to a geminate ethyl-ethyl radical pair. There is, however, a small net effect superimposed by an ethyl-pentachloroacetyl radical pair.

In addition to Kaptein's studies, there were several other reports of CIDNP from peroxide decompositions. Walling and Lepley⁵⁰ studied the decomposition of bis-phenyl acetyl peroxide. In this compound, there is no polarization developed in the initial benzyl-benzyl radical pair. They interpreted their results in terms of free radical reactions with solvent derived radicals. Ward and Lawler studied the decomposition of several peroxides in the presence of alkyl iodides⁵¹. They were able to interpret their results in terms of a pair substitution reaction, that is, the alkyl iodides were able to substitute in the radical pair rapidly enough to retain the polarization of the geminate radical pair. In addition to the symmetric diacyl peroxides, there have also been studies which involved the decomposition of mixed peroxides⁵². The results of these studies are quite similar to those reported by Kaptein in his studies of the symmetric peroxides.

At present, there are only preliminary reports indicating the observation of CIDNP during the decomposition of peresters. The first report was the result of Kaptein's work in which

he studied the thermal decomposition of t-butyl perpivalate $((\text{CH}_3)_3\text{CCO}_3\text{C}(\text{CH}_3)_3)$ in chlorobenzene. Kaptein reported that net nuclear polarization was developed by a geminate t-butyl-t-butoxy radical pair. The cage product di-t-butyl ether was observed in emission which lead to the conclusion that $g_{\text{t-butoxy}} < g_{\text{t-butyl}}$. This result was surprising since all the reported values of $g_{\text{t-butoxy}}$ of 2.004 - 2.009 are significantly higher than that of t-butyl radicals (2.0025). A second cage reaction to form iso-butylene and t-butyl alcohol gave net polarization observed in iso-butylene. A radical pair resulting from the free radical encounters of two t-butyl radicals resulted in strong multiplet effect in iso-butane and iso-butylene. The acetone produced did not show any polarization indicating that there is no hyperfine interaction between the protons on the t-butoxy radical and the free electron.

This interpretation has recently been dismissed because of a theoretical evaluation of the properties of the t-butoxy radical ⁵³. As a result of consideration of relaxation effects in this radical, Kaptein concluded that no CIDNP will result from radical pairs containing the t-butoxy radical. Kaptein also studied the decomposition (probably photolytic) of t-butyl peracetate, perbenzoate and perpropionate. There were no results presented other than stating that there was no CIDNP due to the geminate cage.

The second report of CIDNP from peresters involved the thermolysis of di-t-butyl peroxyoxalate ⁵⁴. This compound

decomposes in several steps to eventually lead to methyl radicals. The purpose of this research was to study the free radical reactions of the methyl radical with solvent derived radicals. There was no CIDNP attributed to the initial decomposition of the perester.

The final report exists as a brief section in a communication to the Editor of the Journal of the American Chemical Society by P.D. Bartlett.⁵⁵ Bartlett reported that CIDNP is generated from the triplet decomposition of t-butyl perbenzoate which was present during the thermal decomposition of tetramethyl dioxetane. In this experiment, the t-butyl perbenzoate decomposed after energy transfer from triplet acetone formed by decomposition of the dioxetane. The benzoyloxy -t-butoxy radical pair which was postulated generated nuclear polarization observed in benzene. This radical pair, however, could not generate nuclear polarization in benzene since there is no interaction of the protons of the benzoyloxy radical with the odd electron. A more feasible radical pair would be the phenyl-t-butoxy or a phenyl-trichloromethyl (solvent derived) pair.

RESULTS AND DISCUSSION

The mechanism by which nuclear polarization is developed during perester decompositions is strongly influenced by the nature of the solvent. Hydrocarbon solvents and hexachloroacetone produced spectra which were markedly different from those obtained by decomposition of the perester in aromatic solvents. This provided a logical division with which to separate the reactions of the peresters.

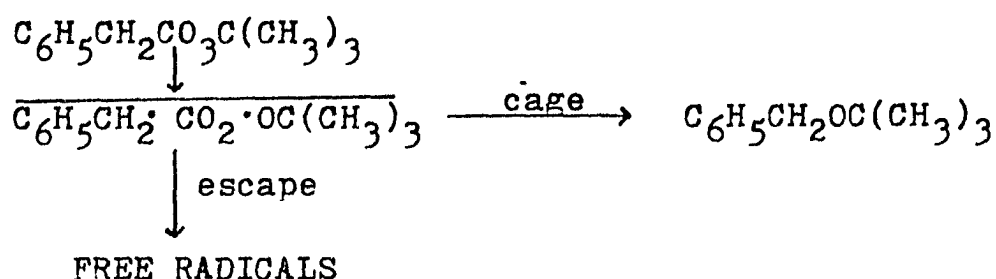
The first section will deal with the decomposition of each perester in various non-aromatic solvents (usually decane and hexachloroacetone). The next section will deal with the decomposition of each perester in aromatic solvents (usually chlorobenzene).

A final brief section, which does not involve CIDNP, reports the isolation and identification of two isomeric cage ethers from the decomposition of t-butyl diphenylperacetate.

The Decomposition of Peresters in Non-Aromatic Solvents.

Decomposition of *t*-Butyl Phenylperacetate (1).

The thermal decomposition of *t*-butyl phenylperacetate (1) has been studied in considerable detail²⁸. This compound is known to decompose via a concerted cleavage of the O-O bond and loss of carbon dioxide. This initial decomposition leads to a geminate benzyl-*t*-butoxy radical pair which may either couple or diffuse apart to give free radicals.



The benzylic protons of the ether formed by this process would be expected to show strong CIDNP effects in their NMR spectrum since they have a large hyperfine coupling in the benzyl radical and the *g*-factors of the two interacting radicals should be different⁵⁶. However, there are no CIDNP effects observed during the decomposition of this perester in decane at 140°C despite the fact that the ether is formed in approximately 14% yield (by NMR intergration). This lack of nuclear polarization was somewhat troublesome to explain. The possible implications of this effect include: 1) decomposition of this perester involves a non-concerted loss of CO₂ from the acyloxy radical, 2) ether formation does not involve radicals, 3) coupling of the

benzyl-t-butoxy radical pair occurs before nuclear polarization can develop or 4) the benzyl-t-butoxy radical pair is unable to develop nuclear polarization.

Possibility 1 was dismissed since there is considerable chemical evidence which indicates that the decomposition of this compound leads directly to a benzyl-t-butoxy radical pair²⁵. CIDNP studies of the corresponding peroxide (big-phenylacetyl peroxide) gave no indication of the existence of the phenylacetoxo radical within the time scale necessary to develop CIDNP (10^{-9} - 10^{-10} sec)⁵⁰. It would be difficult to rationalize that the phenylacetoxo radical has a longer lifetime during perester decompositions (140°C) than during the peroxide decomposition (40°C). Attempted chemical reactions to trap the phenylacetoxo radical have been unsuccessful²⁸.

Possibility 2 would be hard to reconcile with the formation of both benzyl and t-butoxy free radicals. Chemical evidence indicates that the formation of the ether involves a cage coupling of these radicals. Possibility 3 is difficult to reconcile with the formation of any ether. Decomposition of 1 in a more viscous solvent would be expected to slow down the rate of cage escape³⁹ giving sufficient time to develop nuclear polarization. The decomposition of 1 was carried out using mineral oil as the solvent, however, there was still no nuclear polarization observed for the benzyl-t-butyl ether.

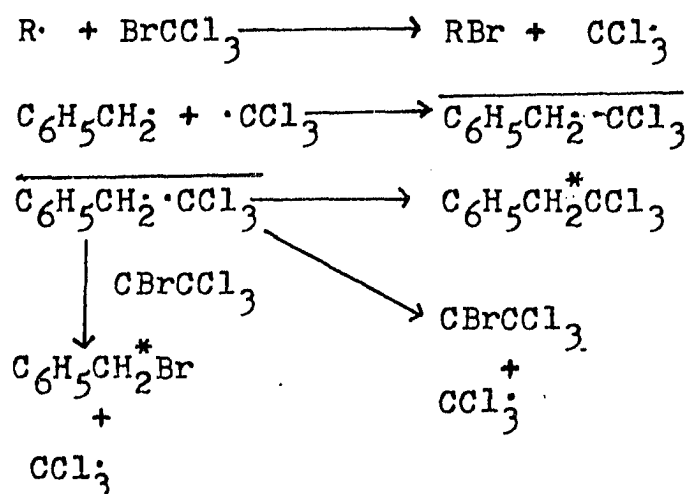
The only remaining possibility is that the benzyl-

t-butoxy radical pair cannot generate nuclear polarization. It has been suggested that the t-butoxy radical is subject to rapid electron spin relaxation due to a degeneracy in the oxygen p orbital in which the odd electron is localized ⁴⁵. Local fields arising from electrons in nearby orbitals cause a fluctuating g-tensor and provide an effective mechanism for spin relaxation. For this reason, the t-butoxy radical cannot be observed in solution by ESR spectroscopy. This spin relaxation would disrupt the spin correlation needed to generate CIDNP in the products of this radical pair. The possibility that rapid spin relaxation could interfere with the generation of nuclear polarization has been suggested by Kaptein as a complication which may arise when studying metal-centered radicals via CIDNP ⁵⁷. A theoretical discussion of the effect of electron relaxation of CIDNP has recently appeared. In this work, Kaptein suggests that the CIDNP effects produced by peroxyesters are entirely due to free radical reactions, in agreement with our conclusions ⁵³.

Since the t-butoxy radical is unable to generate nuclear polarization, we should expect that all peroxyesters will not lead to nuclear polarization from geminate pairs when decomposed in hydrocarbon solvents. This was found to be true when various ring substituted (p-CH₃-, p-Br-, p-Cl-, etc.), phenyl or methyl substituted t-butyl phenylperacetates were investigated (vide infra).

To confirm the presence of benzyl radicals, the decomposition of 1 was carried out in the presence of

bromotrichloromethane. Under these conditions, strong CIDNP was observed for the benzylic protons of benzyl bromide (4.45 δ E) and 2,2,2-trichloroethylbenzene (4.00 δ A) (see figure IX). The CIDNP produced is generated by dif-⁵⁸
fusive encounters of the benzyl and trichloromethyl radicals.



These effects are consistent with Kaptein's rules since in this radical pair the trichloromethyl radical has the greater g-factor ($g=2.0025$ for benzyl vs. $g=2.009$ for CCl_3) and the observed protons have a negative hyperfine coupling in the benzyl radical. Kaptein's rules predict

$$\begin{array}{l}
 \Gamma = \mu \cdot \Delta g \cdot a_i \\
 \Gamma = + + - - = + \quad \text{absorption}
 \end{array}$$

for the coupling product 2,2,2-trichloroethylbenzene and

$$\Gamma = + - - - = - \quad \text{emission}$$

for the escape product benzyl bromide. There is additional polarization observed during the decomposition in the aromatic region of the spectra. These resonances are due to the aromatic protons on the benzyl radical. It is well

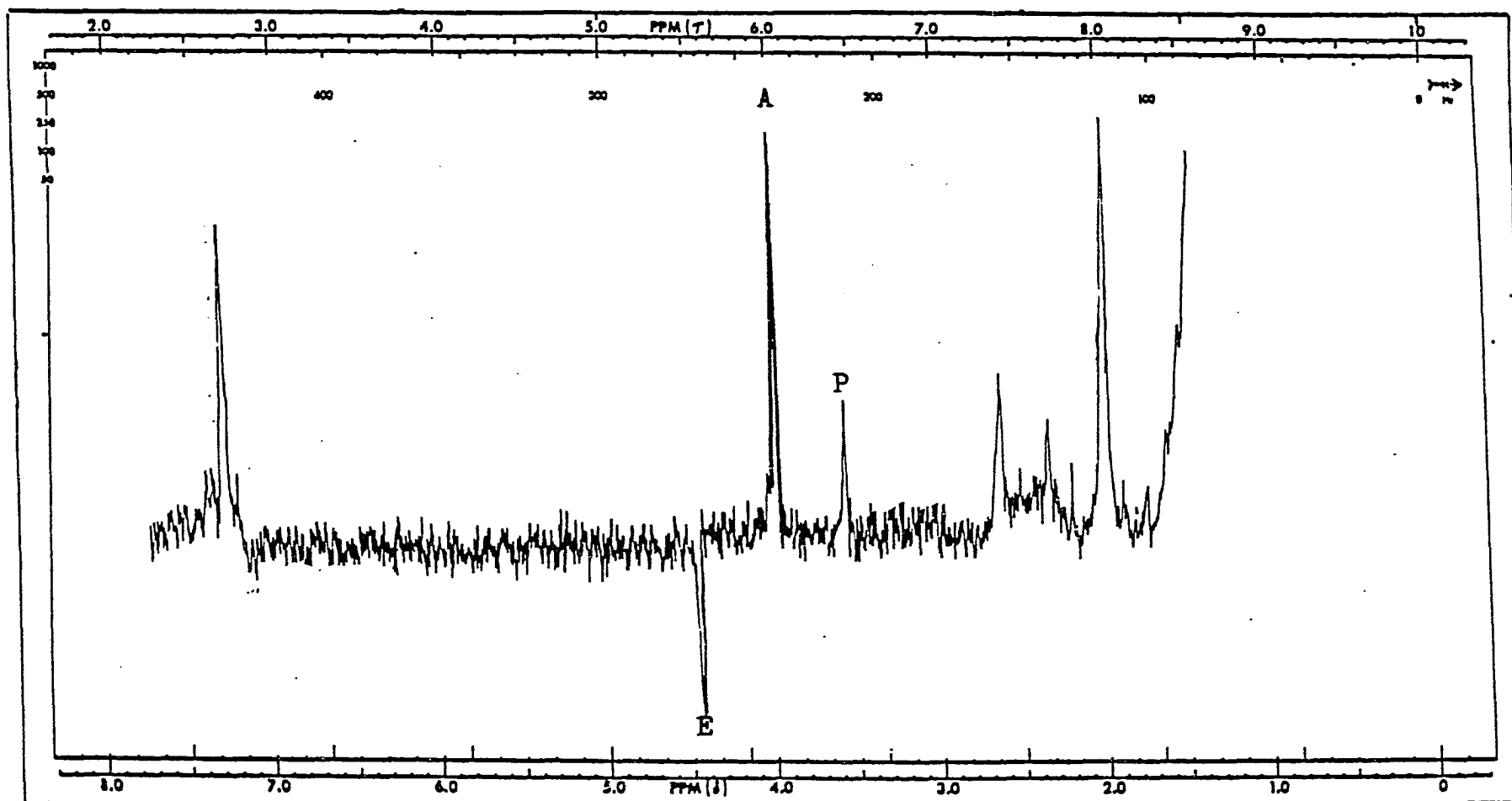


Figure IX. Decomposition of t-butyl phenylperacetate (1) in decane containing 0.05 M BrCCl_3 . Resonances marked A are enhanced, E are emission and P are the original perester.

Known that the aromatic protons have appreciable hyperfine coupling to the odd electron in the benzyl radical. However, we have not analyzed these in detail. The detection of acetone and t-butyl alcohol, known products resulting from t-butoxy radicals, is obscured by strong absorption due to the solvent decane.

These results and similar observations with other peresters lead to the conclusion that no CIDNP is produced in the geminate cage during perester decompositions. For this reason, we can expect to learn very little about the initial decomposition of these compounds using this technique. We can, however, study the free radical reactions of the alkyl radicals and the radicals derived from the various solvents or added trapping agents.

Decomposition of 1 in The Presence of Hexachloroacetone

The decomposition of 1 in hexachloroacetone (HCA) was found to give strong polarization as shown in figure X. The polarized resonances at 5.00, 4.45 and 3.80 δ have been assigned to benzyl 2-(pentachloropropenyl) ether, benzyl chloride and 4-phenyl-1,1,1,3,3-pentachlorobutanone respectively. There was no CIDNP observed for the protons on benzyl-t-butyl ether, acetone or other products derived from the t-butoxy radical. Since HCA has been shown to be an effective trap for alkyl radicals¹², it was expected that these spectra could be explained in terms of diffusive encounters of benzyl-pentachloroacetyl (PCA) radical

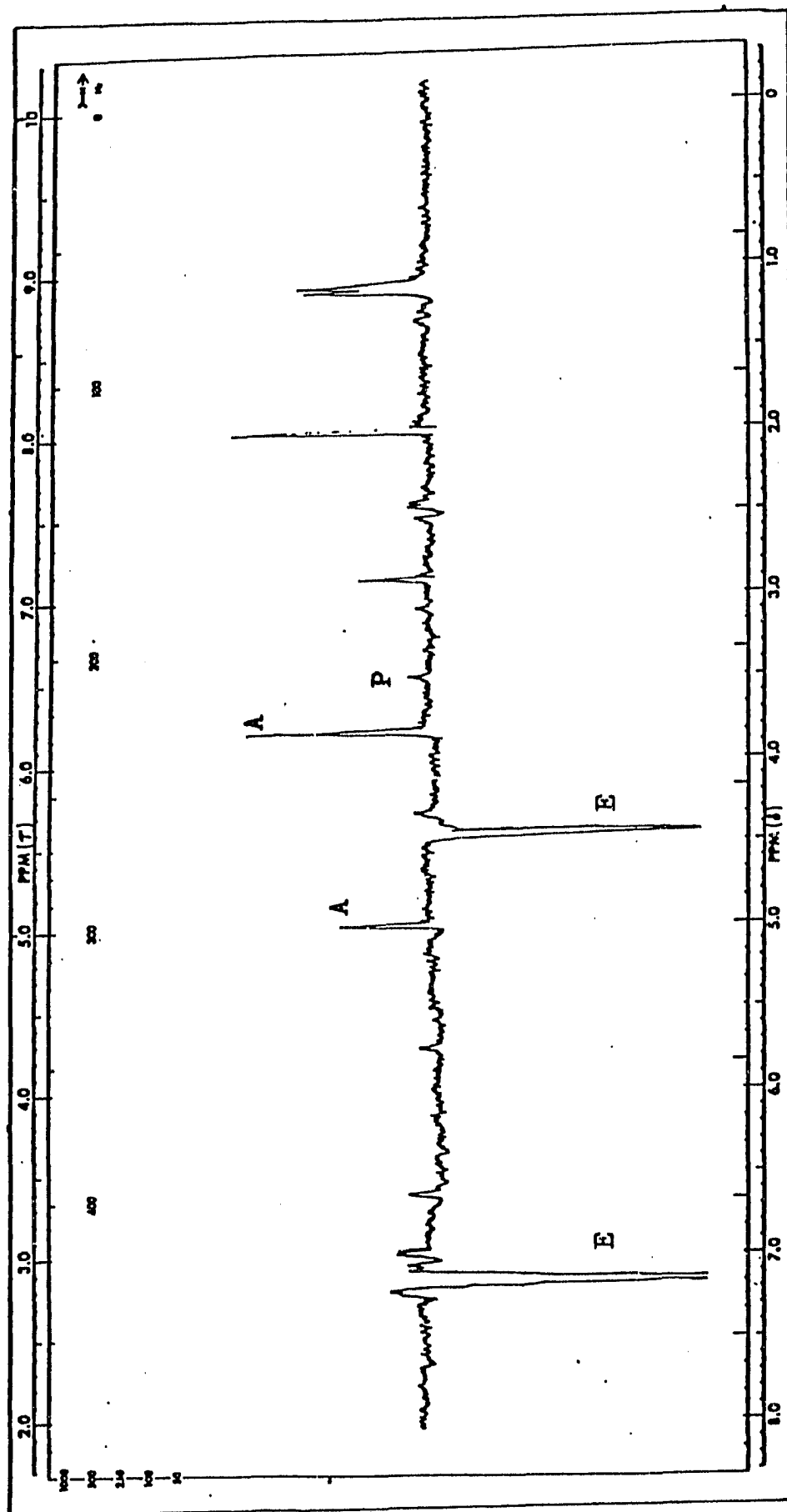
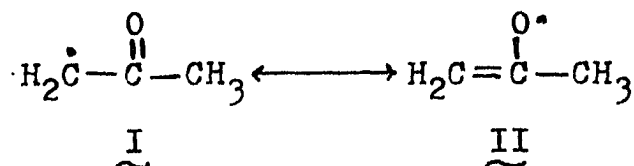


Figure X. Decomposition of *t*-butyl phenylperacetate (1) in hexachloroacetone

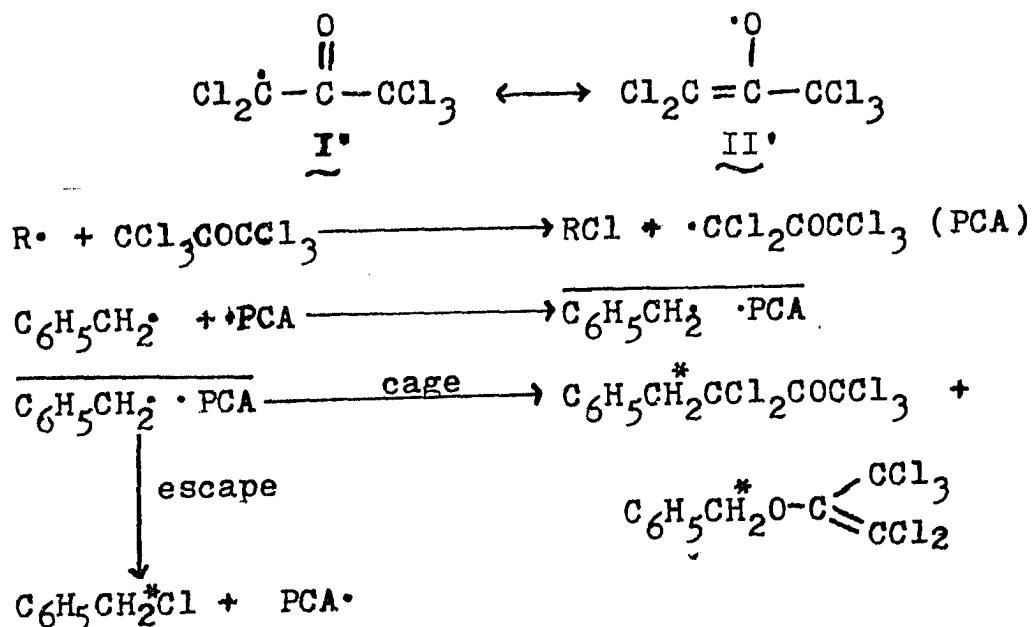
pairs.

Acetonyl radicals have been the subject of interest since they may exist as a hybrid of two forms. (I and II) ⁵⁹



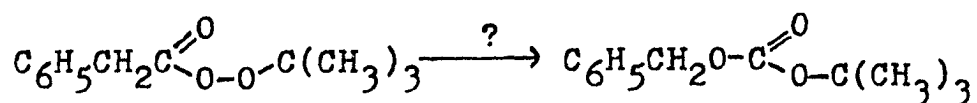
This was suspected since they are iso-electronic with the allylic radical and has been confirmed by ESR spectroscopy. These studies indicate that there is an abnormally high barrier to rotation about the C_1-C_2 bond which implies the participation of structure II. ⁶⁰ There are, however, no reports of products derived from reactions of radical II.

The observed spectra can now be easily explained by a mechanism which is similar to that used to explain the decomposition of 1 in the presence of BrCCl_3 but has been modified to include both resonance forms (I' and II') of the PCA radical.

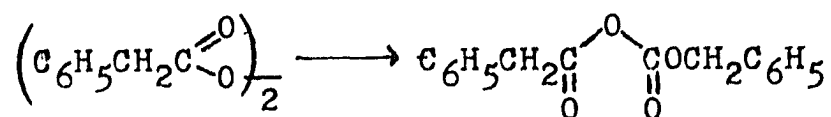


Since the pentachloroacetyl radical has a g-factor which is greater than that of the benzyl ($g_{PCA}=2.008$), cage products would be expected to exhibit enhanced absorption while the escape products should show emission. This is in agreement with the observed spectra.

Assignments of the structures to the resonance at 3.80 δ and 4.45 δ was based upon suitable model compounds (3.80 δ by comparison to 2,2,2-trichloroethylbenzene at 3.88 δ ⁵⁰ and 4.45 δ by comparison to authentic benzyl chloride). The resonance at 5.00 δ was somewhat more difficult to assign since suitable enolic ethers were unavailable. The fact that the protons causing this signal are benzylic was easily confirmed by the decomposition of t-butyl phenylperacetate- α -d₂ under the reaction conditions. In this case, there were no CIDNP effects observed. The appearance of a benzylic proton at 5.00 δ indicates that it must be attached to an electronegative element which is itself electron deficient. The assignment of the 5.00 δ peak to benzyl 2-(pentachloropropenyl) ether was based on a comparison to a suitable model compound, benzyl acetate 5.10 δ .⁶¹ At this point, two compounds may be suspected to be present in our reaction and cause a resonance at 5.00 δ , the assigned ether and benzyl-t-butyl carbonate. The carbonate is a possible result of a carboxy inversion reaction which is unknown in



perester decompositions³⁷. Similar carboxy inversion products are known to be formed during the thermal decomposition of the corresponding peroxide, but have been shown to be the result of non-radical mechanisms^{50, 62}.



Additional information which leads away from the assignment of the carboxy inversion product is that this resonance is not present in reactions where other radical traps are used. It would be difficult to reconcile the formation of a carboxy inversion product in solutions containing traps such as HCA or other chlorinated ketones but not in solutions containing no radical trap or bromotrichloromethane or carbon tetrachloride. It then appears reasonable to assign the resonance at 5.00 to benzyl 2-(pentachloropropenyl) ether.

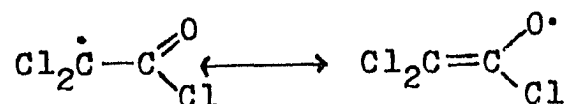
An additional polarized signal (A) is observed at 5.80 δ but remains unassigned. The product responsible for this resonance may be the result of secondary reactions with product derived radicals. Polarization is also observed in the aromatic region of the spectrum due to the various benzyl containing products.

Enolic Structure of α -Carbonyl Radicals

Since PCA exists as a hybrid of two forms, we decided to briefly study the structure of radicals which are adjacent to a carbonyl group. With this in mind, we studied the decomposition of 1 in decane solutions containing

various radical traps. Representative spectra are shown in figures XI-XV and are summarized in table 1.

It was found that both forms of these acetonyl radicals can be observed in the pentachloroacetonyl and tetrachloroacetonyl radicals. Similar results were obtained when trichloro or dichloroacetyl chloride were used as a radical trap. In this case, the radical which is produced by abstraction of the α chlorine atom is capable of existing as a hybrid of the two forms shown:



The decomposition of 1 in the presence of trichloro dichloroacetic acid resulted in CIDNP for only 3-phenyl-2,2-dichloropropanoic acid, the result of C-C coupling. This may indicate that the enolic form in this radical does not substantially contribute to the structure of the radical.

There was no CIDNP observed in several systems. This probably indicates that the added trap was unable to compete with the solvent which is a weak hydrogen donor. These systems and comparison to traps which could not give enolic radicals are summarized in Table 1.

Decomposition of Ring Substituted t-Butyl Phenylperacetates

The decompositions of several ring substituted t-butyl phenylperacetates were investigated for the following reasons: since it is known that the initial decomposition

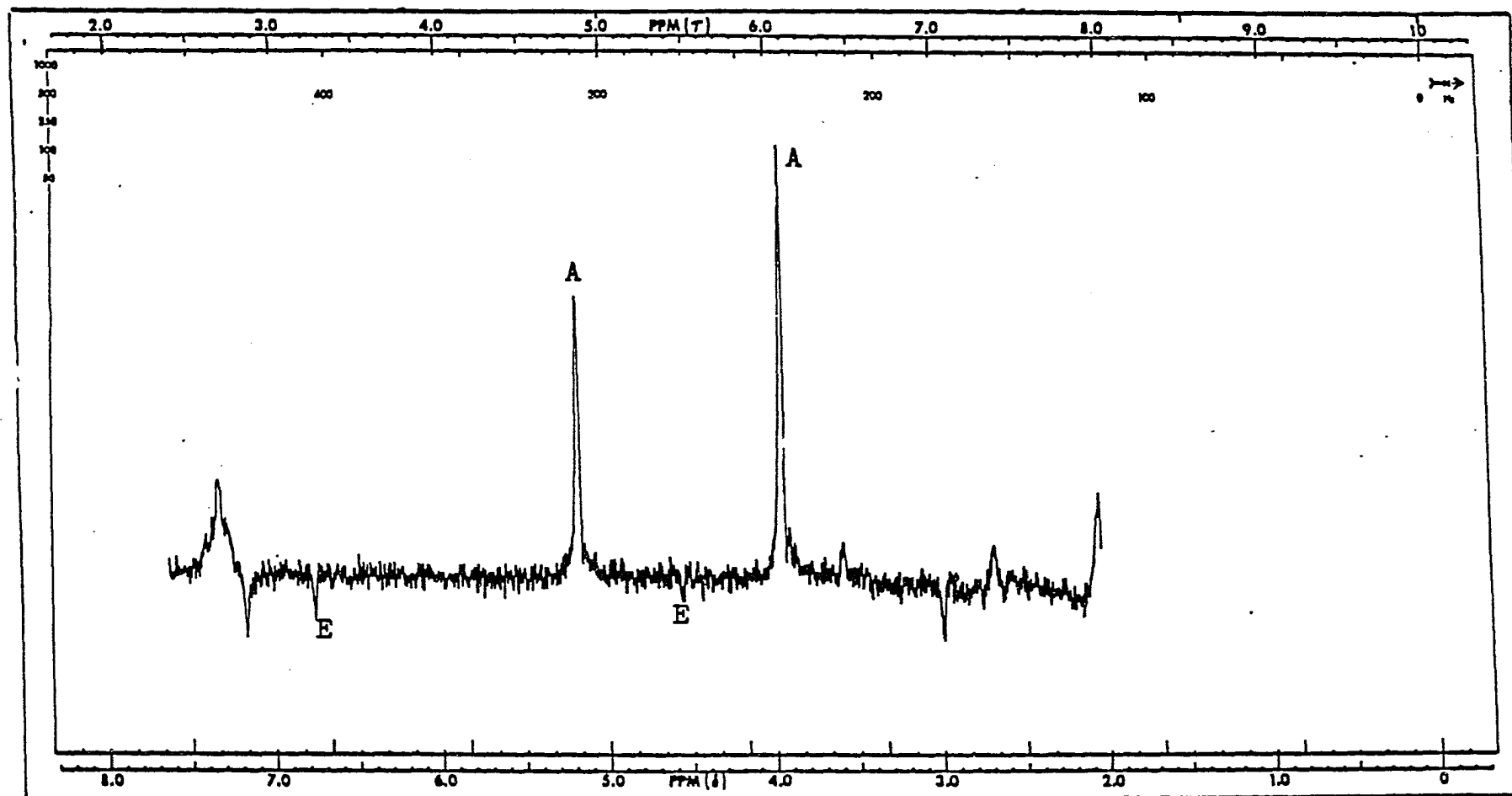


Fig. XI. Decomposition of t-butyl phenylperacetate (1) in decane containing 0.1 M hexachloroacetone.

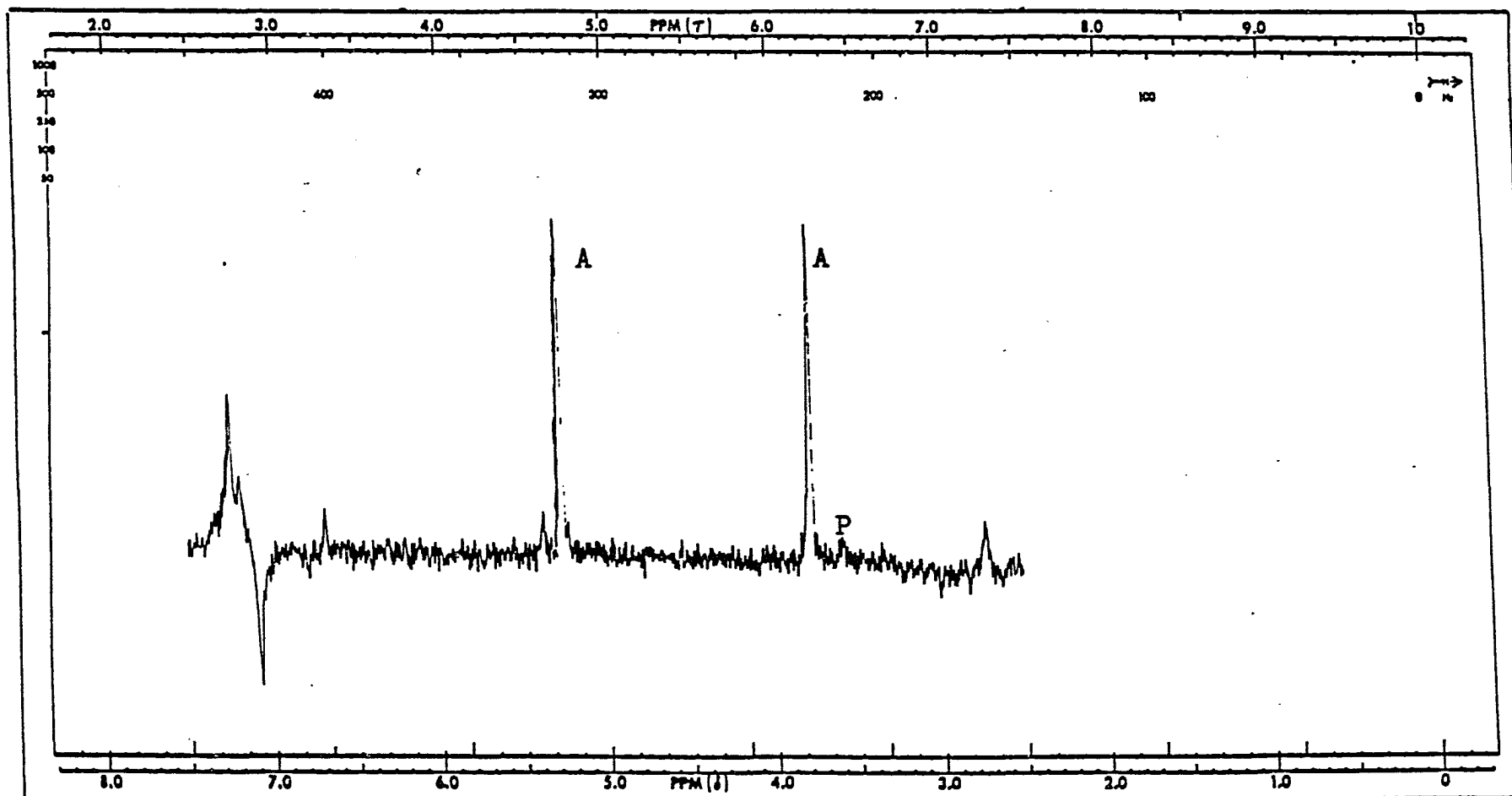


Fig. XII. Decompositon of *t*-butyl phenylperacetate (1) in decane containing 0.1 M pentachloroacetone. Resonance at 6.73 δ reduces intensity during the decomposition.

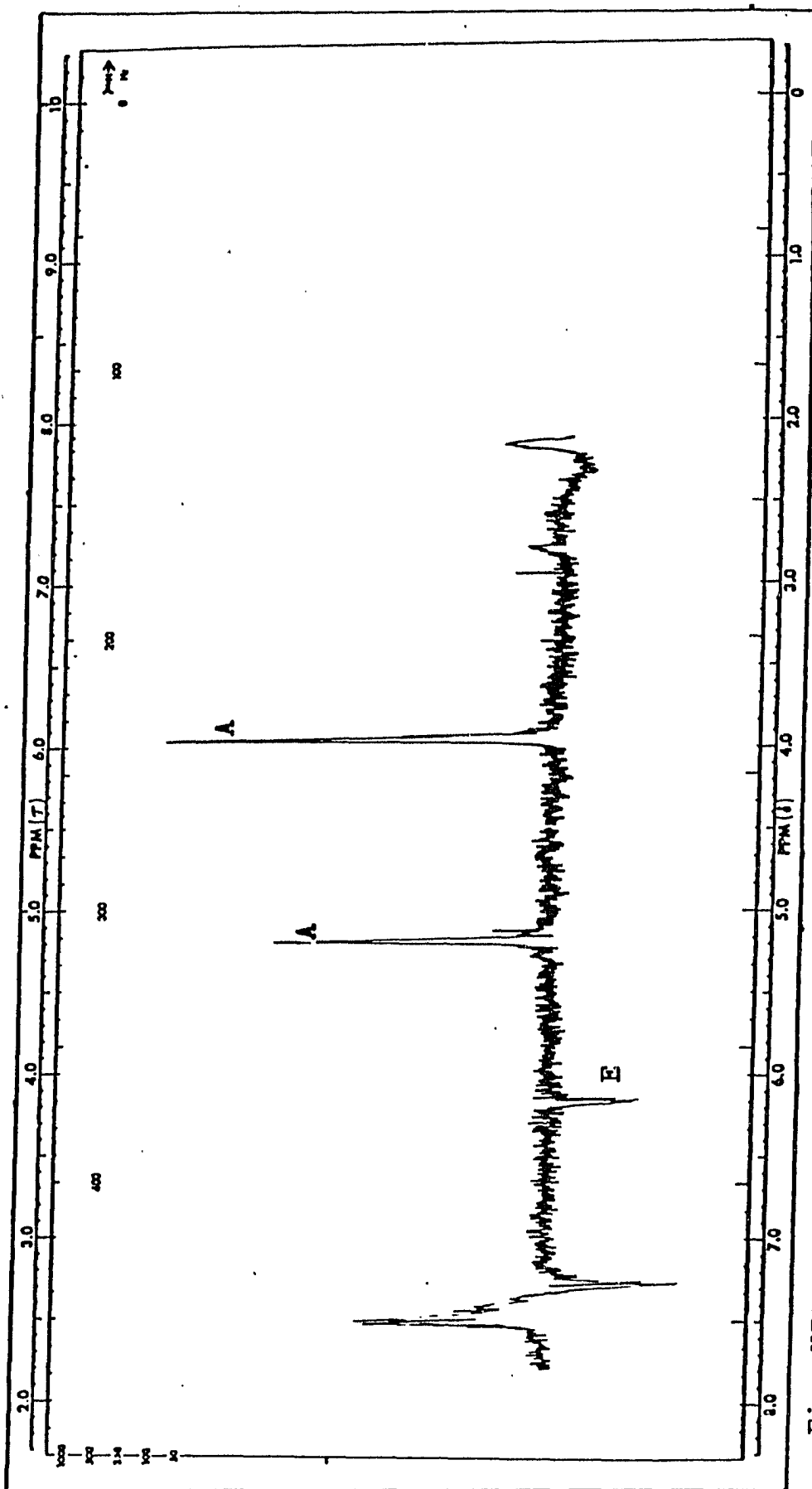


Fig. XIII. Decomposition of *t*-butyl phenylperacetate (1) in decane containing 0.1 M trichloroacetyl chloride.

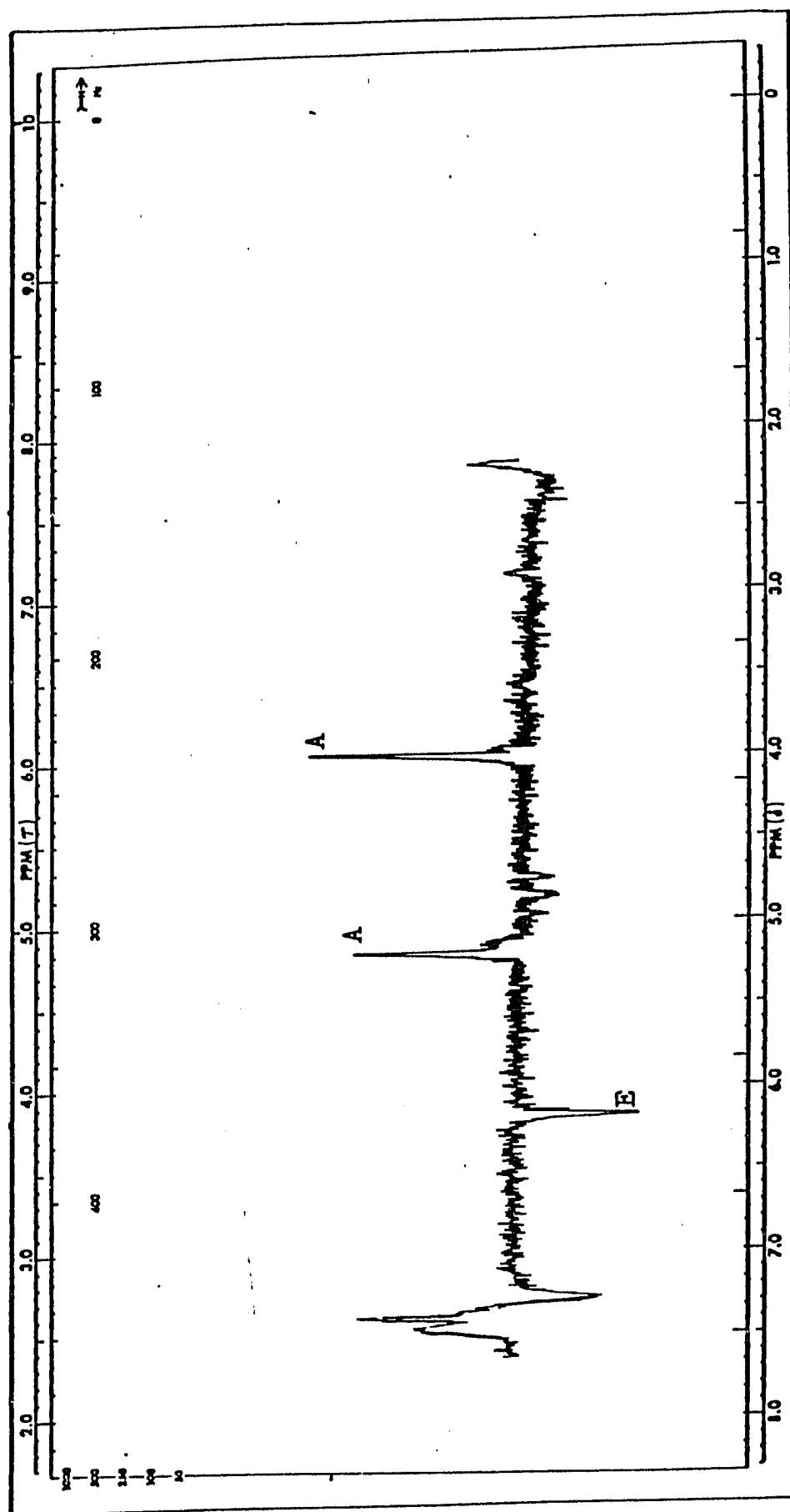


Fig. XIV. Decomposition of t-butyl phenylperacetate (1) in decane containing 0.1 M dichloroacetyl chloride.

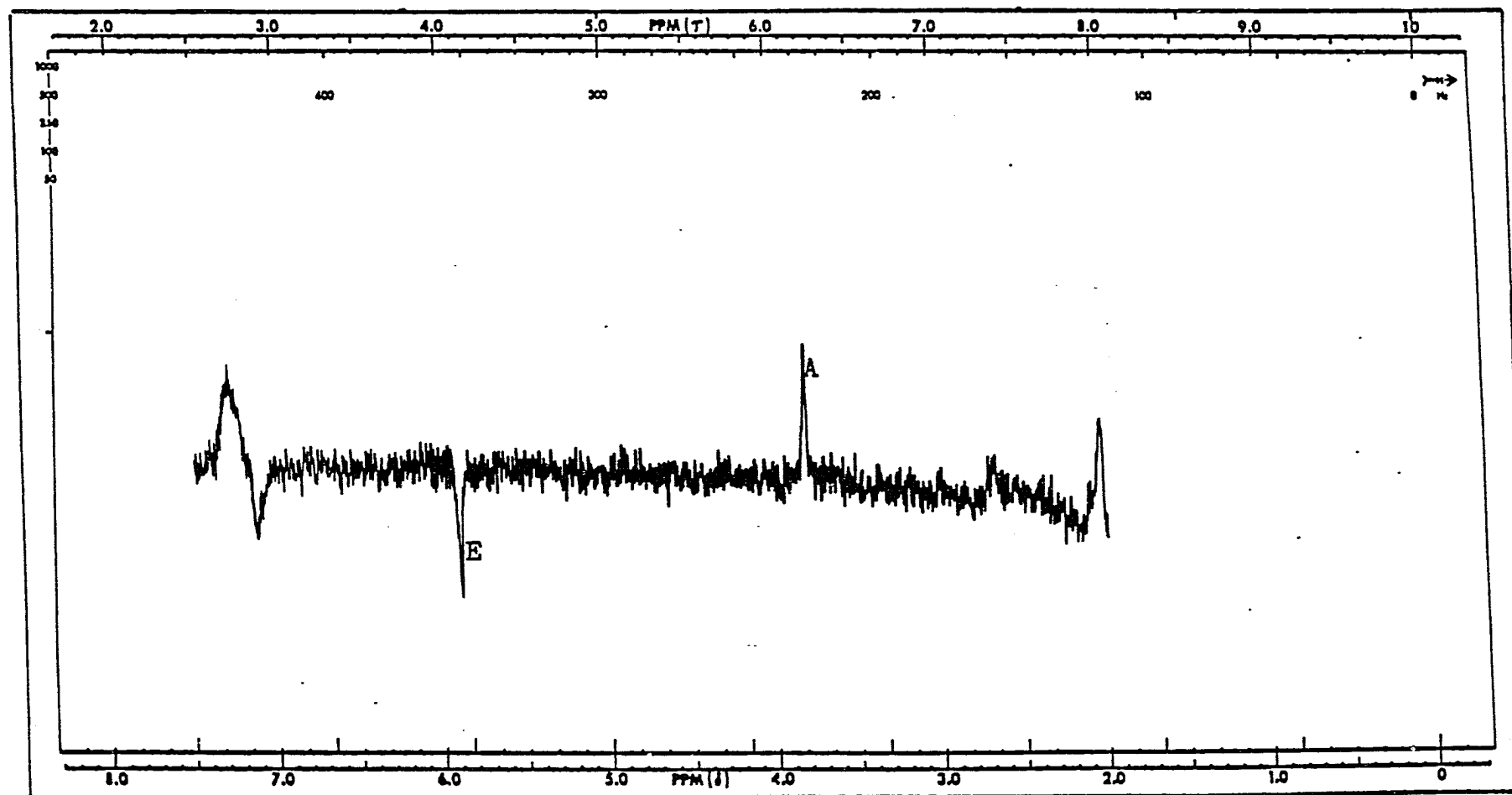


Fig. XV. Decomposition of t-butyl phenylperacetate (1) in decane containing 0.1 M dichloroacetic acid.

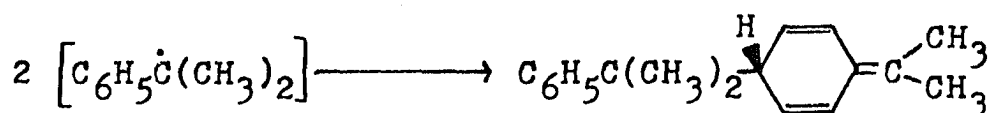
Table 1
CIDNP in systems involving α -keto-radicals

<u>Trap</u>	<u>PhCH₂R</u>	<u>PhCH₂R'</u>	<u>RH</u>	<u>comments</u>
CCl ₃ COCCl ₃	3.97 (A)	5.16 (A)	6.73 (E)	Fig. XI
CCl ₂ HCOCCl ₃	3.83 (A)	5.30 (A)	6.70 (E)	Fig. XII
(CCl ₂ H) ₂ CO	3.83 (A)	5.33 (A)	6.30 (E)	5.50 s (E) 5.07 t (E) 4.50 s (E) 3.45 t (A)
CCl ₃ COCl	3.92 (A)	5.18 (A)	6.16 (E)	Fig. XIII
CCl ₂ HCOCl	3.96 (A)	5.17 (A)	6.18 (E)	Fig. XIV 4.80 t (E)
Ph-OCH ₂ COCl	3.60 t (A)	5.00 (A)		5.18 t (E)
CCl ₂ HCO ₂ H	3.97 (A)		6.80 (E)	Fig. XV
CHCl ₂ CCl ₃	4.10 (A)		6.20 (E)	
CCl ₃ H	4.00 (A)			
CCl ₄	3.90 (A)			
CH ₂ ClCOCl				no CIDNP
(PhCH ₂) ₂ CO				no CIDNP

PhCH₂R=normal coupling product

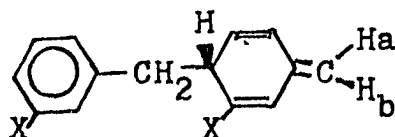
PhCH₂R'=enolic coupling product

of the compounds is analogous to the unsubstituted perester,³³ we could expect to observe the same polarizing pairs. The g-factor of the substituted benzyl radicals, however, differ¹³ from the unsubstituted benzyl radical. By studying these peresters, we were able to insure that the lack of polarization in the geminate cage product (benzyl-t-butyl ether) was not the result of an accidental equivalence of the g-factors of the two interacting radicals. A second result expected from these studies was that they would help in the assigning of structures to the polarized resonances. The benzylic protons of the various products should show a characteristic and predictable shift depending on the substituent. A final purpose was to determine if any polarized products from aromatic ring attack could be detected. While these products are unknown from the coupling of benzyl radicals, there is evidence that they are formed by the coupling of cumyl, diphenylmethyl and triphenylmethyl radicals.⁶³



These quinoid dimers are the result of radical attacks on the ortho or para positions on the aromatic ring. The unsubstituted 1 is unsuitable for studying these products since the spectra of their benzylic protons would exhibit only a single line. The study of ortho and meta substituted peresters would remove the equivalence of the "benzylic" hydrogens (H_a and H_b) in the ring coupled product,

making any multiplet effect clearly observable.



Representative spectra are shown for p-methoxy-1 (figure XVI), p-bromo-1 (figure XVII), p-methyl-1 (figure XVIII), and m-chloro-1 (figure XIX). When these peresters are decomposed in hexachloroacetone, strong CIDNP is observed for the products corresponding to those described for the unsubstituted perester. In no case was there any nuclear polarization observed for the benzyl-t-butyl ether. This information is in agreement with our expectations based on the study of 1.

Table 2 summarizes the chemical shifts of all of the substituted t-butyl phenylperacetates studied. It can be seen that the shift caused by the substituent in the starting perester is apparent in all of the resonances which were assigned to benzylic protons. This correlation of chemical shifts was considered to be a strong indication of the benzylic nature of these resonances and support of the assigned structures. There would be poor correlation expected had these resonances been due to other products resulting from product derived radicals.

The CIDNP generated upon decomposition of m-chloro-1 in HCA (figure XIX) does not show any multiplet effect polarization attributable to the ring coupled dimer. Investigations of other systems in which ring coupling

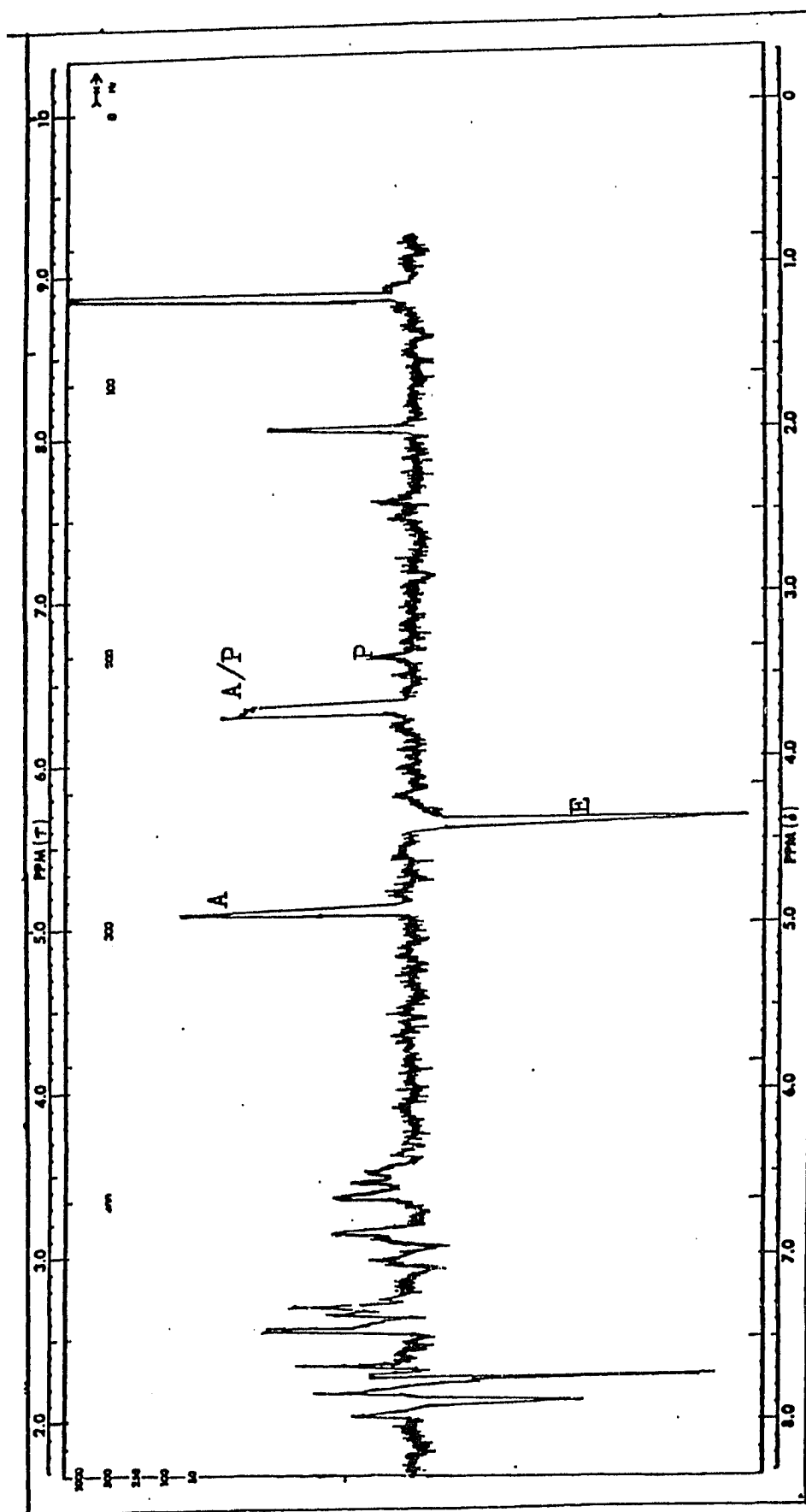


Fig. XVI. Decomposition of *t*-butyl *p*-methoxyphenylperacetate in hexachloroacetone

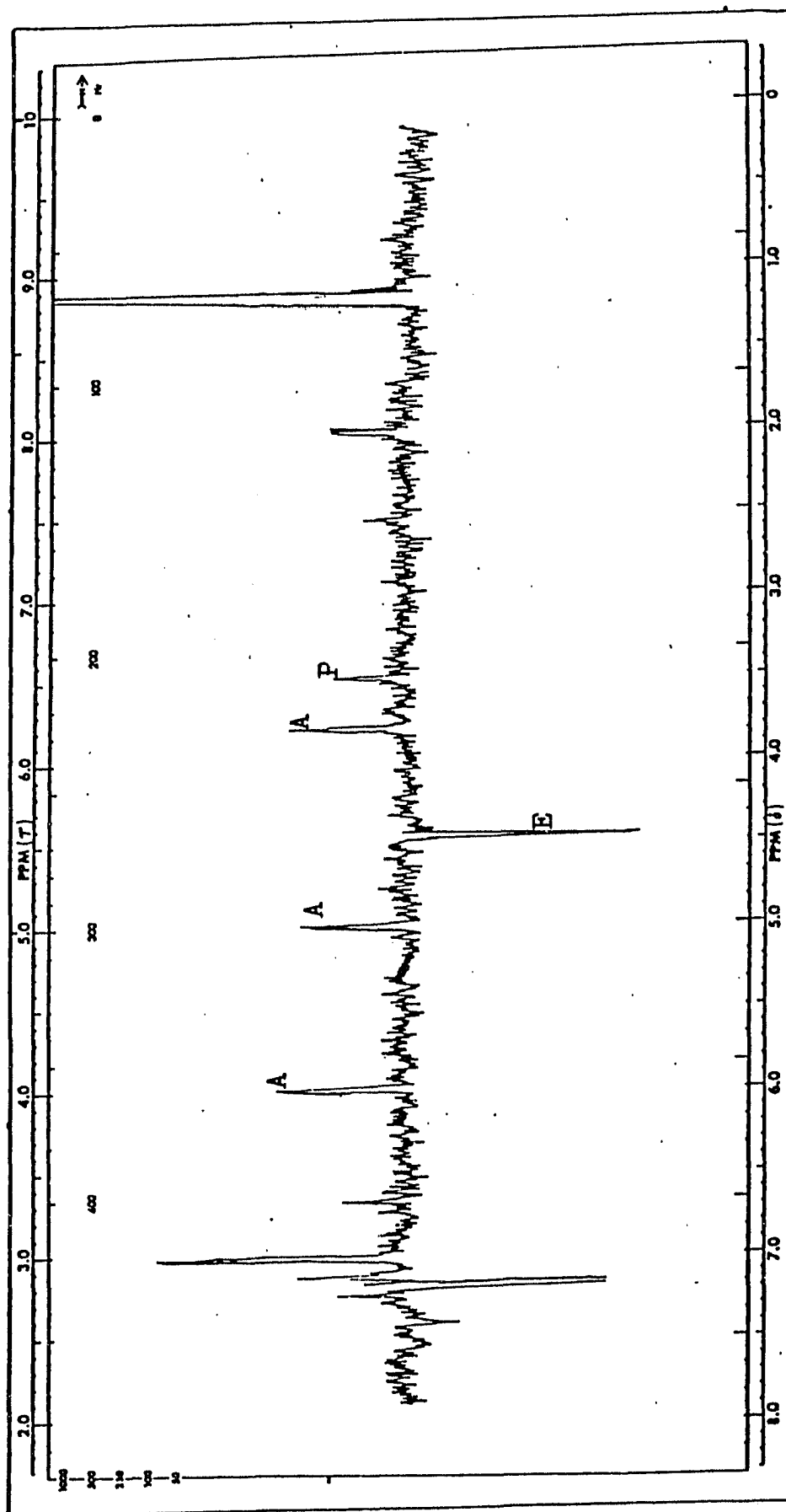


Fig. XVII. Decomposition of *t*-butyl *p*-bromophenylperacetate in hexachloroacetone.

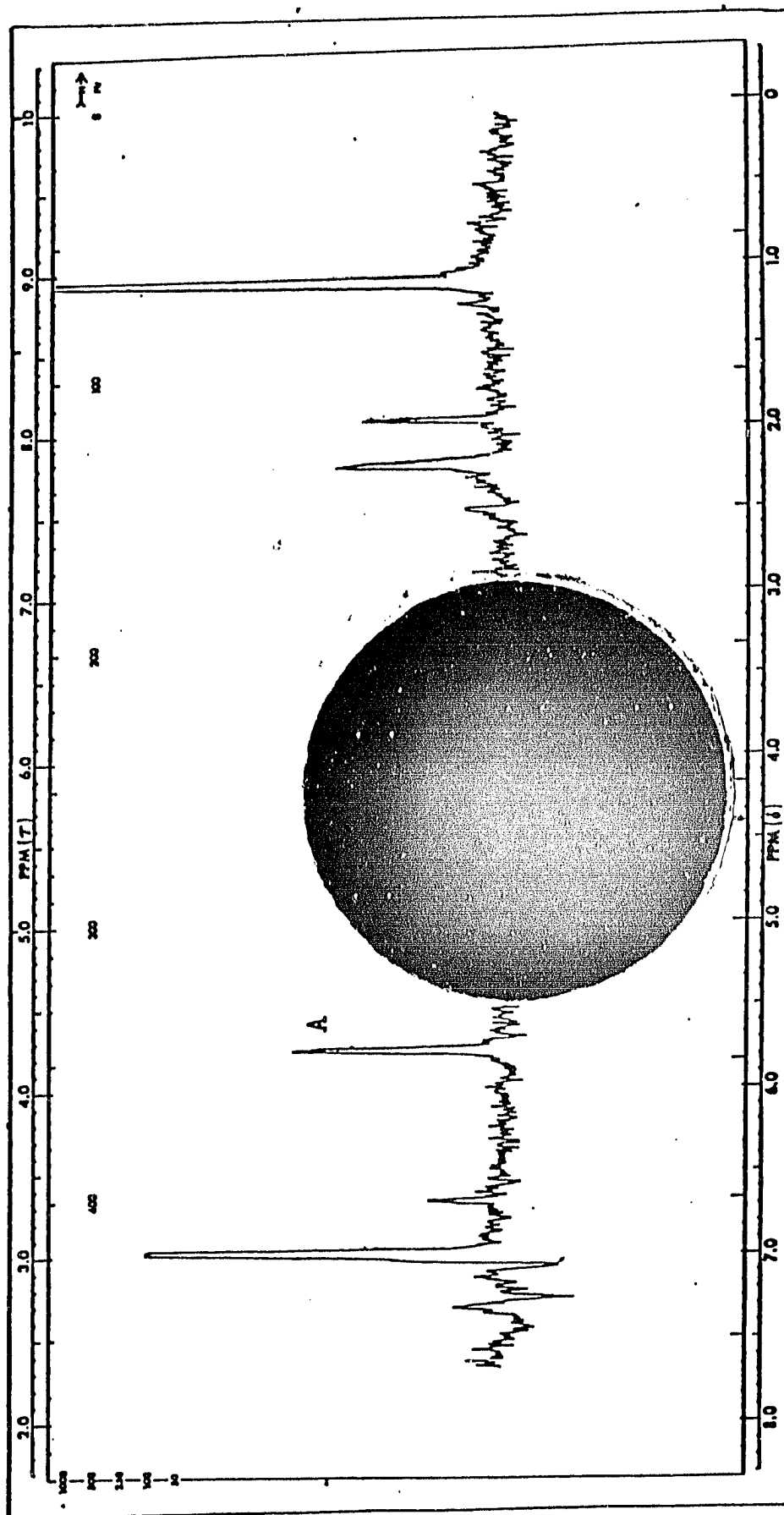


Fig. XVIII. Decomposition of t-butyl p-methylphenylperacetate in hexachloroacetone.

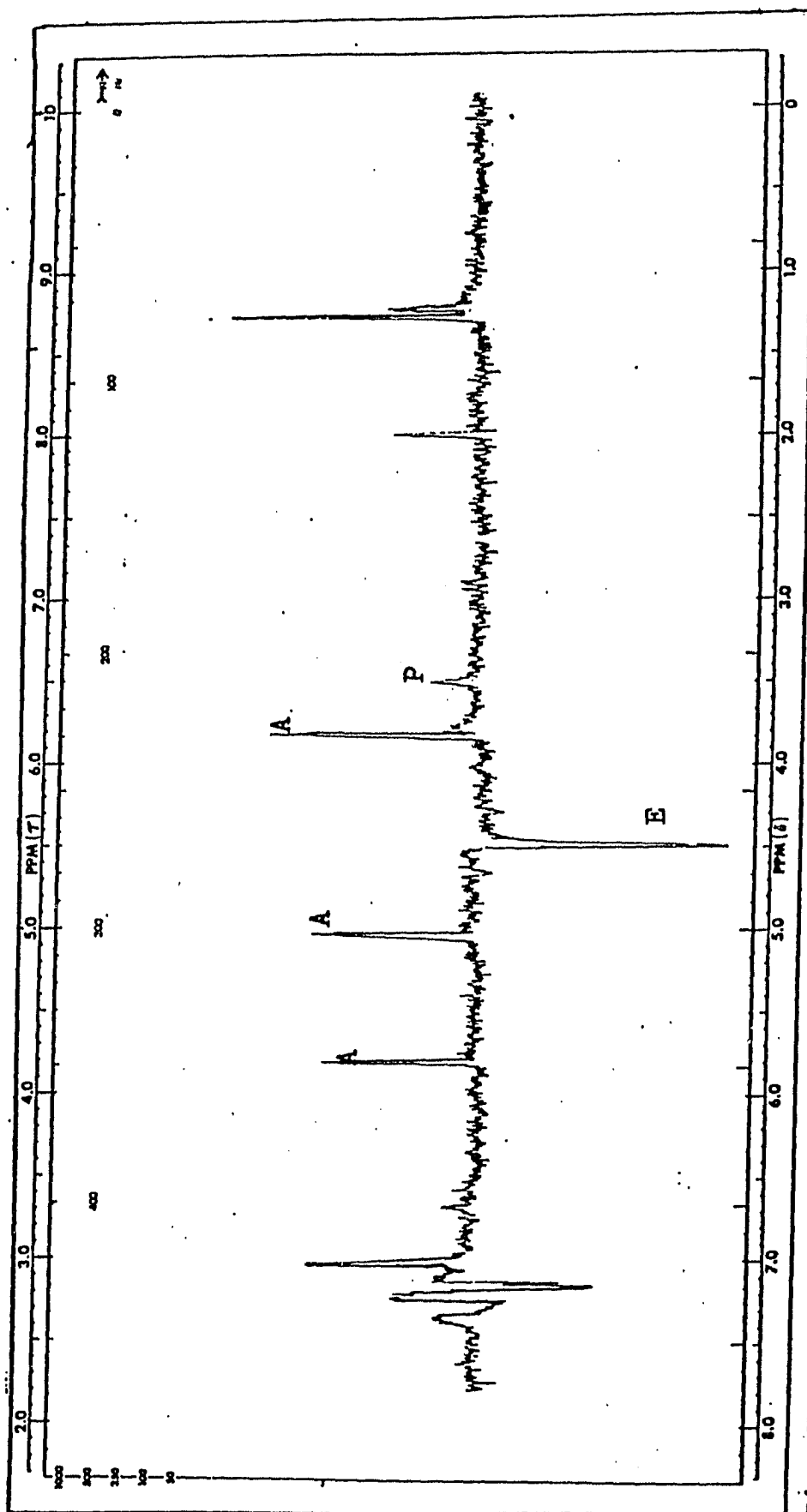


Fig. XIX. Decomposition of *t*-butyl *m*-chlorophenylperacetate in hexachloroacetone

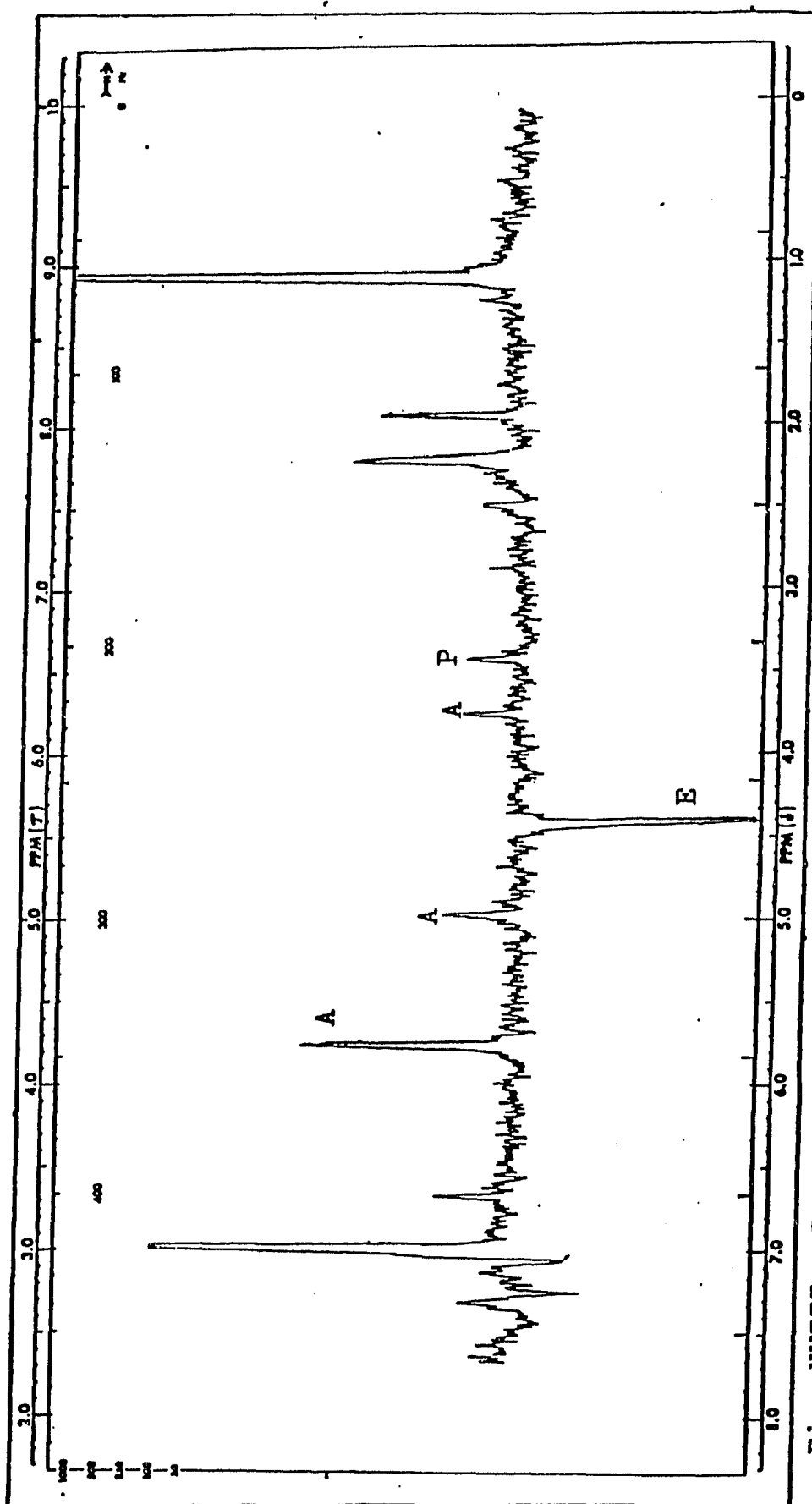


Fig. XVIII. Decomposition of t-butyl p-methylphenylperacetate in hexachloroacetone.

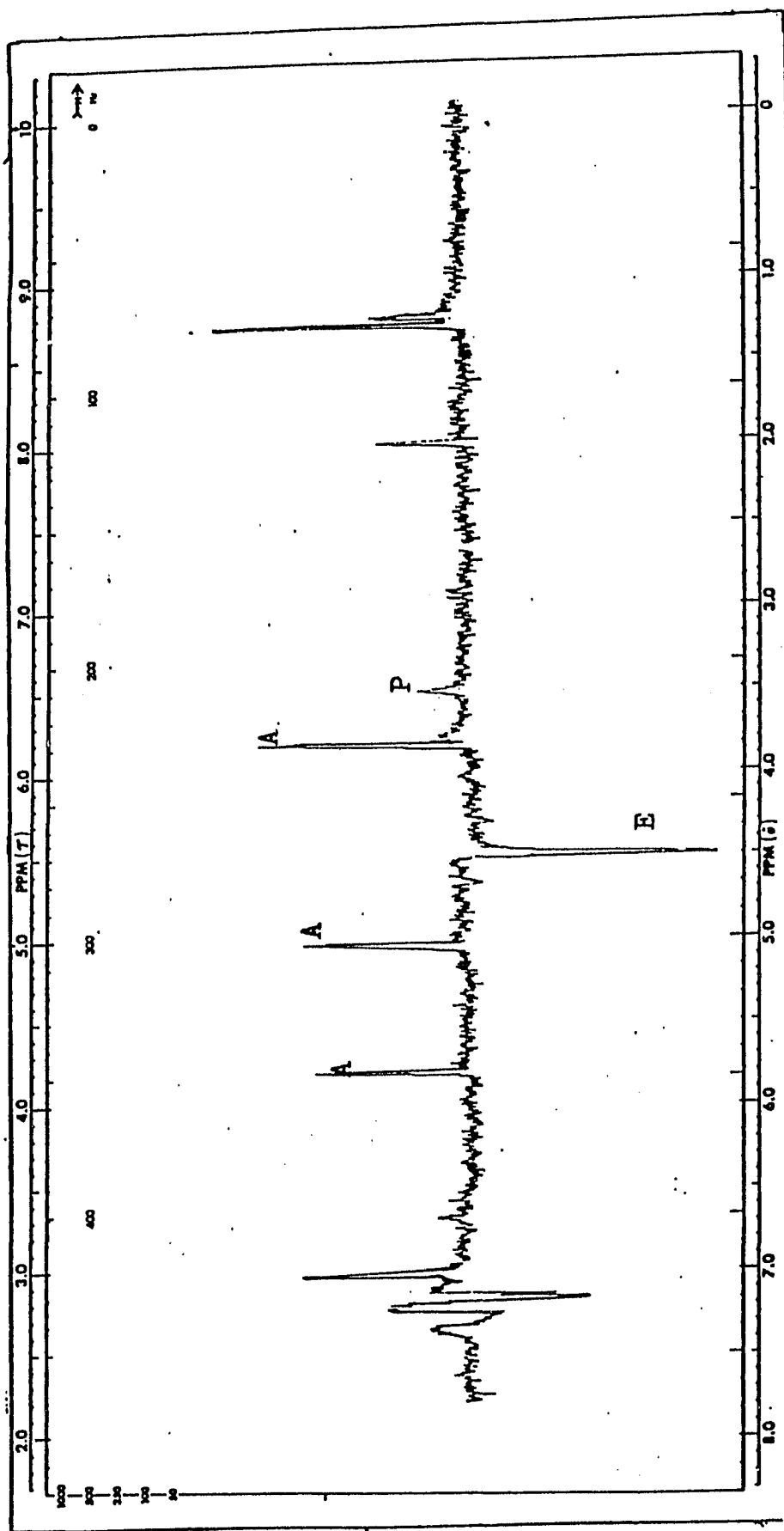


Fig. XIX. Decomposition of t-butyl m-chlorophenylperacetate in hexachloroacetone

Table 2
Chemical Shifts of the Benzylic Protons of the Products of t-butyl phenylperacetates

R	$\text{RCO}_2\text{C}(\text{CH}_3)_3$	RCl	$\text{RCCl}_2\text{COCCl}_3$	$\text{ROC} \begin{smallmatrix} \diagup \text{CCl}_3 \\ \diagdown \text{CCl}_2 \end{smallmatrix}$
$\text{C}_6\text{H}_5\text{CH}_2-$	3.60 δ	4.45 δ	3.80 δ	5.00 δ
<i>p</i> -Br- $\text{C}_6\text{H}_4\text{CH}_2-$	3.65	4.50	3.83	5.02
<i>p</i> -Cl- $\text{C}_6\text{H}_4\text{CH}_2-$	3.60	4.50	3.80	5.03
<i>m</i> -Cl- $\text{C}_6\text{H}_4\text{CH}_2-$	3.53	4.49	3.86	5.03
<i>o</i> -Cl- $\text{C}_6\text{H}_4\text{CH}_2-$	3.50	4.45	3.82	5.00
<i>p</i> -F- $\text{C}_6\text{H}_4\text{CH}_2-$	3.49	4.44	3.80	5.00
<i>p</i> -CH ₃ - $\text{C}_6\text{H}_4\text{CH}_2-$	3.67	4.66	3.98	5.13
<i>p</i> -CH ₃ O- $\text{C}_6\text{H}_4\text{CH}_2-$	3.33	4.28	3.56	4.76
<i>m</i> -CH ₃ O- $\text{C}_6\text{H}_4\text{CH}_2-$	3.40	4.35	3.65	4.82

might be expected to be observable (o-chloro-1 and m-methoxy-1) also failed to indicate that this process was present. These results should not be interpreted to indicate that ring coupling does not occur since the lack of CIDNP may be due to other effects. It is entirely possible that the quinoid dimer is extremely unstable and is rapidly converted to either a polymer or rearranged product.

Decomposition of t-Butyl Diphenylperacetate (2)

The decomposition of t-butyl diphenylperacetate (2) occurs by a mechanism which is similar to that followed by 1. There can be little doubt that this perester decomposes by a concerted cleavage of the O-O bond and loss of carbon dioxide. In this case, the diphenylacetoxo radical which would result from a step-wise decomposition would be particularly unstable relative to the diphenylmethyl radical. This compound has been thoroughly studied to determine the nature of the cage products³⁷. It was postulated that there are two cage ethers produced during the decomposition of this compound; the expected coupling ether and a compound resulting from the attack of t-butoxy radicals on the ring of a diphenylmethyl radical. Based on the information obtained from the decomposition of 1, we would expect that neither cage ether would be polarized. As expected, there is no CIDNP observed when this compound is decomposed in hydrocarbon solvents. This was also true when the perester was decomposed in mineral oil where the

cage coupling of peresters in this solvent is known to be very efficient (90%)³⁷.

Nuclear polarization was obtained when this perester was decomposed in solutions of hexachloroacetone (figure XX). The CIDNP obtained is somewhat unusual since only enhanced absorption is observed at 6.33 and 5.41 δ . There is no emission observed except in the aromatic hydrogens. The two enhanced resonances are attributable to 1,1-diphenyl-2,2,4,4,4-pentachlorobutanone (5.41) and diphenylmethyl 2-pentachloropropenyl ether (6.33). These products result from the coupling of diphenylmethyl radicals with the two forms of the PCA radical. The expected escape product, diphenylmethyl chloride, is not observed since the lifetime of the diphenylmethyl radical is longer than the nuclear relaxation time in the radical. Addition of a more efficient radical trap such as bromotrichloromethane results in emission for diphenylmethyl bromide (6.27 δ). This observation is similar to that reported by Closs in reactions involving the benzyl-diphenylmethyl radical pair¹³.

The origin of CIDNP during the decomposition of 2 in HCA is explained in terms of free radical encounters of the benzhydryl and pentachloroacetonyl radicals. The g-factor of the benzhydryl radical is equal to that of the benzyl radical (2.0025) and the α proton would be expected to have a negative hyperfine coupling constant. Application of Kaptein's rule:

$$P = \mu \cdot \epsilon \cdot \Delta g \cdot a_1$$

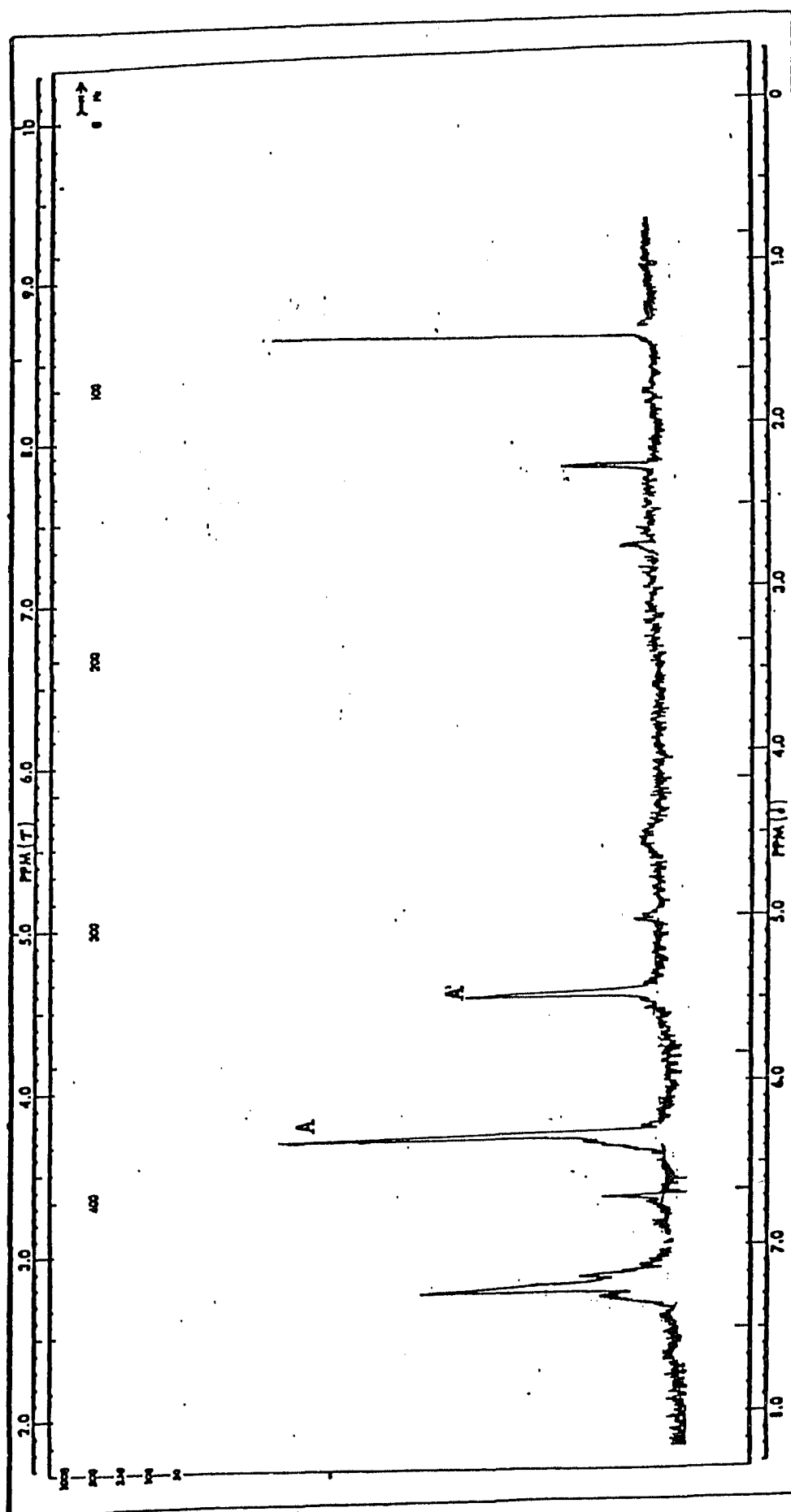


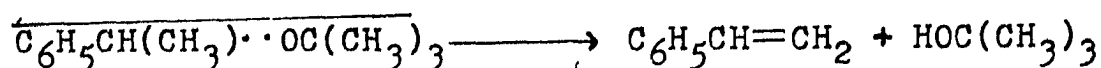
Fig. XX. Decomposition of t-butyl diphenylperacetate in hexachloroacetone.

$$= (+)(+)(-)(-) \Rightarrow A \text{ enhanced absorption}$$

predicts enhanced absorption of both recombination products of this radical pair which is in agreement with the observed spectra.

Decomposition of t-Butyl 2 Phenylperpropionate (3)

The introduction of a methyl group into the α position of a benzyl radical enables the radical to undergo disproportionation as an alternative cage reaction to simple coupling. CIDNP spectra obtained during the decomposition of t-butyl 2-phenylperpropionate (3) in HCA (figure XXI) does not indicate the formation of polarized t-butyl alcohol as a result of the following reaction:



As with other peresters, there is no polarization observed for the cage coupling product 1-phenylethyl-t-butyl ether. Both of these results are consistent with the theory that no nuclear polarization will be developed in radical pairs involving the t-butoxy radical.

Nuclear polarization attributable to the recombination of 1-phenylethyl PCA radical pair, is observed in the vinyl hydrogens of styrene ($H_\alpha = 6.48, H_\beta = 5.55$ δ both multiplets), pentachloroacetone (6.75 δ E), 1-phenylethyl-2-pentachloro-

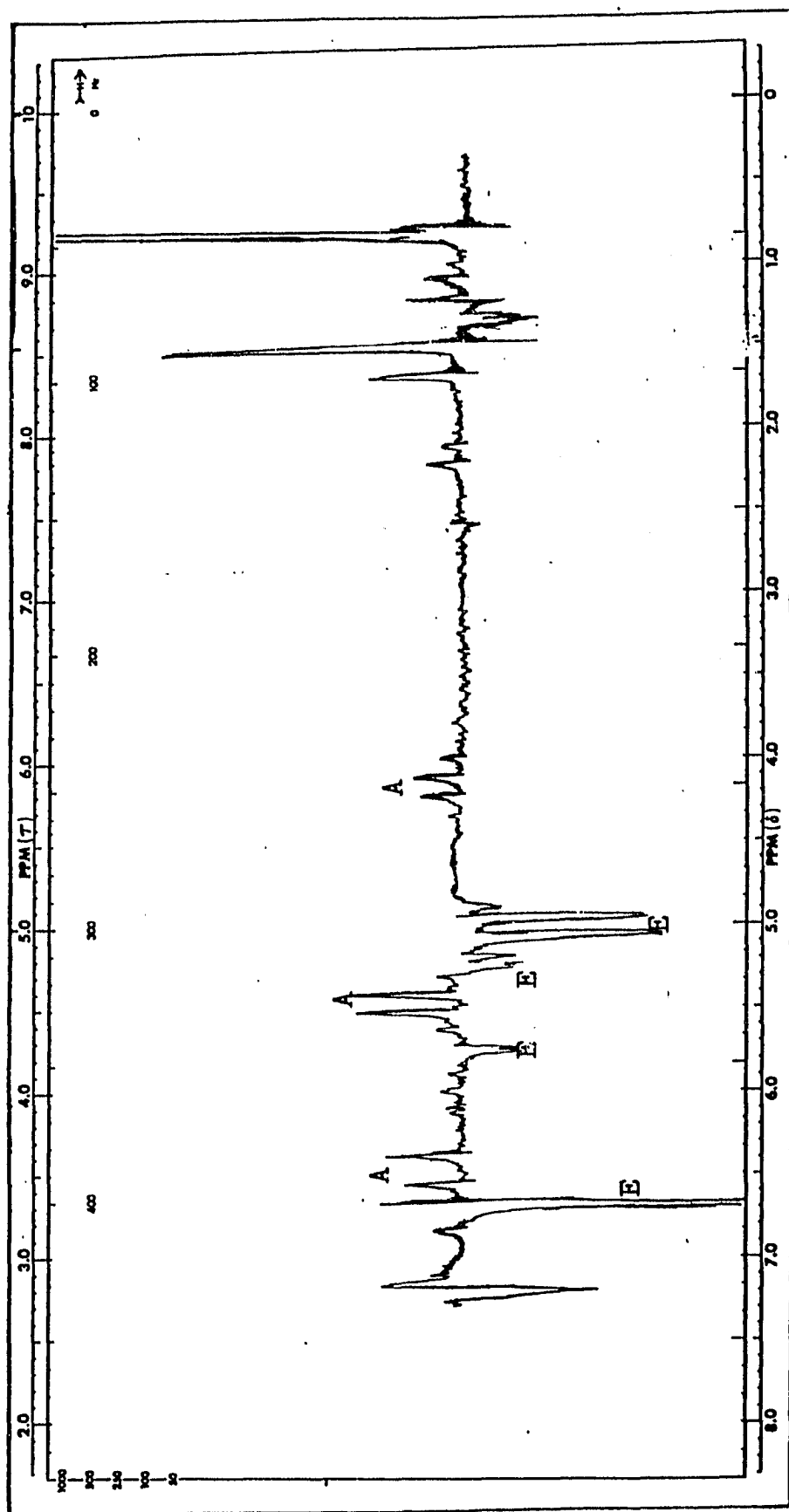
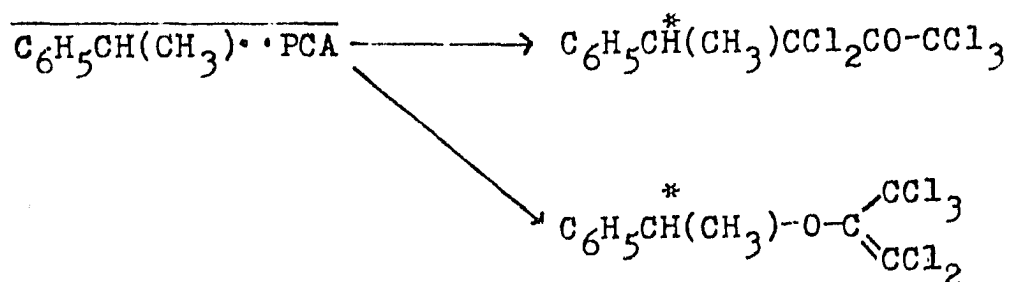


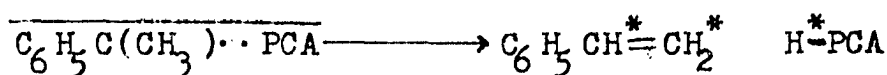
Fig. XXI. Decomposition of t-butyl 2-phenylperpropionate in hexachloroacetone.

propenyl ether (5.52 δ quartet $J=6.7\text{Hz}$. A). and 4-phenyl-1,1,1,3,3-pentachloro-2 pentanone (4.20 δ quartet $J=6.7\text{Hz}$. A). The escape product 1-phenylethyl chloride appears in emission (5.07 δ quartet $J=6.9\text{Hz}$.). Additional polarization in the methyl groups of these products appears from 1.72 to 1.50 δ , the overlap of these resonances make product assignments to these signals uncertain.

The origin of the observed CIDNP is from diffusive encounters of the 1-phenylethyl-PCA radical pair. Coupling of this radical pair results in the formation of the pentanone and 1-phenylethyl-2-pentachloropropenyl ether.



The g-factor of the 1-phenylethyl radical (2.0025) is less than that of the PCA radical (2.008). The coupling of the α hydrogens is negative and the coupling of the β hydrogens is positive. Using Kaptein's rules, enhanced absorption is predicted for the α protons while emission is predicted for the β protons. The alternate recombination reaction involves disproportionation:



Application of Kaptein's rules to this reaction predicts enhanced absorption for the α proton of styrene and emission for the β protons and pentachloroacetone.

Escape from this diffusive pair produces 1-phenylethyl chloride which is expected in emission. These results are consistent with the observed spectra.

Decomposition of t-Butyl 2,2-Diphenylperpropionate (4)

Further substitution of the α position results in radicals which have no α protons. In the previous reactions, the α protons were strongly polarized and easily assigned to products. In the absence of these protons, little information could be expected.

The decomposition of t-butyl 2,2-diphenylperpropionate (4) in HCA (figure XXII) results in strong polarization for pentachloroacetone (6.73 δ E) and in diphenylethylene (5.35E). These products indicate the disproportionation of a diphenyl ethyl-PCA radical pair. The phase of the CIDNP is consistent with a diffusive encounter of these radicals. As expected, there is nuclear polarization observed for the aromatic and methyl protons of products. These resonances were not be assigned to particular products. The signals which are marked SSB are the result of spinning side bands of polarized resonances.

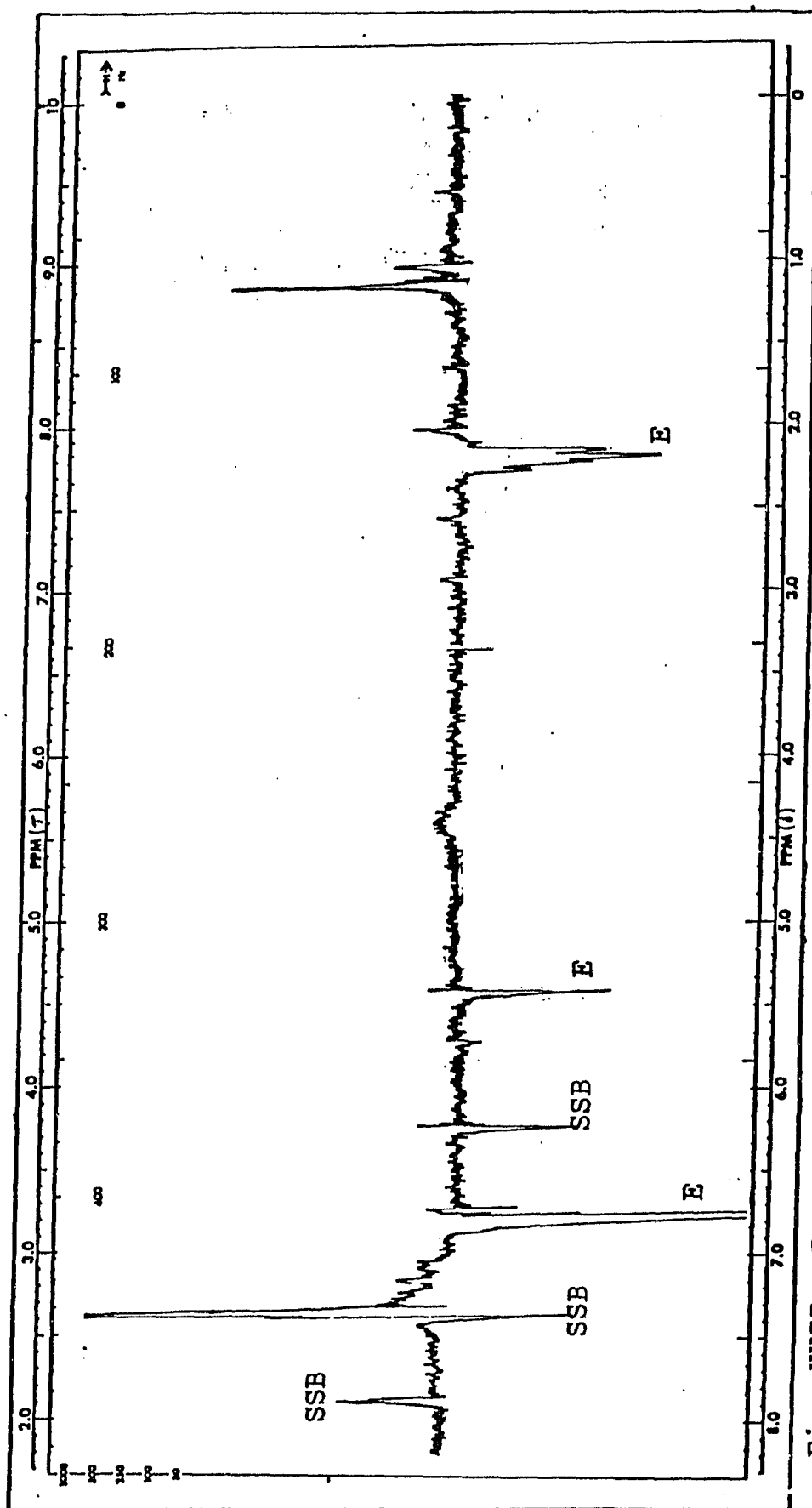
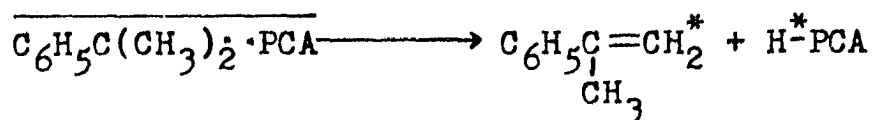


Fig. XXII. Decomposition of t-butyl 2,2-diphenylperpropionate (4) in hexachloroacetone

Decomposition of t-Butyl α -Phenylperoxy-iso-Butyrate (5)

The decomposition of t-butyl α -phenylperoxy-iso-butyrate (5) results in emission for pentachloroacetone (6.75 δ E) and α -methyl styrene (5.30, 5.10 and 2.2 δ) (figure XXIII). In this case, both the vinylic and allylic protons of α -methyl styrene are visible in emission. There is enhanced absorption observed for the methyl protons of an unidentified product. The products and the observed CIDNP are consistent with free radical encounters of the cumyl-PCA radical pairs and the following reaction.



Decomposition of t-Butyl Perpivalate (6)

The final perester studied in this series of methyl and phenyl substituted peracetates is t-butyl perpivalate (6) (pivalate=trimethylacetate). CIDNP is observed when this compound is decomposed in HCA (figure XXIV) for pentachloroacetone and isobutylene (3.88 δ). The polarization is caused by diffusive encounters of t-butyl-PCA radical pairs.

The products and polarizations for the methyl and phenyl peracetates are summarized in table 3. The attempted decomposition of t-butyl peroxy-iso-butyrate

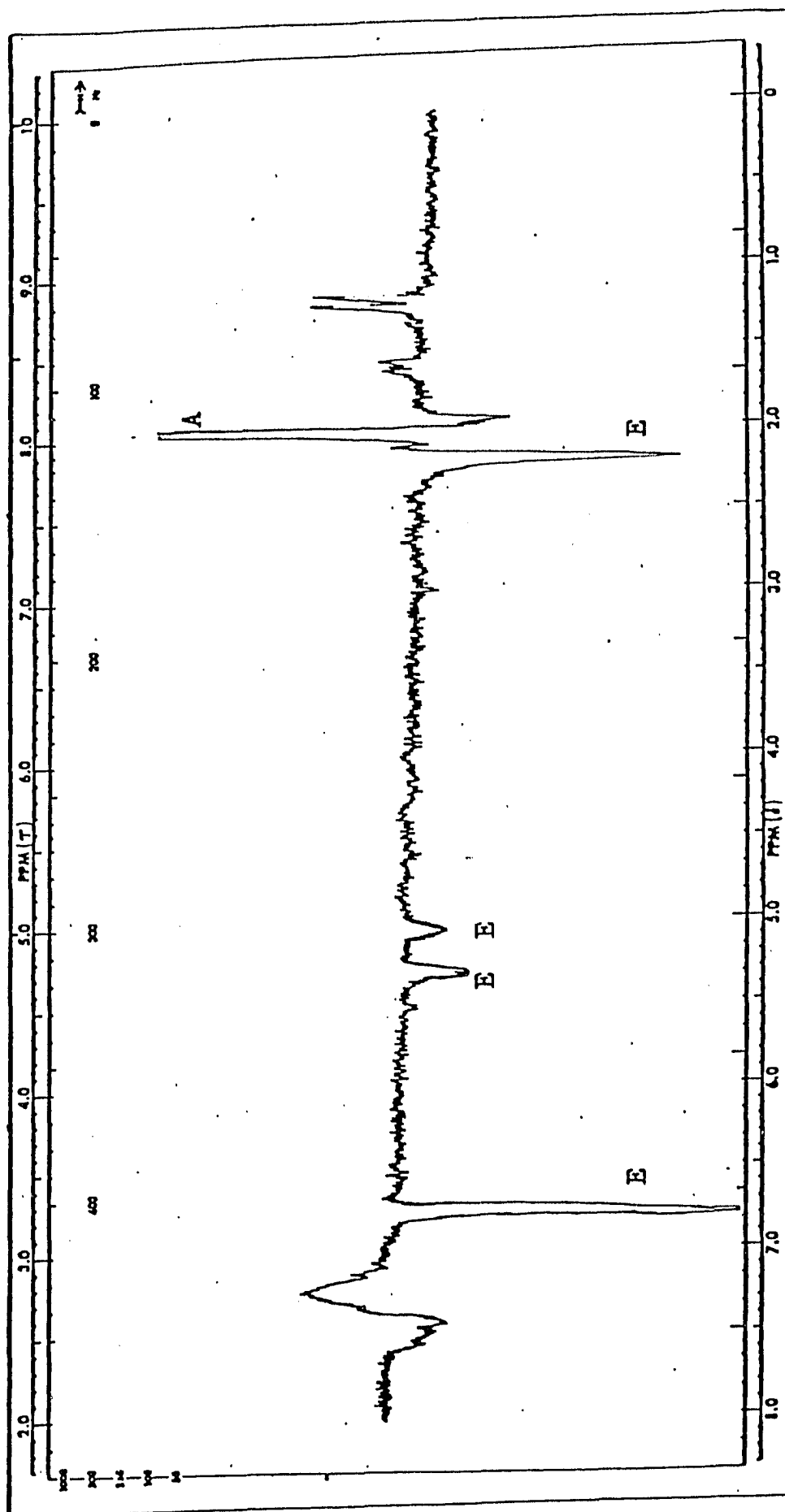


Fig. XXIII. Decomposition of t-butyl α-phenylperoxy-iso-butyrate in hexachloroacetone.

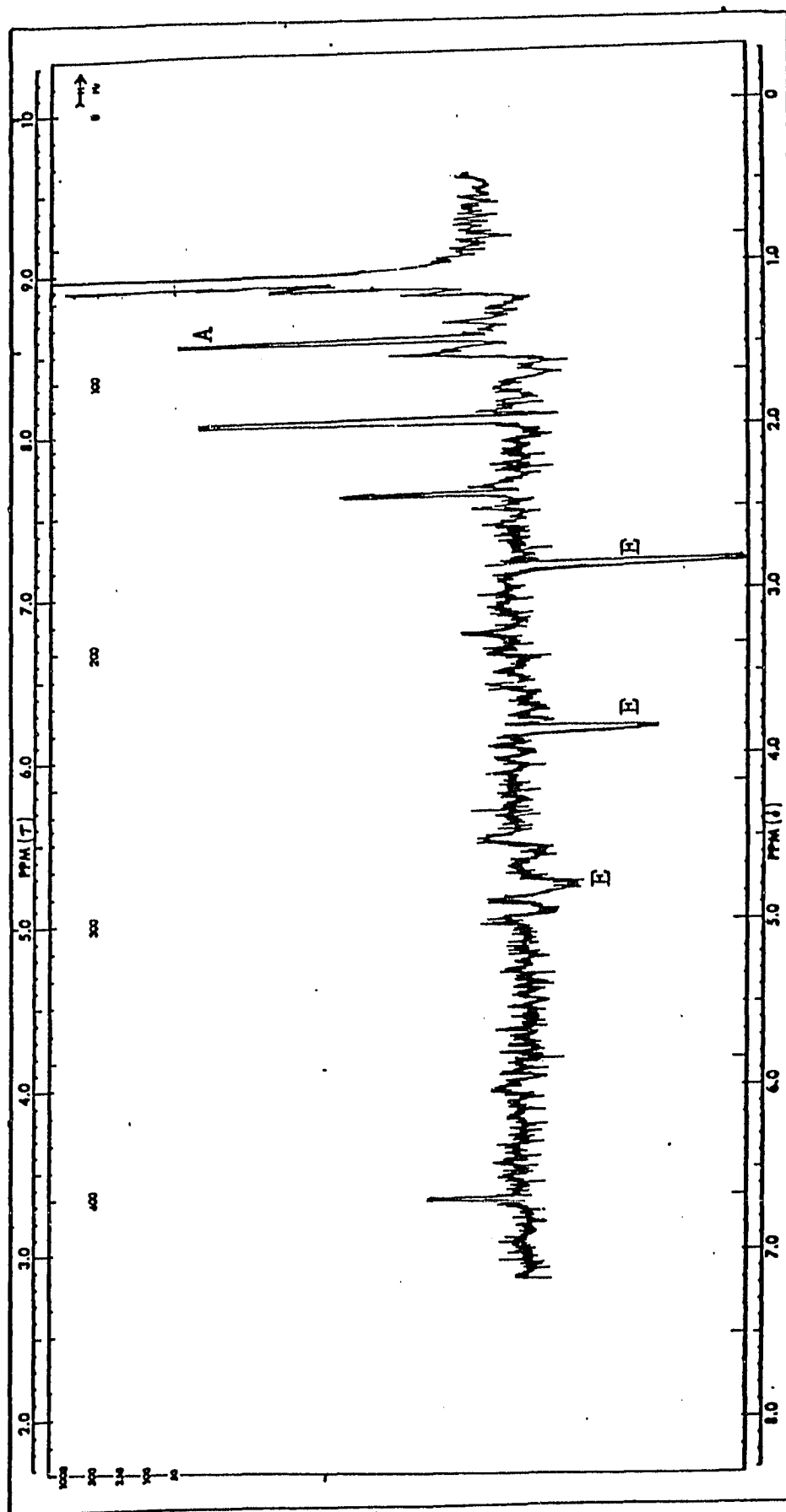


Fig. XXIV. Decomposition of t-butyl perpivalate in hexachloroacetone.

Table 3

Summary of CIDNP from Several Substituted Peracetates in Hexachloroacetone

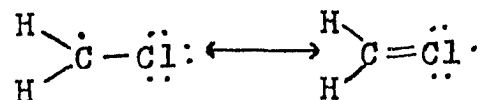
R	RC1	RCCl ₂ COCCl ₃	ROC $\begin{smallmatrix} \text{CCl}_3 \\ \text{CCl}_2 \end{smallmatrix}$	R(-H)	HCcl ₂ COCCl ₃
C ₆ H ₅ CH ₂ -	4.45 δ	3.80	5.00		
C ₆ H ₅ CH(CH ₃)-	5.33	4.50	5.75	5.56-6.10 6.78	6.93
C ₆ H ₅ C(CH ₃) ₂ -	2.18	n.o.	n.o.	5.30 5.10	6.70
(C ₆ H ₅) ₂ C(CH ₃)-	n.o.	n.o.	n.o.	5.36	6.73
(CH ₃) ₃ C-	n.o.	n.o.	n.o.	4.80 2.81	

n.o.= not observed as polarized

and perpropionate did not result in CIDNP in HCA. These peresters did not decompose at a rate which would produce the necessary concentration of free radicals at temperatures below 200°C.

Decomposition of t-Butyl α Halo-Peroxyesters

The presence of a halogen atom has been shown to stabilize the resulting radical of peroxide and perester decompositions. This is a result of the overlap of the unshared p orbitals on the halogen with the odd electron on the carbon. Resonance structures as shown below indicate that the odd spin may reside on either the carbon or the halogen atoms.



Since the haloalkyl radicals resulting from the decomposition of these peresters are considerably more stable than the methyl or the phenyl radical, the decomposition of these peresters would be expected to occur via a concerted cleavage of the O-O bond and loss of carbon dioxide. This has been clearly demonstrated for t-butyl peroxytrichloro-²acetate which decomposes 10 times more rapidly than t-butyl peracetate²⁸. This rate increase is a result of the stability of the trichloromethyl radical reducing the activation energy of the decomposition when a concerted process is followed. There are no published reports on

the kinetic behavior of other halo-peresters (except trifluoroperacetate which we did not study) but the temperature of their decomposition in HCA (to give CIDNP) is considerably lower than t-butyl peracetate. Exceptions to this pattern were t-butyl bromoperacetate and 2-bromoperpropionate which like t-butyl peracetate did not decompose at a substantial rate at 200°C. This thermal instability of the chloro-peresters indicates that the halogen atom is increasing the rate of decomposition which is only to be expected if a concerted mechanism is followed. This process would be expected to be less efficient for bromine, whose outer shell electrons are more diffuse.

Decomposition of t-Butyl Chloroperacetate (7)

The decomposition of 7, like the benzylic peresters, did not result in observable CIDNP when decomposed in dodecane. This is in agreement with our established properties of the t-butoxy radical.

The decomposition of 7 in HCA provides strong CIDNP (figure XXV) resulting from free radical encounters of the chloromethyl-PCA radical pair. The two coupling products of these radicals 1,1,1,3,3,4-hexachlorobutanone (4.32 δ) and chloromethyl 2-pentachloropropenyl ether (5.70 δ) appear enhanced while the escape product methylene chloride (5.20 δ) is in emission. In this radical pair, the PCA radical has the higher g-factor ($g=2.008$ for PCA

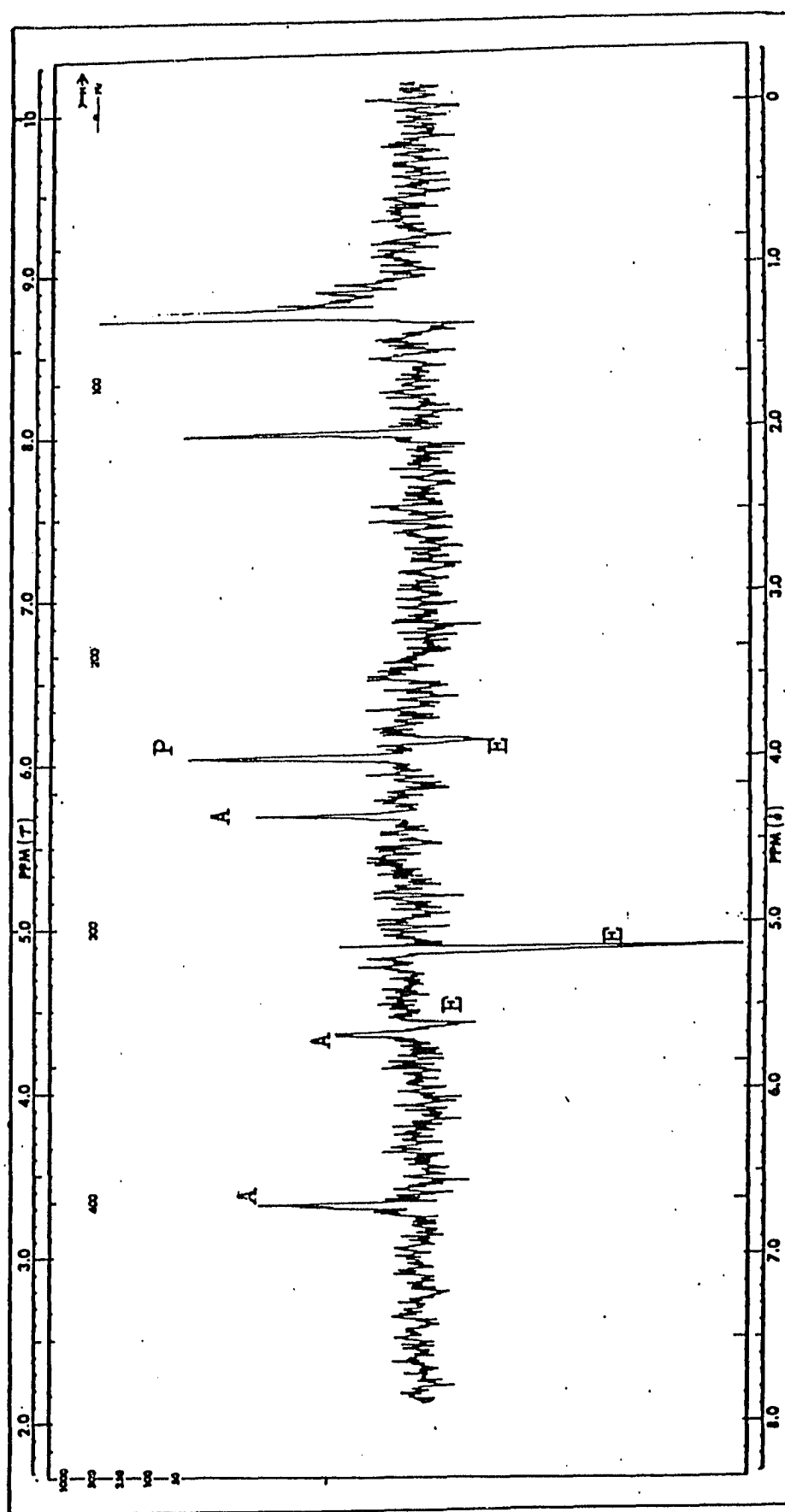


Fig. XXV. Decomposition of t-butyl chloroperacetate (7) in hexachloroacetone.

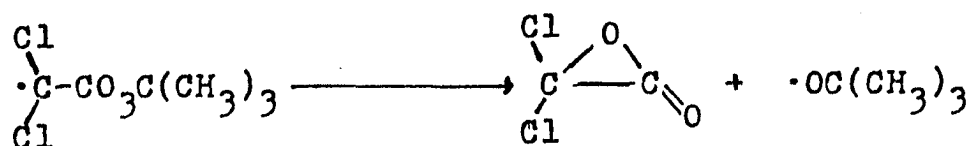
and 2.008 for CH_2Cl) and the hyperfine coupling of the hydrogens of the chloromethyl radical are negative. Application of Kaptein's rule predicts that the recombination products will be enhanced while the escape products will appear in emission. This is in agreement with the observed spectra. Besides these resonances, there are two emission signals which appear at 5.63 δ and 3.85 δ . The structure of the products responsible for these signals has not been determined. They may be due to a radical derived from another component in the reaction mixture. This should be expected since the starting perester and the known products (methylene chloride, etc.) may act as radical traps.

Decomposition of t-Butyl Dichloroperacetate (8)

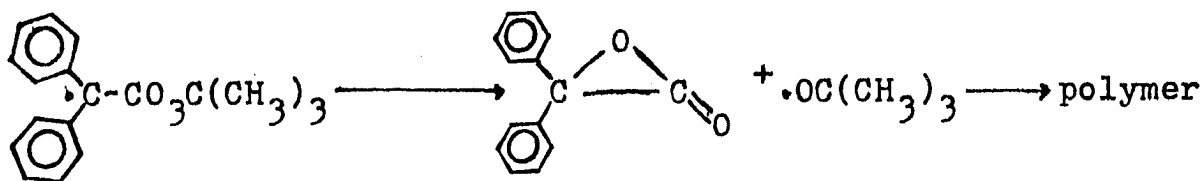
The decomposition of 8 in decane leads to strong emission for two products at 6.47 and 4.50 δ . The emission at 6.47 δ has been assigned to the starting perester which has been reformed by a radical reaction. In this case, 8 can be expected to be an effective radical trap. Decomposition of one perester molecule results in radicals which will abstract hydrogen atoms from the perester.



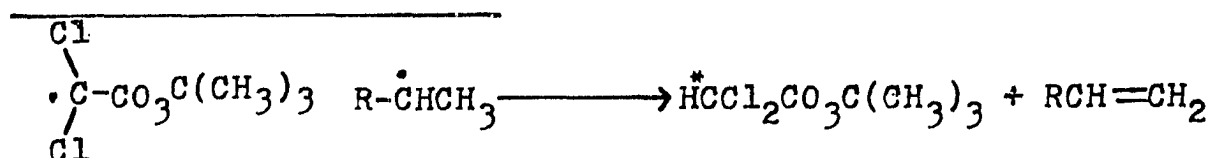
The radical thus formed may then decompose:



or undergo polarizing encounters as free radicals. The structure of this perester derived radical is similar to that observed from the decomposition of di-t-butyl peroxy-diphenylmalonate.



The resulting α -lactone will then undergo a radical induced polymerization. The polarized perester must be formed by a disproportionation reaction between the perester derived radical and a unknown radical. Since the perester derived radical does not have any hydrogens, the polarized proton of the perester must reside on the other partner in the radical pair.



The structure of the other product appearing at 4.50 was not assigned. It may be due to an alkene formed by the disproportionation reaction which formed the perester. The decomposition of this perester is an unusual case, there was, however, no indication of polarization resulting from reactions of the t-butoxy radical. Further study of the

decomposition of this perester in hydrocarbon solvents was not attempted since large parts of the spectrum are obscured by the solvent absorption.

When this perester is decomposed in HCA (figure XXVI), polarization is observed at 7.27(E) and 7.52 δ (A). These resonances have been assigned to chloroform and dichloromethyl 2-(pentachloropropenyl) ether respectively. In this case, the g-factor of both radicals are approximately 2.008. There is, however, a small difference in g-factors between these two radicals which provides the net polarization. In this case, the PCA radical has the higher g-factor leading to enhanced absorption in the coupling products. This same radical pair is responsible for the emission observed in the escape product chloroform. Since the Δg term in this radical pair is small, polarizations in this reaction are weak. Because of the low intensity, only one coupling product of the PCA radical has been observed. The alternate product heptachlorobutanone is obscured by the resonance of the initial perester (6.48) or of pentachloroacetone.

Decomposition of t-Butyl Trichloroperacetate (9)

This perester would be expected to be an effective radical trap as was the dichloroacetate. When t-butyl trichloroperacetate is decomposed in decane, the CIDNP produced is identical to that produced by the dichloroperacetate. This serves to confirm that the polarization

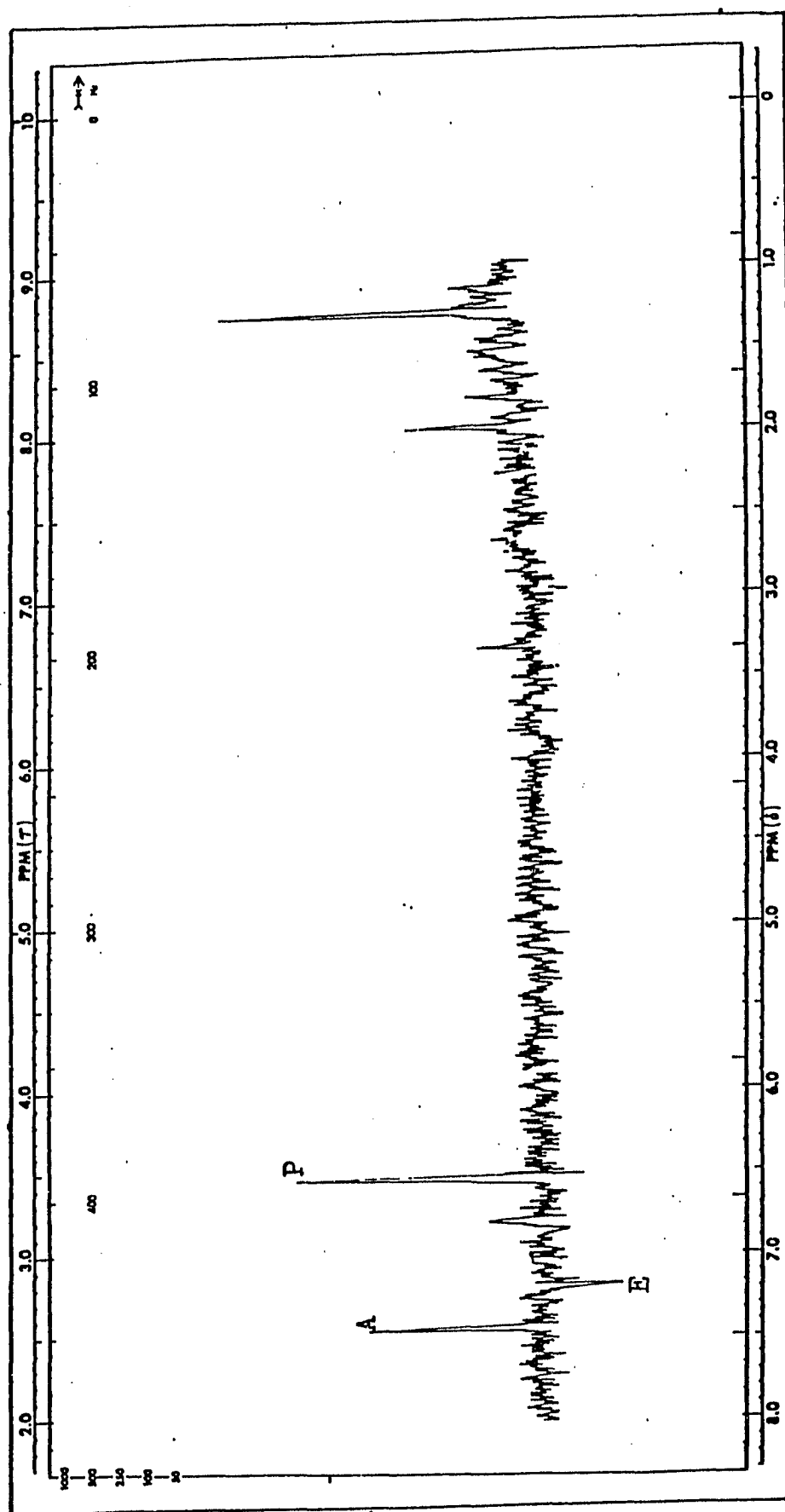
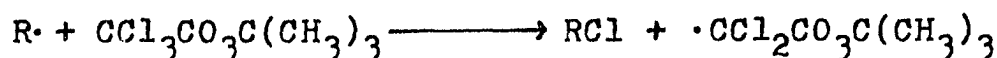
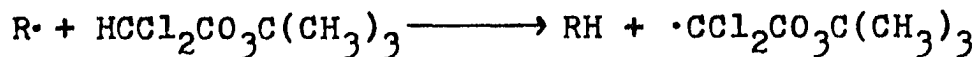


Fig. XXVI. Decomposition of t-butyl dichloroperacetate (8) in hexachloroacetone.

was due to perester derived radicals since the same radical will be derived from each source.



The observation of polarized t-butyl dichloroperacetate is the result of subsequent reactions of the perester derived radicals.

There was no CIDNP observed when this perester was decomposed in HCA. This is not surprising since the expected products do not have any hydrogens which are coupled in the precursor radical pairs. But it does seem to indicate that polarizations are not generally derived from methyl or product derived radicals.

Decomposition of t-Butyl Peroxy 2-Chloropropionate (10)

The decomposition of 10 is expected to be quite similar to the decomposition of t-butyl 2-phenylperpropionate (3). Both peresters decompose to give 1-substituted ethyl radicals which may either couple or disproportionate.

Decomposition of 10 in HCA (figure XXVII) results in nuclear polarization observed for: pentachloroacetone (6.73 δ weak E) 1-chloroethyl 2-pentachloropropenyl ether

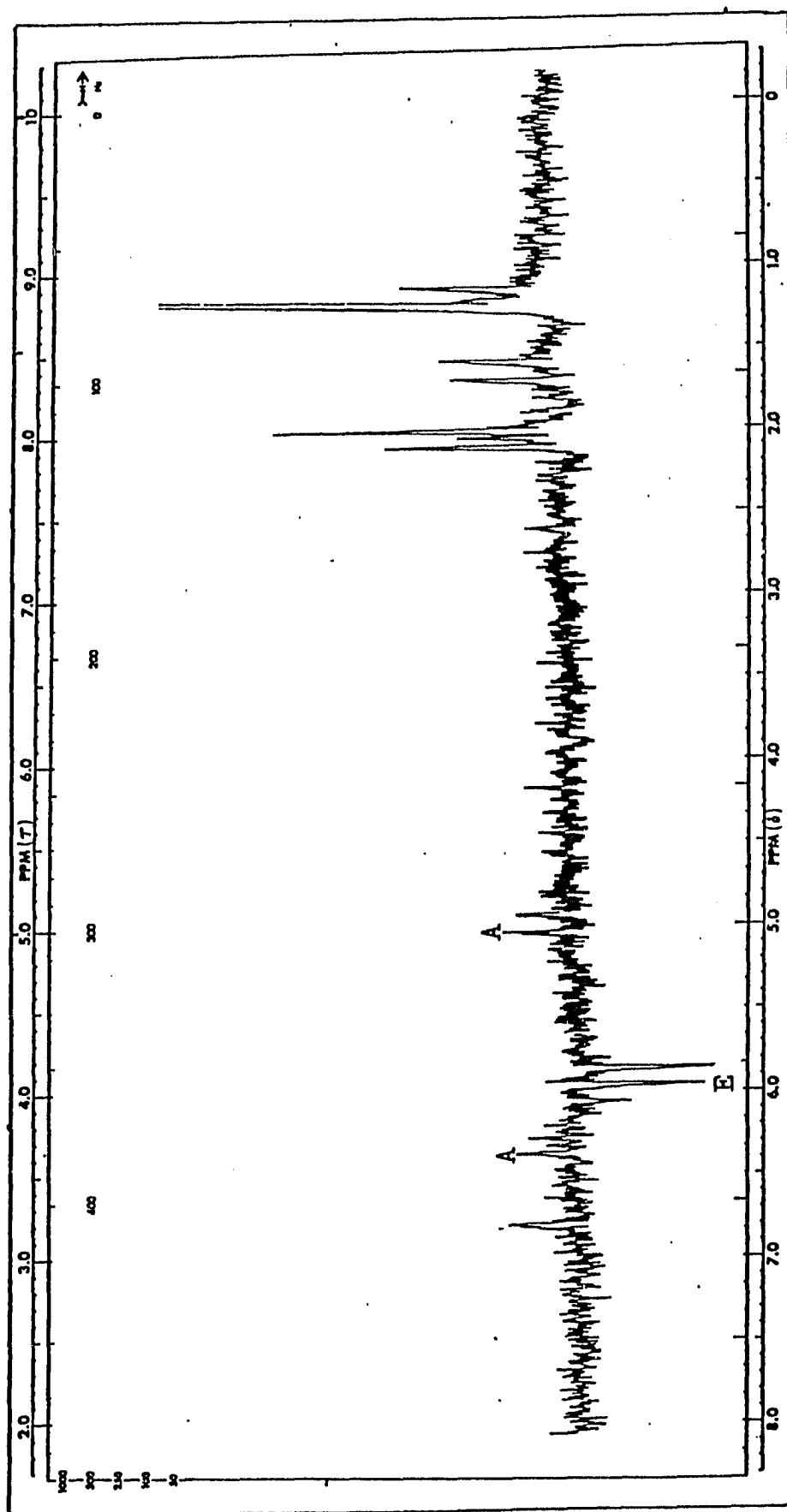


Fig. XXVII. Decomposition of t-butyl 2-chloropropionate (10) in hexachloroacetone.

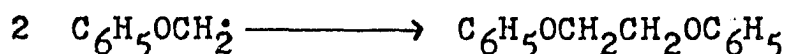
(6.28 δ quartet $J=6$ Hz. A) 1,1-dichloroethane (5.86 δ quartet $J=6$ Hz. E) and 1,1,1,3,3,4-hexachloropentane-2-one (5.05 δ quartet (only central lines visible) $J=6$ Hz. A). These products all result from free radical encounters of the 1-chloroethyl-PCA radical pair. The mechanism for the formation of these products is analogous to that proposed for perester 3. The only apparent difference between the polarization observed in 10 from that of 3 is the occurrence of disproportionation of the ethyl-PCA radical pair. When the ethyl radical is phenyl substituted the formation of styrene must enhance the rate of disproportionation vs. coupling. This is the result of both conjugation in the styrene and steric hindrance in the coupling products which are less important for the chloroethyl-PCA radical pair.

Decomposition of t-Butyl Phenoxyperacetate (11)

The presence of an oxygen in the α position of a peroxy-ester has been shown to greatly increase the rate of decomposition. This can be rationalized by stabilization occurring due to polar effects in the transition state leading to the formation of radicals⁶⁶.

Decomposition of t-butyl phenoxyperacetate in HCA results in CIDNP observed only for the aromatic protons. It seems likely that the relatively stable phenoxymethyl radical is acting as a trap for any free radicals formed. Diffusive encounters of the phenoxymethyl radicals result

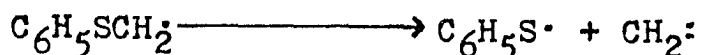
in multiplet effect polarization visible in the aromatic protons of the coupling product 1,2-diphenoxyethane:



The interaction of the unpaired electron with the ring protons has been demonstrated by ESR studies of the phenoxymethyl radical⁶⁷. Since the phenoxymethyl radical is acting as an effective radical trap, there is no opportunity to observe the formation and reactions of PCA radicals.

Decomposition of t-Butyl Thiophenoxyperacetate (12)

Like oxygen, sulfur is able to accelerate the decomposition of peroxyesters. The resulting thiophenoxymethyl radicals can further decompose to give thiophenoxy radicals and methylene⁶⁸.



Product studies in benzene indicate the formation of 1,2-bis-(thiophenoxy)ethane (1%) dithiophenoxymethane (2%) and diphenyldisulfide (31%)⁶⁸. These results indicate that the decomposition of the thiophenoxymethyl radical is rapid and efficiently produces the carbene. Trapping studies with styrene yields phenylcyclopropane in low yield.

The CIDNP produced in reactions involving carbenes has been thoroughly studied and recently reviewed by Roth⁶⁹. It is known that nuclear polarization is generated after methylene abstracts a chlorine atom from the solvent

creating a chloromethyl solvent derived radical pair. The multiplicity of the precursor carbene is retained in the radical pair. When methylene was generated from the photolysis of diazomethane in carbon tetrachloride, CIDNP was observed in both the coupling ($\text{CH}_2\text{ClCCl}_3$) and escape (CH_2Cl_2) products.

The decomposition of 12 in HCA (figure XXVIII) shows strong polarization at 6.70, 5.97 and 3.00 δ as well as in the aromatic region. An unusually short lived (about 30 seconds) emission which was attributed to phenyl chloromethyl sulfide appears at 4.99 δ . There were no traces of products resulting from methylene insertion into the C-Cl bond of HCA (methylene chloride or hexachlorobutanone). A detailed investigation of this perester was not attempted because of the difficulty in assigning products and the unavailability of suitable model compounds.

Decomposition of di-*t*-Butyl Peroxyoxalate (13)

This perester is known to decompose in several steps to give *t*-butoxy radicals³⁹,



In viscous solvents there can be a substantial amount of cage coupling to give di-*t*-butyl peroxide as a cage product³⁹. Escape from this geminate cage will result in trapping by the solvent (SH) or decomposition of the *t*-butoxy radical.

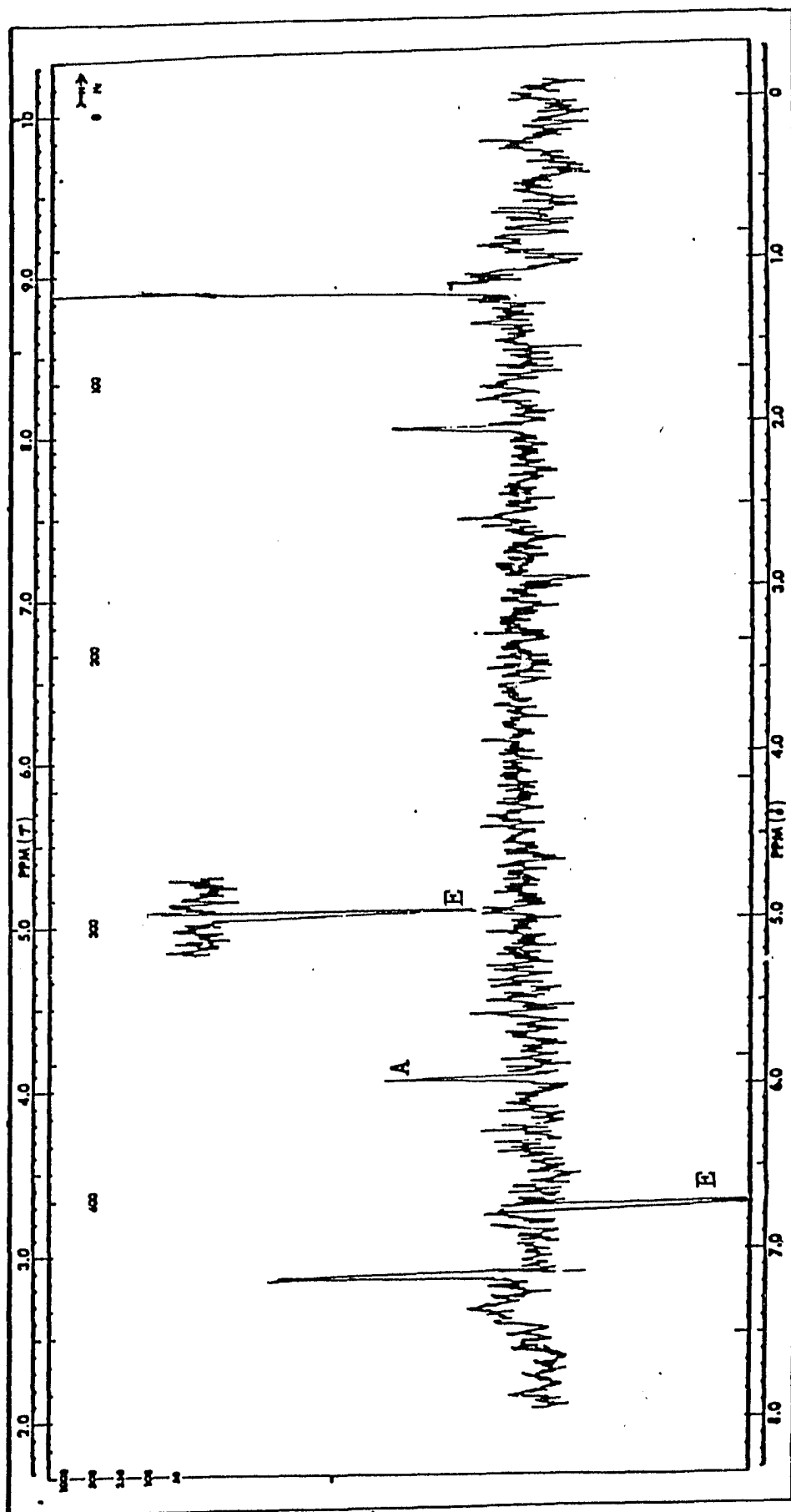


Fig. XXVIII. Decomposition of t-butyl thiophenoxypacetate (12) in hexachloroacetone.

Because of these reactions, 13 can be used to study the reactions involving the free t-butoxy or methyl radicals.

The decomposition of this compound in chlorinated hydrocarbons gives unusual results. When 13 is decomposed in carbon tetrachloride, strong CIDNP is observed for methane (0.15 δ E), methyl chloride (2.83 δ E), 1,1,1-trichloroethane (2.65 δ A) and chloroform (7.27 δ E) (figure XXIX). The polarization is developed during diffusive encounters of methyl-trichloromethyl radical pairs. The trichloroethane is the result of the coupling of these pairs and exhibits the expected (from Kaptein's rule) enhanced absorption. Escape from this pair will result in the scavenging of both the methyl and trichloromethyl radicals to give methyl chloride or methane and carbon tetrachloride. What is unusual in this reaction is the nuclear polarization observed in chloroform. This cannot be due to the initial polarizing pair since there are no protons on the trichloromethyl radical to retain the polarization. Instead this emission is the result of the abstraction of a polarized proton (in a product such as methyl chloride) by the trichloromethyl radical. This "transfer effect" has been postulated by den Hollander and requires that the trichloromethyl radical attack the newly formed methyl chloride before nuclear spin relaxation destroys the nuclear polarization.⁷⁰ This may be shown by the following reactions:

,

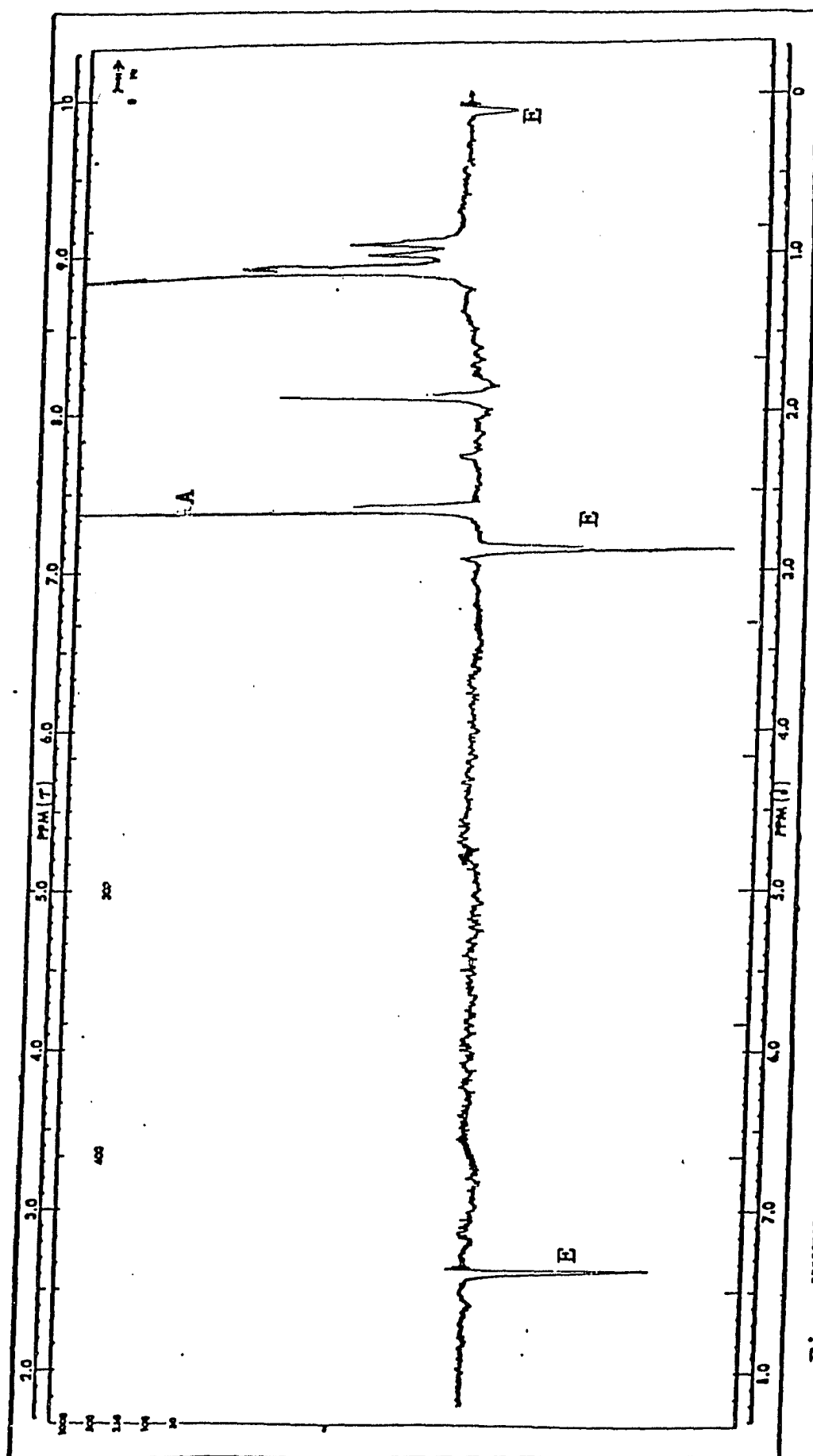
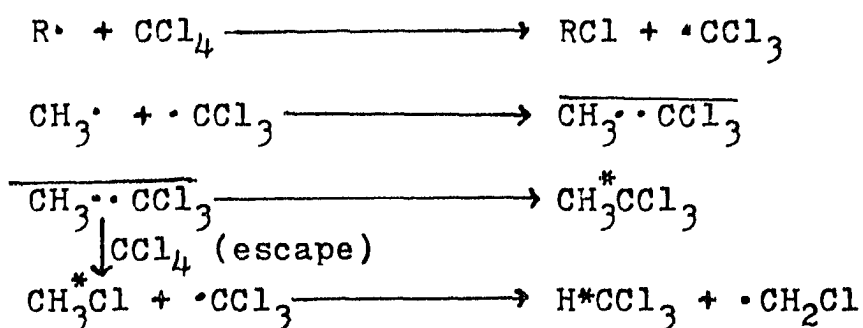


Fig. XXIX. Decomposition of di-t-butyl peroxyoxalate in carbon tetrachloride.



The resulting chloromethyl radicals may combine with tri-chloromethyl radicals giving weakly polarized 1,1,1,2-tetrachloroethane (A). The polarization of this compound is developed in the diffusive encounters of the chloromethyl-trichloromethyl radical pair. The escape product, of this pair, methylene chloride, is not observed presumably due to a low intensity of the resonance and relaxation effects in the radical.

Similar observations of the transfer of a polarized proton were observed in the decomposition of 13 in chloroform-d (figure XXX) and in hexachloroacetone (figure XXXI).

In figure XXX the 1,1,1-trichloroethane (coupling of methyl-trichloromethyl pairs) appears enhanced at 2.62 δ and the escape product methane-d₁ appears as a 1:1:1 triplet at 0.10 δ . Weak emission is observed from chloroform via transfer of the methane polarization.

The polarization observed in HCA is considerably more complex. The initial polarizing pair (methyl-PCA) leads to enhanced absorption for 1,1,1,3,3-pentachlorobutan-2-one (2.38 δ) and methyl pentachloropropenyl ether (3.34 δ) as well as emission for methyl chloride and methane. These

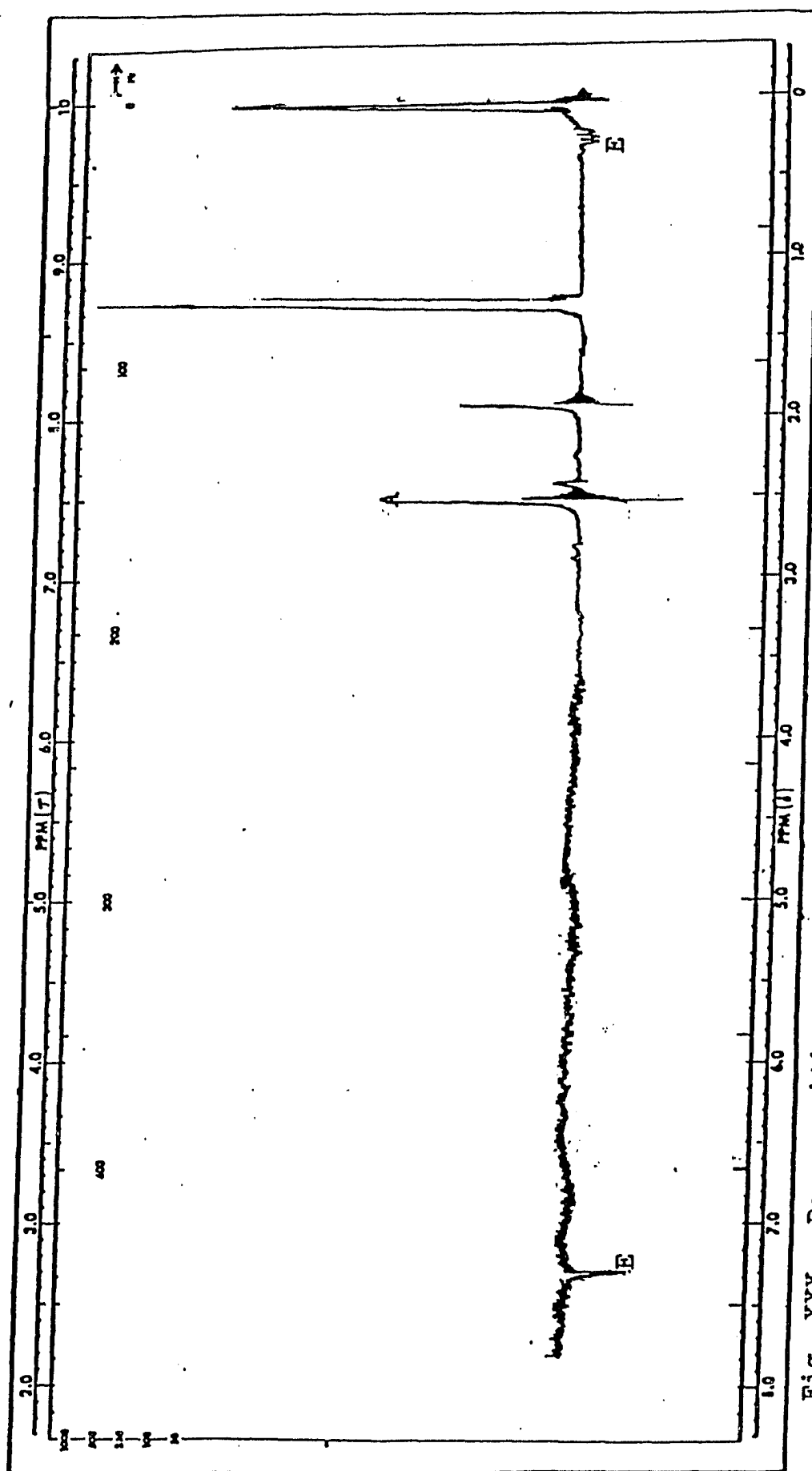


Fig. XXX. Decomposition of di-*t*-butyl peroxyoxalate in chloroform-*d* containing 1% TMS.

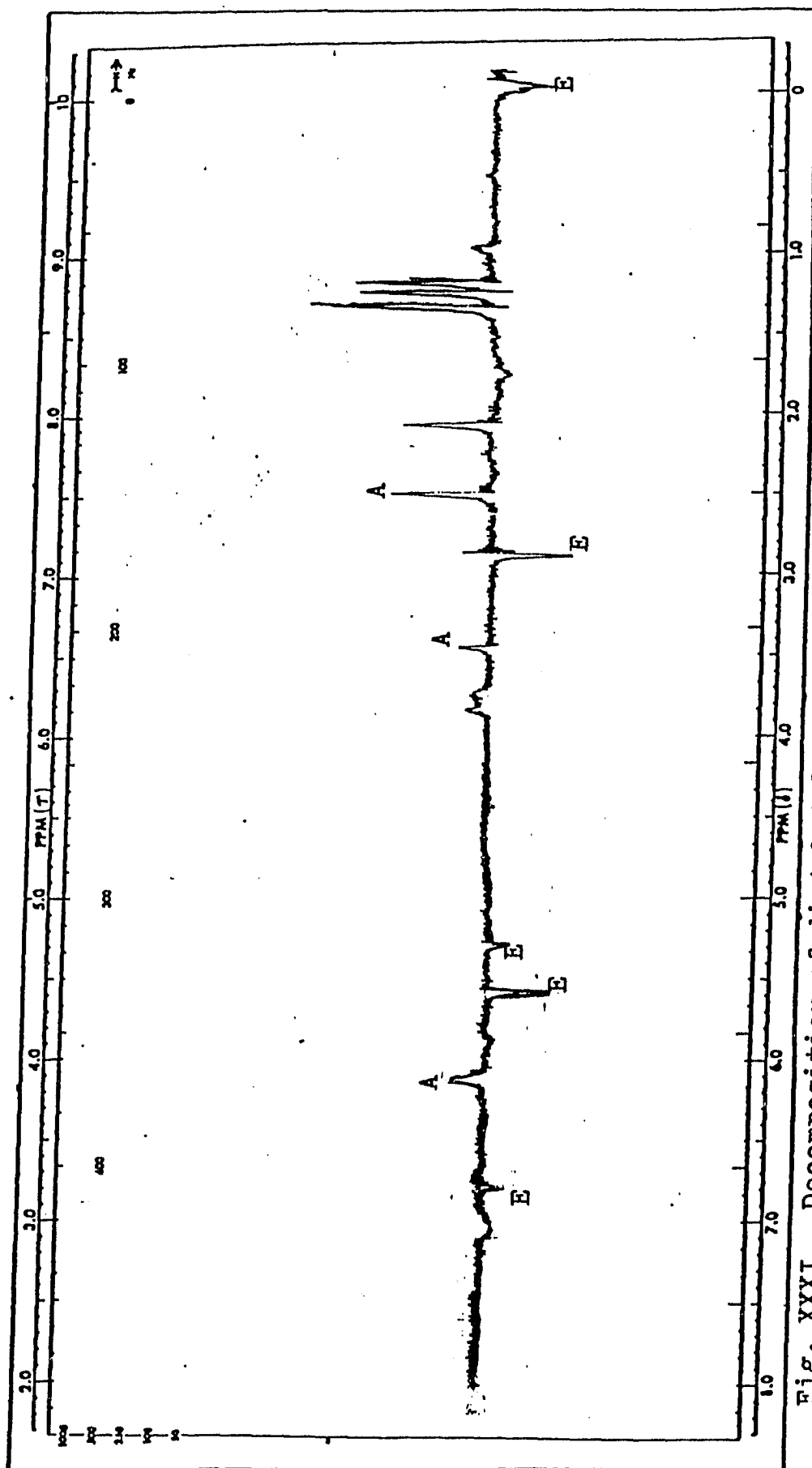
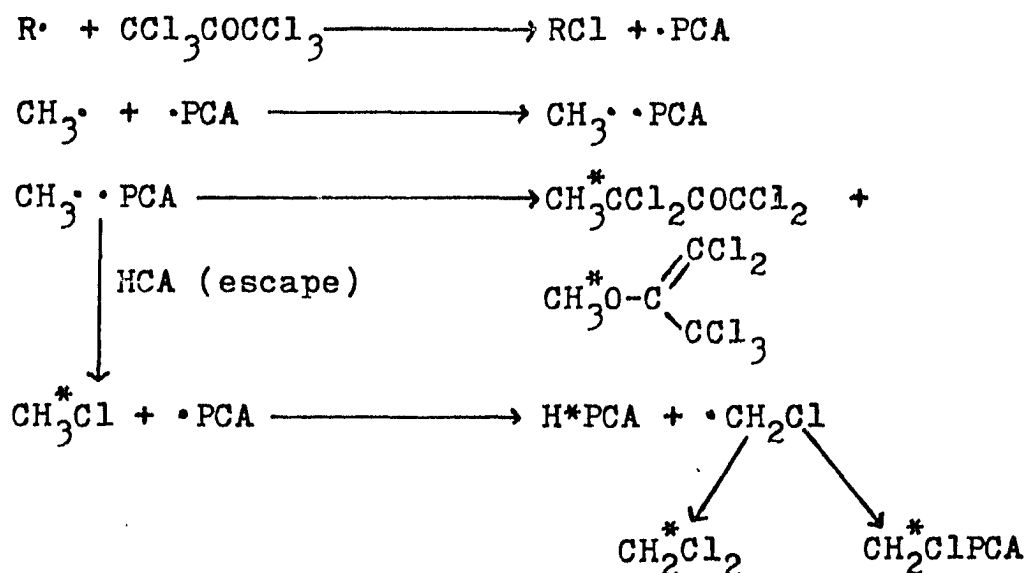


Fig. XXXI. Decomposition of di-*t*-butyl peroxyoxalate in hexachloroacetone.

enhanced products are formed as a result of the coupling of two forms of the PCA radical with methyl radicals. The products appearing in emission are the result of escape and subsequent trapping of polarized methyl radicals. Polarized pentachloroacetone (6.73δ E) is formed by transfer of a polarized proton from methyl chloride. Products of a secondary polarizing pair, chloromethyl-PCA, appear at 4.60δ (hexachlorobutanone A) and 5.15δ (methylene chloride). There are two unidentified resonances at 6.01δ (A) and 5.40δ (E).



Polarization was not observed when 13 was decomposed in bromotrichloromethane or carbon tetrachloride containing 0.1M. carbon tetrabromide. These systems obviously trap free methyl radicals so effectively that there are no diffusive methyl-tribromomethyl radical pairs formed.

Decomposition of Peresters in Aromatic Solvents

The reactivity of free radicals are often greatly changed in the presence of aromatic solvents. The t-butoxy radical has been shown to both coordinate to and react with aromatic solvents. To study the effect of the aromatic solvents, the decomposition of several peresters were carried out in chlorobenzene.

Decomposition of t-Butyl Phenylperacetate (1)

The nuclear polarization generated by 1 in chlorobenzene (figure XXXII) is very different from the decomposition of 1 in HCA. CIDNP is observed in the products identified as benzyl t-butyl ether (4.32 δ A), chlorodiphenylmethane (3.99 δ E), ethyl benzene (2.49 δ quartet 1.07 triplet A/E), toluene (2.12 δ A) and methane (.15 δ A). Additional polarization is observed at 4.84 δ (A) but remains unidentified. Products observed with normal spin distributions include: bibenzyl (2.76 δ), acetone (1.75 δ), and several different t-butoxy groups (1.08 δ).

In this reaction, we have our first example of multiplet effect polarization. The multiplet effect observed for ethyl benzene indicates the polarization is generated by a radical pair where Δg equals zero. This condition is met by the benzyl-methyl pair in which both radicals have $g=2.0025$. To predict the phase of this signal, we must know the hyperfine coupling constants in both the benzyl and methyl radicals (both coupling constants are negative)

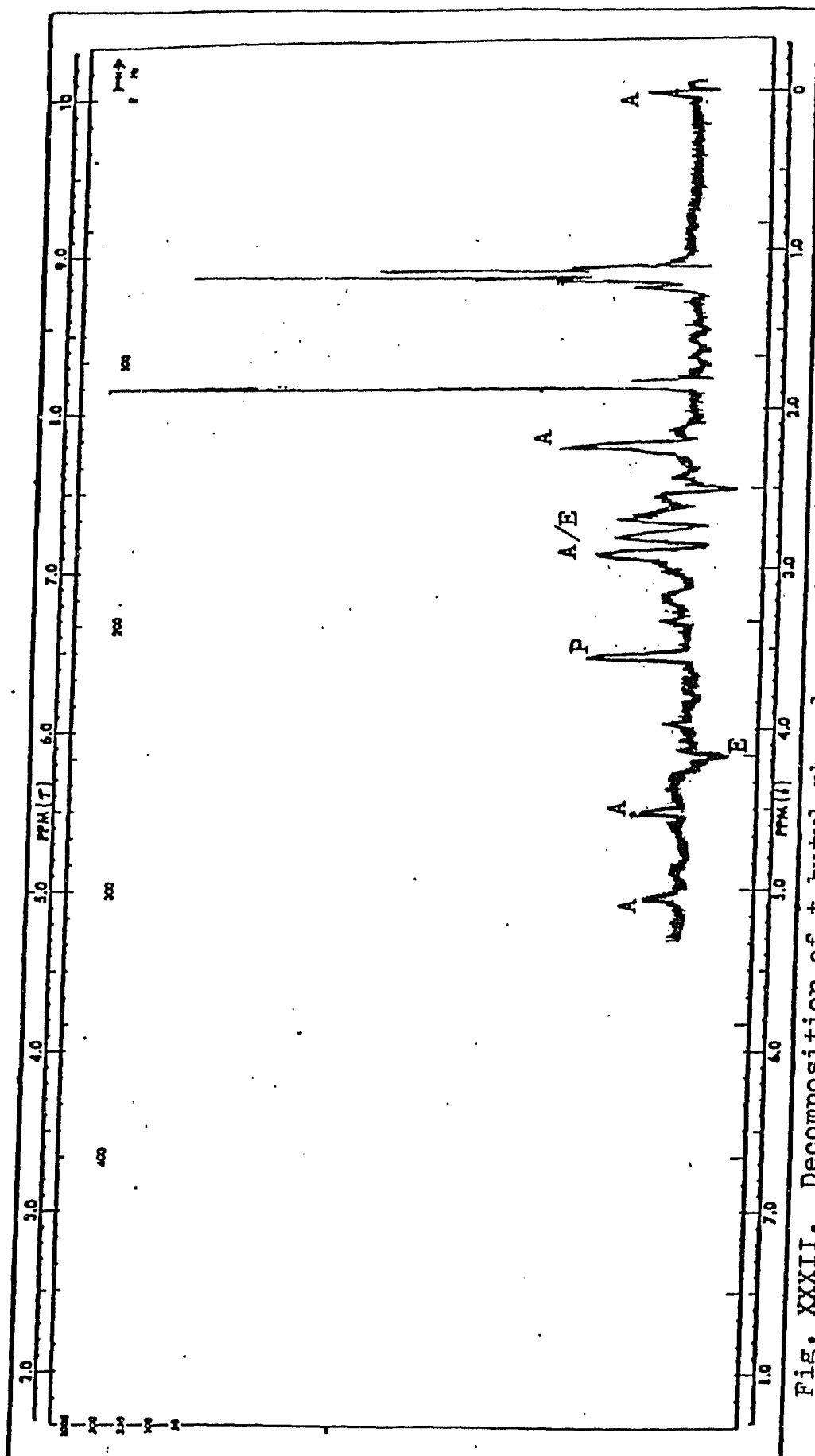


Fig. XXXII. Decomposition of *t*-butyl phenylperacetate in chlorobenzene.

and the sign of the nuclear spin-spin coupling constant.

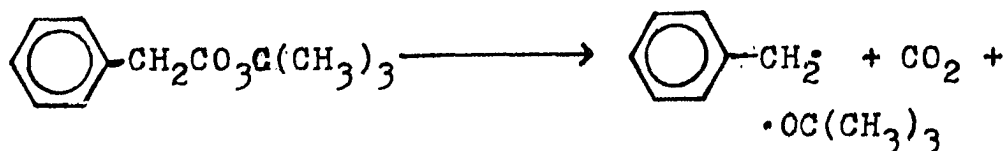
The J_{H-H} in freely rotating ethane molecules is positive.

Using Kaptein's rule for the multiplet effect, we find that A/E is observed for a triplet or free radical pair.

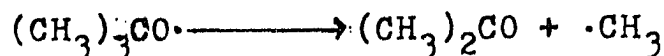
$$\Gamma = \mu \epsilon a_i a_j J_{ij} \sigma_{ij}$$

$$= (+)(+)(-)(-)(+)(-) = A/E$$

It is not difficult to rationalize the formation of ethyl benzene as a product of free radical reactions in this system. The benzyl radical is produced as a product of the initial decomposition,



and the methyl radical is a known decomposition product of the t-butoxy radical.



These radicals are polarized during diffusive encounters in solution. CIDNP is observed in the coupling product ethyl benzene. There is no CIDNP expected for the escape products of this radical pair (bibenzyl, ethane, toluene or methane) since each of these compounds exhibits a single line in the NMR spectrum (excluding the aromatics). The same radical pair may be generated from independent sources of methyl and benzyl radicals. To confirm this, we decomposed di-t-butyl peroxyoxalate in chlorobenzene containing 1.0 molar toluene. The CIDNP observed in this system is similar in phase to that generated by 1 in

chlorobenzene (figure XXXIII A and B).

The net effect observed in benzyl t-butyl ether is in marked contrast to the absence of polarization when the perester is decomposed in HCA or decane. We have already established that no CIDNP will be produced by radical pairs involving the t-butoxy radical. A possible explanation for this polarization is that the aromatic solvent may coordinate to the t-butoxy radical lifting the degeneracy of the odd electron. The polarization observed can then result from the interactions of a singlet benzyl-t-butoxy/chlorobenzene pair in the geminate cage. This mechanism was abandoned because addition of low concentrations of radical traps (below .1M of carbon tetrachloride, bromotrichloromethane or HCA) results in the quenching of the ether polarization. If this ether is formed as a cage product, its formation will be unaffected by low concentration of free radical traps. The possibility that the polarized ether is formed by free radical interactions of the same radical pair remains but is dismissed in favor of a mechanism which can explain all of the net polarizations.

The net effect observed for benzyl-t-butoxy ether, toluene, methane and chlorodiphenyl methane, requires a radical pair where Δg is non-zero. We interpret the polarization as being due to diffusive encounters of alkyl (benzyl or methyl) radicals with substituted cyclohexadienyl radicals (CHD). The formation of the CHD radicals is the result of the addition of either methyl or t-butoxy radicals

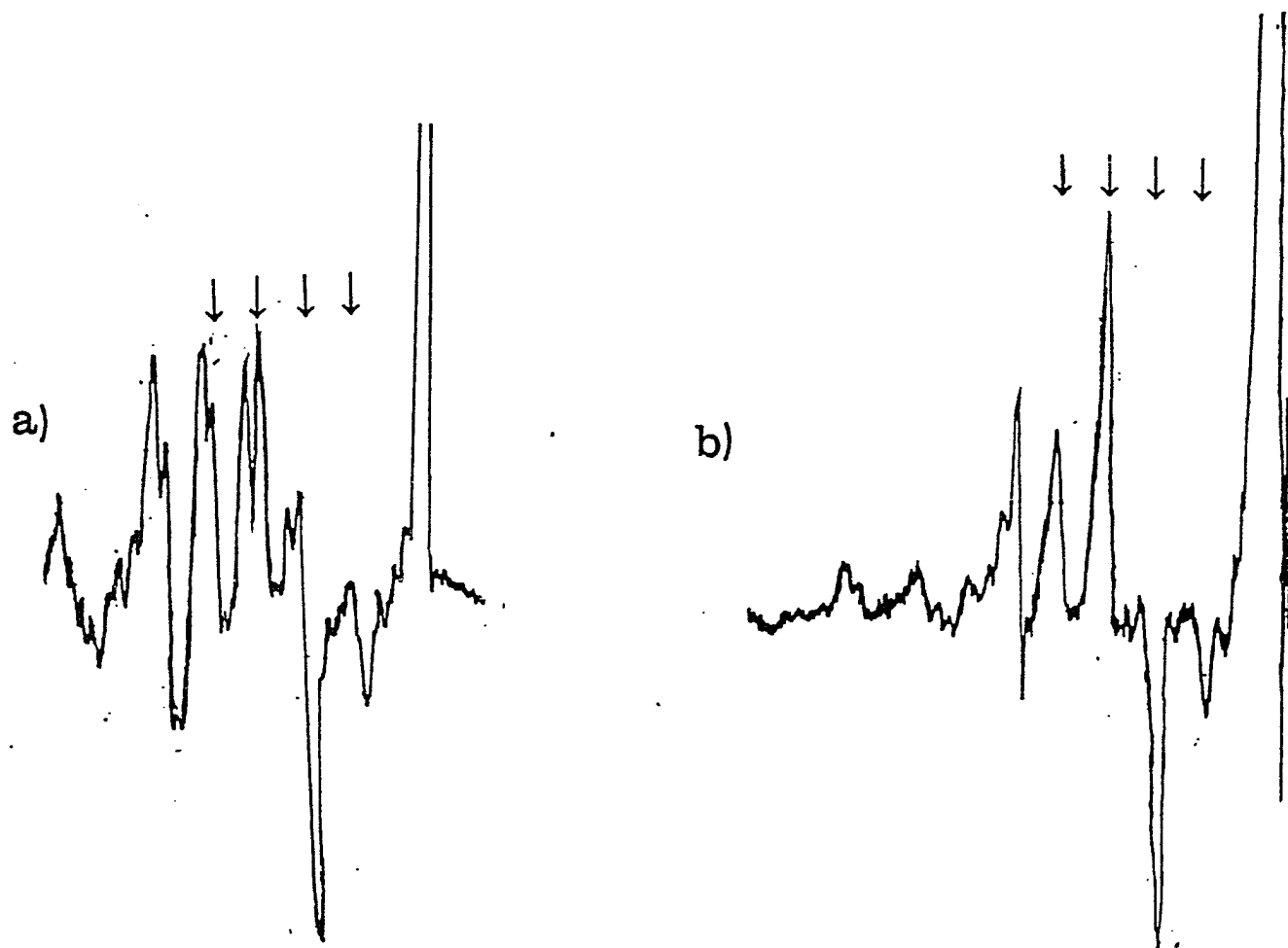
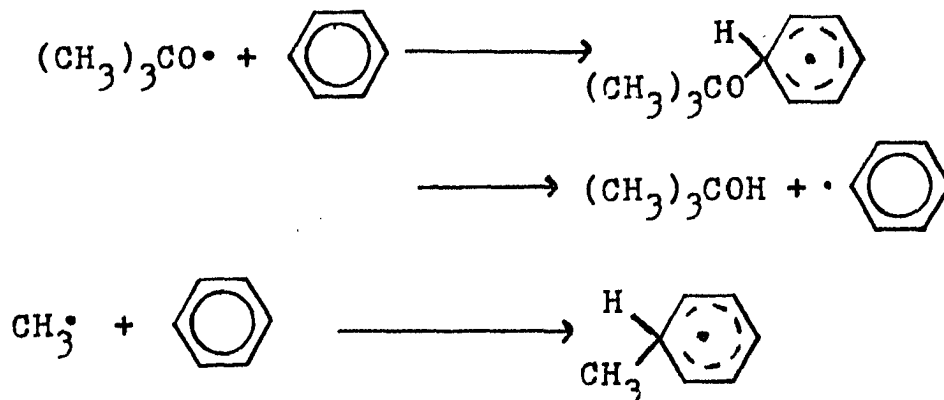
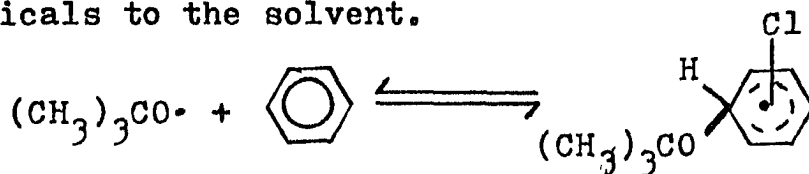


Fig. XXXIII. Ethylbenzene quartet observed during perester decompositions;
a) Decomposition of t-butyl phenylperacetate in chlorobenzene
b) Decomposition of di-t-butyl peroxyoxalate in chlorobenzene containing 1.0 M toluene.
The arrows indicate the ethylbenzene quartet.

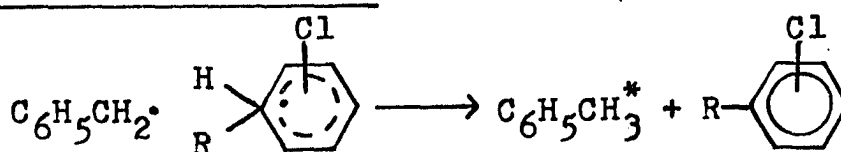
to the solvent. It is known that t-butoxy radicals may either add to or abstract hydrogen from benzene and that methyl radicals will react only by addition to benzene⁷¹⁻².



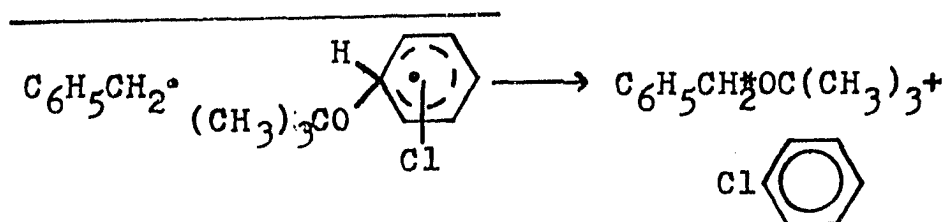
The CIDNP produced by 1 in chlorobenzene may be explained in terms of a reversible addition of t-butoxy radicals to the solvent.



Polarization is generated in diffusive encounters of the benzyl and CHD radicals. The cage products of this pair toluene and benzyl-t-butyl ether both exhibit enhanced absorption. The toluene is formed by a simple disproportionation of the benzyl-CHD radical pair.



The polarized ether is formed by decomposition of the CHD radical in the cage with the benzyl radical. This requires that the addition of t-butoxy radicals to the aromatic solvent is reversible.



Similar effects observed for the cyclohexadienyl radicals formed by addition of a pentafluorobenzoyloxy radical to aromatic solvents have been extensively studied by CIDNP¹⁹. It was found that the addition of this radical to the solvent was reversible.

Polarization generated in the benzyl-CHD radical pair is retained in the subsequent benzyl-t-butoxy pair and is observed in the products of the second pair. A similar effect has been observed during the decomposition of acetyl peroxide by Kaptein⁴. In this peroxide, net polarization developed in a methyl-acetoxy radical pair is observed in ethane. In this case, the acetoxy radical decomposes giving a methyl radical and carbon dioxide. The methyl-methyl pair collapses giving ethane but retaining the nuclear polarization of the methyl-acetoxy radical pair. This effect has been termed the "memory effect" by Kaptein. The observation of the memory effect requires that both the fragmentation of the initial radical and the formation of the product in the new radical pair be competitive with

diffusion from the polarizing cage. In the case of the benzyl-t-butoxy pair, if the coupling must be rapid to retain polarization (memory effect) it will not be destroyed by spin relaxation (of the t-butoxy radical).

The phase of the polarization from the benzyl-CHD radical pair may be rationalized using Kaptein's rule,

$$\Gamma = \mu \epsilon \Delta g a_i \\ = (+)(+)(-)(-) = A$$

for the benzylic protons of the benzyl-t-butyl ether and the two protons on the toluene which originally resided on the benzyl fragment. In this application of Kaptein's rule, we have assumed that the g-factor of the CHD radical is greater than the g-factor of the benzyl radical. This assumption is justified since heavy atoms usually increase the g-factor of radicals. Further support of this assumption has been found during the decomposition of substituted phenyl- and dichloroperacetates (vide infra). The third proton of the toluene methyl group, which originated on the CHD radical, will also appear enhanced since the hyperfine coupling of the allylic protons in the CHD radical are positive ¹⁹. Kaptein's rule predicts this proton will be enhanced.

$$\Gamma = \mu \epsilon \Delta g a_i \\ = (+)(+)(+)(+) = + A$$

This result was confirmed by the decomposition of 1-ox-d₂. When this perester is decomposed, there is enhanced absorption observed for the benzylic protons of toluene

$\alpha\alpha$ -d₂ (2.12 δ 1:2:2:1 quartet J=2 Hz.) (figure XXXIV). In this case, only the proton which resides on the CHD fragment will be observed.

The escape products of the benzyl radical will appear in emission. Of the possible products (toluene, ethylbenzene, bibenzyl and chlorodiphenylmethane), only the chlorodiphenylmethane appears polarized. Observation of the polarization in other products is obscured by other mechanisms forming these products more efficiently.

Production of chlorodiphenylmethane may be rationalized in either (or both) of two mechanisms. The first involves polarization of a benzyl radical by CHD and observation of this product as the result of escaping and subsequent trapping by a chlorophenyl radical. The phase of the polarization which is consistent with this mechanism is:

$$\begin{aligned}\Gamma &= \mu \ e \ \Delta g \ a_1 \\ &= (+)(-)(-)(-) = E\end{aligned}$$

An alternate mode of product formation is simply the free radical coupling of a benzyl-chlorophenyl radical pair. In this pair, the chlorophenyl will be expected to have the higher g-factor. The phase of the polarization by this mechanism will be:

$$\begin{aligned}\Gamma &= \mu \ e \ \Delta g \ a_1 \\ &= (+)(+)(-)(-) = A\end{aligned}$$

The observation of emission in this product indicates that the polarization results from the first mechanism. This does not imply that the second mechanism does not

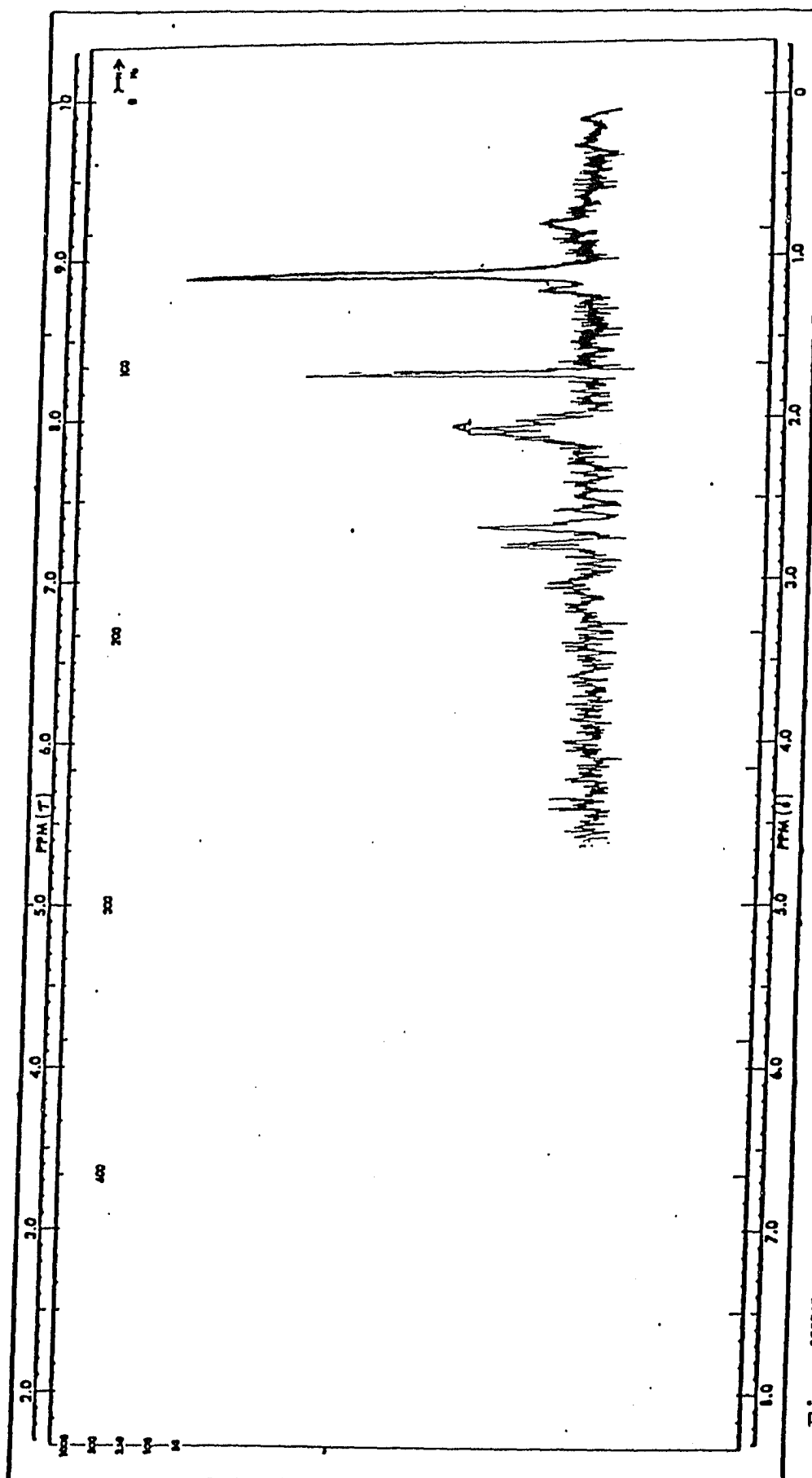


Fig. XXXIV. Decomposition of t-butyl phenylperacetate- $\alpha\alpha$ - d_2 in chlorobenzene.

occur or even that the first mechanism is the dominant pathway to the formation of chlorodiphenylmethane.

The final polarized product, methane, results from free radical encounters of a methyl CHD pair. The polarization observed should be the same phase as that produced by the benzyl-CHD pair in forming toluene. The observed enhanced absorption may be rationalized in the same manner as was the toluene.

The CIDNP generated in the decomposition of 1 was explained by the interaction of radicals in bulk solution. Since the CIDNP was independent of the reactions in the geminate cage, we were able to produce similar spectra by the decomposition of di-t-butyl peroxyoxalate in chlorobenzene containing toluene. The polarization resulting from this reaction is similar in both products and phase to that generated by 1. There is, however, no polarization observed for benzyl-t-butyl ether. This is possibly due to the low concentration of t-butoxy substituted CHD radicals.

The reactions leading to nuclear polarization in both 1 in chlorobenzene and di-t-butyl peroxyoxalate in toluene chlorobenzene are summarized in figures XXXV and XXXVI, respectively.

Before concluding the discussion of this perester, I feel it is necessary to mention that CIDNP is an extremely sensitive technique. The radical concentrations needed to

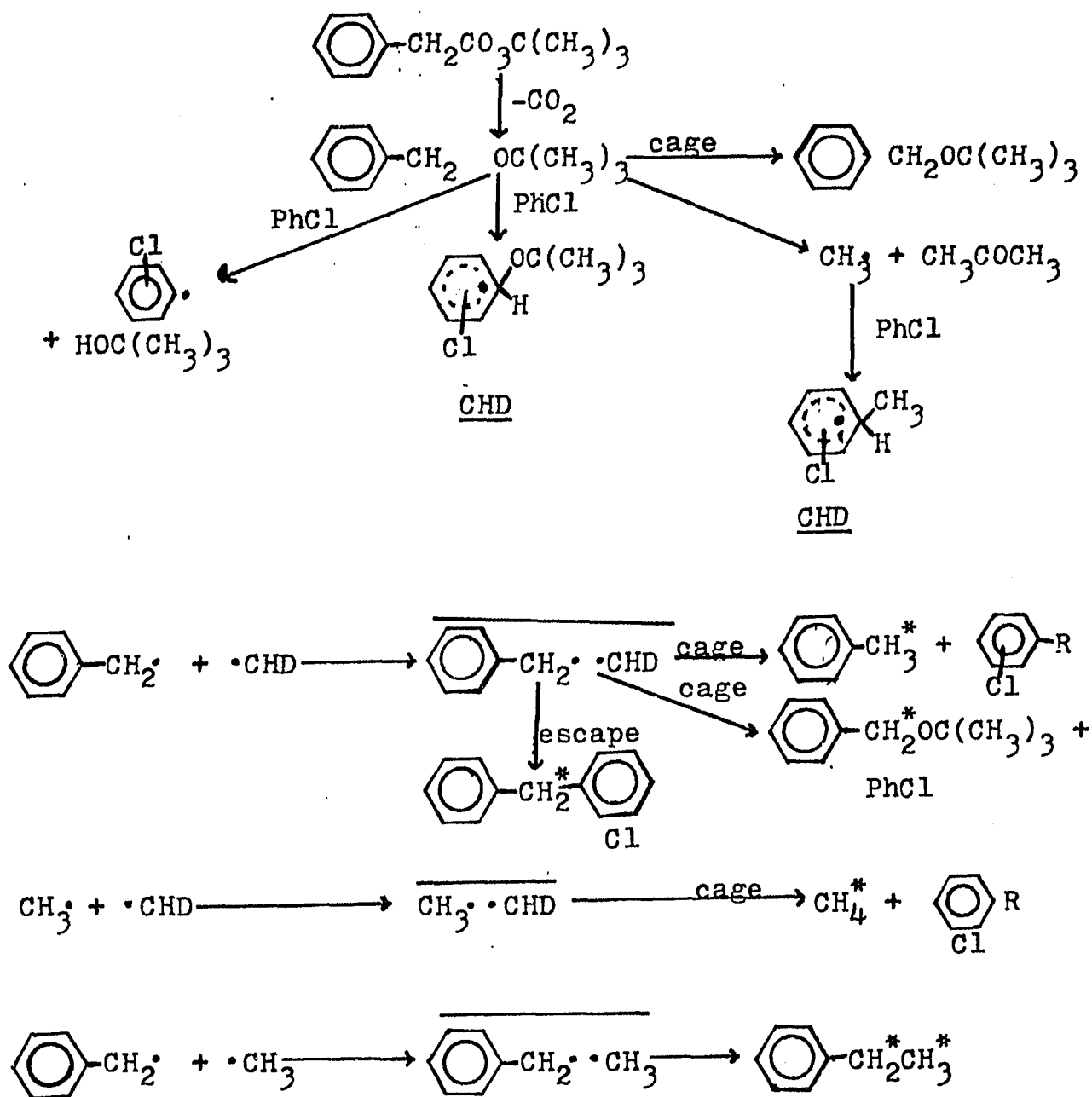


Fig. XXXV. Reactions leading to CIDNP during the decomposition of t-butyl phenylperacetate in chlorobenzene. R = CH_3 - or $(\text{CH}_3)_3\text{CO}-$.

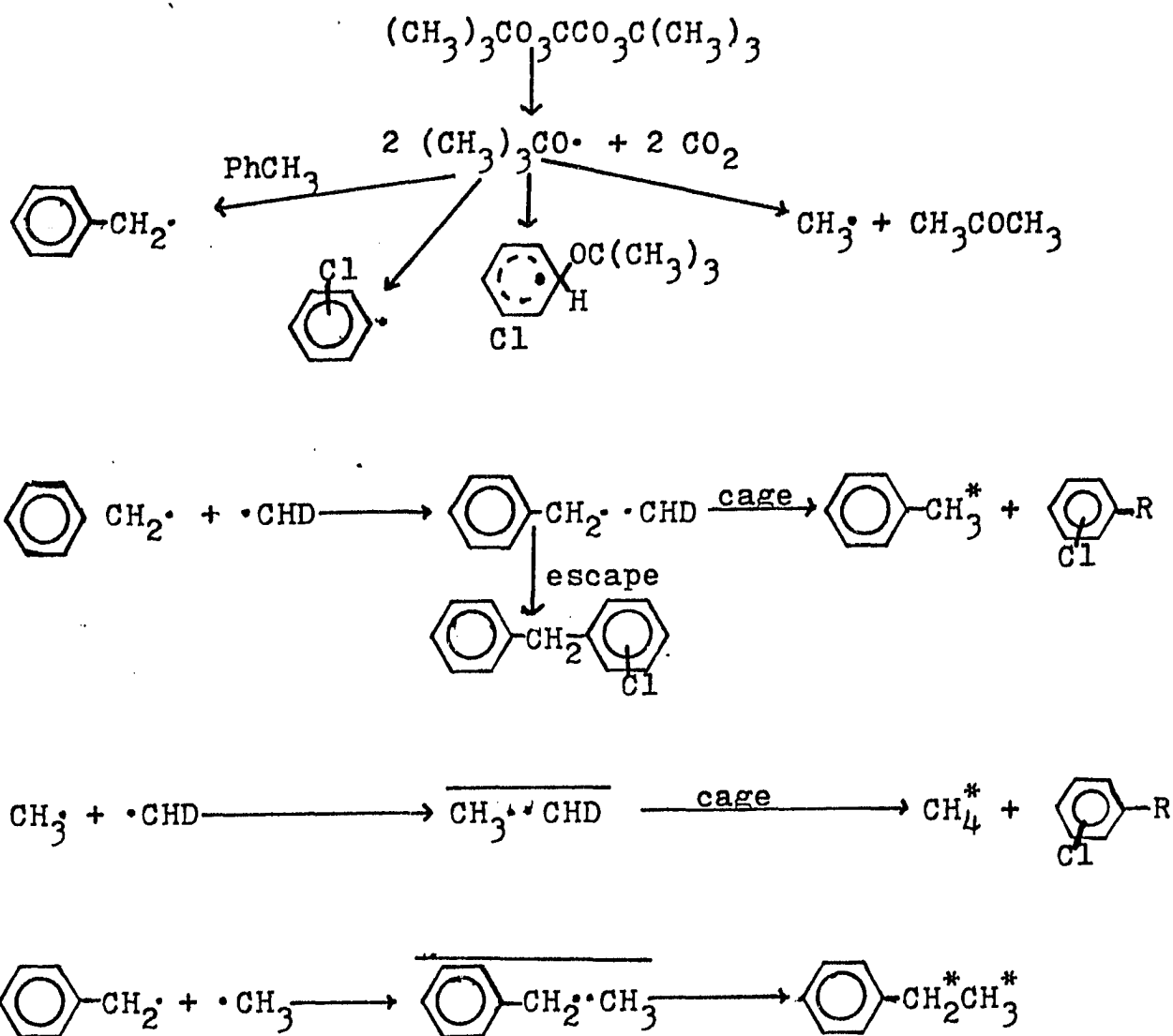


Fig. XXXVI. Reactions leading to CIDNP during the decomposition of di-*t*-butyl peroxyoxalate in chlorobenzene containing 1.0 M toluene. R = CH₃-or (CH₃)₃CO-.

produce observable nuclear polarization are extremely low. It has been estimated that, under favorable conditions, CIDNP can be observed at radical concentrations of about 10% of that needed for ESR observation. In the preceding discussion, we have shown that there are many pathways occurring during the decomposition of 1 that are not unexpected but have gone undemonstrated until now. These pathways are responsible for very little product formation but produce large CIDNP effects. To estimate the extent to which this mechanism contributes to the products formed, we carried out a careful product search. Major products of the decomposition of 1 in benzene are: benzyl-t-butyl ether (the cage product), acetone, t-butanol, toluene and bibenzyl. Additional minor products were: biphenyl, diphenylmethane and another benzyl containing product (base peak 91 m/e in the mass spectrum was the only peak visible). We were unable to detect any ethylbenzene or phenyl t-butyl ether by gas chromatography using either hydrogen flame detectors or total ion current (from GS-MS). Under these conditions, we would have easily seen 0.1% of either compound. These analysis indicate that the nuclear polarization is the result of only the minor pathways in the decomposition of this perester.

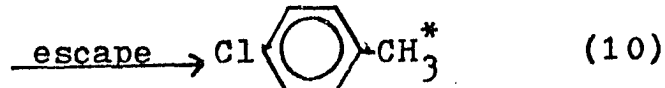
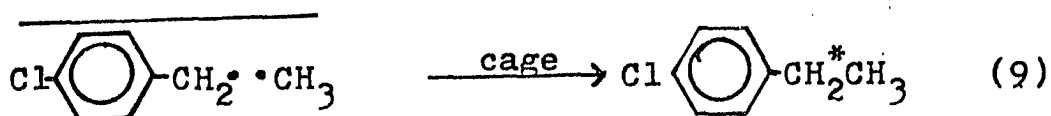
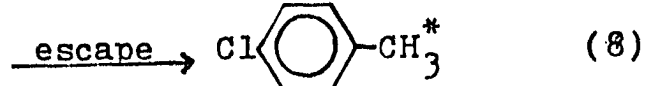
The Decomposition of p-Chloro and p-Bromophenyl Peracetates

The preceding results assumed that the g-factor of the CHD radical was greater than that of alkyl radicals (2.0025).

To confirm this, we prepared and studied the decomposition of p-chloro and p-bromophenylperacetates (p-Cl-1 and p-Br-1). These compounds decompose to give p-chlorobenzyl and p-bromobenzyl radicals which have g-factors of 2.0030 and 2.0050 respectively^{13a}.

When p-Cl-1 is decomposed in chlorobenzene (figure XXXVII), CIDNP is observed for p-chloro substituted: toluene (2.00 δA), benzyl-t-butyl ether (4.61 δA), ethylbenzene (2.25 δ ?/E), chlorodiphenylmethane (4.06 δE) and methane (0.05 δA). In this system, there are several different radical pairs which are operating simultaneously to generate CIDNP. A careful evaluation of each pair is necessary to evaluate the role of each pair.

Polarized toluene will be formed by three different reactions.



Assuming that the CIDNP in recombination products must be more intense than in the escape products, the net CIDNP from reactions 7 and 8 will be determined by reaction 7. Since little polarization is observed from the methyl-p-chlorobenzyl pair in the coupling product p-chloroethyl-

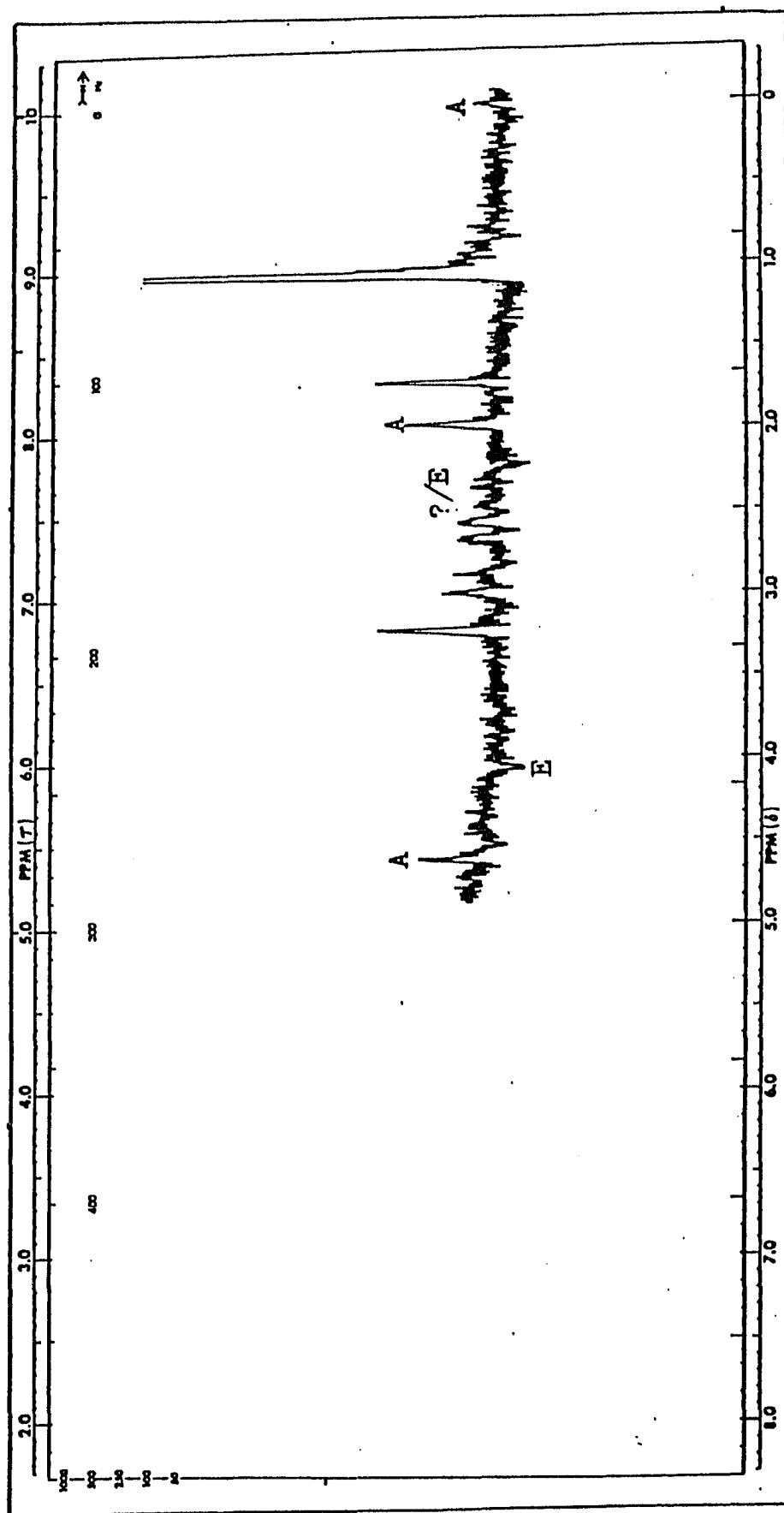
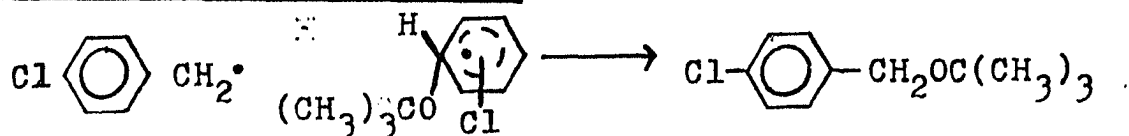


Fig. XXXVII. Decomposition of t-butyl p-chlorophenylperacetate in chlorobenzene.

benzene (reaction 9), we would expect that little polarization will be observed from reaction 10. We can, therefore, assume that the major route to the production of polarized toluene will be reaction 7. As in the case of the unsubstituted perester, enhanced absorption will be observed if g_{CHD} is greater than g_{benzyl} .

The formation of p-chlorobenzyl t-butyl ether occurs by only one reaction which produces nuclear polarization.



Enhanced absorption indicates that g_{CHD} is greater than g of the chlorobenzyl radical confirming the interpretation of the toluene resonance. Other products are formed by mechanisms which are identical to those discussed for the unsubstituted perester.

The decomposition of p-Br-1 (figure XXXVIII) leads to strong polarization which is reversed in phase to that produced by both the unsubstituted or the p-chlorophenyl peracetate. Emission is observed for the p-bromo substituted: ethylbenzene (2.37 δ J=7 Hz. E), bibenzyl (2.40 δ E), toluene (2.00 δ E) and benzyl-t-butyl ether (4.95 δ E). Methane which appears as emission is also reversed as is p-bromochlorodiphenylmethane (4.15 δ).

The reversal of phase of the ether indicates that the g -factor of the CHD radical is now less than that of the p-bromobenzyl radical. This polarized ether will only be

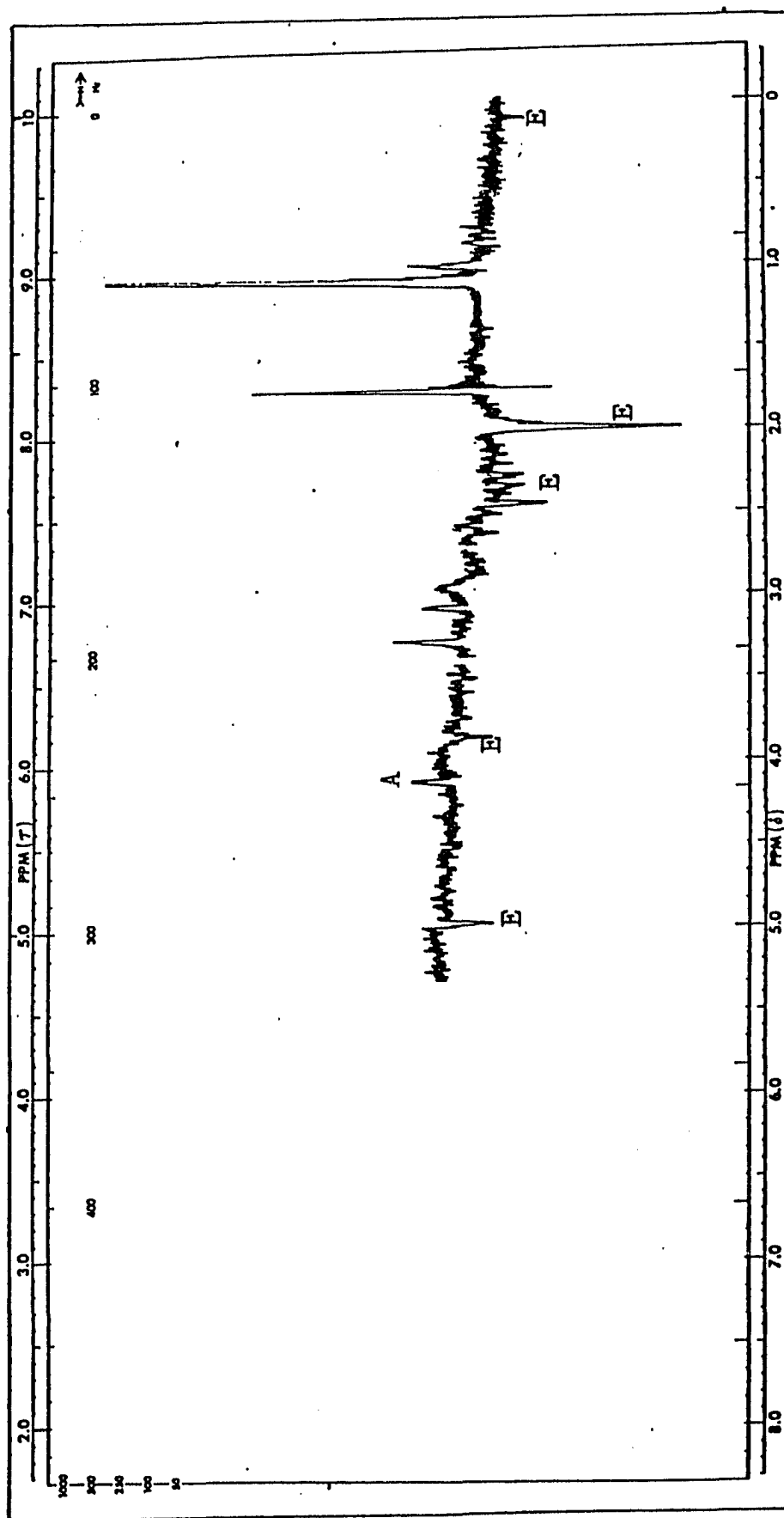
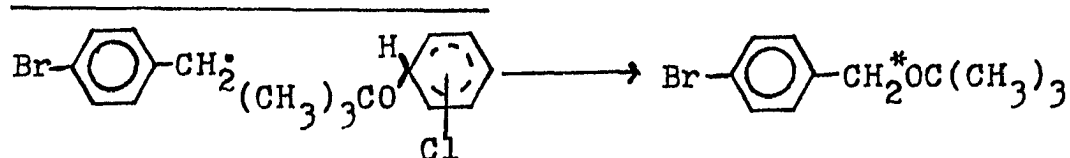


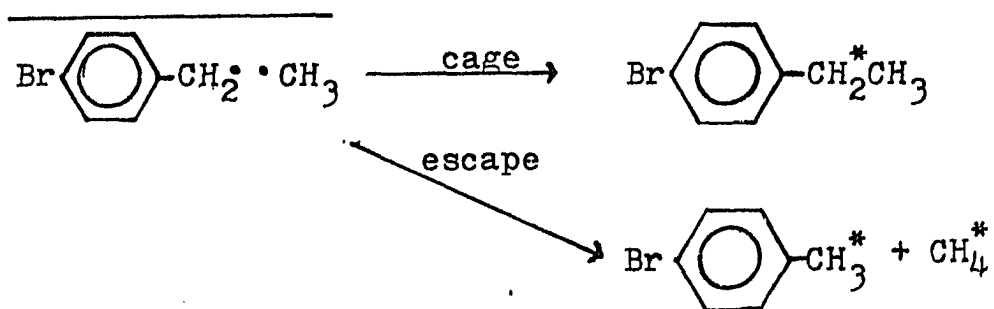
Fig. XXXVIII. Decomposition of t-butyl p-bromophenylperacetate in chlorobenzene.

formed by:



Application of Kaptein's rule will indicate that the benzyl radical must have a higher *g*-factor. The other product of this radical pair is *p*-bromotoluene which will be expected in emission.

Another radical pair which is generating net polarization is the methyl-*p*-bromobenzyl pair. The possible products of this pair are *p*-bromoethylbenzene, *p*-bromotoluene and methane by the following reactions:



In this pair, the *p*-bromobenzyl radical has the higher *g*-factor and the hyperfine coupling constants of both the benzylic and the methyl hydrogens are negative. Net polarization will be expected in the ethylbenzene (quartet E and triplet A) formed by cage recombination and in the toluene (A) and methane (E) formed by escape from this pair.

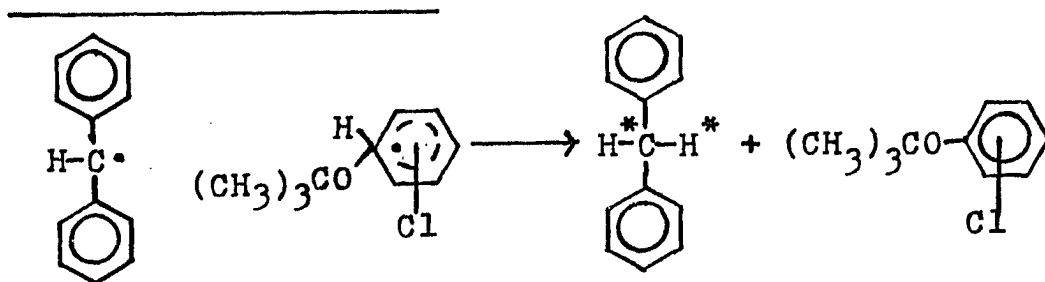
In this perester, two independent mechanisms generate *p*-bromotoluene which is polarized with opposite signs. The observed effect is dominated by the CHD-*p*-bromobenzyl

radical pair which polarizes the product more efficiently.

Decomposition of t-Butyl Diphenylperacetate (2)

When this compound is decomposed in chlorobenzene, strong nuclear polarization is observed for diphenyl methane (3.78 δ A), diphenyl ethane (3.84 δ quartet $J=7.2$ Hz. A/E) and methane (A)(figure XXXIX). These products are the result of the recombination of the diphenylmethyl-CHD and diphenylmethyl-methyl radical pairs. It is established that CIDNP is not observed in the escape products of the diphenylmethyl radical^{13,73}. This is a result of a relatively long lifetime of this radical when it is compared to its nuclear spin relaxation rate.

The appearance of polarized diphenylmethane indicates the involvement of the diphenylmethyl-CHD pair. This radical pair will undergo a cage disproportionation giving diphenylmethane and chlorophenyl t-butyl ether.



The enhanced absorption generated by this pair is consistent with Kaptein's rule.

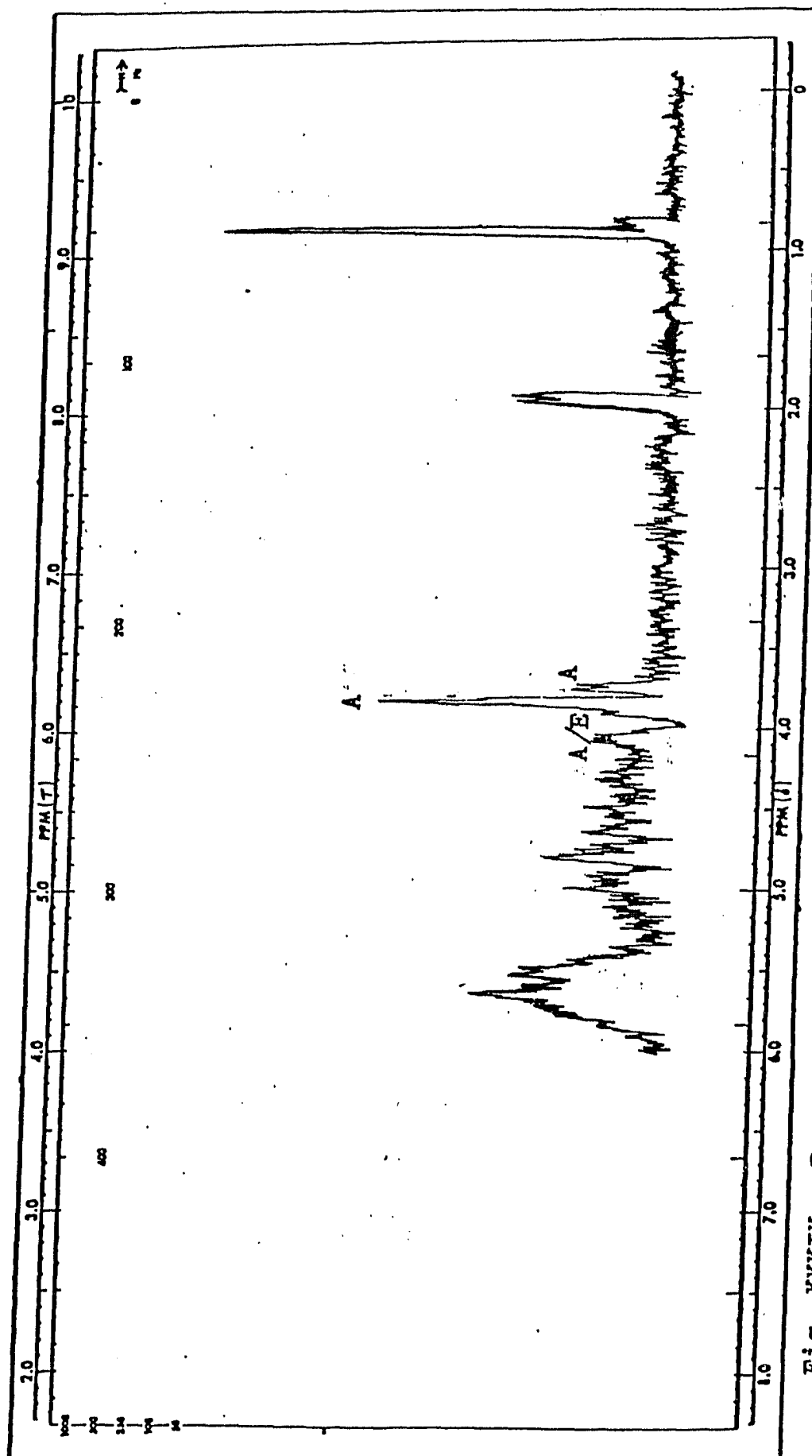
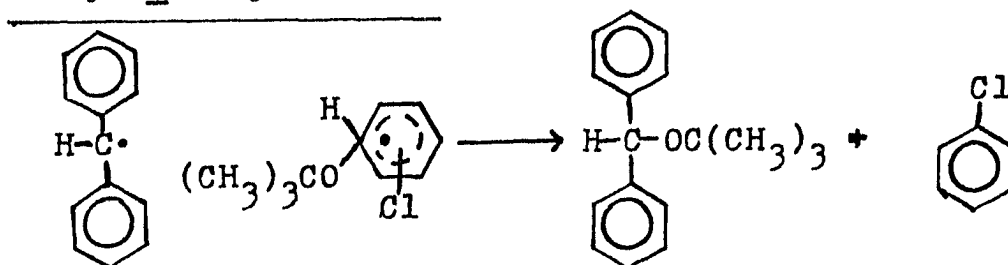


Fig. XXXIX. Decomposition of *t*-butyl diphenylperacetate in chlorobenzene.

An alternate reaction of this radical pair would involve the decomposition of the CHD radical to give diphenylmethyl t-butyl ether.



The coupling of the intermediate diphenylmethyl-t-butoxy radical pair apparently is not rapid enough to retain polarization via the memory effect. During the decomposition of t-butyl phenylperacetate, the ether formed by the corresponding reaction does exhibit nuclear polarization. It is not surprising that the coupling of t-butoxy to benzyl radicals is more rapid than its coupling to diphenylmethyl.

Methane is formed by the disproportionation of the methyl-CHD radical pair. The reactions and explanation for the phase of the polarization is identical to that described in the decomposition of 1 in chlorobenzene.

The multiplet effect observed in diphenylethane is the result of the recombination of the diphenylmethyl-methyl radical pair. In this pair, Δg equals zero so that only the multiplet effect will be observed. The spectrum observed for this product contains additional polarized resonances. These may result from either small coupling to the aromatic hydrogens of diphenylethane or from an additional product which appears in the same area.

The facile decomposition of 2 allowed us to study the decomposition in benzene. When 2 is decomposed in benzene, the diphenylmethane produced is weakly polarized (figure XLa). The single resonance line exhibits both absorption and emission. The low intensity of this polarization is due to the fact that the g -factor of the diphenylmethyl radical is almost equal to the g -factor of the CHD radical. In this case, the CHD radical derived from benzene, does not have the chlorine which was increasing the g -factor of the CHD radical derived from chlorobenzene. Since the larger net effect is not present, low intensity multiplet effects become visible. A small coupling to the aromatic ring protons which is usually unobserved provides the necessary multiplet to observe this weak polarization.

The participation of the aromatic solvent in the polarizing reactions can be confirmed by the decomposition of 2 in benzene- d_6 . In this solvent, weak CIDNP is observed for a 1:1:1 triplet ($J=2$ Hz.) of diphenylmethane α - d_1 (figure XLb). In this case, each line of the triplet exhibits the unusual A/E multiplet effect which also was observed in benzene solution.

The decomposition of t-butyl diphenyl peracetate- d_1 in chlorobenzene (figure XLc) produces diphenylmethane- d_1 which is enhanced. In this case, the net effect is observed since the g -factor of the CHD radical is high due to the presence of the chlorine. In this reaction, the polarized proton originally resided on the CHD radical.

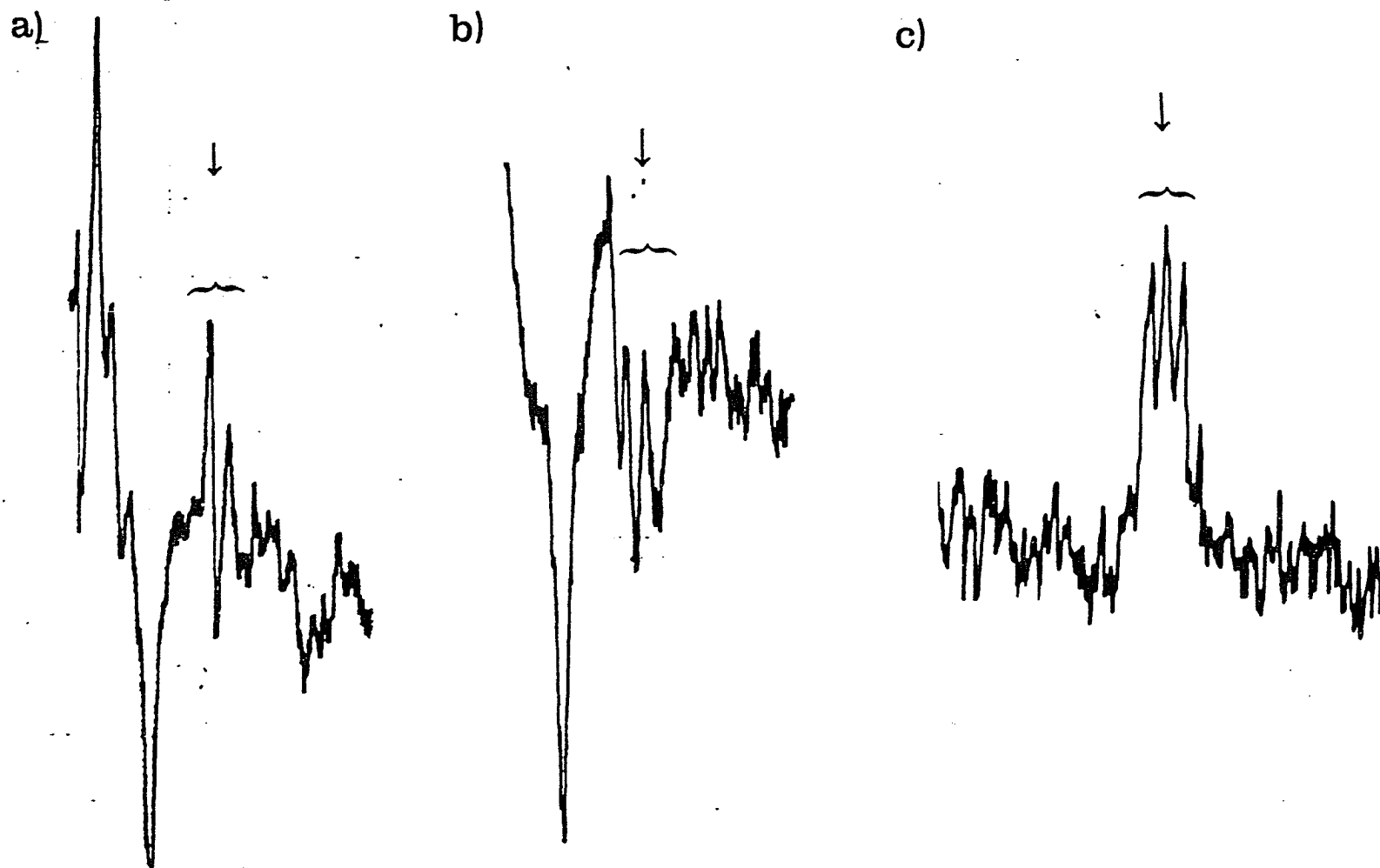
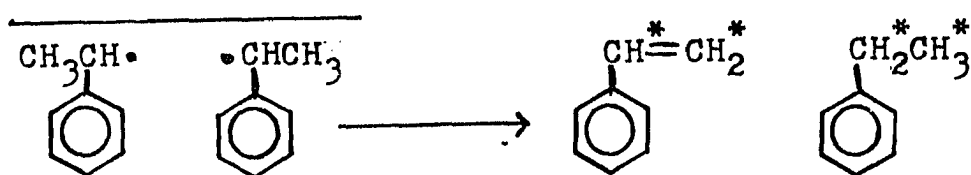


Fig. XL. CIDNP observed for diphenylmethane formed by the decomposition of *t*-butyl diphenylperacetate. a) Decomposition of *t*-butyl diphenylperacetate in benzene- H_6 . b) Decomposition of *t*-butyl diphenylperacetate in benzene- D_6 . c) Decomposition of *t*-butyl diphenylperacetate- $-D_1$ in chlorobenzene. Arrows indicate the resonance assigned to diphenylmethane. The large multiplet effect, in spectra a) and b), is due to diphenylethane.

Decomposition of t-Butyl 2-Phenylperpropionate (3)

The decomposition of 3 results in the formation of 1-phenylethyl radicals which are able to undergo disproportionation reactions. The only CIDNP observed during the decomposition of 3 in chlorobenzene is a strong multiplet effect (A/E) in both the quartet and triplet of ethylbenzene (figure XLI). This is consistent with the disproportionation of the two phenylethyl radicals.



The polarization is not observed in the other product, styrene, since this area of the spectrum is obscured by the strong solvent absorption. The polarization in this system is due to free radical encounters of two phenylethyl radicals. The multiplet effect is observed since the two interacting phenylethyl radicals must have the same g-factor. The phase of the CIDNP is easily rationalized using Kaptein's rule for the multiplet effect:

$$\begin{aligned} \Gamma_{\text{mult. effect}} &= \mu \epsilon a_i a_j J_{ij} \sigma_{ij} \\ &= + + - + + + = - A/E \end{aligned}$$

This indicates that both the quartet and the triplet should be expected to exhibit the same (A/E) multiplet effect which is consistent with the experimental result.

The CIDNP effects due to the solvent derived CHD radicals are not observed in this system. This is due to

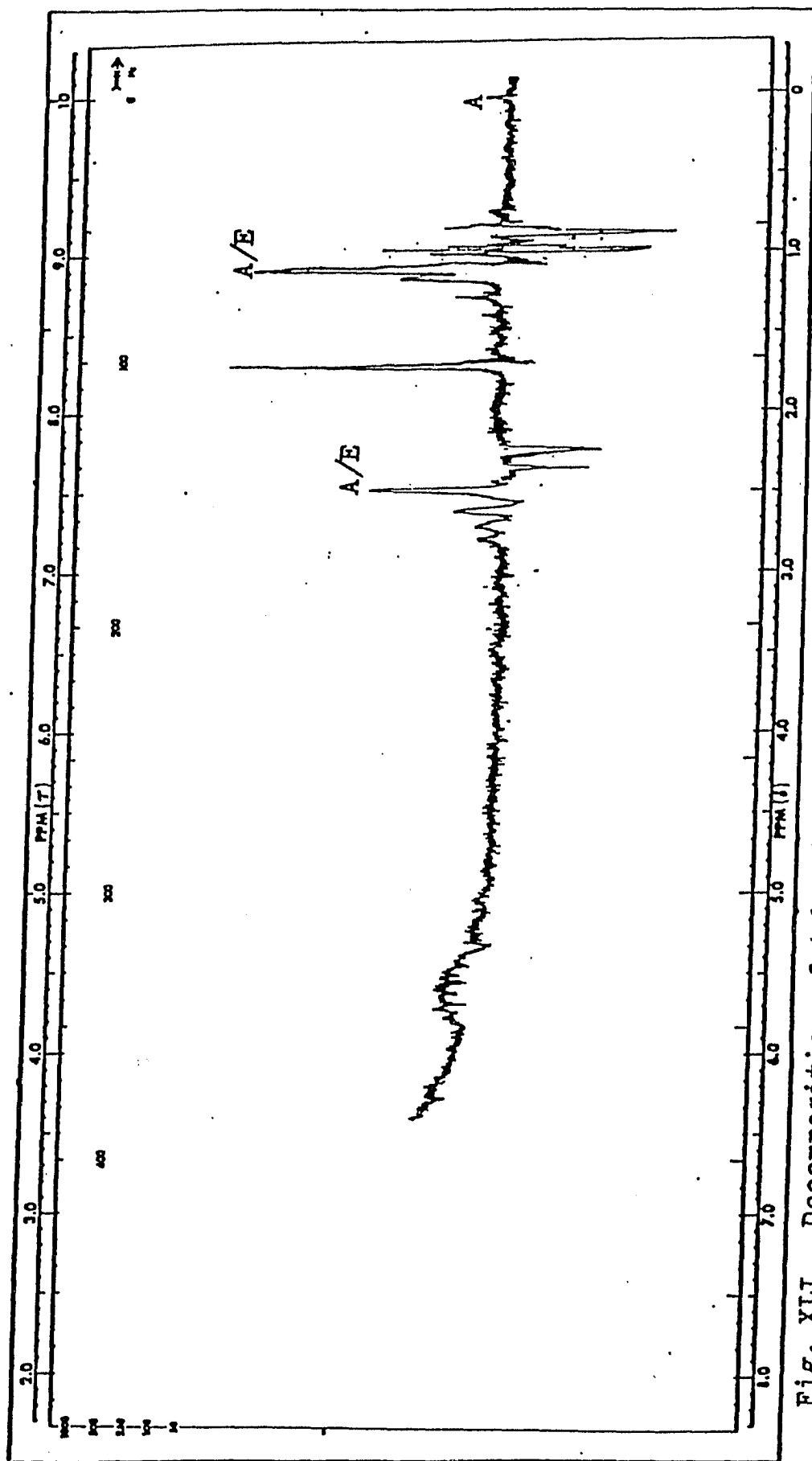
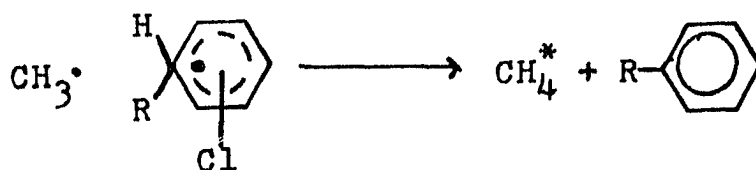


Fig. XLI. Decomposition of t-butyl 2-phenylperpropionate (3) in chlorobenzene.

the strong multiplet effect masking any net polarization which would appear in the ethylbenzene. The presence of CHD radicals is indicated by the polarization of methane. This is due to the interaction of methyl-CHD radical pairs.



The methane formed from the disproportionation of the methyl-phenylethyl radical pair would not be polarized. Both radicals have the same g-factor and the resulting multiplet effect could not be observed in methane.

The Decomposition of t-Butyl 2,2-Diphenylperpropionate (4)

The decomposition of this perester provides strong polarization (figure XLII) for the methyl protons of diphenylethane (1,27 doublet $J=7$ Hz. A/E) and net polarization for methane (A). These products indicate the participation of 1,1-diphenylethyl 1,1-diphenylethyl radical pairs and methyl CHD radical pairs. The mechanism for the generation of CIDNP is similar to that described in the section on the decomposition of t-butyl 2-phenylperpropionate.

The resonances at 2.38 and 1.50 δ are unidentified.

The decomposition of t-Butyl α -Phenylperoxy-iso-Butyrate

The decomposition of this perester in chlorobenzene provides strong CIDNP (figure XLIII) observed for cumene (2.50 δ multiplet, 1.02 A/E) & methane. The cumene is formed

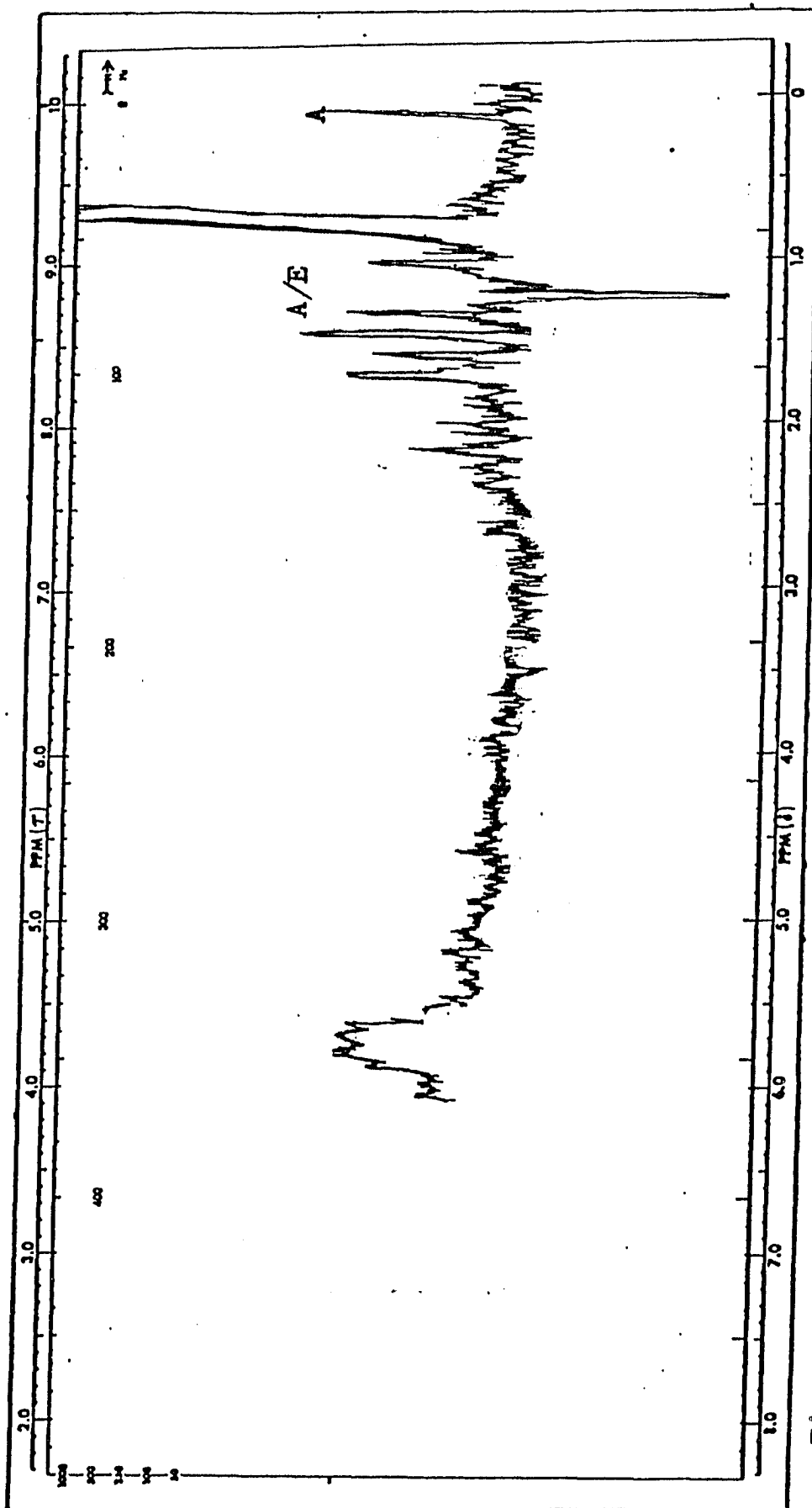


Fig. XLII. Decomposition of t-butyl 2,2-diphenylperpropionate in chlorobenzene.

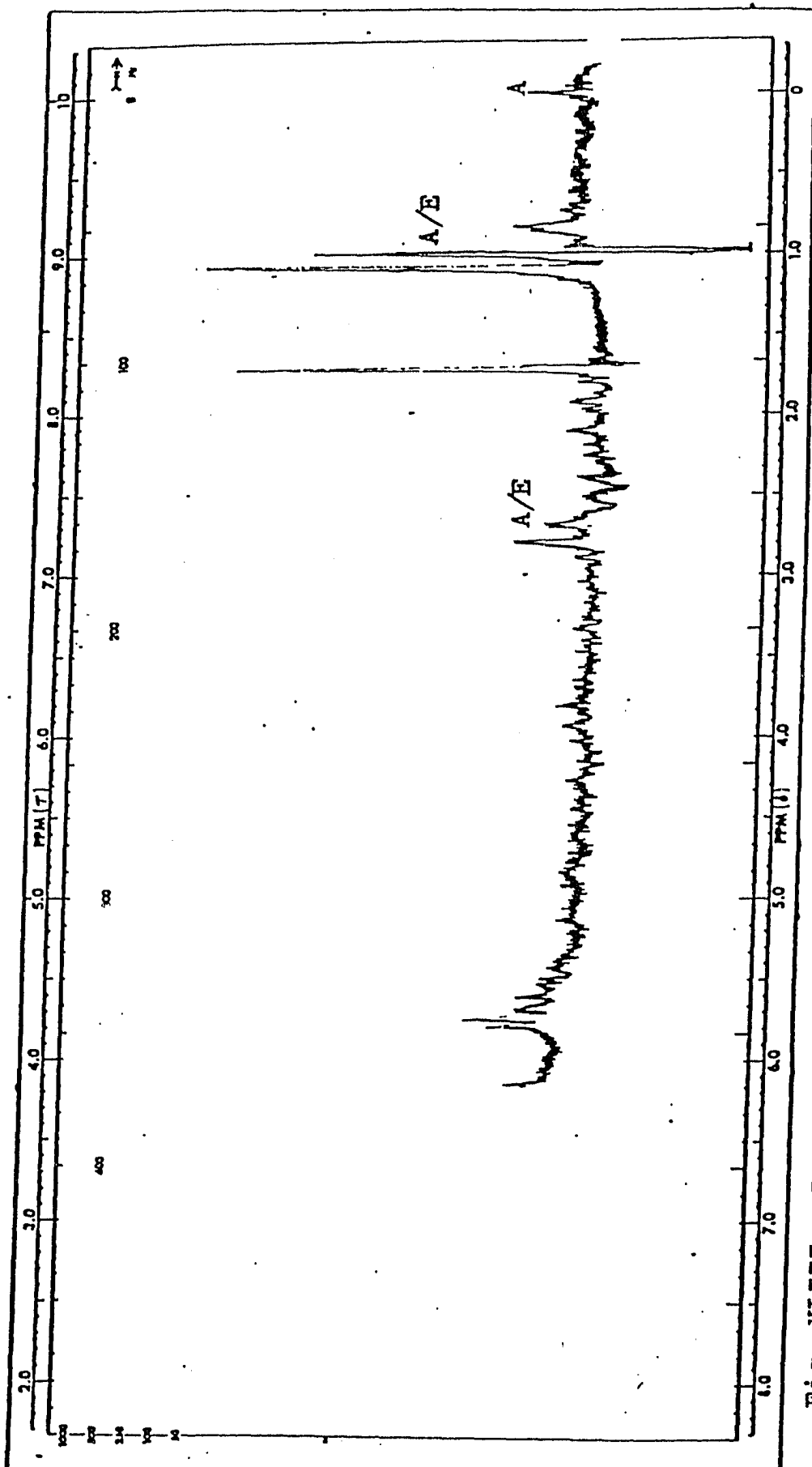
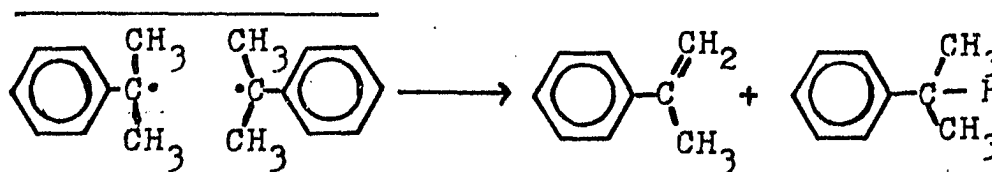


Fig. XLIII. Decomposition of t-butyl 2-phenylperoxy-iso-butrate in chlorobenzene.

during free radical encounters of two 2-phenyl propyl radicals (cumyl).



The allylic protons of 2-phenyl propene formed should exhibit the same A/E multiplet effect that is observed in cumene. This, however, was not observed.

Methane formed in this reaction is the result of the disproportionation of the methyl-CHD radical pair.

The Decomposition of t-Butyl Perpivalate

This perester deserves special comment since it is the only perester included in Kaptein's survey of peroxides.¹² His original explanation involved the interaction of the geminate t-butyl-t-butoxy radical pair. This leads to a reported polarization for di-t-butyl ether and net effects observed in the iso-butylene formed. Additional nuclear polarization was generated from free radical encounters of two t-butyl radicals resulting in multiplet effects observed in iso-butane and iso-butylene. This original interpretation has recently been retracted after theoretical calculations indicated that no polarization could be generated by radical pairs containing the t-butoxy radical.

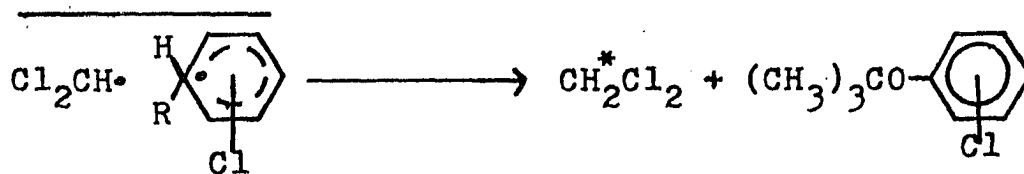
The CIDNP observed during the decomposition of t-butyl perpivalate in chlorobenzene (figure XLIV) is observed in iso-butylene (4.60 A/E) and iso-butane (1.45 δ multiplet A/E and 1.17 δ doublet A/E). There is no resonance corresponding to di-t-butylether as originally reported by Kaptein.

These results are consistent with our observation on other peresters with all CIDNP being due to free radical reactions. The radical pair responsible for all the CIDNP in this system is the t-butyl-t-butyl pair.

Decomposition of t-Butyl Dichloroperacetate

This perester would not decompose rapidly enough to generate CIDNP in chlorobenzene so the higher boiling solvent o-dichlorobenzene was employed. The only polarizations observed in this decomposition are emission for methylene chloride (5.15 δ) and enhanced absorption for methane (figure XLV).

The polarization observed in methylene chloride is the result of dichloromethyl-CHD radical pairs. Methylene chloride is the product of disproportionation of this pair.



In this pair, the dichloromethyl radical will have the greater g-factor, therefore, emission should be expected for both the protons of the dichloromethyl and the CHD

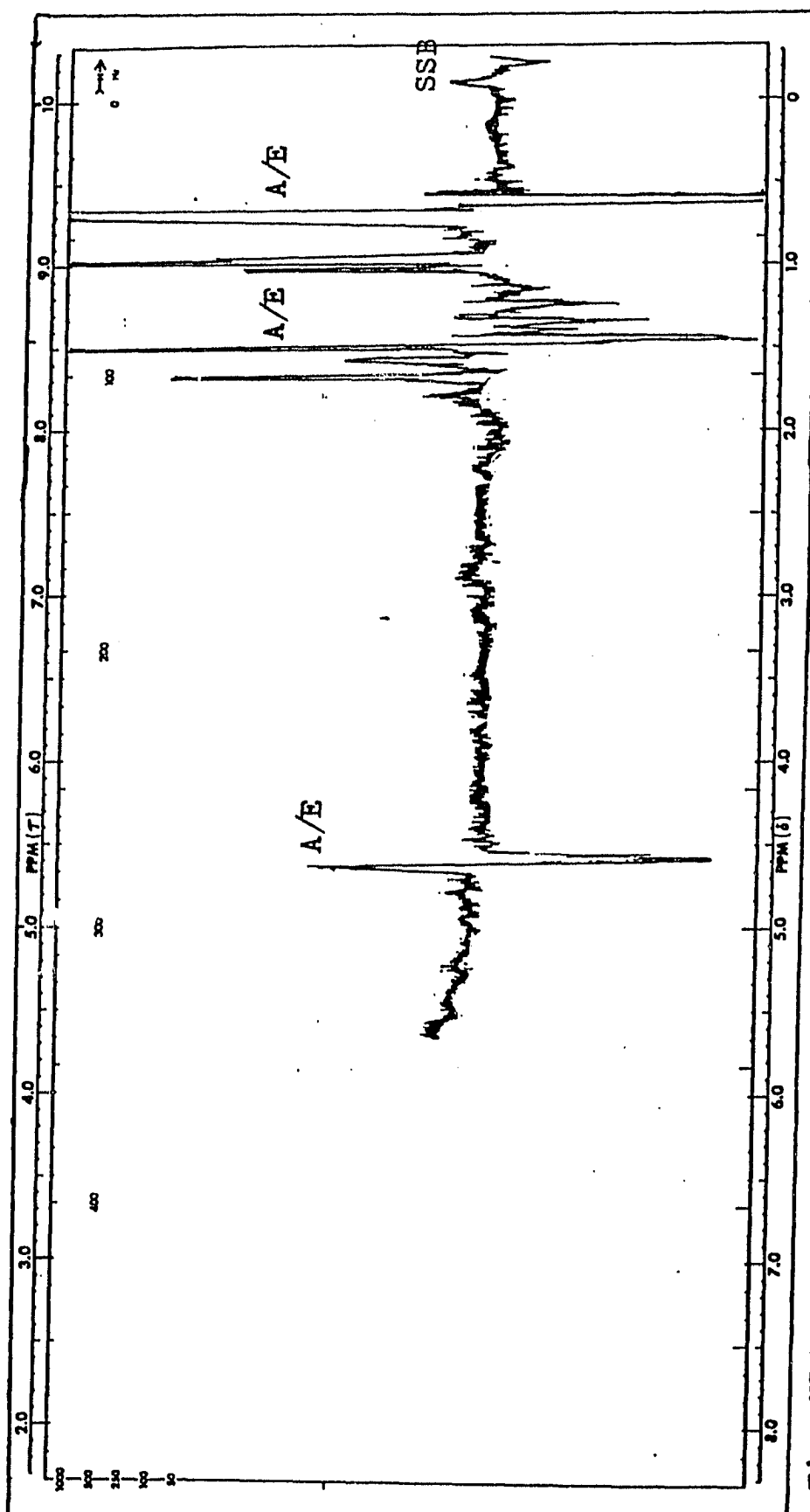
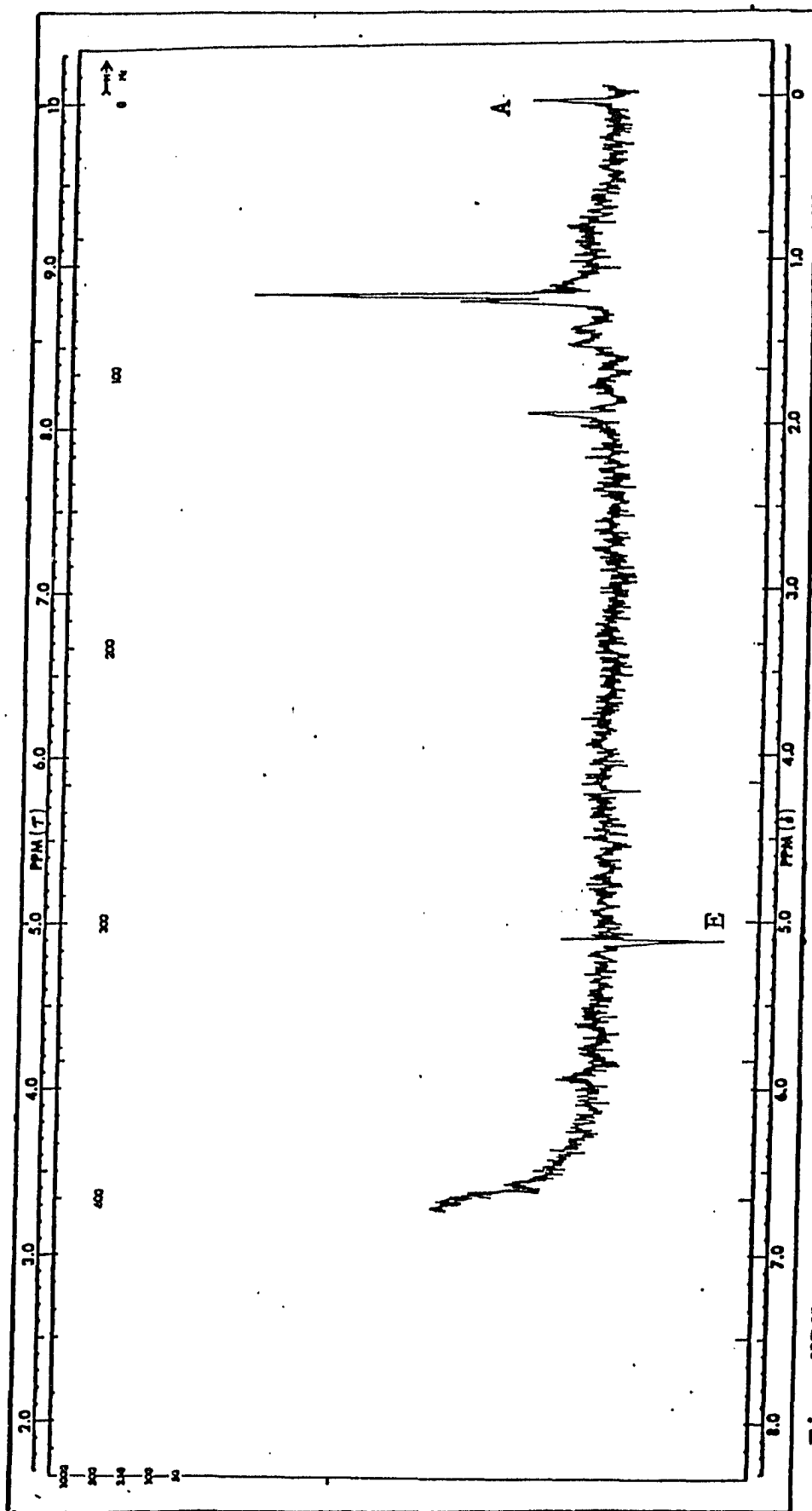


Fig. XLIV. Decomposition of *t*-butyl perphosphate in chlorobenzene.



radicals.

Methane is formed from the methyl-CHD encounters and appears in the expected enhanced absorption.

Decomposition of t-Butyl 2-Chloropropionate

The CIDNP (figure XLVII) produced by this decomposition shows both the effects due to the chloroethyl-CHD and chloroethyl-chloroethyl pairs. Polarization is observed for ethyl chloride (δ .37 δ quartet O/E) and methane (A) as well as some unidentified methyl groups (δ 1.40 δ).

The polarization of the ethyl chloride is the result of two super-imposed effects. The A/E multiplet effect results from the interaction of two chloroethyl radicals; the net emission is due to the chloroethyl-CHD radical pair. Each radical pair produces ethyl chloride and the final result is a cancelling of the absorption half of the multiplet and a reinforcing of the emission.

The phases of the polarization are consistent with Kaptein's rules.

Summary of the CIDNP Effects in Aromatic Solvents

It appears that there are two independent mechanisms which will generate CIDNP in these solvents. If the alkyl radicals generated by the decomposition of the perester can disproportionate, then the dominant polarization will result from the interaction of two alkyl radicals. The reactions leading to CIDNP in these peresters are summarized

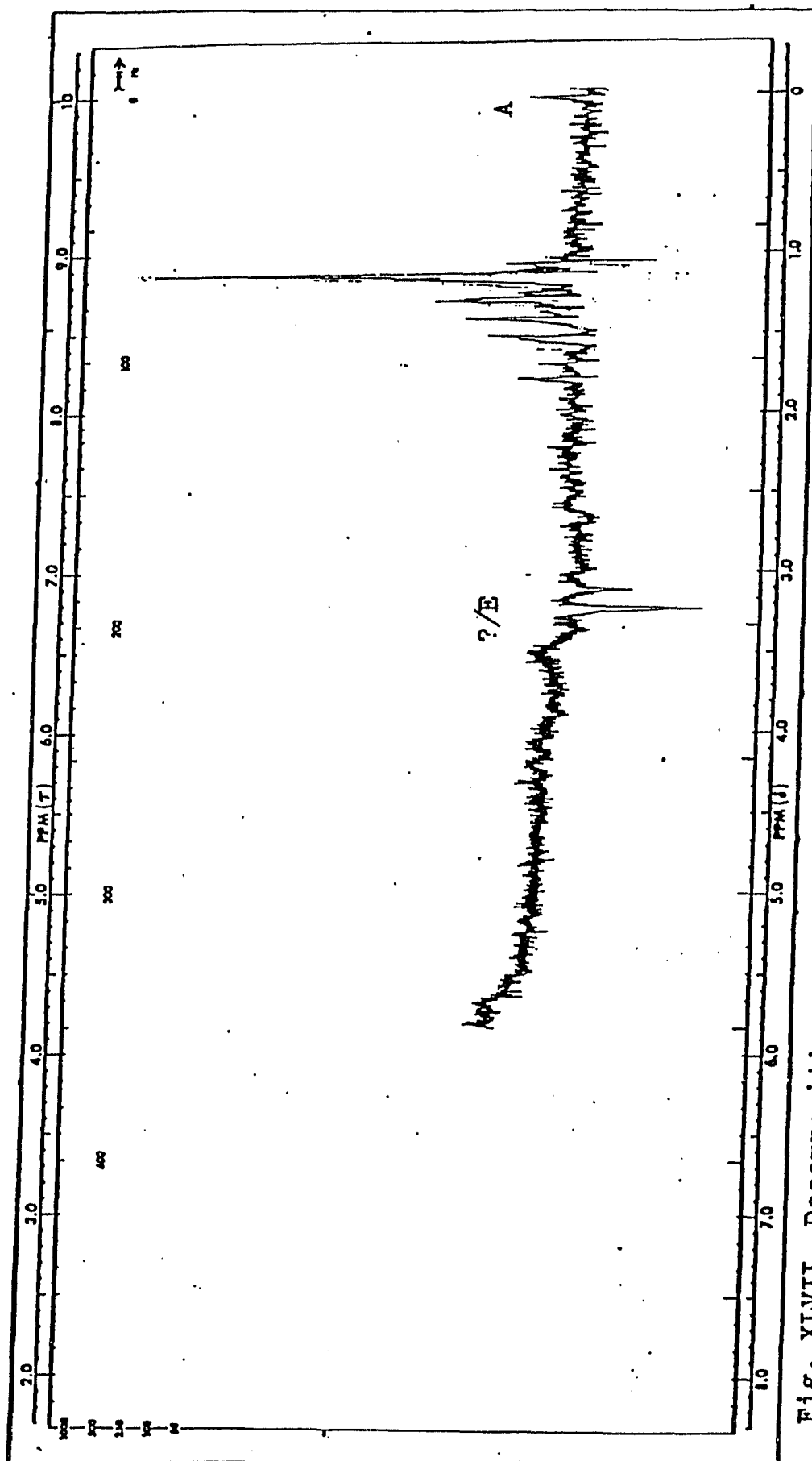


Fig. XLVII. Decomposition of t-butyl 2-chloropropionate in chlorobenzene.

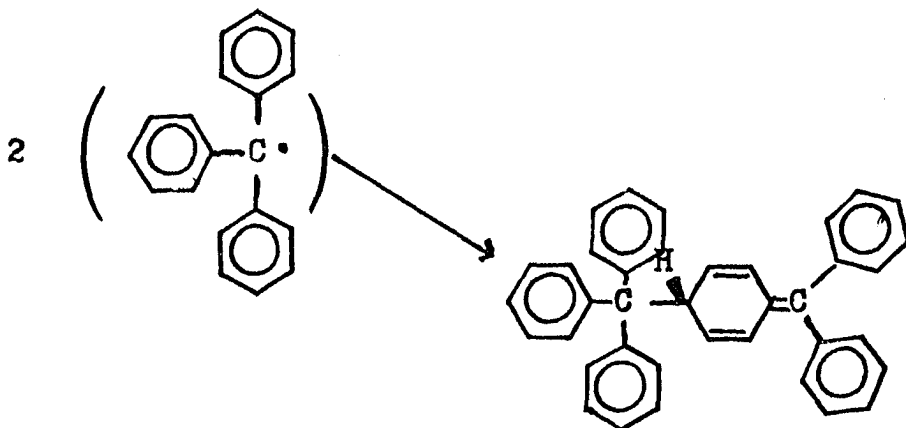
in figure XLVIII.

In peresters where the alkyl radicals produced cannot disproportionate, the dominant CIDNP is generated by the alkyl-CHD radical pairs. The reactions generating CIDNP in these systems are summarized in figure XLIX.

In either case, the polarization observed for methane is due to the interaction of methyl-CHD radical pairs.

Ring Coupled Products from Benzylic Radicals

The attack of the ring positions of benzylic radicals has been demonstrated in a few systems.⁶³ It is known that the dimer resulting from the coupling of two triphenylmethyl radicals has the quinoid structure.



Similar products appear to be formed by the coupling of two cumyl radicals. In this case, the NMR structure of the dimer has been assigned⁷⁴ giving us an ideal model compound to aid in product assignments. There are no polarized resonances which are attributable to the ring

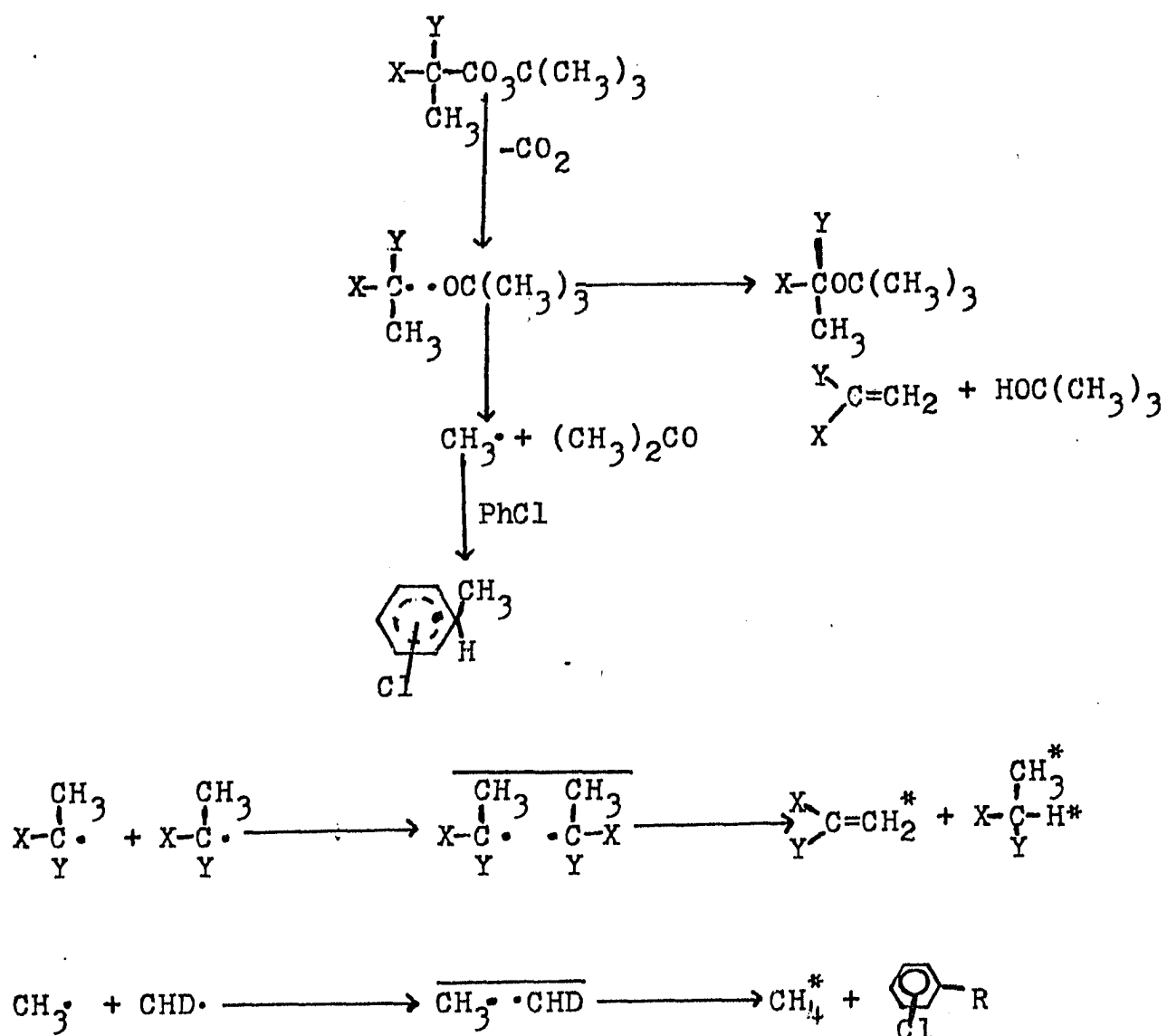


Fig. XLVIII. Reactions leading to CIDNP during the decomposition of peresters whose alkyl radicals can disproportionate. X = C₆H₅, Cl or CH₃. Y = C₆H₅, or CH₃. R = CH₃ or OC(CH₃)₃.

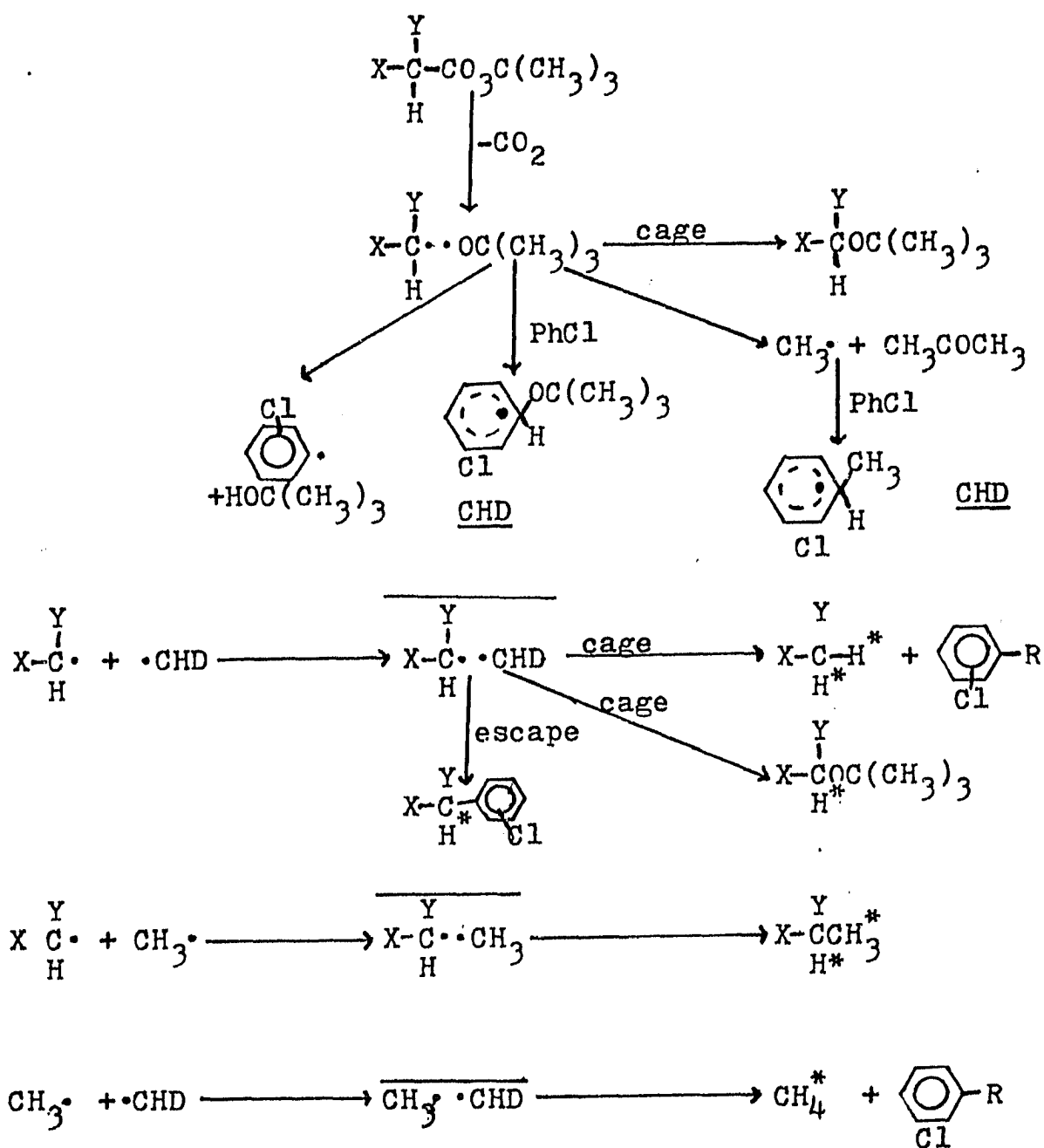


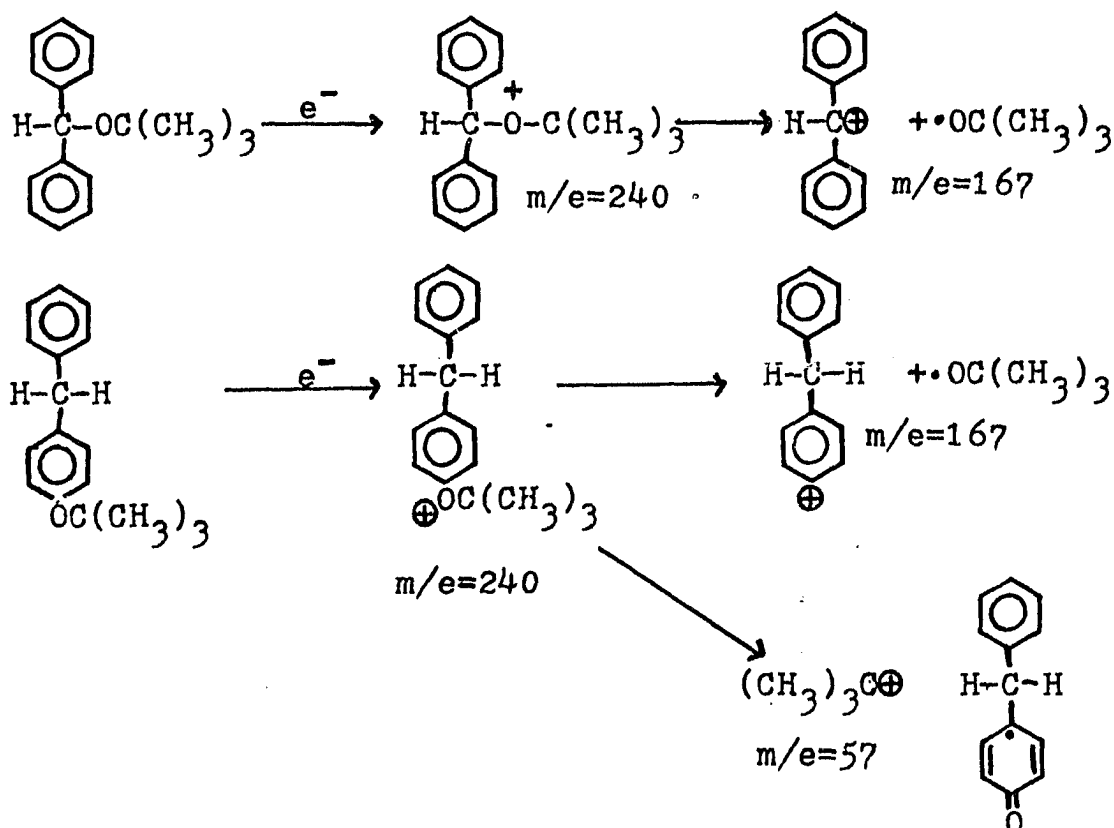
Fig. XLIX. Reactions leading to CIDNP during the decomposition of peresters whose alkyl radicals cannot disproportionate. $\text{X} = \text{C}_6\text{H}_5$ -, substituted C_6H_5 -, Cl or H . $\text{Y} = \text{C}_6\text{H}_5$ - or Cl . $\text{R} = \text{CH}_3$ or $\text{OC}(\text{CH}_3)_3$

coupled dimer of any of the benzylic peresters studied. In investigations of the corresponding azo compounds, there was no mention of any products attributable to the ring coupled dimers of the benzylic radicals¹³. This was in spite of the fact that the normal α - α dimer exhibited strong CIDNP. We can offer no explanation for the absence of CIDNP in these products.

Another form of ring attack involves the addition of the t-butoxy radical to the para position of benzylic radicals. This was proposed as an alternate cage reaction which is available to peresters when the α - α coupling is sterically hindered.⁷⁵ Lorand suggested that the cage coupling of the t-butoxy radical to the diphenyl methyl radical produces two isomeric ethers. This was based on the difference between the isolated cage ether and the cage effect estimated from trapping studies. Lorand was, however, unable to isolate the ring coupled product. We would not expect to observe CIDNP in this product since the t-butoxy radical would be required in the polarizing cage. Careful product studies, however, indicate the presence of two isomeric diphenylmethyl t-butyl ethers. Separation of the products from the decomposition of t-butyl diphenylperacetate in benzene by preparative gas chromatography produces two products of molecular weight 240 amu. Fragmentation patterns in the mass spectrum of each compound are markedly different.

Ethers decompose after electron bombardment to give

carbonium ions in the mass spectrometer. This fragmentation occurs so as to give the most stable carbonium ion. Comparison of the two ethers will lead us to predict the following initial decompositions:



This initial decomposition should easily distinguish the two isomeric compounds by mass spectroscopy.⁷⁶ The normal ether gives a large peak at m/e 167 (base peak) corresponding to the diphenylmethyl cation with the peak at m/e 57 equal to about 5% relative intensity. The para-coupled ether again has the base peak at 167 due to the p-benzyl phenyl cation but the peak corresponding to the t-butyl cation is now 46.3%. The complete assignment of the major peaks in each of the mass spectra appear in table 4 (for the normal ether) and table 5 (for the ring coupled ether).⁷⁶

These results confirm the prediction of Lorand that the coupling of t-butoxy radicals to diphenyl methyl can give two cage ethers. The quinoid ether, the second cage ether, could rapidly isomerize to give the more stable p-t-butoxy diphenylmethane which was identified by its mass spectrum:

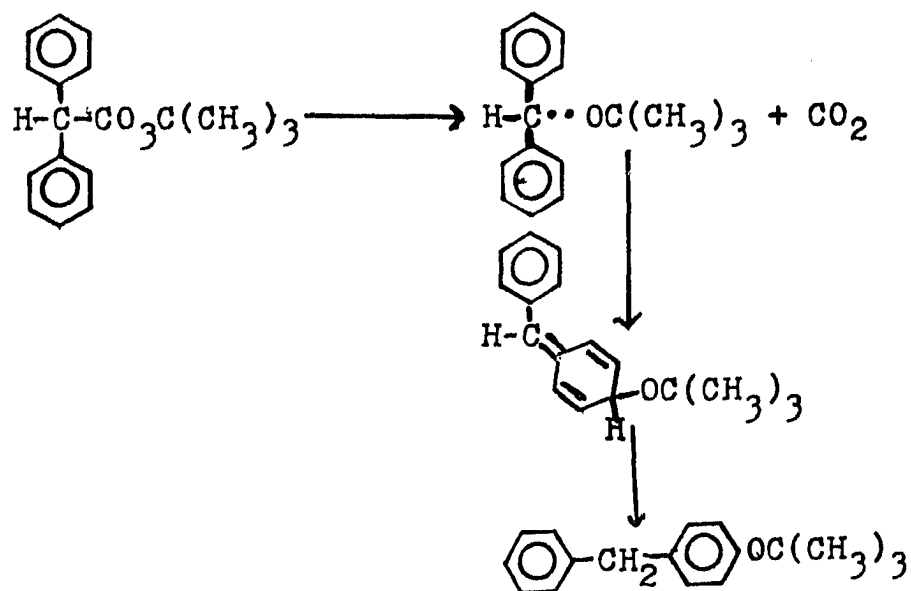


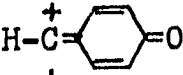
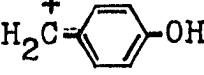
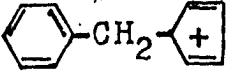
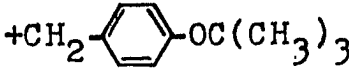
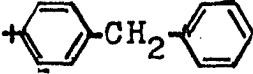
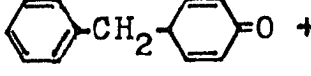
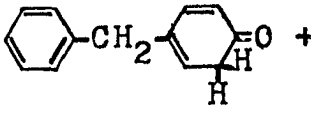
Table 4

Mass Spectrum of Diphenylmethyl t-Butyl Ether

<u>m/e</u>	<u>Relative Intensity</u>	<u>Assignment</u>
57	5.7	$+C(CH_3)_3$
77	8.5	$+C_6H_5$
105	7.5	$C_6H_5C\equiv O^+$
152	13.5	
165	30.8	
166	11.3	
167	100.	$(C_6H_5)_2CH^+$
168	22.5	$(C_6H_5)_2CH_2^+$
240	15.0	Parent Ion

Table 5

Mass Spectrum of p-t-Butoxy Diphenylmethane

<u>m/e</u>	<u>Relative Intensity</u>	<u>Assignment</u>
57	46.3	+C(CH ₃) ₃
77	25.0	+C ₆ H ₅
78	22.9	+C ₆ H ₆
79	13.7	+ 
105	34.2	H-C ⁺ = 
107	54.7	H ₂ C ⁺ = 
152	13.7	
155	11.6	
163	11.5	+CH ₂ - 
165	31.0	
166	14.7	
167	100	+ 
168	17.1	(C ₆ H ₅) ₂ CH ₂ ⁺
183	9.0	 +
184	27.2	 +
240	31.0	Parent Ion

INSTRUMENTATION

NMR spectra - CIDNP spectra were recorded using a Varian A-60-A NMR spectrometer which was equipped with a Varian variable temperature controller. The sample for study was placed in the pre-heated probe and spectra were recorded using a rapid scan (500 Hz./100 sec.). These rapid scans served to locate polarized resonances and maximize the resolution controls of the spectrometer. Temperature was adjusted so as to give maximum CIDNP signals during the one to three minute time period. After this procedure, small sections (60-80 Hz.) of the spectra were repeatedly scanned at a rate of 500 Hz./250 sec. using fresh samples of the perester for each section. Each area of the spectrum was recorded using this procedure. CIDNP spectra appearing throughout this work are composites of between 5 and 8 smaller sections.

Product spectra were recorded after the perester had completely decomposed (10-30 minutes). Chemical shifts were measured by reference to known products of the reaction mixture such as acetone or pentachloroacetone and by addition of known compounds.

Routine analytical spectra were recorded using the A-60-A or a Varian T-60 NMR spectrometers. These spectra were recorded in deuteriochloroform containing 1% tetramethylsilane as a reference material.

Mass Spectra were recorded using a Varian Mat CH-7 mass spectrometer⁷⁶. In most cases, the samples were

introduced after chromatographic separation of the reaction mixture. These separations were accomplished using a Varian Aerograph 2700 gas chromatograph which was connected to the spectrometer via a helium separator. For these chromatographs, the ion current measured by the spectrometer was used to indicate the elution of the material from the column.

The isomeric diphenylmethyl t-butyl ethers were identified entirely from their mass spectra. In these cases, the compounds isolated using preparative gas chromatography were introduced into the mass spectrometer by direct insertion into the ion chamber of the instrument. Fragmentation patterns were recorded at 70 ev while the molecular weight was determined at low ionization energies (about 20 ev.).

Gas Chromatography - analytical separations were performed using a Varian 2700 gas chromatograph which was equipped with a single hydrogen flame ionization detector. Reaction mixtures were separated using a 10% SE-30 on chromosorb-W column (8' by 1/8"). The injector oven was maintained at 200 C and the detector oven was at 300 C. The column oven was varied from ambient to 200 C to obtain maximum separation of the mixtures.

Preparative gas chromatographic separations were carried out using a Varian Aerograph 90-F chromatograph. This instrument contained a 3' by 1/4" 3% SE-30 on chromosorb W column. The material was isolated after separation by

collecting the effluent at the exit port of the instrument in dry ice cooled glass tubes. The detector in this instrument is a thermal conductivity detector. Injections were of approximately 50 microliters and about 20 injections were required to obtain a visible amount of material for the mass spectrometric identification of the ethers.

Solvents

Hexachloroacetone - this compound was obtained from both Eastman and Aldrich Chemical Companies. In either case, the material supplied was a pale yellow liquid which showed proton containing impurities in the NMR spectrum. This material was purified by fractional distillation and the fraction boiling 203-204° C was used for perester decompositions. This colorless liquid contained approximately .2M pentachloroacetone as an impurity (by NMR analysis).

Chlorobenzene - the chlorobenzene used was purchased from J.T. Baker Chemicals. This reagent grade material was used without further purification.

o-Dichlorobenzene - this material was supplied by Matheson Chemical Company. The material obtained was technical grade and was purified by fractional distillation. The material which distilled at 180-181 C (lit. 180.5) was collected and used for perester decompositions.

Benzene - the material used for the decomposition of t-butyl diphenyl peracetate was from J.T. Baker chemicals. This spectro grade material was used without purification.

The same material was used for the product studies of peresters.

Benzene-d₆ - this material was purchased from Aldrich and was used without purification. This solvent had a specified isotopic purity of 99.5%.

Decane - this solvent was purchased from Aldrich Chemicals and had a specified purity of 99+% (gold label). This material was used without purification.

Dodecane - this material was supplied by Aldrich Chemicals and was distilled prior to use. The fraction of the material boiling 216-7 was collected and used for the perester decompositions.

Mineral Oil - this material was used as supplied by Aldrich Chemical Company.

Deuterated Solvents - these materials used for the analytical spectra were purchased from a variety of sources (Aldrich, Norell, Wilmad and Merck Chemical Companies). In all cases, the materials were used without further purification.

Pentane - this material was purchased from both Aldrich and Eastman Chemicals. In either case, the material was dried and stored over molecular sieves.

Hexane - this solvent was obtained from J.T. Baker Chemicals and was dried (as described above) before use.

Diethyl Ether (anhydrous) - this solvent was obtained from J.T. Baker and was not purified before use.

Preparation of Peresters

The peresters used in this study were prepared as described by Bartlett and Simons unless otherwise noted ²⁹.

t-Butyl Hydroperoxide was obtained from Lucidol Chemical Company ⁷⁷. This material was supplied with an estimated purity of 90% with the impurities being t-butanol and water. This material was purified by evaporating the impurities at reduced pressure. After this procedure, the peroxide was stored at 0°C over molecular sieves until use.

The pyridine used for the synthesis of peresters was obtained from J.T. Baker Chemicals. The reagent grade material was dried over potassium hydroxide pellets and distilled prior to use. This material was stored over molecular sieves prior to use.

Preparation of t-Butyl Phenylperacetate (1)

In a typical preparation, a solution of 3.10 g. (0.02 moles) of phenylacetyl chloride (Eastman) in 10ml. of pentane was added at 0-5 C to a solution of t-butyl hydroperoxide (1.8 g. 0.02 moles) and pyridine (1.6 g. 0.02 moles) in pentane. When addition was complete, the mixture was allowed to react at 0°C for one hour. After this period, the reaction mixture was poured into ice cold water and the organic phase separated. The pentane layer was then extracted two times using 10% solution of sulfuric acid and then washed with water. The pentane layer

was then washed twice using 10% sodium hydroxide and then again with water. The temperature of each extraction and washing was kept at 0-5°C. The organic layer was then dried over anhydrous sodium sulfate and the solvent removed at reduced pressure. The crude perester was then purified by chromatography over fluorosil using pentane to elute. Evaporation of this solution gave the purified perester as a pale yellow oil (2.20 g. 53% yield).

A convenient modification of Bartlett's procedure involves filtering the original reaction mixture to remove the precipitate of pyridine hydrochloride formed. The residue was then washed with 50-75 ml of cold pentane (0-10°C) and the filtrate and washings combined. This solution was then cooled to -68°C at which time the desired perester separated as an oil. The solvent was then decanted and the crude perester was subject to column chromatography as above. This purified perester gave identical NMR spectra to the perester purified by washing and chromatography.

NMR analysis of the perester in CDCl_3 gave three singlets, 7.35 δ (5 protons), 3.66 δ (2 protons) and 1.22 δ (9 protons). There were no traces of any impurities in the perester before decomposition.

Preparation of t-Butyl Phenylperacetate- $\alpha,\alpha\text{-d}_2$

The deuterium exchange was carried out using 1.20 g. (0.01 moles) of benzyl cyanide (Pfaltz and Bauer) in 20 ml.

of 20% NaOD (Aldrich 40% NaOD in Norell D₂O) and a catalytic amount of benzyltriethylammonium chloride (Aldrich). This two phase reaction was rapidly stirred for thirty minutes and a sample was removed for NMR analysis. The benzyl cyanide was found to be about 95% deuterium enriched (the remaining benzyl cyanide was α -d₁). The NaOD-D₂O layer was then removed and 10 ml. of fresh solution was added. This reaction was then refluxed over night to both complete the exchange and hydrolyse the nitrile. Acidification of the aqueous reaction mixture resulted in a precipitate of phenylacetic acid- α,α -d₂. This material was purified by recrystallization from petroleum ether. The yield after hydrolysis was 1.08 g. (79%). NMR analysis indicated that the compound was completely deuterated (greater than 98%).

The acid was refluxed with excess thionyl chloride (Pfaltz and Bauer) for 6 hours to give 0.76 g. (62%) of phenylacetyl chloride- α,α -d₂. (boiling point - 112-4°C at 30 mm.)

The perester was prepared by the reaction of this acyl chloride (0.76 g. 2.7 mmoles) with an equimolar amount of t-butyl hydroperoxide and pyridine in pentane. The perester was purified as described for the non-deuterated compound by extractions and chromatography. The evaporation of the solvent gave 0.415 g. of the desired perester (71%). NMR analysis on this compound gave two singlets 7.35 δ (5 protons) and 1.22 δ (9 protons).

Preparation of p-Bromophenylacetyl Chloride

This material was prepared from 10 g. (0.04% moles) of p-bromophenylacetic acid (Aldrich) with excess thionyl chloride. After 5 hours the excess thionyl chloride was removed and the acyl chloride was distilled at reduced pressure to give 8.85 g. (0.38 moles 81%), boiling point 136-8 at 20 mm. (Lit. 125°C at 8 mm.⁷⁸).

Preparation of t-Butyl p-Bromophenylperacetate

This perester was prepared from 4.66 g. (.02 moles) by the method described for the unsubstituted compound. Purification by column chromatography gave 3.04 g. (53%) of a pale yellow perester which solidified upon storage at -20°C. NMR analysis gave an AB quartet for the 4 aromatic protons at 7.30 δ and singlets at 3.65 δ (2 protons) and 1.23 δ (9 protons).

Preparation of p-Chlorophenylacetyl Chloride

This acyl chloride was prepared by refluxing 10 g. (0.058 moles) of p-chlorophenylacetic acid (Aldrich) with 75 ml (124 g. 1.05 moles) thionyl chloride. This reaction was allowed to reflux for 5 hours after which time the excess thionyl chloride was removed by distillation. The acyl chloride was then purified by vacuum distillation to give 9.67 g. (0.051 moles 88%) p-chlorophenylacetyl chloride, boiling point 128°C at 18 mm. (Lit 119°C at 14 mm.³³).

Preparation of t-Butyl p-Chlorophenylperacetate

This perester was prepared by the same procedure used for the unsubstituted perester. The reaction used 4.56 g. (0.02 moles) of the p-chlorophenylacetyl chloride with an equal amount of t-butyl hydroperoxide and pyridine in pentane. The crude perester was purified by chromatography over fluorosil to give 2.32 g. (48%) of the desired perester. NMR analysis of the perester in CDCl_3 gave the following spectrum: 7.30 δ (4 protons), 3.55 δ (2 protons) and 1.17 δ (9 protons).

Preparation of m-Chlorophenylacetyl Chloride

The acyl chloride was prepared from 5.00 g. of m-chlorophenylacetic acid (Aldrich) by reaction with thionyl chloride. The product was purified by vacuum distillation to give 3.70 g. (.02 moles) of the desired material boiling point 121°C at 18 mm. (Lit. 121°C at 17 mm.³³).

Preparation of t-Butyl m-Chlorophenylperacetate

This perester was prepared from 2.33 g. of acid by the usual method. Column chromatography gave 1.28 g. (5.28 mmoles 44%) of the desired perester. NMR of this compound gave a multiplet for the four aromatic hydrogens 7.25 δ and two singlets at 3.60 δ (2 protons) and 1.23 δ (9 protons).

Preparation of o-Chlorophenylacetyl Chloride

This material was prepared from 5.0 g. of o-chloro-

phenylacetic acid and an excess of thionyl chloride. The reaction was allowed to reflux for 5 hours at which time the excess thionyl chloride was removed by distillation. The crude acid chloride was purified by vacuum distillation to give 3.95 g. (72% yield) of the desired acyl chloride. boiling point 110°C at 16 mm.

Preparation of t-Butyl o-Chlorophenylperacetate

The perester was prepared from the reaction of 2.28 g. (0.01 moles) of o-chlorophenylacetyl chloride with excess t-butyl hydroperoxide. The crude perester was then purified by passing through a column of fluorosil. The final perester was obtained in 57% yield (1.39 g.) which gave the following NMR spectrum: 7.20 δ multiplet (4 protons), 3.50 δ singlet (2 protons) and 1.18 δ singlet (9 protons).

Preparation of p-Fluorophenylacetyl Chloride

This acyl chloride was prepared from 5.00 g. of the corresponding carboxylic acid (Aldrich) by reaction with thionyl chloride. The acyl chloride was isolated by vacuum distillation to give 4.4 g. (79%), boiling point 112°C at 18 mm.

Preparation of t-Butyl p-Fluorophenylperacetate

The perester was prepared from the reaction of the acyl chloride with t-butyl hydroperoxide in pentane. The material obtained by this procedure was purified by

chromatography over fluorosil to give 1.17 g. (51%) of the desired perester. NMR in CDCl_3 gave 7.4 - 6.9 δ multiplet (5 hydrogens), 4.55 singlet (2 hydrogens) and 1.22 singlet (9 hydrogens).

Preparation of p-Methylphenylacetyl Chloride

The chloride was prepared from 10.0 g. of p-methylphenylacetic acid (K&K labs) and thionyl chloride. The thionyl chloride was then removed and the acyl chloride vacuum distilled to give 6.66 g. of the desired product (60%) boiling at 102-3°C at 18 mm. (Lit. 108-11°C at 20 mm.³³).

Preparation of t-Butyl p-Methylphenylperacetate

The perester was prepared from 5.04 g. (0.03 moles) of the acyl chloride and t-butyl hydroperoxide under the usual conditions. The yield from this procedure was 5.45 g. (66%) of the desired perester. NMR of this compound gave: 7.05 δ (5 hydrogens, singlet) 3.40 (2 hydrogens, singlet) 2.20 (3 hydrogens, singlet) and 1.12 (9 hydrogens, singlet).

Preparation of p-Methoxyphenylacetyl Chloride

The acyl chloride was prepared by the reaction of thionyl chloride with p-methoxyphenylacetic acid 10.0 g. (Ald.). The product was isolated by vacuum distillation to give (66%) of the desired acyl chloride. (boiling point 150°C at 14 mm. Lit. 127-8°C at 9 mm.³³).

Preparation of t-Butyl p-Methoxyphenylperacetate

This perester was prepared as described for the unsubstituted compound from the reaction of 3.70 g. (0.02 moles) of the acyl chloride. Column chromatography gave 1.52 g. (32%) of the desired perester. M.P. 37-8°C.

NMR gave: 7.06 δ AB quartet (4 protons), 3.81 δ singlet (3 protons), 3.60 δ singlet (2 protons) and 1.26 δ singlet (9 protons). (Lit. M.P. 38.6 - 38.9°C.³³).

Preparation of m-Methoxyphenylacetyl Chloride

The acyl chloride was prepared by the action of thionyl chloride on 5.00 g. of m-methoxyphenylacetic acid. Distillation of the product at reduced pressure afforded 4.36 g. (77%) of the chloride boiling point 127-9°C 15 at mm. (Lit. 126°C at 15 mm.).

Preparation of t-Butyl m-Methoxyphenylperacetate

This perester was prepared as described previously from the reaction of 3.70 g. (0.02 moles) of the acyl chloride with excess t-butyl hydroperoxide. Column chromatography gave 1.79 g. of the desired perester (38%) which gave the following NMR spectrum: 7.50-6.70 δ multiplet (4 protons), 3.40 δ singlet (2 protons), 1.19 δ singlet (9 protons).

Preparation of Diphenylacetyl Chloride

Diphenylacetic acid (Eastman) (40.0 g. 0.19 moles) was

refluxed for three hours with 75 ml of thionyl chloride. The thionyl chloride was then removed by distillation to give a thick green oil which crystallized upon cooling to room temperature. The crude acid chloride was then purified by recrystallization from hexane to give 34.0 g. (79%) of diphenylacetyl chloride m.p. $51\pm 2^{\circ}\text{C}$ (Lit $51-2^{\circ}$ ⁷⁵ 56° ⁷⁹).

Preparation of t-Butyl Diphenylperacetate (2)

Diphenylacetyl chloride (10.42 g. 0.044 moles) was dissolved in 30 ml of dry ether. This solution was added to 50 ml of pentane containing 8.0 g. (0.88 moles) of *t*-butyl hydroperoxide and 3.5 g. of pyridine at $0-5^{\circ}\text{C}$. After addition, the solution was stirred for 30 minutes. Ether was added when the precipitate of pyridine hydrochloride became too thick for stirring. The reaction was then allowed to warm up to room temperature and the solution was filtered to remove the precipitate. The residue was then washed several times with diethyl ether. The filtrate and washings were combined and then evaporated at reduced pressure to give 6.0 g. of the crude perester. The product was then recrystallized three times from pentane and finally from 3:1 pentane-benzene mixture. The final product 3.50 g. (27%) gave mp $58-60^{\circ}\text{C}$ (Lit. $57.5 - 60^{\circ}\text{C}$ ^{37b}). NMR of the purified product gave 7.20 multiplet (10 protons), 4.98 δ singlet (1 proton) and 1.20 δ singlet (9 protons). An additional resonance at 5.50 δ was

attributed to a 7% impurity of diphenylmethyl t-butyl ether.

Preparation of Diphenylacetic Acid- d_1

Diphenylacetic acid (4.24 g.) was refluxed with 30 ml of methanol- d_1 (Stohler 99% d) containing 3.0 g. of potassium t-butoxide (K&K labs). After 18 hours, NMR indicated about 66% of the desired protons had been exchanged. The reaction mixture was evaporated at reduced pressure. and 30 ml of fresh methanol- d_1 containing 1.0 g. of potassium t-butoxide was added. The reaction was then refluxed for 16 hours at which time the NMR indicated only a small amount of proton containing acid was present. The reaction was then cooled and 100 ml of 10% HCl was added. The precipitated acid was then removed by extraction with diethyl ether. The ether layer was washed with water and dried and evaporated. The yield by this procedure was 3.07 g. of diphenylacetic acid- α - d_1 which was approximately 90% deuterated.

Preparation of Diphenylacetyl Chloride- α - d_1

The deuterium containing acid was refluxed with thionyl chloride for 4 hours. The excess thionyl chloride was then distilled and the product was recrystallized twice from hexane to give 2.55 g. of the acyl chloride (m.p. 52-3°C).

Preparation of t-Butyl Diphenylperacetate- α -d₁

The deuterated perester was prepared by addition of 2.55 g. of the acyl chloride dissolved in 10 ml ether to a solution containing an excess of t-butyl hydroperoxide and pyridine in pentane. The perester was isolated as described for the non-deuterated compound to give 0.68 g. (21%) of the desired perester. NMR indicated that the perester was about 90% deuterated.

Preparation of 2-Phenylpropionyl Chloride

The acyl chloride was prepared by addition of 5.0 g. (0.033 moles) 2-phenylpropionic acid (hydratropic acid, Eastman) to 20 ml of thionyl chloride. This mixture was refluxed for 2 hours and allowed to react at room temperature overnight. After this period, the excess thionyl chloride was removed and the desired acyl chloride was vacuum distilled (BP 92°C at 11 mm.) to yield 3.99 g. (85%). (Lit 93-4°C at 11 mm.⁸⁰).

Preparation of t-Butyl 2-Phenylperpropionate (3)

The acid chloride (3.99 g. 0.026 moles) was dissolved in 30 ml of pentane and slowly added to a solution of t-butyl hydroperoxide (2.31 g.) and pyridine (2.05 g.) in 100 ml of pentane at 0°C. After one hour at 0°C, 50 ml of cold water was added and the layers separated. The organic layer was then washed with dilute acid and base and then water. The pentane was then dried and removed at reduced

pressure. The final perester was purified by chromatography to give 3.02 g. (54%) of product. NMR analysis gave a singlet at 7.30 δ (5 protons), quartet at 3.75 δ (1 proton), doublet at 1.54 δ (3 protons) and 1.20 δ singlet (9 protons).

Preparation of α -Phenyl-iso-Butyryl Nitrile

Benzyl cyanide (60.0 g. 0.5 moles, P&B Chemicals) in 100 ml. of anhydrous tetrahydrofuran was slowly added to a suspension of 60.0 g. of sodium amide (Alfa Inorganics) in 500 ml. of THF. This mixture was refluxed under a nitrogen atmosphere for three hours with rapid stirring. During the initial addition of the cyanide, the reaction turned bright orange which darkened to a deep red during the reflux. After the three hours, 70.0 g. of methyl iodide (0.5 moles) was slowly added. The mixture turned orange after addition of the methyl iodide and a fine precipitate of sodium iodide formed. The reaction was then refluxed again at which time, it again became dark red. After three hours, an additional 100 g. of methyl iodide was added and the reaction turned a pale orange. The reaction was then refluxed overnight and then hydrolysed by addition of water. The organic layer was then removed, dried and evaporated to give 64.5 g. of 2-phenyl-iso-butyryl nitrile (89%).

Preparation of α -Phenyl-iso-Butyric Acid

The hydrolysis of the nitrile was carried out in both acid and base to give the desired carboxylic acid.

Acidic Hydrolysis - 30 g. of the crude nitrile was refluxed for 5 days with 100 ml of 48% hydrobromic acid. The reaction was then diluted with 400 ml of water and extracted with ether. The organic layer was washed with two portions of water and then extracted with 10% sodium hydroxide. Upon acidification of this extract, a pale brown oil separated which crystallized upon cooling to room temperature. The Product was then recrystallized two times from hexane to yield 23.4 g. of the desired acid. (mp 75-6°C yield 70%) (Lit. 77°C)²⁸.

Alkaline Hydrolysis - the crude nitrile (34.5 g.) was refluxed with 30% potassium hydroxide in 50% aqueous methanol for three days. The reaction was then extracted with ether and the aqueous phase acidified to give an oil which crystallized upon cooling. The product was then recrystallized twice from hexane to give 19.5 g. of the desired carboxylic acid. (yield 50% mp 75-6°C).

Preparation of α -Phenyl-iso-Butyryl Chloride

The acyl chloride was prepared by the addition of 10.0 g. of the recrystallized acid to thionyl chloride. The reaction was then refluxed for 4 hours and the excess thionyl chloride was removed by distillation. The acyl

chloride was then purified by vacuum distillation to give 8.68 g. (77%) boiling point 110-2°C at 11 mm. (Lit. 77°C at 0.2 mm. ²⁸).

Preparation of t-Butyl α -Phenyl Per-iso-Butyrate (5)

The perester was prepared by the reaction of the acyl chloride (5.46 g.) with excess t-butyl hydroperoxide in pentane-ether solution. The reaction was allowed to react overnight at 0°C. The mixture was then extracted with water, dilute acid and dilute base. The organic layer was then dried and evaporated to give the crude perester. This compound was then purified by chromatography over fluorosil to give 0.93 g. of the desired perester. (16% yield) NMR analysis of the perester gave 7.5-7.2 multiplet (5 hydrogens), 1.47 singlet (6 hydrogens) and 1.20 singlet (9 hydrogens).

Preparation of 2,2-Diphenylpropionyl Chloride

The acid chloride was prepared by treatment of 2,2-diphenylpropionic acid (Aldrich)(4.24 g. 0.020 moles) with 50 mls. of thionyl chloride. The reaction was refluxed overnight and the excess thionyl chloride was then removed by distillation. The residue was then recrystallized from hexane giving 2.60 g.(55%) of the desired acyl chloride m.p. 37-8°C. (Lit. 39.0-42.5°C ³⁷).

Preparation of t-Butyl 2,2-Diphenylperpropionate (4)

The attempted preparation of this perester, by our

usual procedure, was unsuccessful. The product recovered from this reaction contained only the original carboxylic acid resulting from the hydrolysis of the acyl chloride.

This perester was successfully prepared by the reaction of the acyl chloride with the sodium salt of t-butyl hydroperoxide in methylene chloride. This procedure is analogous to that used by Lorand to prepare t-butyl triphenylperacetate ^{63b}.

Sodium t-butyl hydroperoxide was prepared by the addition of 18.0 g. of t-butyl hydroperoxide in 50 ml of anhydrous ether to 9.6 g. of sodium hydride (50% dispersion in oil, Alfa Inorganics) in 200 mls. of ether at 0°C. During the addition, there was considerable evolution of hydrogen gas. After two hours at 0°C, the solution was filtered and the residue washed with dry ether. This anhydrous sodium t-butyl hydroperoxide was dried at reduced pressure.

The perester was prepared by the addition of 2.44 g. of 2,2-diphenylpropionyl chloride in 20 ml. of methylene chloride to a suspension of sodium t-butyl hydroperoxide (4.0 g.) in methylene chloride. After addition of the acyl chloride, the reaction was stored at -20°C for 24 hours. The reaction was then filtered through Celite and the filtrate was removed at reduced pressure. The crude perester was then recrystallized from pentane to give 1.89 g. (0.0063 moles, 63%) m.p. 69-70°C. with decomposition. The NMR spectrum of this compound consisted of three singlets:

7.30 δ (10 protons), 1.28 (3 protons) and 1.15 (9 protons).

Preparation of t-Butyl Perpivalate (6)

This perester was prepared by the addition of pivaloyl chloride (Aldrich) (3.60 g. 0.03 moles) to t-butyl hydroperoxide under the usual conditions. After extractions with both dilute acid and dilute base, the organic layer was evaporated and the crude perester purified by column chromatography over fluorosil. This purified compound was obtained as a colorless oil in 43% yield (2.25 g.) and gave the following NMR spectrum: 1.25 δ (9 protons) 1.17 δ (9 protons).

Preparation of t-Butyl Chloroperacetate (7)

This perester was prepared by acylation of t-butyl hydroperoxide by chloroacetyl chloride (Aldrich, 1.31 g.) in pentane containing pyridine. The perester was purified by column chromatography over fluorosil to give a 48% yield (0.79 g.) of the desired compound. NMR of this compound in CDCl₃ gave two singlets at 4.18 δ (2 protons) and 1.32 (9 protons).

Preparation of t-Butyl Dichloroperacetate (8)

This perester was prepared by the usual procedure using 0.02 moles of the corresponding acyl chloride (Aldrich). This compound was purified by passing it through a column of fluorosil to give 2.21 g. of the

desired perester (58%). NMR analysis of this compound gave two singlets at 6.05 (1 proton) and 1.28 (9 protons).

Preparation of t-Butyl Trichloroperacetate (9)

This perester was prepared by the reaction of 1.8 g. (.01 mole) of trichloroacetyl chloride (Pfaltz and Bauer) with t-butyl hydroperoxide in pentane containing one equivalent of pyridine. The crude perester was purified by column chromatography over fluorosil to give 0.84 g. of the desired perester. NMR analysis of this compound gave a single resonance at 1.19 δ .

Preparation of t-Butyl 2-Chloroperpropionate (10)

This perester was prepared by the addition of 2 chloropropionyl chloride (Aldrich, 1.26 g.) to a solution of pentane containing t-butyl hydroperoxide and pyridine. The desired perester was obtained after chromatography in 43% yield (0.83 g.) and gave the following NMR spectrum: 4.47 δ quartet (1 hydrogen) 1.70 doublet (3 hydrogens) and 1.18 singlet (9 hydrogens).

Preparation of t-Butyl Phenoxyperacetate (11)

The perester was prepared by the reaction of phenoxyacetyl chloride (Aldrich, 1.70 g.) with t-butyl hydroperoxide in pentane containing pyridine. The purified perester was obtained in 22% yield (0.52 g.) by recrystallization from pentane. The product obtained melted at

21-3°C with decomposition. NMR analysis gave the following results 7.4-6.8 δ multiplet (5 hydrogens), 4.7 δ singlet (2 hydrogens) and 1.20 singlet (9 hydrogens).

Preparation of t-Butyl Thiophenoxyperacetate (12)

The acyl chloride used in this preparation was obtained by treatment of thiophenoxyacetic acid (Aldrich) with thionyl chloride. This acyl chloride was then used to prepare the perester. Reaction of the acyl chloride (1.86 g.) with t-butyl hydroperoxide in pentane containing an equimolar amount of pyridine⁶⁶ provided 0.81 g. 32% of the desired perester. NMR analysis of this perester gave 7.5-7.2 δ multiplet (5 hydrogens) 3.46 singlet (2 hydrogens) and 1.15 singlet (9 hydrogens).

Preparation of di-t-Butyl Peroxyoxalate (13)

The di-perester was obtained by the reaction of oxalyl chloride with two equivalents of t-butyl hydroperoxide under the usual conditions. The reaction mixture was filtered to remove pyridine hydrochloride which is formed as a by-product of the acylation and the filtrate was then cooled to -68°C. The perester was obtained in good yield (94%) as a white crystalline material. Freshly prepared material gave a sharp decomposition point of 49-51°C and showed no impurities in the NMR spectrum (single line at 1.19 δ). This material should be used shortly after preparation since there are

obvious decomposition products in the NMR of week-old material which was stored at -20°C . Freshly prepared perester should be handled carefully since this material, when pure, is sensitive to shock and explodes with little provocation. Care should be exercised when transferring the perester from the Buchner funnel as any scraping of the dried perester will cause it to explode.

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