LIN, LIANGCHAO

THE CHEMISTRY OF QUATERNARY AMMONIUM SALTS ALPHA-SUBSTITUTED WITH PHOSPHORUS FUNCTIONAL GROUPS

City University of New York PH.D. 1980

THE CHEMISTRY OF QUATERNARY AMMONIUM SALTS α-SUBSTITUTED WITH PHOSPHORUS FUNCTIONAL GROUPS

BY

LIANGCHAO LIN

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1980

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosphy.

date	Chairman of Examining Committee
8 August 1980 date	David C. Locke Executive Officer

Supervisory Committee

The City University of New York

Abstract

THE CHEMISTRY OF QUATERNARY AMMONIUM SALTS α-SUBSTITUTED WITH PHOSPHORUS FUNCTIONAL GROUPS

by

Liangchao Lin

Adviser: Professor Neil McKelvie

Diethoxy phosphonomethyltriethylammonium chloride, and ethoxy phenylphosphinomethyltriethylammonium chloride have been prepared from a one-step intramolecular trans-alkylation reaction. A series of diphenylphosphinomethyltrialkylammonium salts were made from the N-alkylation of N,N-dimethylaminomethyldiphenylphosphine. No P-alkylation was observed. Further alkylation of these quaternary ammonium salts gave a series of bis-(phosphonium-ammonium) salts.

DEDICATION

To Lee-fong (麗鳳)

and

To Grace and Elbert

ACKNOWLEDGEMENT

The writer would like to express his thanks to Professor Neil McKelvie for suggesting the problem, and for his advice and encouragement throughout the course of this work.

TABLE OF CONTENTS

INTRODUCTION

With the development of the olefin synthesis by Wittig and Schöllkopf[1] in 1954, interest in ylids grew and led to the preparation of a wide variety of ylids. Phosphonium ylids (I) are well-known and well-studied stable ylids. In contrast, simple nitrogen ylids (II) are far less stable. A decomposition step has been suggested leading to amines and carbene intermediates by Wittig and Polster[2].

$$R_3\overset{+}{P}\text{-}\overset{-}{C}H_2 \longleftrightarrow R_3P{=}CH_2$$

(I)

$$(CH_3)_3\overset{+}{N}\text{-}\overset{-}{C}H_2 \longrightarrow (CH_3)_3N: + [CH_2:] \longrightarrow (CH_2)_n$$

(II)

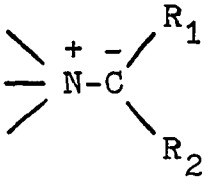
The standard explanation for this great difference in the stability is that an ammonium group is capable of stabilizing an adjacent carbanion only by an electrostatic interaction between the opposite charges.

1. G. Wittig and U. Schöllkopf, Chem. Ber. 87 1318 (1954)
2. G. Wittig and R. Polster, Ann. 599 1 (1956)

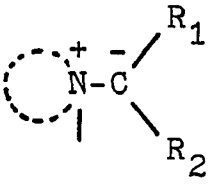
Being a first row element with filled 2s- and 2p-orbitals, the next available empty orbital is the 3s-orbital which is at a much higher energy level. In contrast, phosphorus, being a second row element with filled 3s- and 3p-orbitals, has as its next available empty orbitals the 3d-orbitals which are at a moderately higher energy level and therefore more available for overlap with considerable stablization of the carbanion, especially when the phosphorus carries a positive charge. The carbanion can also be stabilized by the much greater polarizability of the other three σ-bonds to the phosphorus atom (as compared to nitrogen-carbon σ-bonds), which allows electron density from a neighboring unshared pair to feed into σ^* antibonding orbitals. (i.e., $H_2\overset{-}{C}\text{-}\overset{+}{P}R_3 \leftrightarrow H_2C{=}PR_2 \;\; :R^-$)

The nitrogen ylids can be subdivided into ammonium (III), cycloammonium (IV), immonium (V), cycloimmonium (VI), nitrile (VII), and diazonium (VIII) ylids according to the nature of the nitrogen atom[3].

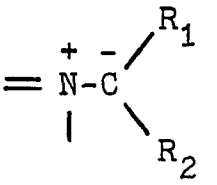
3. I. Zugravescu and M. Petrovanu, N-Ylid Chemistry, McGraw-Hill International Book Co., (1976)



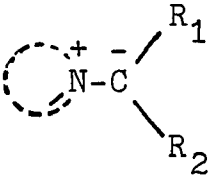
(III)



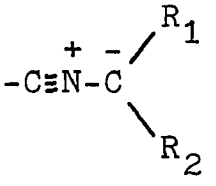
(IV)



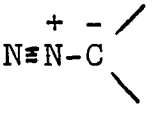
(V)



(VI)

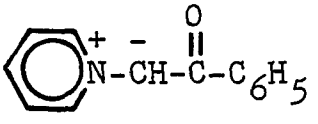


(VII)

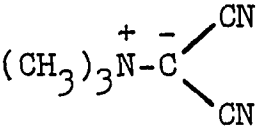


(VIII)

There are indeed stable nitrogen ylids, but in all cases the unshared pair on carbon is stabilized by conjugation with other groups (e.g., IX[4], X[5]). The nitrogen atom plays no role other than affording electrostatic stabilization for the carbanion.



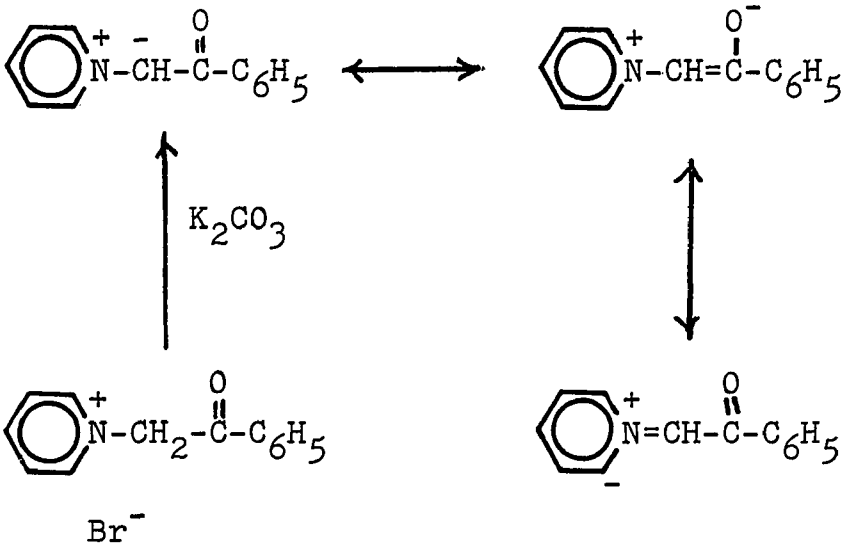
(IX)



(X)

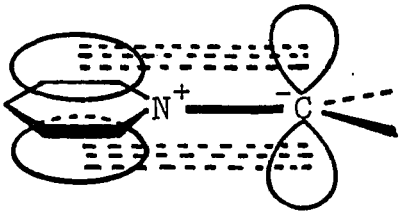
4. F. Kröhnke, Chem. Ber. 68 1173 (1935)
5. Z. Arnold, Chem. & Ind., London, 1478 (1960)

The stability of cycloimmonium ylids (VI) is mainly determined by three factors, (a) Delocalization of the charge on the carbon ylid by the electro-withdrawing substituents (e.g., C_6H_5CO-, -CN, ... etc.); (b) The coulombic attractive force between the opposite charges; (c) The resonance interaction between the N-ring and the carbanion.

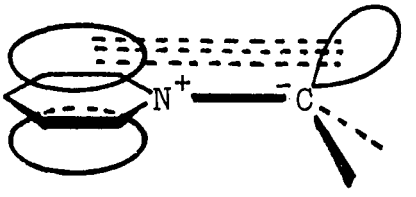


The coulombic interaction energy is not very high and it is not able to stabilize ylids, ammonium (III) or cycloammonium (IV) ylids for example, when R_1 and/or R_2 do not possess a strong anion-stabilizing character. In the cycloimmonium ylids the nitrogen atom of the ylid is sp^2-hybridized. The carbon atom can be sp^2- or sp^3-hybridized. When it is sp^2 (XI) hybridized there is

an important overlap between the doubly-occupied 2p-orbital of this carbon atom and the π-aromatic ring cloud. When it is sp^3 (XII) hybridized this overlapping becomes less important.



(XI)



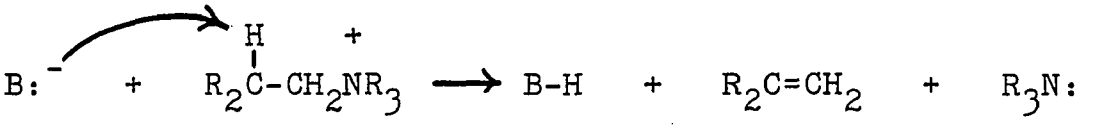
(XII)

The stability of nitrogen ylids is determined by two important factors: the structures of the 'onium group and of the anionic part. The greater the capacity of the groups attached to both the nitrogen atom and the carbanion to accept the two charges, the higher the stability of ylids.

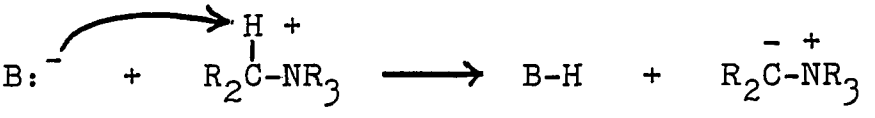
In general, quaternary ammonium salts may be expected to react with base at three different position[6]: (a) at an α-carbon to yield the free amine and alkylated base;

6. C. R. Hauser and S. W. Kantor, J. Am. Chem. Soc., 73 1437 (1951)

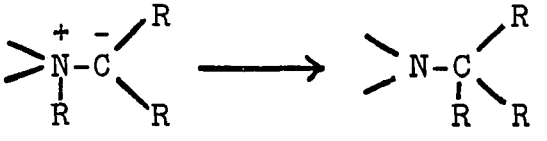
(b) at a β-hydrogen to yield alkene, amine, and the conjugated acid of the attacking base via a Hofmann elimination;



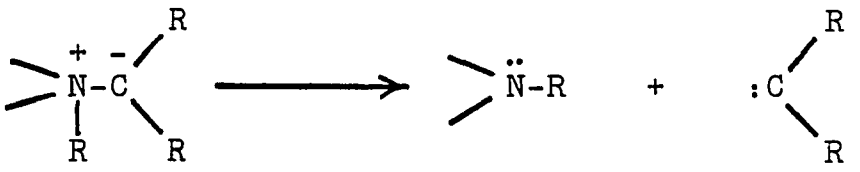
(c) at an α-hydrogen which yields the conjugated acid of the base and a carbon-nitrogen ylid.



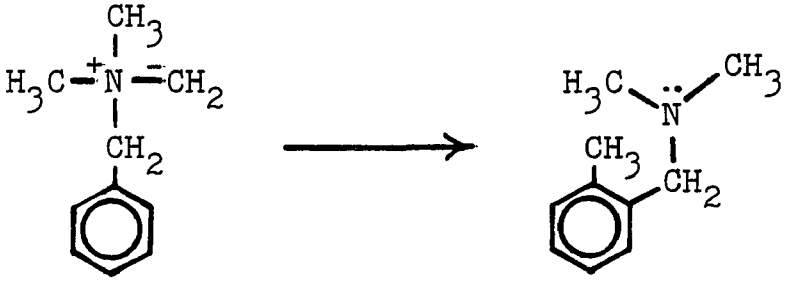
Assuming that all R-groups attached to the carbanion are hydrogen or alkyl groups, no stable ammonium- and cycloammonium ylids have been made. Such types of compounds could not be isolated as they undergo either a Stevens rearrangement[7], or a heterolytic breaking of the N-C bond giving tertiary amines and carbenes.



7. T. S. Stevens, E. M. Creighton, A. B. Gordon, and M. MacNicol, J.Chem. Soc., 3193 (1928)

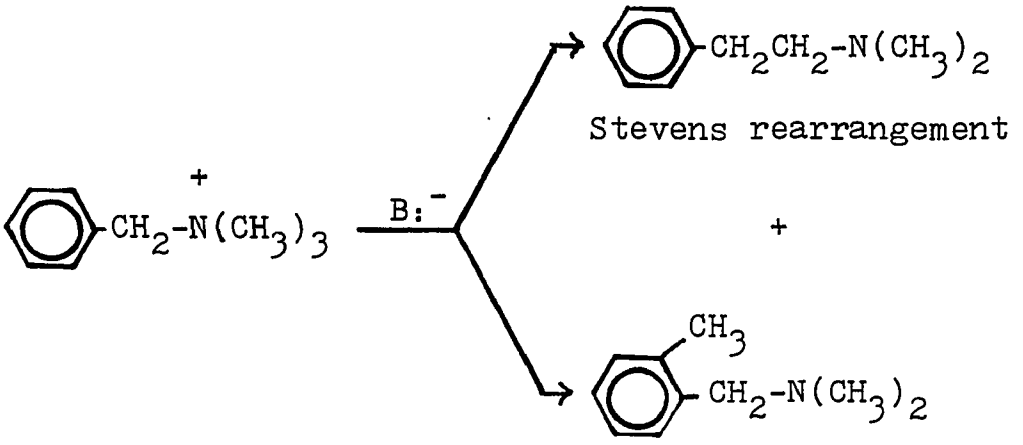


In nitrogen ylids having an alkylaromatic group substituted in the N'onium part, the molecule may be stabilized in turn by a Sommelet-Hauser type rearrangement[6,8].



When structurally feasible, both the Stevens and Sommelet-Hauser rearrangements may occur simultaneously, although experimental conditions markedly affect the relative amounts of the competing pathways.

8. M. Sommelet, Compt. Rend., 205 56 (1937)



It occurred to us that a type of ylid yet to be investigated would be one with the plus charge on one side of the carbanion and the "available d-orbital" on the other (XIV). If one could synthesize an α-phosphino-substituted quaternary ammonium salt (XIII), removal of a proton should produce an ylid (XIV) of the indicated type.

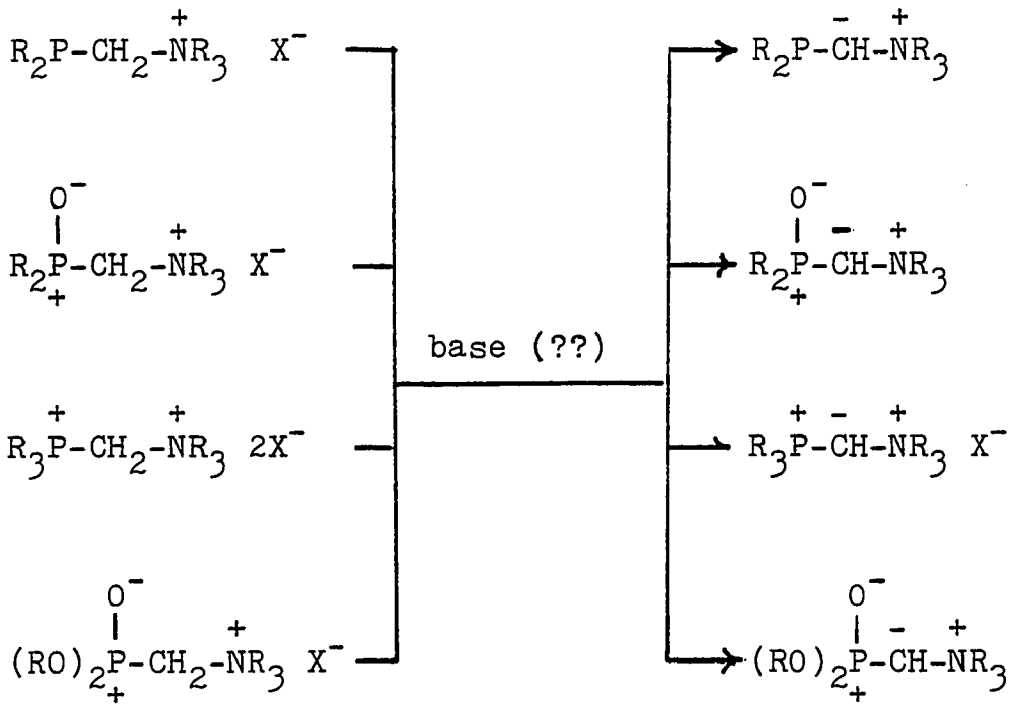
$$(C_6H_5)_2P\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_3\ I^- \xrightarrow{-H^+} (C_6H_5)_2P\text{-}\overset{-}{C}H\text{-}\overset{+}{N}(CH_3)_3$$

(XIII) (XIV)

Clearly, other lower-row elemente such as silicon or sulfur could replace the phosphorus atom.

We have (a) synthesized a variety of α-phosphino-substituted quaternary ammonium salts, and studied the action

of bases on these with the intent of making α-phosphino-substituted ammonium ylids; (b) synthesized also quaternary ammonium salts α-substituted with other phosphorus functions (phosphine oxide, phosphonium salt, phosphonate ester, etc.) and studied the action of bases on these.



The chemistry of diphenylphosphinomethyltrimethylammonium iodide and of (diphenylmethylphosphonium-trimethylammonium)-methylene diiodide has been studied.

HISTORICAL SURVEY

(A) Nitrogen Ylids

During the first two decades of this century, several chemists attempted to synthesize organic derivatives containing pentavalent nitrogen. To this purpose, Schlenk and Holtz[9] treated tetramethylammonium chloride with sodium triphenylmethide and with benzyl sodium, isolating tetramethylammonium triphenylmethide (XV) and tetramethylammonium benzylide (XVI), respectively. These compounds were thought at the time to be pentavalent nitrogen compounds.

$$(C_6H_5)_3CNa + Cl\text{-}N(CH_3)_4 \rightarrow (C_6H_5)_3C\text{-}N(CH_3)_4 + NaCl$$

(XV)

$$C_6H_5CH_2Na + Cl\text{-}N(CH_3)_4 \rightarrow C_6H_5CH_2N(CH_3)_4 + NaCl$$

(XVI)

With the same purpose in view, Hager and Marvel[10] treated benzyltriethylammonium bromide with ethyllithium,

9. W. Schlenk and J. Holtz, Ber. 49 603 (1916); 50 274 (1917)
10. F. D. Hager and C. S. Marvel, J. Am. Chem. Soc. 48 2689 (1926)

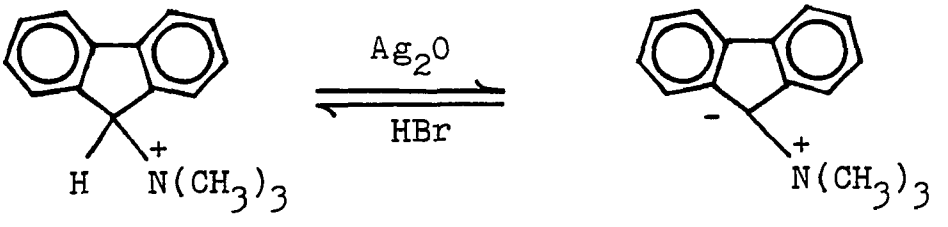
but failed to isolate the expected "benzyltetraethylammonium (XVII)" having all five groups σ-bonded to nitrogen.

$$C_6H_5CH_2\overset{+}{N}(C_2H_5)_3\ Br^- + C_2H_5Li \longrightarrow \text{"}C_6H_5CH_2N(C_2H_5)_4\text{"} + LiBr$$

(XVII)

From this observation, they concluded that the materials prepared by Schlenk and Holtz were tetraalkylammonium salts of the relatively stable triphenylmethyl and benzyl carbanions rather than derivatives of pentavalent nitrogen.

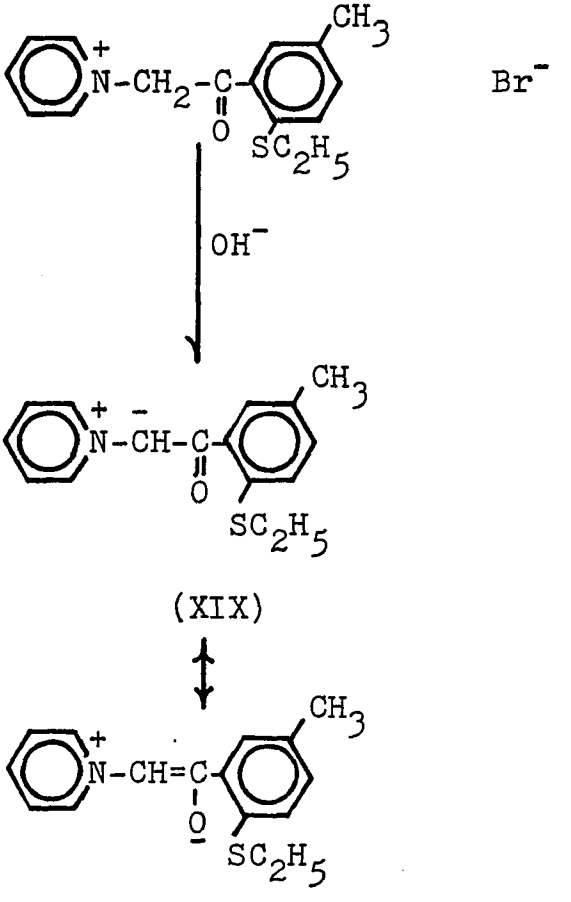
In 1929, Ingold and Jessop[11] noted a deep-purple color occurring when 9-fluorenyltrimethylammonium bromide was treated with silver oxide; the color disappeared in the presence of acids. They suggested that this was due to conversion of the hydroxide to trimethylammonium fluorenylide (XVIII).



(XVIII)

11. C. K. Ingold and J. A. Jessop, J. Chem. Soc., 2359 (1929)

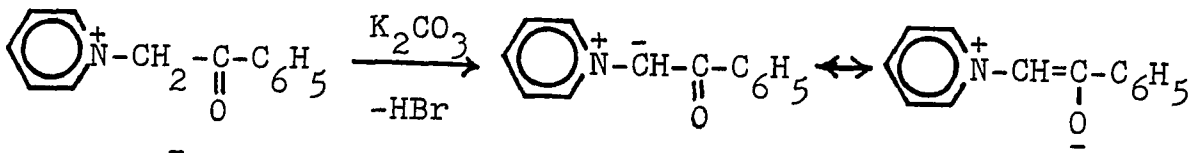
A carbanion-substituted pyridinium-methylide compound (XIX) to which a nitrogen ylid structure may be assigned was prepared by Krollpfeiffer and Müller[12] in 1933. A stable orange crystalline product was isolated by treating an aqueous solution of N-(2-ethyl-mercapto-5-ethyl-phenacyl)-pyridinium bromide with sodium hydroxide.



(12)

12. F. Krollpfeiffer and A. Müller, Ber. 66 739 (1933)

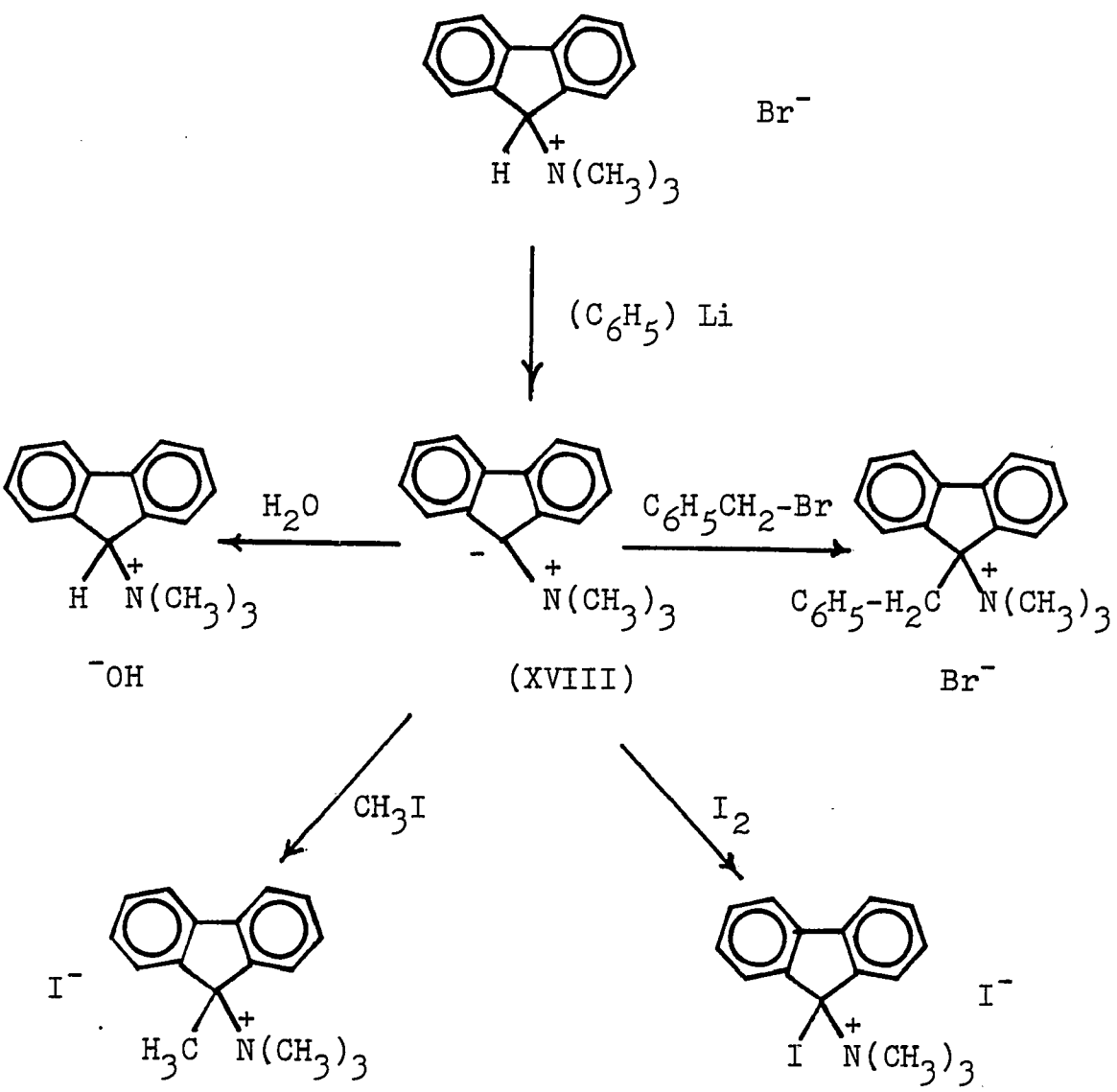
Two years later, Kröhnke[4] isolated a crystalline product from the treatment of phenacylpyridinium bromide with potassium carbonate and he assigned to it an enol-betaine structure (IX).



(IX)

In 1944, Wittig and Felletschin[13] began a reinvestigation of the pentavalent nitrogen problem and succeeded in isolating a red powder from the treatment of a 9-fluorenyltrimethylammonium bromide with phenyllithium in ether. Identification of benzene in the reaction mixture and especially the addition of different reagents to product (XVIII) proved the dipolar "ylid" structure of the deep colored product.

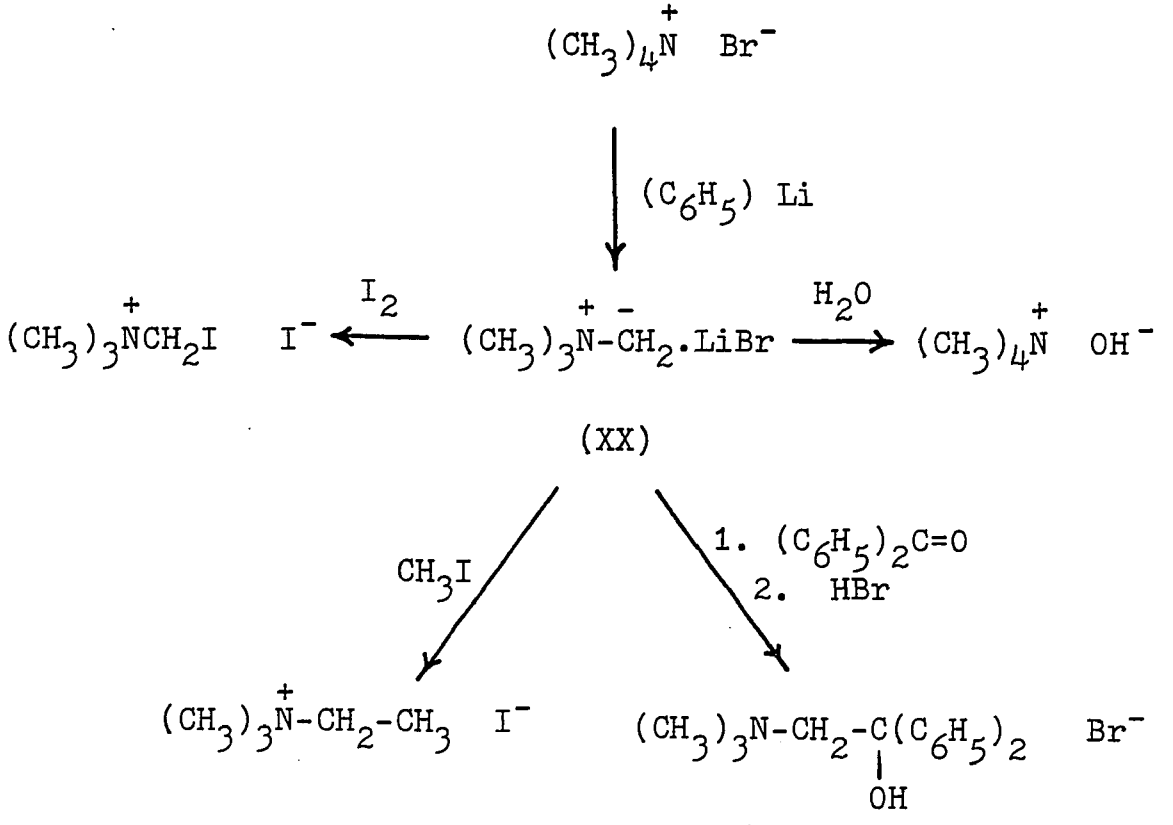
13. G. Wittig and G. Felletschin, Ann. 555 133 (1944)



Following this initial preparation of the stable trimethylammonium-fluorenylide (XVIII), the chemistry of numerous nitrogen ylids has been studied.

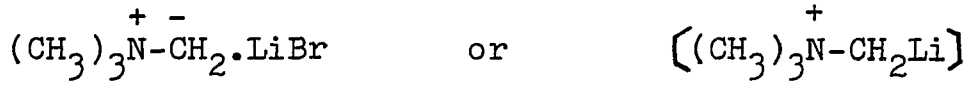
I. Ammonium Ylids

In 1947, Wittig and Wetterling[14] examined the reaction between tetramethylammonium bromide and phenyllithium in ether. The ylid (XX) was insoluble in ether and was held in suspension along with the starting material during the course of reaction. The presence of the ylid was shown by its reactions with water, iodine, methyl iodide and benzophenone.



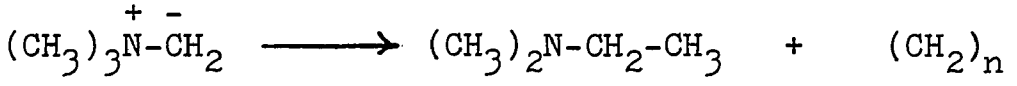
14. G. Wittig and M. H. Wetterling, Ann. 557 193 (1947)

In 1956, Wittig and Polster[2] noted that the structure of this simplest ylid, trimethylammoniummethyl lithium bromide complex, was a lithium complex.



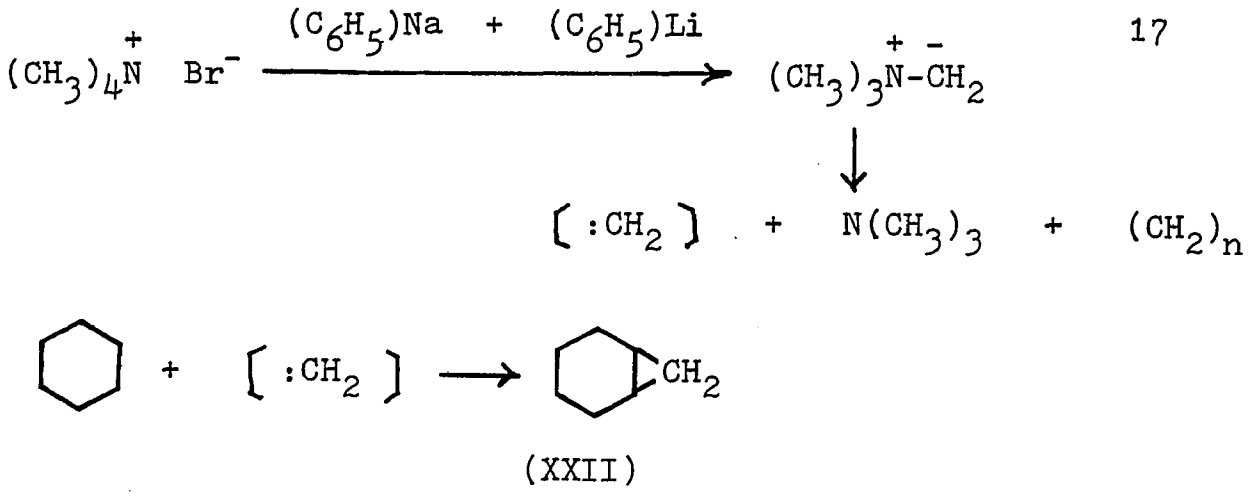
(XX) (XXI)

They indicated further that this ylid could not be prepared salt free, for if the lithium ion was removed by complexation with dimethoxyethane or if phenylsodium was used in its preparation, the unstabilized ylid decomposed to give dimethylethylamine and polyethylene[15].



Franzen and Wittig[16] claimed that a solution of the ylid prepared by a mixture of phenylsodium and phenyllithium, converted cyclohexene to norcarane (XXII) in 5-18% yield.

15. G. Wittig and D. Krauss, Ann. 679 34 (1964)
16. V. Franzen and G. Wittig, Angew. Chem. 72 417 (1960)



(XXII)

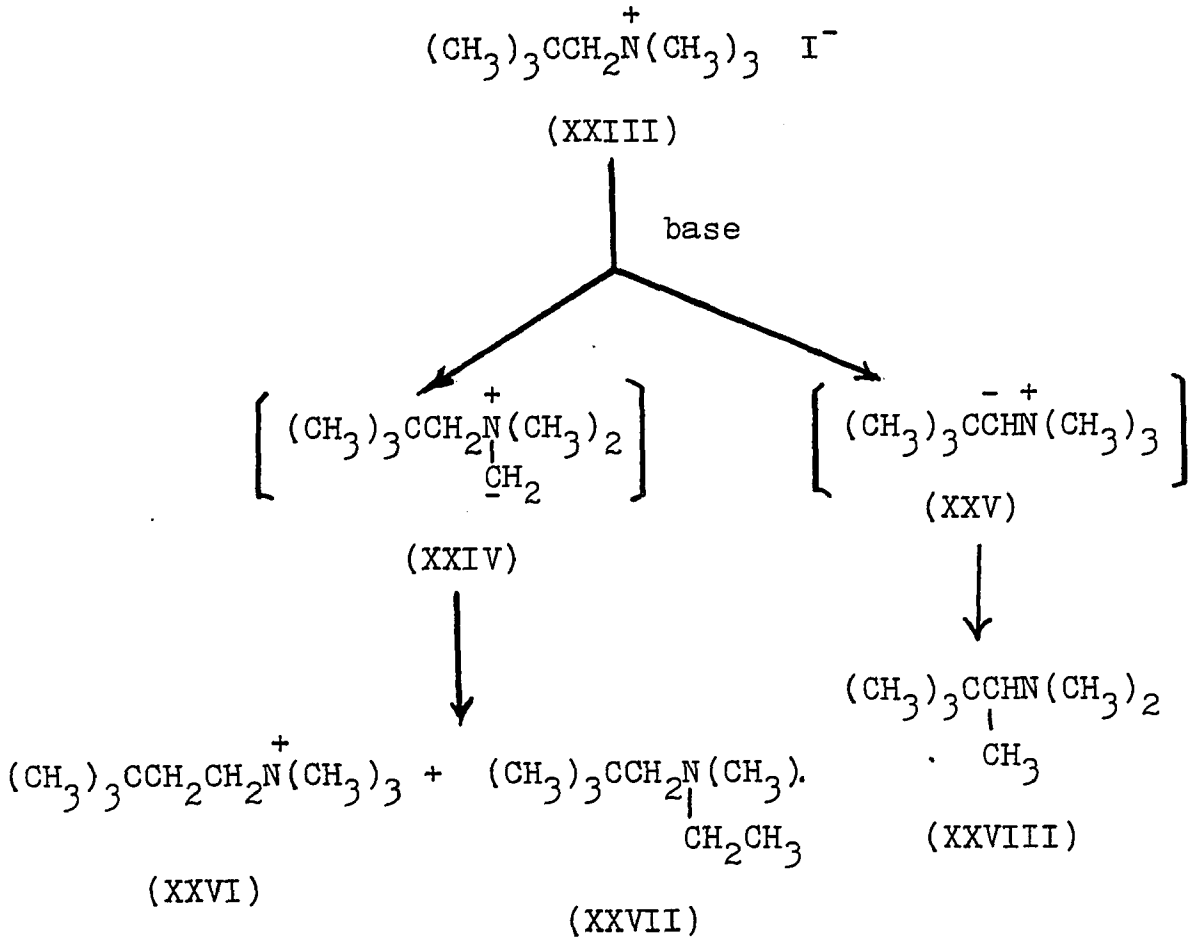
Weygand et al[17] proposed that the ylid decomposed to trimethylamine and methylene and the latter polymerized, from C^{14}-labeling studies.

Since reviews of earlier work on nitrogen-ylids and on the Stevens and Sommelet-Hauser rearrangements are available[3, 18, 19, 20], more recent contributions are emphasized here.

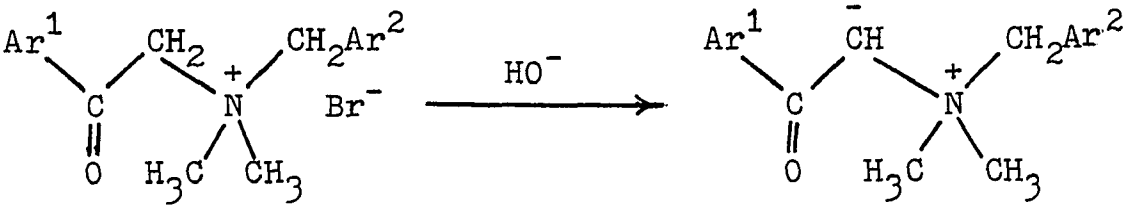
Pine et al[21] treated N,N,N-trimethylneopentylammonium iodide (XXIII) with a series of base-solvent systems, leading to three different Stevens rearrangement

17. F. Weygand, H. Daniel and A. Schroll, Ber. 97 1217 (1964)
18. A. W. Johnson, Ylid Chemistry, Academic Press, New York (1966)
19. W. K. Musker, Fortscher. Chem. Forsch. 14(3) 295-365 (1970)
20. S. H. Pine, Org. Reactions, 18 403-464 (1970)
21. S. H. Pine, B. A. Catto and F. G. Yamagishi, J. Org. Chem. 35(11) 3663 (1970)

products, (XXVI), (XXVII), and (XXVIII), with 3,3,N,N-tetramethyl-1-butylamine (XXVI) predominant in all cases. They treated also N,N,N-trimethyl-2,2,2-triphenylethyl-ammonium iodide with a series of bases, and obtained only the product analogous to (XXVI). They suggested that a combination of steric and electronic factors may be involved.



Ollis et al[22] found that treatment of an aqueous solution of benzyldimethylphenacylammonium bromide (XXIX) with aqueous sodium hydroxide at 0°C yields the crystalline ylid (XXXa) as a monohydrate, mp= 71°C. They identified these ylids by ir-spectra which show no absorption in the localized carbonyl region and are characterized by two strong absorption bands in the 1600-1500 cm^{-1} region, and by H-nmr spectra which show a singlet (δ ca=5) assigned to the benzylic methylene group.

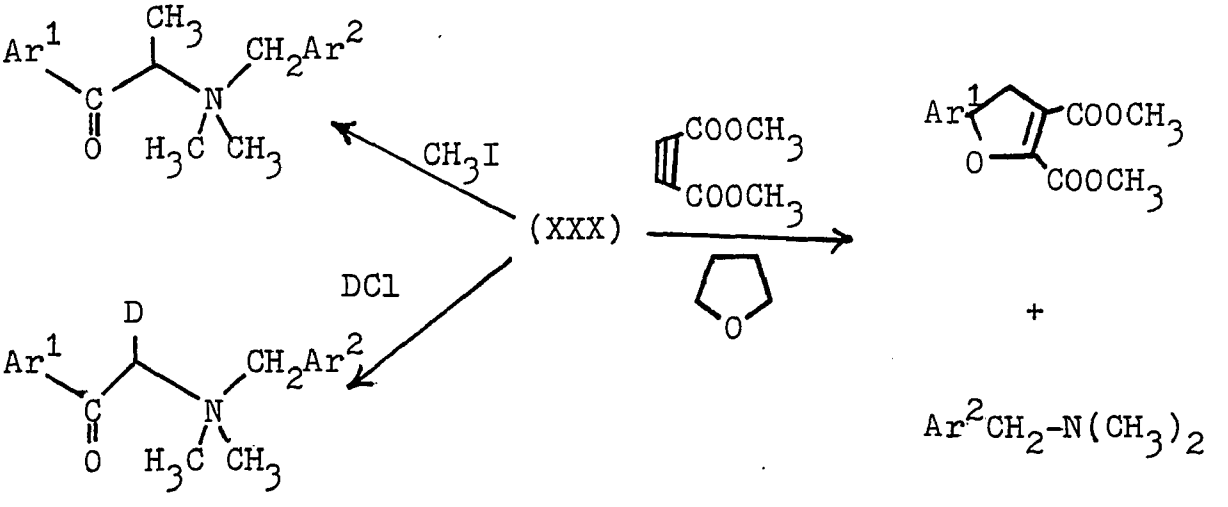


(XXIX) (XXX)

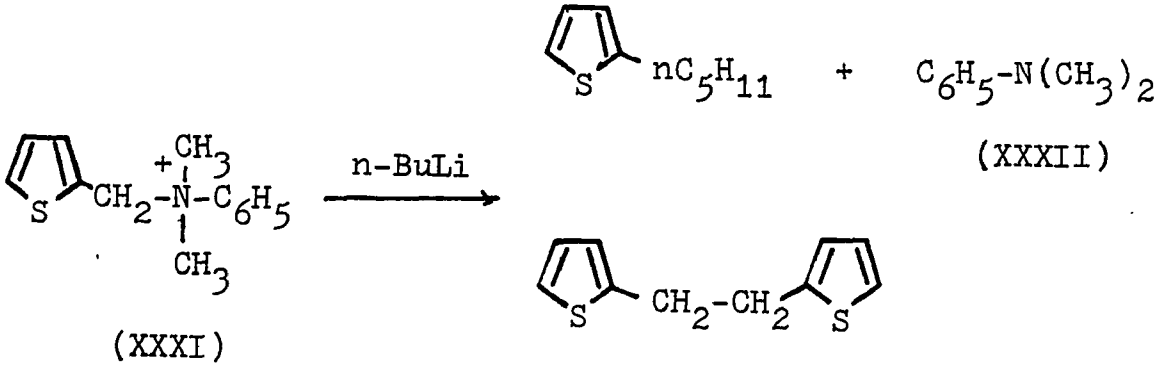
a. Ar^1= Ph; Ar^2= Ph
b. = p-$O_2NC_6H_4$; = Ph
c. = p-BrC_6H_4; = Ph
d. = p-PhC_6H_4; = Ph
e. = Ph; = p-$CH_3C_6H_4$
F. = Ph; = Ph-C≡C-

22. W. D. Ollis, R. W. Jemison, S. Mageswaran, S. E. Potter, A. J. Pretty, I. O. Sutherland and Y. Thebtaranonth, Chem. Comm. 1201 (1970)

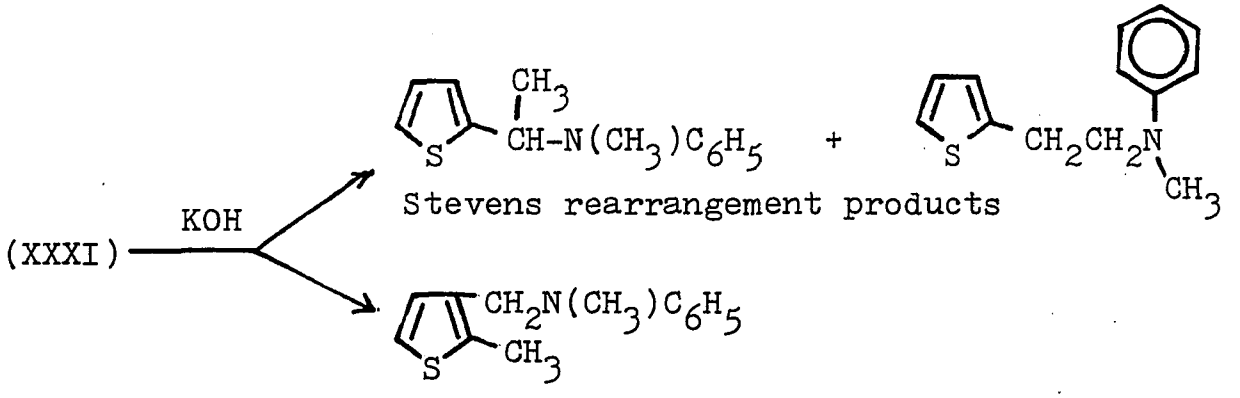
The presence of ylids was shown also by their reactions with hydrobromic acid, deuterium chloride, methyl iodide, and dimethyl acetylenecarboxylate in tetrahydrofuran.



Giumanini and Lercker[23] reported that n-butyllithium under a variety of experimental conditions converts N-(2-thenyl)-N,N-dimethylanilinium chloride (XXXI) into N,N-dimethylaniline (XXXII), in up to 86% yield, and several neutral products.

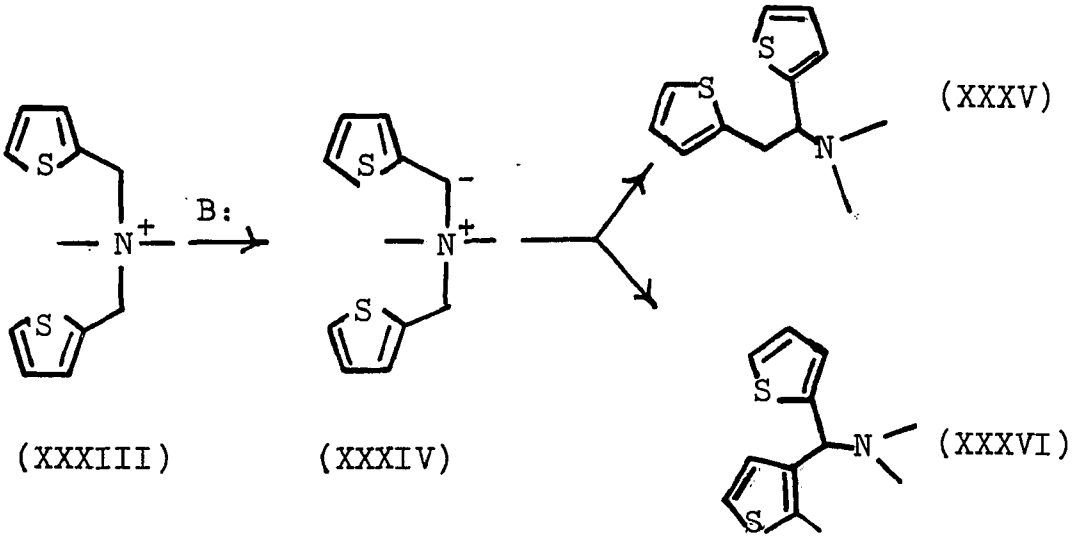


Stevens and Sommelet-Hauser rearrangements were noted, when N-(2-thenyl)-N,N-dimethylanilinium chloride (XXXI) was treated with potassium hydroxide.



Giumanini et al[24] have shown that the presence of two thenyl groups as substituents on nitrogen in the N,N-di-(2-thenyl)-dimethylammonium ion (XXXIII), gave base-promoted rearrangement producing high yields of amines (XXXV) and (XXXVI) as the only products.

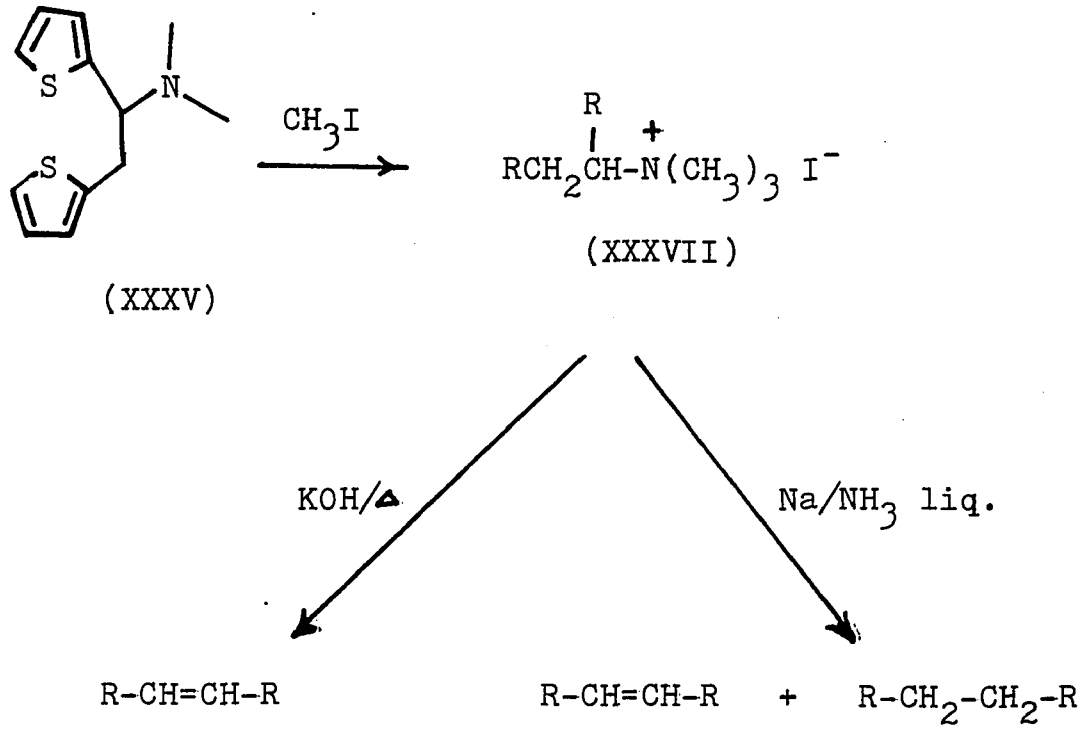
23. A. Giumanini and G. Lercker, Gazzetta. Chimica. Italiana. 104 415 (1974)
24. A. Giumanini, C. Trombini, G. Lercker and A. R. Lepley, J. Org. Chem. 41(12) 2187 (1976)



(XXXIII) (XXXIV)

They suggested that an ylid of (XXXIV) participated in the rearrangement mechanism.

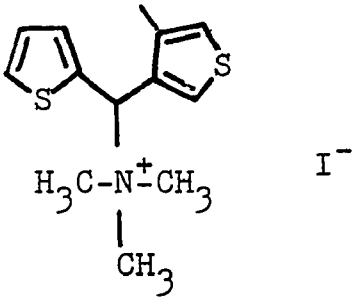
Amine (XXXV) upon treatment with excess methyl iodide gave the corresponding quaternary ammonium salt (XXXVII). This salt upon treatment with hot aqueous potassium hydroxide led to the elimination product (XXXVIII). Reduction of this salt with sodium in liquid ammonia yielded (XXXVIII) and (XXXIX).



(XXXV)

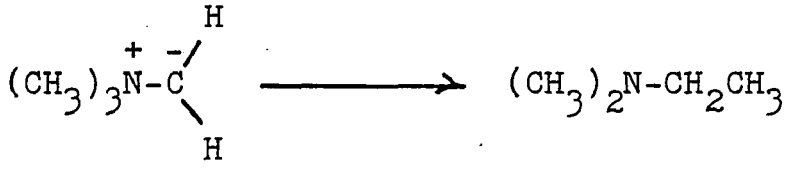
(XXXVII)

A quaternary ammonium salt (XXXX) could also be obtained from the Sommelet amine (XXXVI) with methyl iodide but (XXXX) did not react with any of the reagents used on (XXXVII).



(XXXX)

Dewar and Ramsden[25] have reported the results of MINDO/3 calculations on a concerted (but Woodward-Hoffman "forbidden") pathway for the Stevens rearrangement of trimethylammonium methylide (XXXXI). For this strongly exothermic reaction (ΔH= -87 Kcal mol^{-1}) the transition state was found to be reactant-like, and the activation energy for the process was only 4 Kcal mol^{-1}. They suggested that the Stevens rearrangement may very well take place by a concerted pericyclic path but did not allow a distinction between this and the radical pair mechanism. In the case of (XXXXI), MINDO/3 predicts the dissociation to radicals ($(CH_3)_2NCH_2\cdot$ + $\cdot CH_3$) to be exothermic (ΔH= -10 Kcal mol^{-1}).

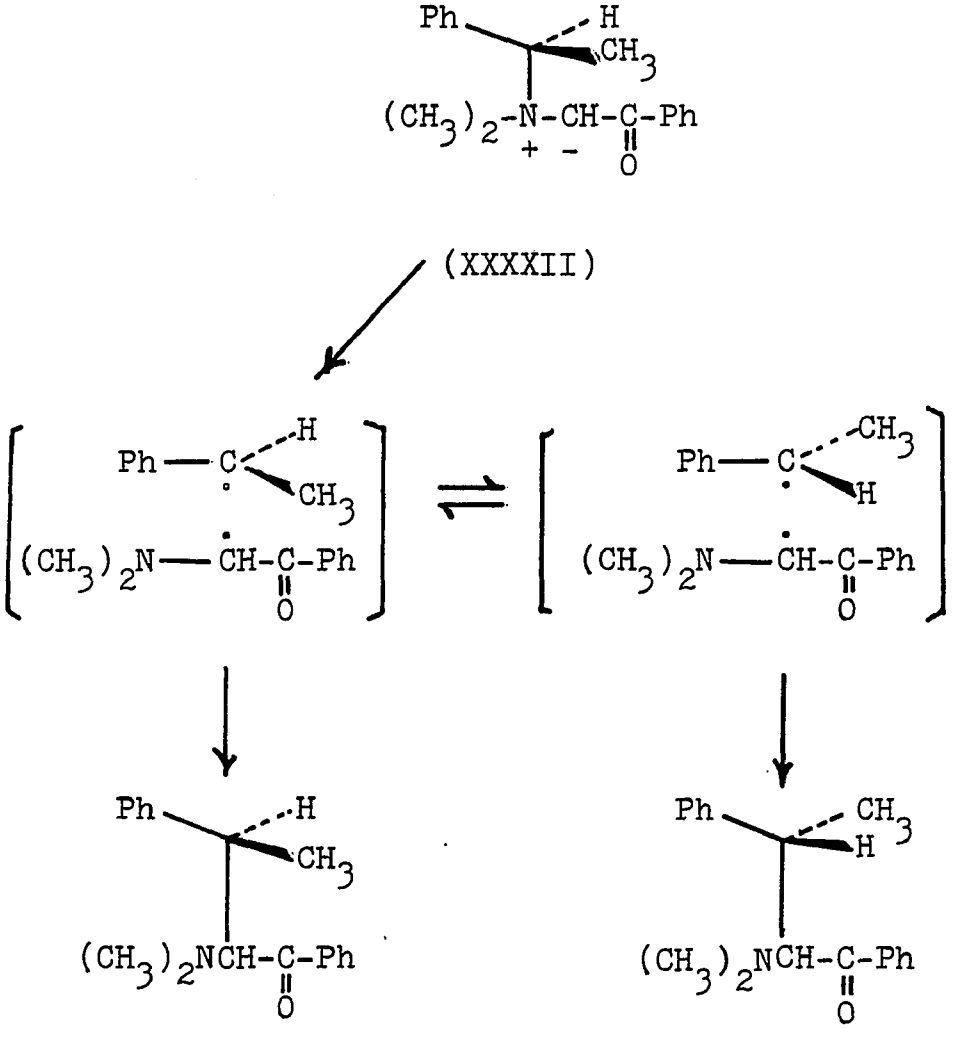


(XXXXI)

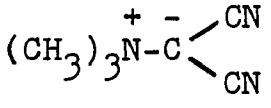
The influence of solvent viscosity and reaction temperature upon the stereoselectivity and intramolecularity of the Stevens rearrangement of the ylid (XXXXII) has been examined by W. D. Ollis, M. Rey and I. O. Sutherland[26].

25. M. J. S. Dewar and C. A. Ramsden, J. Chem. Soc. Perkin I, 1839 (1974)
26. W. D. Ollis, M. Rey and I. O. Sutherland, J. C. S. Chem. Comm. 543 (1975)

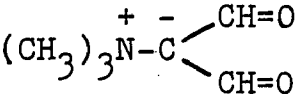
The stereoselectivity of the Stevens rearrangement shows a strong dependence upon solvent viscosity (low viscosity produces a decrease in stereoselectivity), small temperature effects, but no direct relation with solvent polarity. The intramolecularity of the Stevens rearrangement showed strong dependence upon solvent viscosity and large temperature effects. They suggested that a radical pair pathway is at least an important contributor to the reaction mechanism.



Two stable ammonium ylids have been isolated by Arnold et al[5, 27]. (X)[5] was the most stable ammonium ylid reported to date, which was obtained from its conjugate acid with aqueous hydroxide. The ylid has a melting point of 153°C and appeared to be stable in the presence of oxygen and water for indefinite period. Unfortunately, the chemical charateristics of (X) have not been reported. Trimethylammoniodiformylmethylide (XXXXIII)[27] is a crystalline substance which may be sublimed under reduced pressure without decomposition. It is well soluble in polar solvents and its aqueous solution is neutral. As observed by Wittig and co-workers[10] in the preparation of trimethylammonium-methylide, the stability and reactivity of this ylid is markedly affected by the formation of a complex with lithium bromide which is present as a coproduct in the reaction mixture. The attempted nucleophilic substitution of the quaternary ammonium group was not successful. The ylid can be used indirectly for the synthesis of heterocyclic systems substituted by a quaternary ammonium function.



(X)

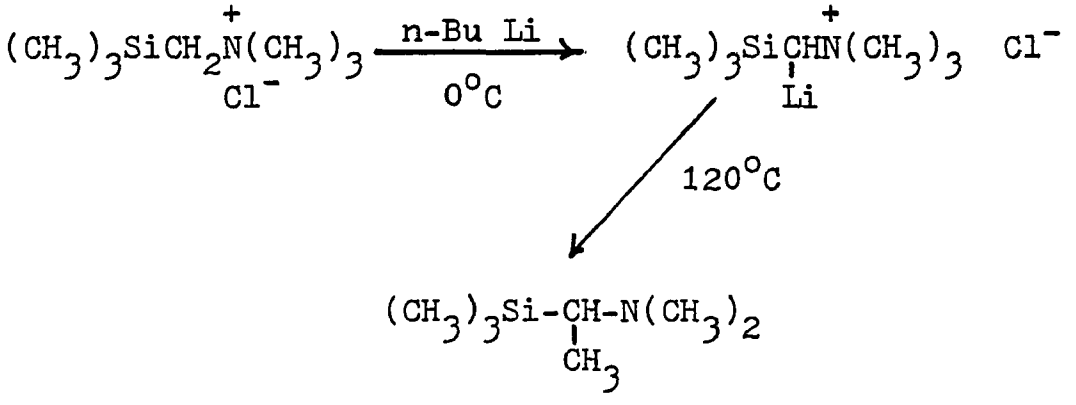


(XXXXIII)

27. Z. Arnold and V. Kral, Coll. Czech. Chem. Comms. 42 3455 (1977)

Two examples of phosphonate-substituted ammonium ylids have been reported. Gross et al[28a] reacted $(CH_3)_2\overset{+}{N}{=}CHCl\ Cl^-$ with two equivalents of triethylphosphite, or alternatively $(CH_3)_2NCH(OCH_3)_2$ with excess diethylphosphite, giving $(CH_3)_2NCH[PO(OC_2H_5)_2]_2$ in each case, which was alkylated with methyl iodide. Deprotonation with sodium ethoxide gave the stable ylid $(CH_3)_3\overset{+}{N}\text{-}\bar{C}[PO(OC_2H_5)_2]_2$. The ylid $(CH_3)_3\overset{+}{N}\text{-}\bar{C}HPO(OCH_2CH{=}CH_2)_2$ was mentioned in a patent application[28b].

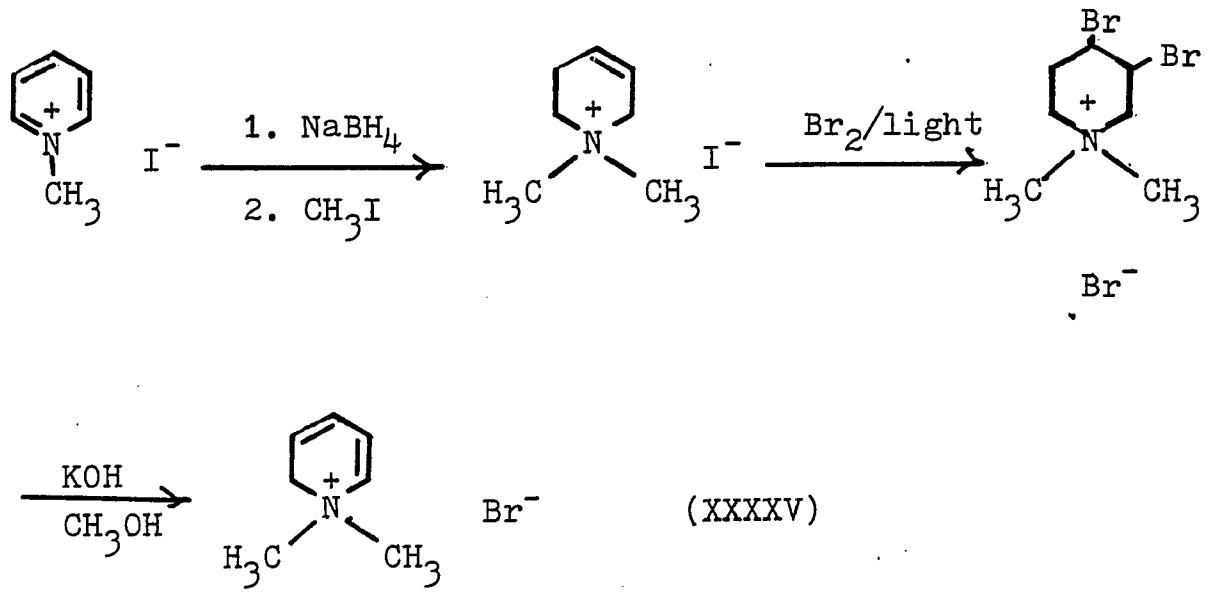
Treatment of trimethylsilylmethyltrimethylammonium chloride with butyllithium at 0°C gave a precipitate which presumably contained the lithium complex of the trimethyl-substituted nitrogen ylid, although this was not directly identified. On removal of solvent and heating to 120°C, a virgorous reaction led to the Stevens product[28c].



28a. Von H. Gross and B. Costisella, Angew. Chem., 445 (1968)
28b. R. Firestone, (Patent Application), through CA 74 p76525y (1969)
28c. N. E. Miller, Inorg. Chem., 4(10) 1458 (1965)

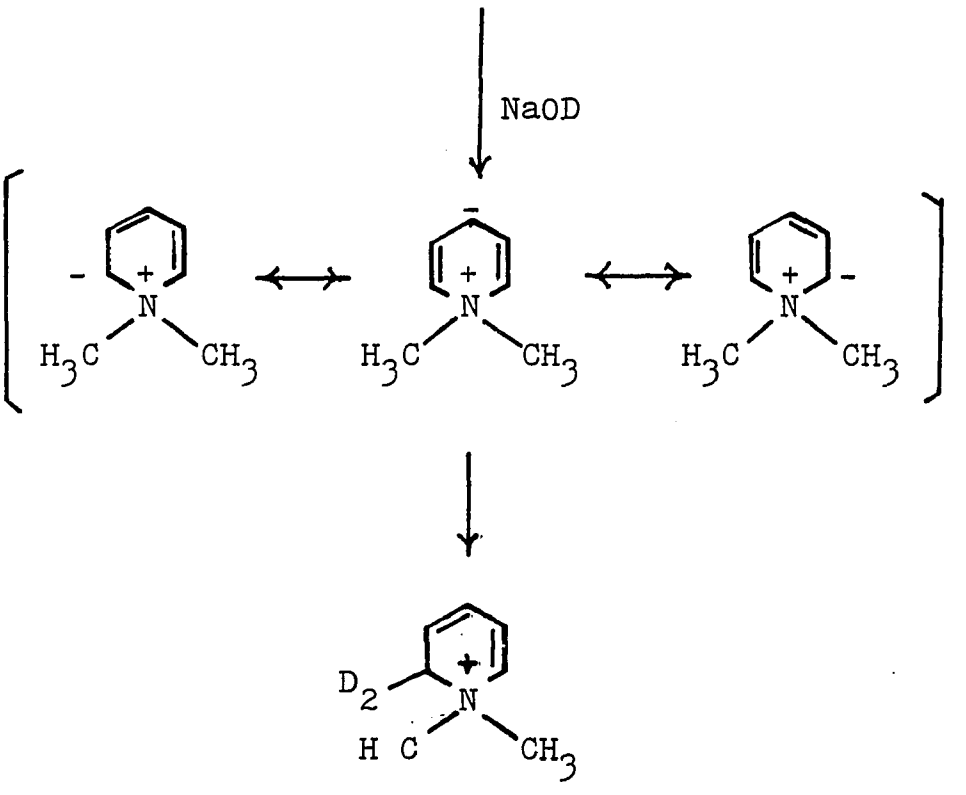
II. Cycloammonium Ylids

The kinetics of aqueous base-catalyzed deuterium exchange of N,N-dimethyl-1,2-dihydropyridinium bromide (XXXXV) has been studied by Saunders and Gold[29], The exchange of the methylene hydrogens in (XXXXV) was faster than exchange in the tetramethylammonium cation[30], by a factor of 1.8×10^{10} at 50°C. The exchange reaction was followed by observing the disappearance of the H-nmr peak area at successive times.



29. M. Saunders and E. H. Gold, J. Am. Chem. Soc., 88(14) 3376 (1966)
30. W. von E. Doering and A. K. Hoffmann, J. Am. Chem. Soc., 77 521 (1955)

(XXXXV)

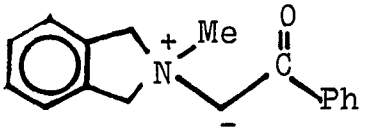


$k = 0{,}494 \pm 0.02$ l mol^{-1} sec^{-1} at $50.0^{o}C$

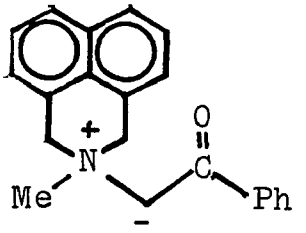
They explained this by postulating the formation of an allylic ylid in which two of the three resonance forms have negative charge adjacent to the quaternary nitrogen.

Ollis et al[22] have prepared some stable cycloammonium ylids. The ylids (XXXXVI), mp 156-7°C, and (XXXXVII),

mp 165°C, were prepared in anhydrous form by crystallization from ethanol-ether .



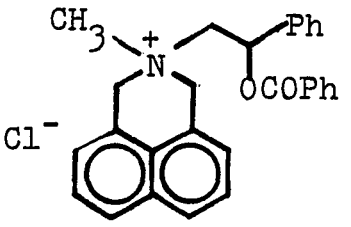
(XXXXVI)



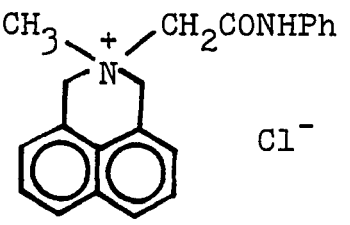
(XXXXVII)

The ylid (XXXXVII) is quite stable at 100°C and at 150°C decomposes to give the amine (XXXXVIII) and tribenzoylcyclopropane. The ylid (XXXXVI) was smoothly transformed at 150°C into the aminoketone (XXXXIX).

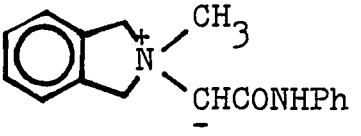
The ylid (XXXXVII) reacts with benzoyl chloride yielding the quaternary enol benzoate chloride (L), mp= 145-7°C, and with phenyl isocyanate, the hydrogen adduct (LI), mp=216-7°C, may isolated. The ylid (XXXXVI) reacts with the phenyl isocyanate to give a new ylid (LII), mp=179-181°C.



(L)



(LI)

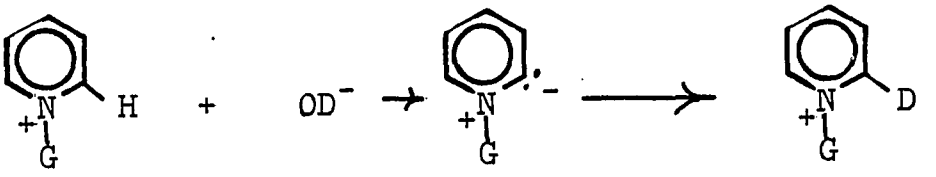


(LII)

The reactions of the carbonyl-stablized cycloammonium ylids with electrophilic reagents may therefore be accompanied in some cases by fission of the +N-CH or the $\bar{C}H$-CO bond of the ylids structure.

III. Cycloimmonium Ylids

N-alkylpyridinium ions underwent base-catalyzed hydrogen-deuterium exchange by simple deprotonation to give intermediates such as (LIII). This has been investigated by Zoltewicz and Helmick[31].



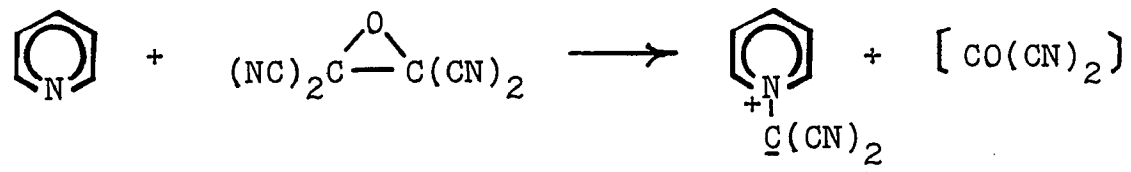
(LIII)

G = $CH_2C_6H_5$, CH_3, C_6H_5

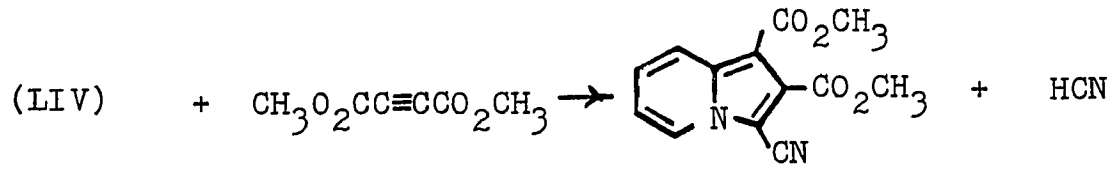
Rates of hydrogen-deuterium exchange of N-substituted pyridinium ion in D_2O at 75°C were obtained by the use of a H-nmr method.

Linn et al[32] treated pyridine with TCNEO (tetracyanoethylene oxide) to give a bright yellow, high-melting, relatively insoluble solid and described it as pyridinium dicyanomethylide (LIV) which condensed with dimethylacetylenedicarboxylate to give dimethyl-3-cyanopyrrocoline-1,2-dicarboxylate (LV).

31. J. A. Zoltewicz and L. S. Helmick, J. Am. Chem. Soc., 92(26) 7547 (1970)
32. W. J. Linn, O. W. Webster and R. E. Benson, J. Am. Chem. Soc., 87(16) 3651 (1965)

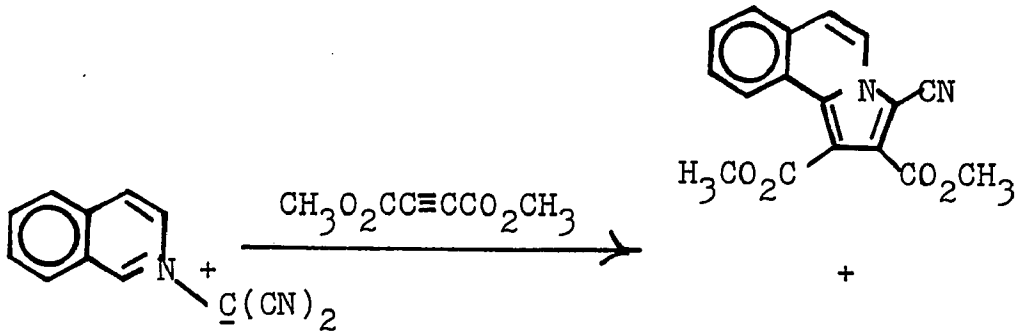


(LIV)

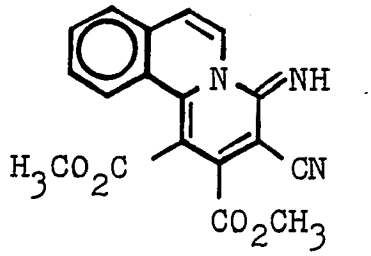


(LV)

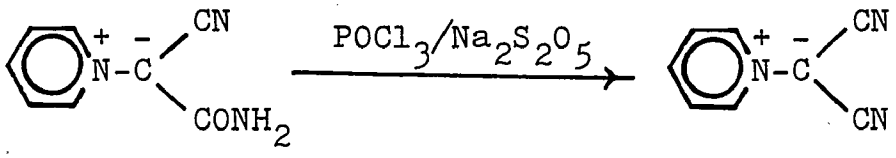
Isoquinolinium dicyanomethylide (LVI) also condensed with dimethyl acetylenedicarboxylate, but in this case two products were isolated.



(LVI)

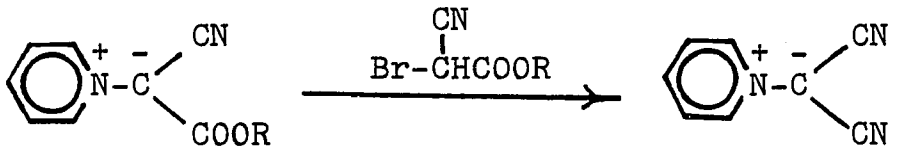


Lenote and Zugravescu[33] prepared the ylid (LIV) by heating cyano-carbamyl-pyridinium-methylid with an excess of $POCl_3$ in the presence of a little amount of sodium pyrosulphite.



(LIV)

They found another easy way to get the ylid (LIV) from the treatment of cyanocarbalkoxypyridiniummethylids with bromocyanoacetic ester.

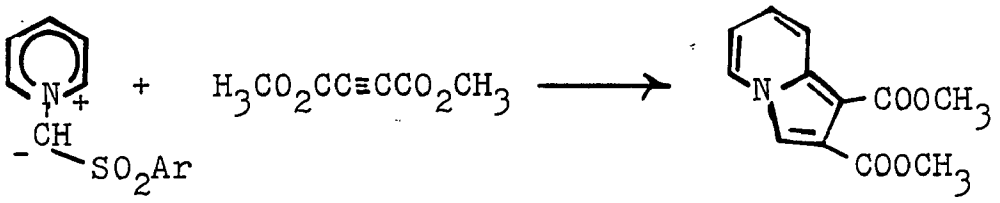


(LIV)

They found also that the ylid (LVI) can be prepared by a similar method. The starting ylids, especially the cyanocarboxymethylids, are easily obtainable from bromocyanoacetic ester and the nitrogen base.

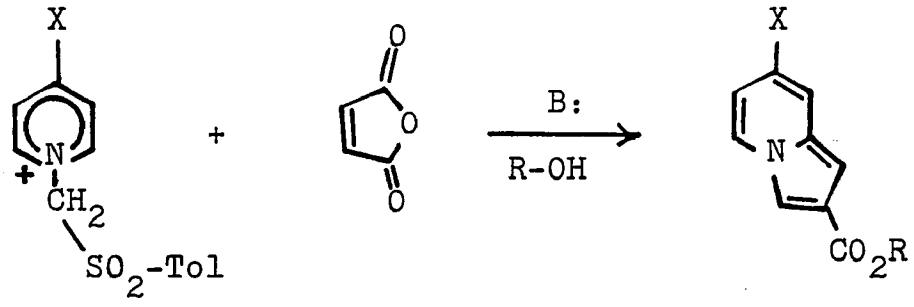
33. C. Lenote and I. Zugravescu, Tetra. Lett. 20 2027 (1972)

Abramovitch and Alexanian[34] reported that the 1,3-dipolar cycloaddition of pyridinium arysulphonylmethylids with dimethyl acetylene carboxylate gives 1,2-dimethoxycarbonylindolizines.



(LVII)

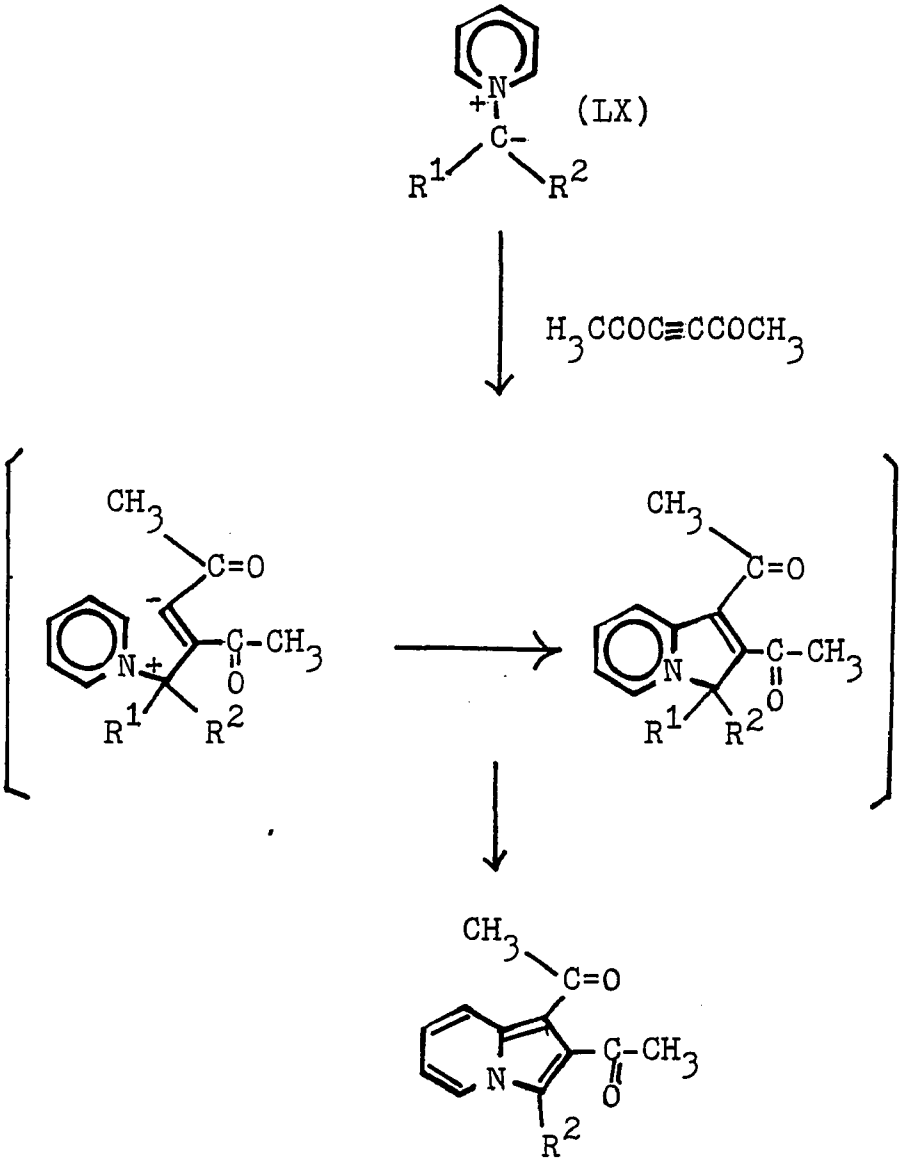
Abramovitch and Mathur reported that the reaction of 4-benzoyl-1-toluenesulphonylpyridinium trifluoromethane sulphonate with maleic anhydride in the presence of triethylamine containing ethanol gave 7-benzoyl-2-ethoxycarbonylindolizine (LVIII), mp 145-7°C; and instead 7-benzoyl-2-methoxycarbonylindolizine (LIX), mp 205°C, when methanol was present.

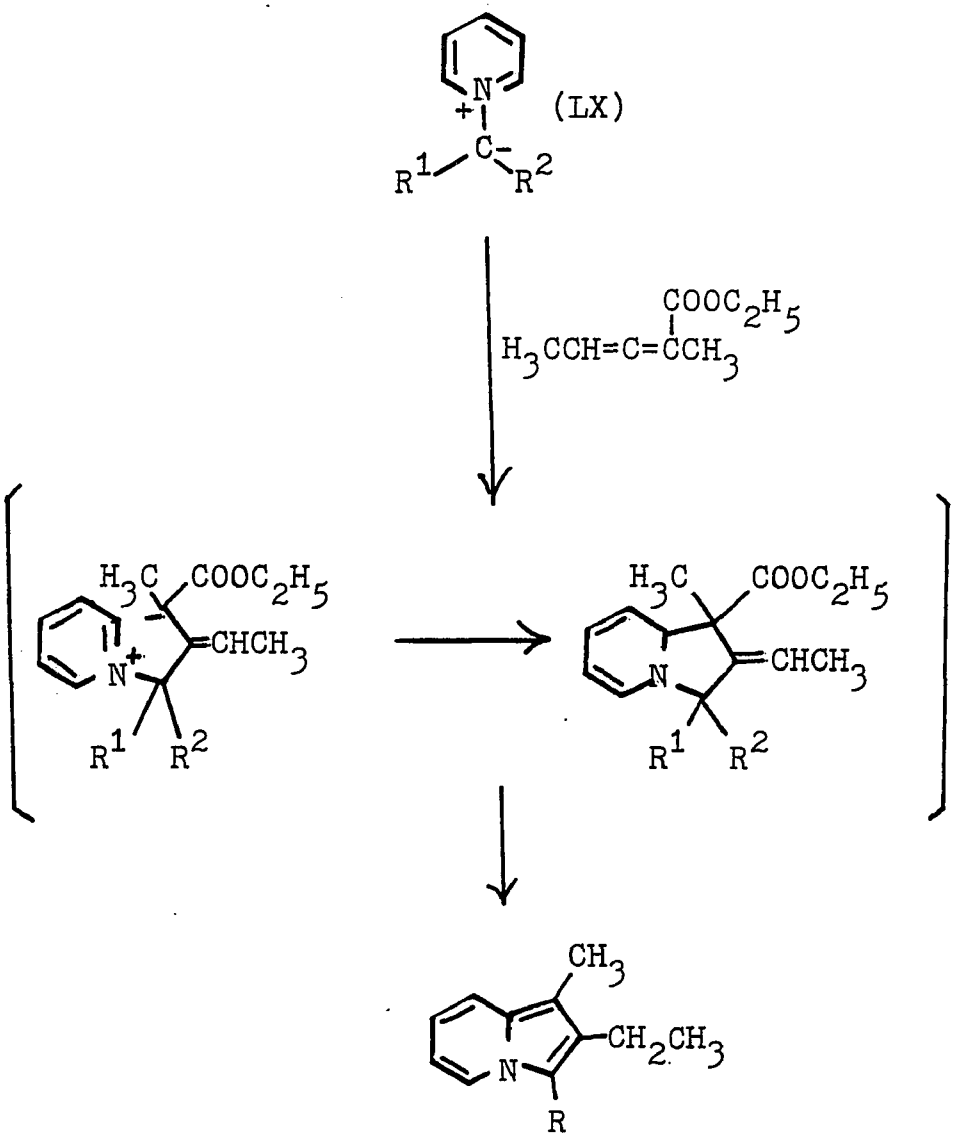


R = C_2H_5 (LVIII)

R = CH_3 (LIX)

Indolizines can also be prepared from the combination of pyridinium ylids and activated acetylenes. Acheson[36] have reported that pyridinium ylids combined with hex-3-yne-2,5-dione lead to indolizines, but no indolizine was formed from 5-hydroxyhex-3-yne-2-one.

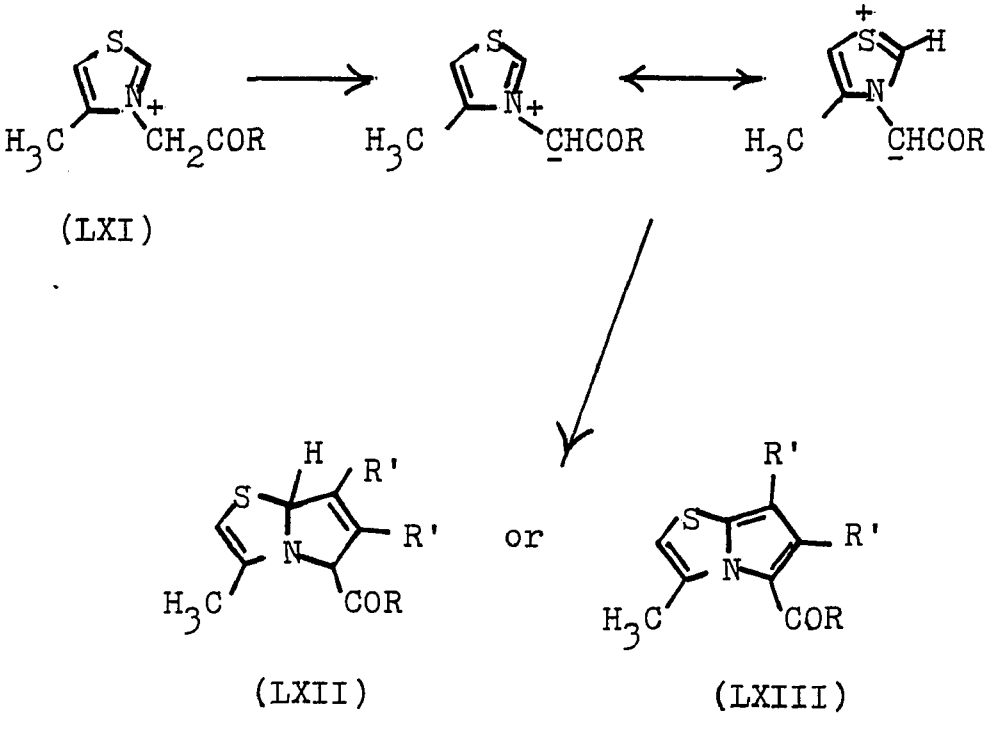




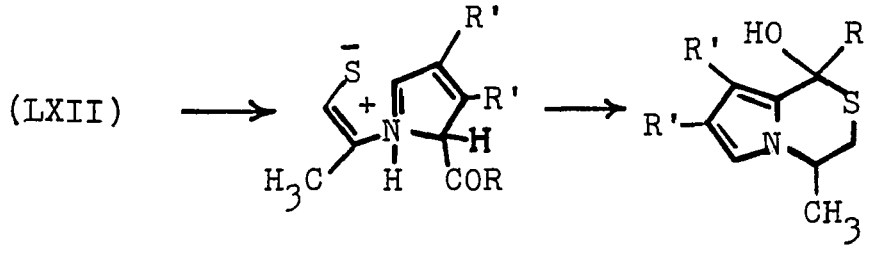
The allenes also combined with the ylid leading to indolizines.

34. R. A. Abramovitch and V. Alexanian, J. Org. Chem. 41 2144 (1976)
35. R. A. Abramovitch and S. S. Mathur, Heterocycles 5 91 (1976)
36. R. M. Acheson, M. G. Bite and M. W. Cooper, J.C.S. Perkin I, 1908 (1976)

Potts et. al.[37] have reported that thiazolium N-ylids can be made from triethylamine and the corresponding salt (LXI) which was prepared from the reaction of 4-methyl-thiazole and 2-bromoacetophenone in boiling ethanol. The ylid gave 1:1 adducts with dimethyl acetylenedicarboxylate and dibenzoyl acetylene in high yields which could be expected to have structure (LXII), or its oxidation product (LXIII).



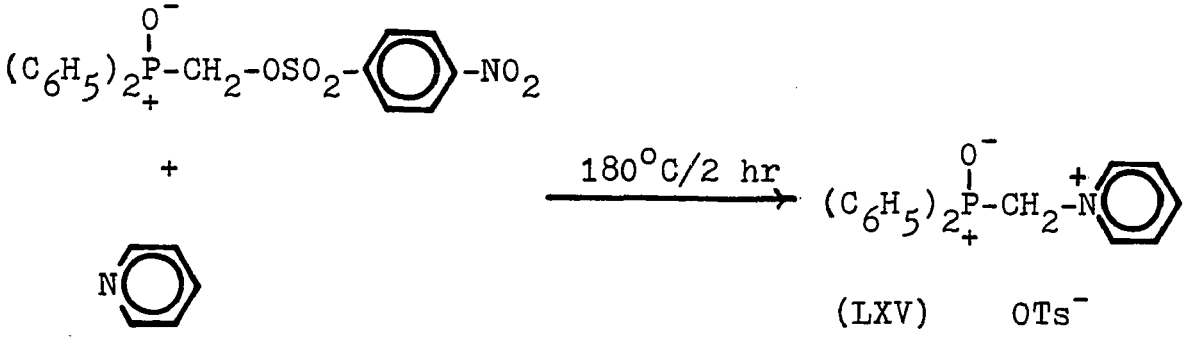
The product (LXII) may easily lead to compound (LXIV) via a rearrangement.



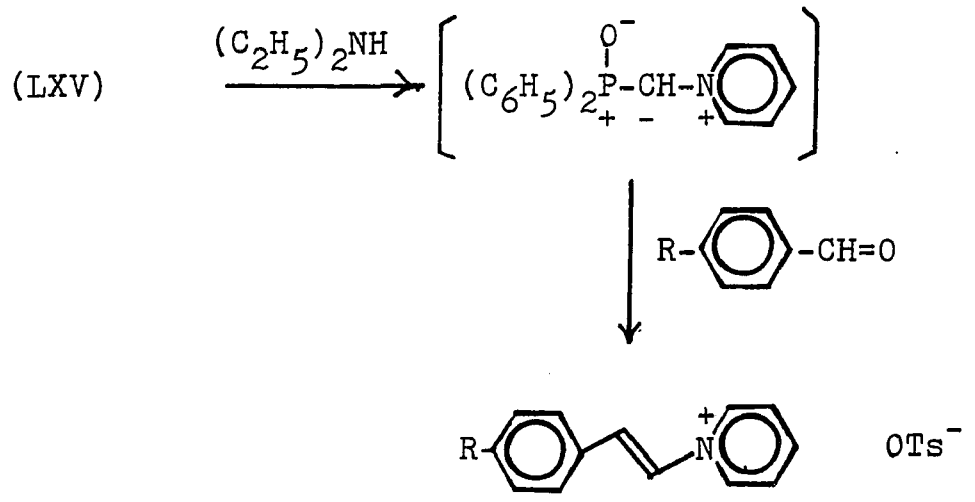
(LXIV)

The structure (LXIV) is consistent with both the H-nmr and C-13 nmr spectra.

There is one recorded example of a phosphorus-substituted cycloimmonium ylid. Wegener and Schlippes[38] reported the formation of a phosphine oxide substituted pyridinium methylide from the corresponding salt (LXV) which was prepared from the treatment of p-nitrobenzenesulphonyldiphenylphosphine oxide with pyridine. The ylid combined with benzaldehyde to give a new pyridinium salt (LXVI).



(LXV)

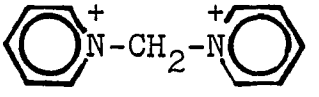


(LXVI)

37. K. T. Potts, D. R. Choudhury and T. R. Westby, J. Org. Chem., 41(2) 187 (1976)
38. W. Wegener and K. Schlippes, Z. Chem. 12(9) 334 (1972)

(B) Bis-'Onium Salts

Numerous methylenedipyridinium salts have been isolated and characterized.



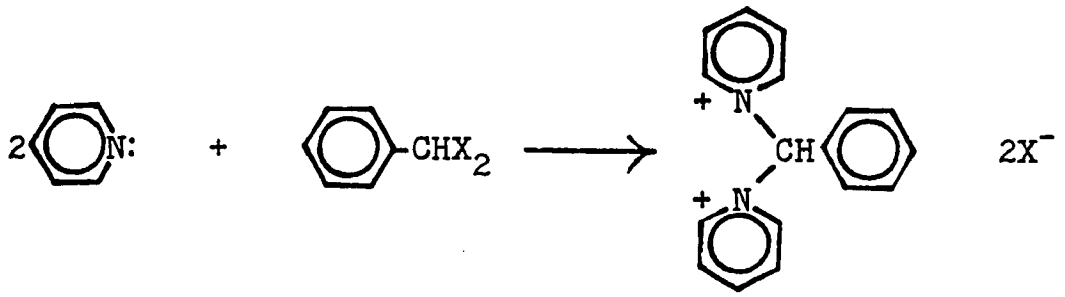
$2\ X^-$

(LXVII)

$X = I^-$ [39], Cl^- [40], Br^- [41], ClO_3^- [42], NO_3^- [43]

Kröhnke prepared another bis-pyridinium salt (LXVIII) by the treatment of two moles of pyridine with one mole of benzal bromide, mp 234°C, and with one mole of benzal iodide, mp 163°C. Unfortunately, there have been no corresponding ylids reported.

39. L. C. King, J. Am. Chem. Soc., 70 242 (1948)
40. K. G. Mizuch, N. M. Kasatkin and Ts. M. Gelfer, J. Gen. Chem. of USSR 27 213 (1957)
41. F. Kröhnke, Ber. 83 50, 56 (1950)
42. F. Kröhnke, Ber. 66 1386, 1391 (1933)
43. O. V. Brody and R. M. Fuoss, J. Am. Chem. Soc.,
44. F. Kröhnke, Ber. 91 1295 (1958)



(LXVIII)

X = Br^-, I^-

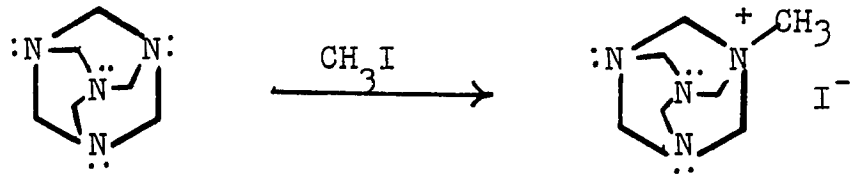
Direct alkylation of tetramethyldiaminomethane with methyl iodide at low temperature to give methylene-bis-(trimethylammonium) di-iodide was achieved by Ehrlich.[45]

$$(CH_3)_2NCH_2N(CH_3)_2 + 2\ CH_3I \xrightarrow[0^oC]{H_2O} (CH_3)_3\overset{+}{N}CH_2\overset{+}{N}(CH_3)_3\ 2\ I^-$$

At temperature above 40°C the compound disproportionates to give $(CH_3)_4N^+\ I^-$ and $(CH_3)_2\overset{+}{N}{=}CH_2\ \ I^-$.

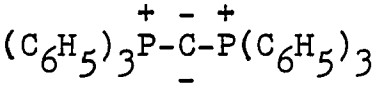
45. R. Ehrlich, J. Chem. Eng. Data, 10(4) 403 (1965)

Treatment of hexamethylene tetramine with methyl iodide[46] gave a mono-alkylated quaternary ammonium salt (LXIX) only.

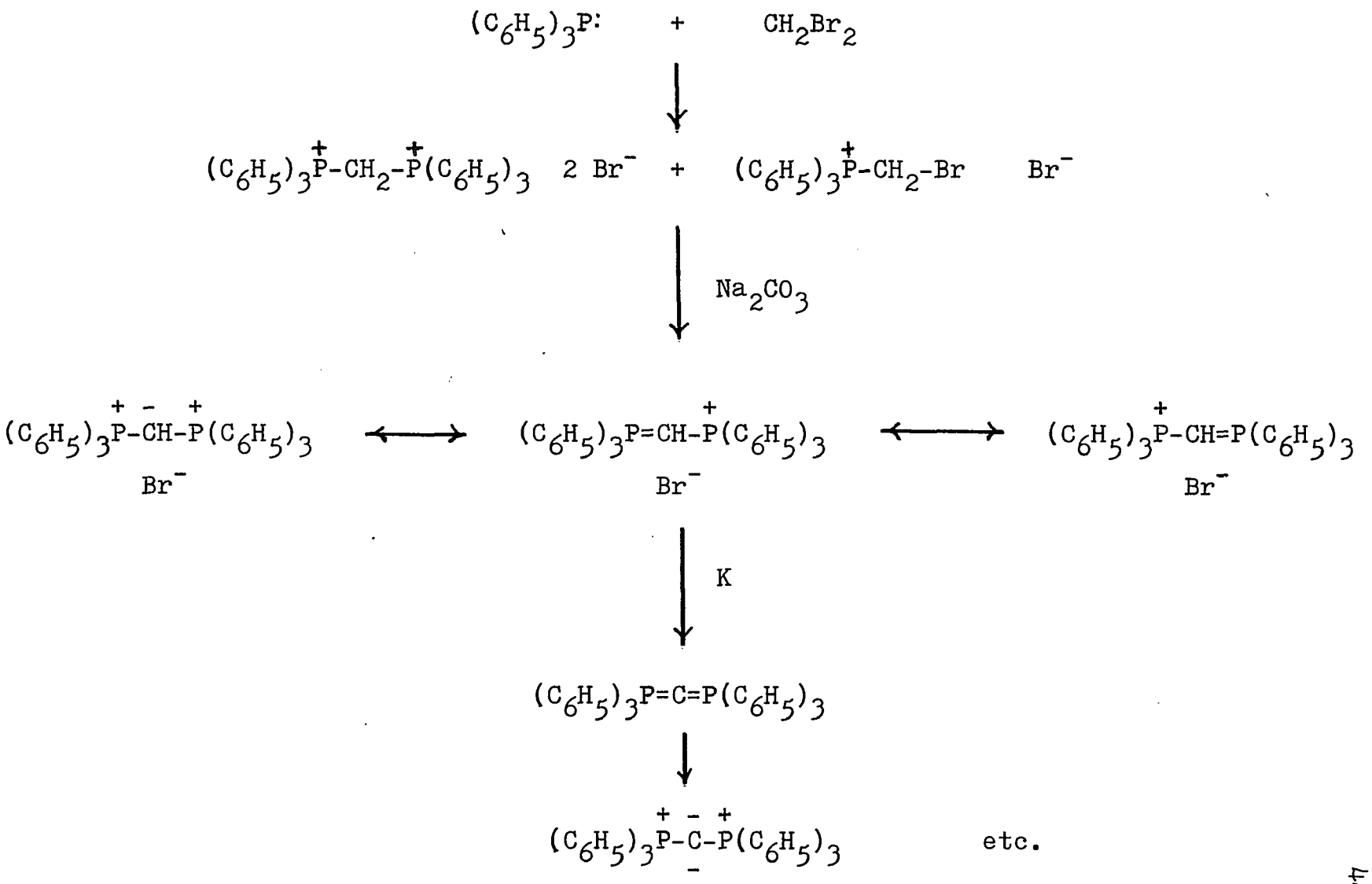


(LXIX)

The interaction of bases with methylene bis-(triphenylphosphonium bromide)[47] led to interesting ylids in which the two positively charged phosphorus-atoms are separated by only one carbon-atom.

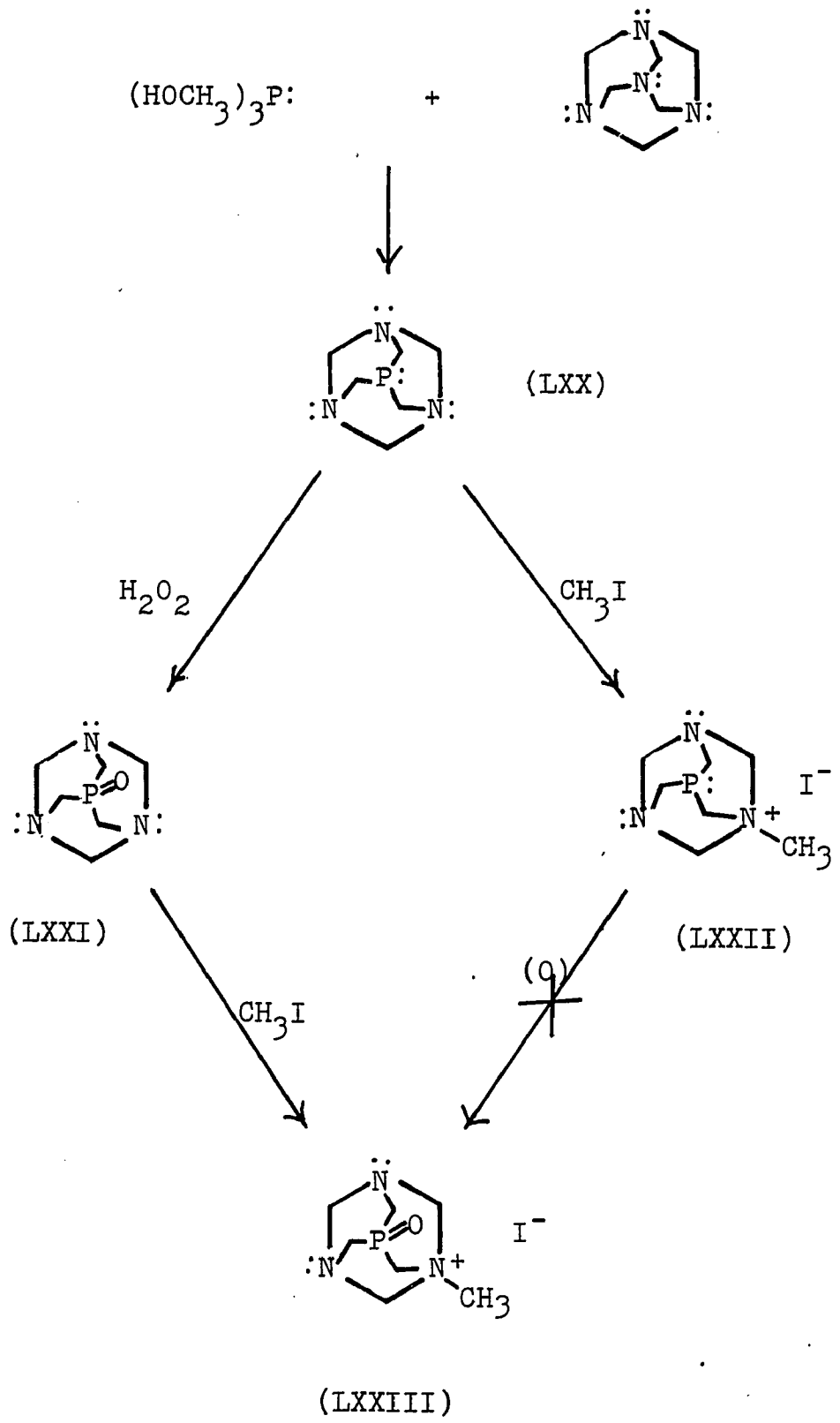


46. M. Dominikiewicz, Arch. Chem. Farm., 2 160 (1935) through Chem. Abs. 30 1030 (1936)
47. F. Ramirez, N. B. Desai, B. Hansen and N. McKelvie, J. Am. Chem. Soc., 83 3539 (1961)


(C6H5)3P: + CH2Br2
(C6H5)3P+-CH2-P+(C6H5)3 2 Br- + (C6H5)3P+-CH2-Br Br-
Na2CO3
(C6H5)3P+-CH-P+(C6H5)3 Br-
(C6H5)3P=CH-P+(C6H5)3 Br-
(C6H5)3P+-CH=P(C6H5)3 Br-
K
(C6H5)3P=C=P(C6H5)3
(C6H5)3P+-C--P+(C6H5)3
etc.

Daigle et al[48] treated a solution containing four moles of formaldehyde and one mole of tris-(hydroxymethyl)-phosphine with one mole of hexamethylenetetramine. A white crystalline compound (LXX) was isolated. The structure shown agreed with the H-nmr spectrum which showed a singlet at δ=4.43 (NCH_2N) and a doublet (J=9 Hz) centered at δ=3.9 (PCH_2N) in the ratio of 1:1. Compound (LXX) can be oxidized to an oxide (LXXI) which showed a strong absorption peak at 8.62 microns charateristic of the P=O stretch. Compound (LXXI) gave a 1:1 methylated corresponding salt (LXXIII). Compound (LXXII) was obtained from methylation of compound (LXX). No bis-('onium) salt from the alkylation of compound (LXX) was isolated.

48. D. J. Daigle, A. B. Pepperman, Jr. and S. L. Vail, J. Heterocyl. Chem., 11 407 (1974)



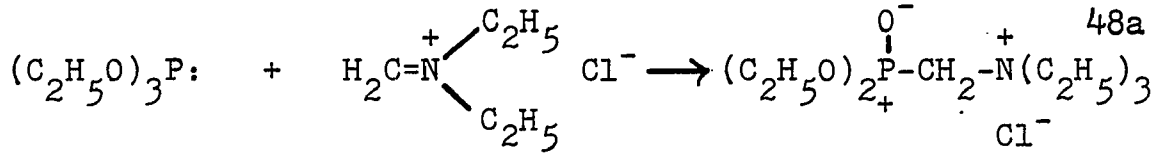
(LXXIII)

RESULTS AND DISCUSSION

I. Quaternary Ammonium Salts α-Substituted With Phosphorus Functions Other Than Phosphino-Groups.

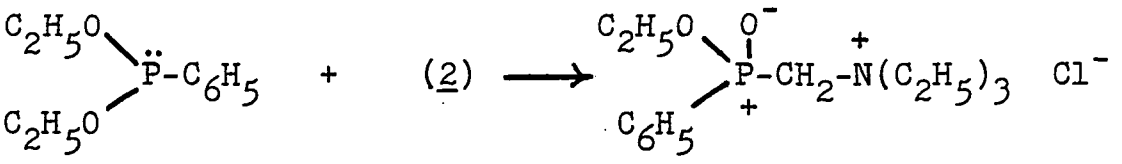
Results

Two quaternary ammonium salts α-substituted with alkoxyphosphonate and withalkoxyphosphinate, namely diethoxylphosphonomethyltriethylammonium chloride (3) and ethoxyphenylphosphinomethyltriethylammonium chloride (4) were prepared by a one-step reaction of N,N-diethylmethyleneiminium chloride (2) with triethylphosphite and with diethyl phenylphosphonite, respectively.



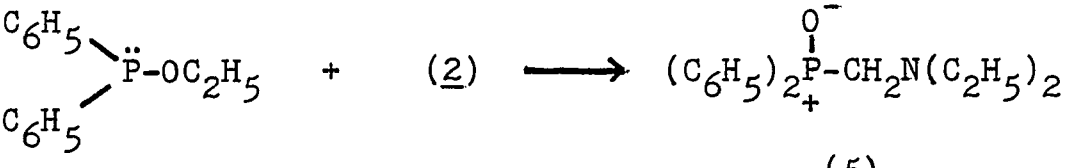
(2) (3)

48a

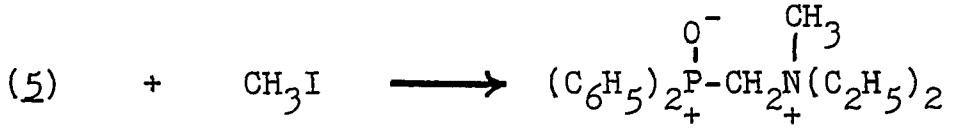


(4)

A quaternary ammonium salt α-substituted with phosphine oxide, diphenylphosphinylmethyldiethylmethylammonium iodide (6) was obtained from the methylation of N,N-diethylaminomethyldiphenylphosphine oxide (5). Compound (5) was a reaction product of compound (2) with ethyl diphenylphosphinite. No ethylated product of compound (5) was observed, when ethyl iodide was employed as alkylating agent.



(5)



(6)

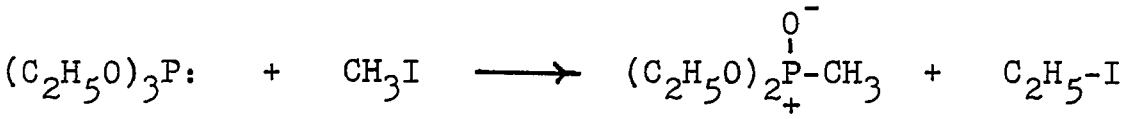
It was not found possible to deoxygenate the $\overset{+}{P}-\overset{-}{O}$ bond of compound (6)

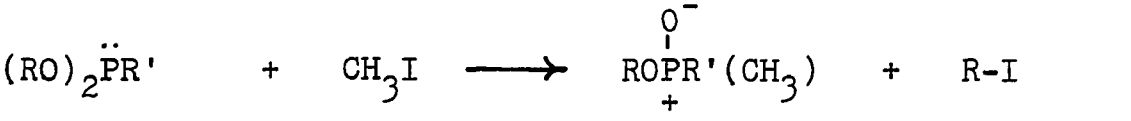
48a. L.P. Divinskaya, V.E. Limanov, E.K. Skvortsova, G.M. Putyatina, A.V. Starkov, N.I. Grinshtein and E.E. Nifantiev, Zh. Obshch. Khim., 36(7) 1244-7 (1966) through CA 65 15418e (1966)

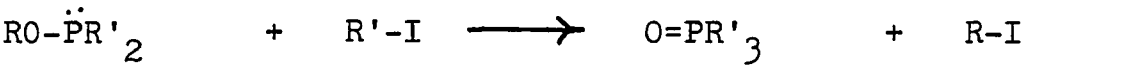
$ClCH_2PO(OC_2H_5)_2 + N(C_2H_5)_3 \rightarrow (C_2H_5)_3\overset{+}{N}CH_2PO(OC_2H_5)_2$ mp=197°C

Discussion

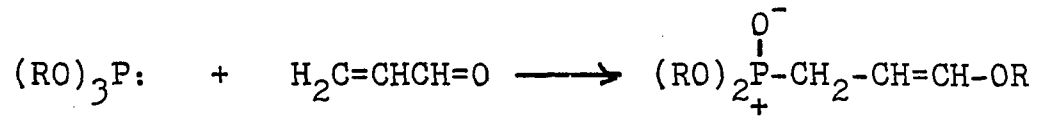
The fundamental characteristic of all trivalent phosphorus compounds is the presence of a lone pair of electrons on the phosphorus atom. As one might anticipate, the trivalent phosphorus compounds give rise to a series of nucleophilic reactions. When the phosphorus nucleophile contains an alkoxy group, the reaction with alkyl halides takes a different course. Thus triethyl phosphite reacts with methyl iodide to give diethylphosphonate. This is known as the Michaelis-Arbusov reaction. It is quite general and may be extended to the synthesis of phosphinates and phosphine oxides[49].



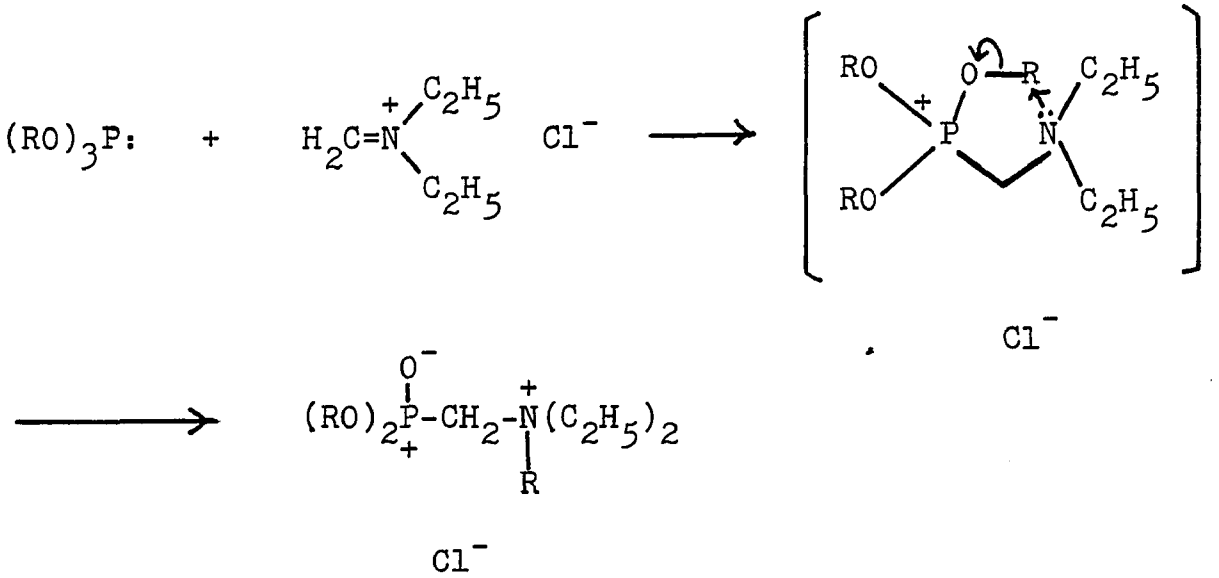




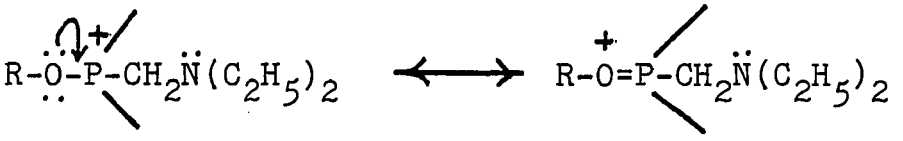
Trivalent phosphorus compounds behave also as nucleophiles towards polarized carbon-carbon multiple bonds[50].



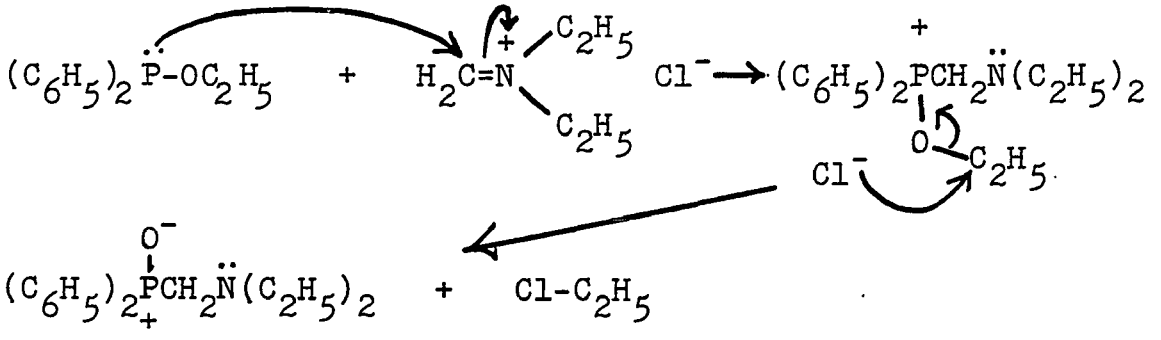
Trivalent phosphorus compounds which contain one or more phosphorus to oxygen σ-bonds, (P-OR), behave as nucleophiles toward polarized carbon-nitrogen double bonds, leading to the formation of quaternary ammonium salts α-substituted with some different phosphorus functions, (phosphonate esters, phosphinate esters, etc.). The initial step, which involves formation of an alkoxy phosphonium salt, is followed by an intramolecular transalkylation via a five-membered cyclic transition state to generate the corresponding quaternary ammonium salts.



Reaction of ethyl diphenylphosphinite (or methyl diphenylphosphinite) with N,N-diethylmethyleneiminium chloride (or N,N-dimethylmethyleneiminium chloride) failed to give the corresponding quaternary ammonium salt. This is thought to be due to the α-P^+ greatly reducing the nucleophilicity of the $-N(C_2H_5)_2$ group. When oxygens are bonded to α-P^+ they reduce the positive charge, making alkylation on nitrogen easier.



Phenyl groups do not conjugate to P^+ nearly as much, because of steric hindrance. The ethyl group on oxygen may be restricted to a backward location and sterically hindered by two bulky phenyl groups. Therefore, the Michaelis-Arbusov mechanism is expected.



Compound (3) and compound (4), very hygroscopic solids, were identified by H-nmr spectra. Compound (3) showed a doublet centered at δ=3.09 (2H, J= 12 Hz) assigned to the methylene protons at $P-CH_2-N^+$; two triplets centered at δ=1.28 (6H, J= 6 Hz) and at δ=1.33 (15H, J= 8 Hz), assigned to methyl groups of ethoxy- and ethyl-group respectively; a quartet centered at δ= 3.31 (6H, J= 8 Hz) assigned to the methylene protons at the ethyl-group bonded at the nitrogen atom; and a multiplet centered at δ=4.04 (4H) assigned to the methylene protons at the ethoxy group bonded to the phosphorus atom.

Compound (4) showed a multiplet centered at δ=1.38 (12H) assigned to the methyl groups; two multiplets centered at δ=3.50 and at δ=4.05 (10H) assigned to methylene protons; and a multiplet centered at δ=7.70 (5H) assigned to protons of a phenyl group.

Compound (5) showed a triplet centered at δ=0.90 (6H, J= 6 Hz) assigned to the methyl protons at the ethyl groups; a quartet centered at δ=2.70 (4H, J= 6 Hz) assigned to the methylene protons of the ethyl groups; a doublet centered at δ=3.26 (2H, J= 6 Hz) assigned to the methylene protons of $\overset{+}{P}-CH_2-N$; and two multiplets centered at δ=7.53 (6H) and at δ=7.93 (4H) assigned to the meta- and para-protons and to the ortho-protons of the two phenyl groups, respectively.

49. J. Emsley and D. Hall, The Chemistry of Phosphorus, Harper & Row Publisher, London 1976
50. G. Kamai and V. A. Kukhtin, Zh. Obsch. Khim. 27 2376 (1957), through Chem. Abs. 52 7127 (1958)

Compound (6) showed an extra singlet at δ=3.30 (3H), compared to the H-nmr spectrum of compound (5). This was assigned to the protons of the methyl groups bonded to a quaternary nitrogen atom. The chemical shift of the methylene protons of $\overset{+}{P}-CH_2-\overset{+}{N}$ was significantly shifted downfield and centered at δ= 4.27 (2H, J= 6 Hz). The ir spectrum of this compound (KBr-pellet) showed a strong absorption band at 1180 cm^{-1} characteristic of the P=O stretch.

The de-oxygenation of compound (6) has been tried. However, all efforts were in vain and led to the recovery of unreacted starting material only, which was identified by its ir spectrum. The deoxygenation reagents, hexachlorodisilane ($Cl_3Si-SiCl_3$)[51], trichlorosilane (Cl_3Si-H)[51], diphenylsilane ($(C_6H_5)_2SiH_2$)[52], work by nucleophilic attack of the P=O $\longleftrightarrow$ $\overset{+}{P}-\bar{O}$ bond on Si-atom. The $-CH_2-\overset{+}{N}$ group presumably stops this by an inductive effect.

51. K. Naumann, G. Zon and K. Mislow, J. Am. Chem. Soc. 91(25) 7012 (1969)
52. O. Dahl and F. K. Jensen, Acta. Chem. Scand. B 29 863 (1975)

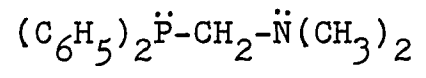
II. Quaternary Ammonium Salts α-Substituted With Phosphino-Groups and Phosphonium Groups.

Results

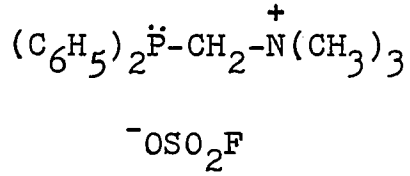
Diphenylphosphinomethyltrialkylammonium salts: diphosphinomethyltrimethylammonium fluorosulfonate (8), diphenylphosphinomethyltrimethylammonium iodide (9), diphenylphosphinomethyltrimethylammonium bromide (10), diphenylphosphinomethyldimethylethylammonium iodide (11), diphenylphosphinomethylbutyldimethylammonium iodide (12), diphenylphosphinomethylbenzyldimethylammonium bromide (13), were made from the alkylation of N,N-dimethylaminomethyldiphenylphosphine (7)[53, 54] with methyl fluorosulfonate, methyl iodide, methyl bromide, ethyl iodide, n-butyl iodide and benzyl bromide, respectively. (Scheme I)

(Diphenylmethylphosphonium-trimethylammonium)-methylene diiodide (14), and (diphenylmethylphosphonium-benzyldimethylammonium)-methylene dibromide were prepared by further alkylation of the corresponding phosphino-substituted quaternary ammonium salts with methyl fluorosulfonate or methyl iodide only.

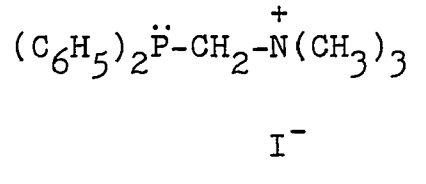
53. A. M. Aguiar, K. C. Hansen and J. T. Mague, J. Org. Chem., 32 2383 (1967)
54. W. E. McEwen, J. H. Smith and E. J. Woo, J. Am. Chem. Soc., 102(8) 2746 (1980)



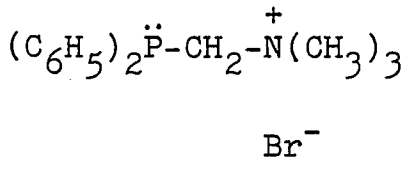
(7)



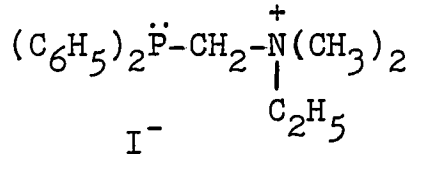
(8)



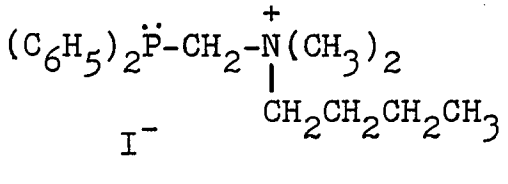
(9)



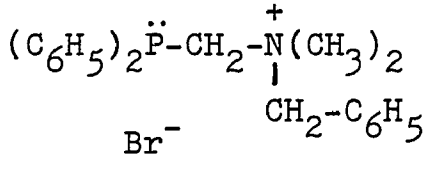
(10)



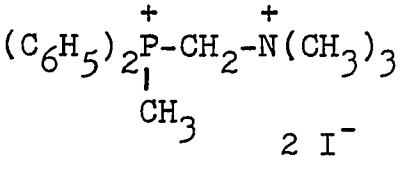
(11)



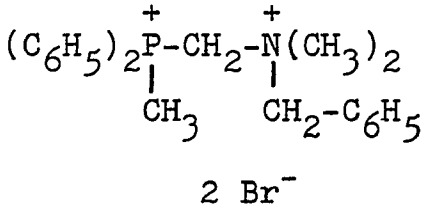
(12)



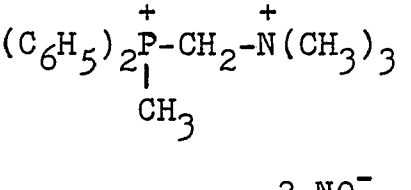
(13)



(14)

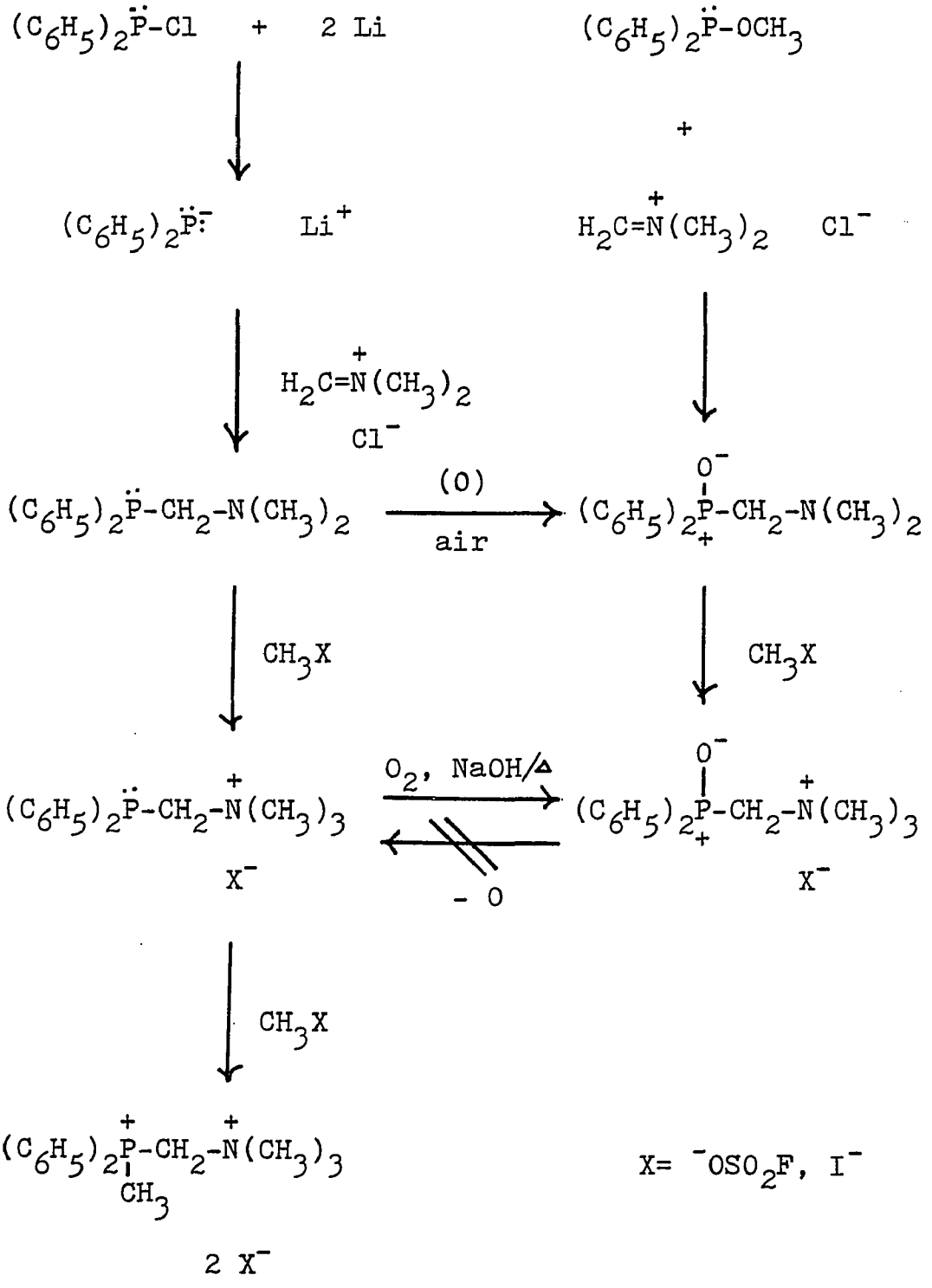


(15)



(16)

Scheme I


(C6H5)2P-Cl + 2 Li
(C6H5)2P-OCH3
+
(C6H5)2P: Li+
H2C=N(CH3)2 Cl-
H2C=N(CH3)2 Cl-
(O)
air
(C6H5)2P-CH2-N(CH3)2
(C6H5)2P-CH2-N(CH3)2
CH3X
CH3X
O2, NaOH/Δ
- O
(C6H5)2P-CH2-N(CH3)3 X-
(C6H5)2P-CH2-N(CH3)3 X-
CH3X
(C6H5)2P-CH2-N(CH3)3
CH3
2 X-
X= -OSO2F, I-

(Diphenylmethylphosphonium-trimethylammonium)-methylene dinitrate (16) was made from the ion exchange of compound (14).

The methylene protons ($\overset{+}{P}-CH_2-\overset{+}{N}$) of compounds (14) and (16) can be exchanged by deuterium in neutral deuterium oxide (D_2O). Those of compound (9) were also hydrogen-deuterium exchangeable in an NaOD-deuterium oxide system.

Compound (9) is stable toward bases in aqueous solvents. The molecule was cleaved upon treatment with sodium hydride in ether, tetrahydrofuran, N,N-dimethylformaldehyde or dimethylsulfoxide. A nucleophilic displacement at the methylene carbon was observed when it was treated with phenyllithium in ether solution.

Discussion

The competitive alkylation, between the nitrogen atom and the phosphorus atom, of a molecule containing the P-C-N linkage, N,N'-dimethylaminomethyldiphenylphosphine for example, seems unusual.

Henderson and Buckler[55] did rate studies on phosphine alkylation with ethyl iodide in acetone, and reported that activation quantities obtained for tri-n-butyl- and triphenylphosphine were as follows (Table I).

Table I

phosphine	ΔH^* (Kcal/mol)	ΔS^* (e.u.)
$(n\text{-}C_4H_9)_3P$:	12.5 ± 0.1	-31 ± 1
$(C_6H_5)_3P$:	14.2 ± 0.1	-33 ± 1

For the corresponding reaction of triethylamine, the enthalpy and entropy of activation are 12.19 Kcal/mol and -38.8 e.u., respectively (reported by Tommila and Kauranen[56]).

55. W. A. Henderson, Jr. and S. A. Buckler, J. Am. Chem. Soc. 82 5794 (1960)
56. E. Tommila and P. Kauranen, Acta. Chem. Scand. 8(7) 1152 (1954)

This means that (i) the activation energy for N-alkylation is less, so at lower temperature, alkylation on tertiary amines should be much faster than on tertiary phosphines, (ii) the steric requirements for N-alkylation are much greater.

Some kinetic measurements of quaternization of tertiary phosphines and amines were investigated by Henderson et. al. (Table II)[55], (Table III)[57] and by McEwen et. al. (Table IV)[58].

Table II

$$RR'R''P: + C_2H_5I \xrightarrow[(CH_3)_2C{=}O,\ 34.97^{\circ}C]{k_2} RR'R''\overset{+}{P}C_2H_5\ I^-$$

phosphine	k_2 (l, mol^{-1}, sec^{-1})
$(CH_3)_3P$:	$2.24 \pm 1.86 \times 10^{-3}$
$C_2H_5\ddot{P}(CH_3)_2$	$8.05 \pm 0.30 \times 10^{-3}$
$(n\text{-}C_4H_9)_3P$:	$1.62 \pm 0.05 \times 10^{-3}$
$(i\text{-}C_4H_9)_3P$:	$1.38 \pm 0.01 \times 10^{-4}$
$(C_6H_5)_2\ddot{P}C_2H_5$	$1.12 \pm 0.01 \times 10^{-4}$
$(C_6H_5)_3P$:	$3.78 \pm 0.05 \times 10^{-5}$

57. W. A. Henderson, Jr. and C. J. Schultz, J. Chem. Soc. 27 4643 (1962)
58. W. E. McEwen, A. B. Janes, J. W. Knapczyk, V.L. Kyllingstad, W. I. Shiau, S. Shore, and J. H. Smith, J. Am. Chem. Soc. 100 7304 (1978)

Table III

$$RR'R''N: + C_2H_5I \xrightarrow[(CH_3)_2C=O,\ 35.00^\circ C]{k_2} RR'R''\overset{+}{N}C_2H_5\ I^-$$

amine	k_2(l, mol^{-1}, sec^{-1})
$(CH_3)_3N$:	$6.53 \pm 0.07 \times 10^{-3}$
$(C_2H_5)_3N$:	$1.82 \pm 0.01 \times 10^{-4}$
$(CH_3)_2\ddot{N}C_6H_5$	$5.47 \pm 0.03 \times 10^{-6}$
$(C_2H_5)_2\ddot{N}C_6H_5$	$1,76 \pm 0.04 \times 10^{-7}$

Table IV

$$RR'R''P: + C_6H_5CH_2\text{-}Br \xrightarrow[\substack{C_6H_6\text{-}CH_3OH\ (3:2)\\ 21.0 \pm 0.1^\circ C}]{k_2} RR'R''\overset{+}{P}CH_2C_6H_5\ Br^-$$

phosphine	k_2(l, mol^{-1}, sec^{-1})
$(C_6H_5)_2\ddot{P}CH_3$	9.86×10^{-4}
$(C_6H_5)_2\ddot{P}C_2H_5$	7.53×10^{-4}
$(C_6H_5)_2\ddot{P}(n\text{-}C_3H_7)$	7.19×10^{-4}
$(C_6H_5)_2\ddot{P}(n\text{-}C_4H_9)$	7.22×10^{-4}
$(C_6H_5)_3P$:	2.00×10^{-4}
$(C_6H_5)_2\ddot{P}CH_2CH_2CH_2OCH_3$	8.67×10^{-4}
$(C_6H_5)_2\ddot{P}CH_2CH_2OCH_3$	9.39×10^{-4}
$(C_6H_5)_2\ddot{P}CH_2OCH_3$	0.00

Table V

$$(n\text{-}C_4H_9)_3P: + R\text{-}X \xrightarrow[(CH_3)_2C{=}O,\ 34.97^{\circ}C]{k_2} (n\text{-}C_4H_9)_3\overset{+}{P}R\ X^-$$

R-X	k_2(l, mol^{-1}, sec^{-1})
CH_3I	$2.60 \pm 0.40 \times 10^{-1}$
C_2H_5I	$1.54 \pm 0.05 \times 10^{-3}$
$n\text{-}C_4H_9Cl$	$2.39 \pm 0.05 \times 10^{-7}$

These results show that (i) the reaction rates of alkylation of tertiary aliphatic amines toward alkyl halides, ethyl iodide for example, decrease as inductive and steric effects on the molecule are increased, (ii) conjugation between phenyl rings and phosphorus seems small judging from the nucleophilicity of aryl phosphines, while conjugation to nitrogen has a very great effect, (iii) the reactivity of phosphines decreases as the size of alkylation reagents increases.

One cannot predict that N-alkylation should be always slower than P-alkylation on the quaternization of a P-C-N system. Dimethylalkylamines, in particular, should alkylate faster than most tertiary phosphines.

Lundberg et al[59] have found that N,N-dimethylaminomethyldimethylphosphine was very reactive toward nucleophiles.

59. K. L. Lundberg, R. L. Rowatt and N. E. Miller, Inorg. Chem., 3 884 (1964)

$$(CH_3)_2\ddot{P}\text{-}CH_2\text{-}\ddot{N}(CH_3)_2$$

They stated that it monoalkylated at more than at one site on treatment with methyl iodide and were not be able to isolate the methylated products. Therefore there was competition between N- and P-alkylation in this system on quaternization.

Our result did show that mono-quaternization of compound (7), $(C_6H_5)_2\ddot{P}\text{-}CH_2\text{-}\ddot{N}(CH_3)_2$, with several alkyl halides in a variety of organic solvent systems, led exclusively to N-alkylation. The quaternary ammonium salts then could be further P-alkylated only with selected alkylating agents such as methyl fluorosulfonate and methyl iodide under reflux conditions.

To demonstrate that the structures derived solely from alkylation on the nitrogen atom, H-nmr and UV spectra of some compounds were carefully examined.

First of all, we took the H-nmr spectra of compound (9) The H-nmr spectrum showed a sharp singlet at δ=3.60 (9H) assigned to the protons of three methyl groups on a quaternary ammonium nitrogen atom. (comparison to the H-nmr spectrum of tetramethylammonium bromide gave a similar chemical shift, see Table VII) A singlet at δ=4.75 (2H) was assigned to the methylene protons of $P\text{-}CH_2\text{-}N^+$, and two groups of multiplets centered at δ=7.60 and δ=7.90 (10H) were assign-

ed to the meta and para and to the ortho protons of the two phenyl groups on phosphorus atom (Fig. I). Upon further alkylation of compound (9) with methyl iodide, compound (14) was obtained.

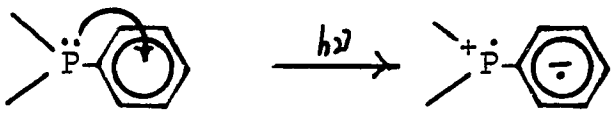
The H-nmr spectrum of compound (14), showed an extra doublet centered at δ=3.19 (3H, J=13 Hz), which perfectly matched the chemical shift and splitting pattern of a methyl group on a quadrivalent phosphorus atom, P^+-CH_3, (Fig. IX, X). Their methylene protons were shifted downfield and became a doublet, aplit by the P^+-atom, centered at δ=5.75 (2H, J=8 Hz) and two groups of multiplets at δ=7.50-8.16 (10H) were assigned to phenyl protons (Fig. VI).

Secondly, we examined compound (13). The H-nmr spectrum (in F_3CCOOH, TMS δ=0.0) showed a singlet at δ=3.24 (6H) assigned as protons of two methyl groups at a quaternary ammonium nitrogen atom; and a multiplet at δ=4.74-4.81 assigned to two methylene protons. The chemical shifts at δ=7.26-7.84 (15H) were thought to be due to overlap of two different groups of phenyl protons (Fig. V). The pattern is different from the pattern of benzyldiphenylphosphine oxide (Fig. XI). Therefore, one can claim that the benzyl group is not on a quadrivalent phosphorus atom.

Compound (13) was further alkylated with methyl iodide. The H-nmr spectrum (in F CCOOH, TMS δ=0.0) of compound (15) showed a new doublet centered at δ=2.34 (3H, J=13 Hz) assigned to a methyl group on the P^+-atom. This is one more piece of evidence to assure quaternization soley on

the nitrogen atom of compound (13). The chemical shift of the methylene protons in $P^+-CH_2-N^+$ was shifted downfield and split into a doublet centered at σ=4.96 (2H, J= 6 Hz) (Fig. VII). All other chemical shifts and signal patterns are similar to the H-nmr spectrum of compound (14).

To provide more evidence for the structure determination, UV spectra were studied. Compound (10) (Fig. XII), (13) (Fig. XIII), and (16) (Fig. XIV) were used for this purpose. The UV spectra of monoalkylated quaternized compounds showed a strong absorption band at between 230 and 260 nm. It is thought to be due to transfer of a lone pair electron on phosphorus to be delocalized over the phenyl ring.



"charge transfer"

The dialkylated product, (16), has no lone pair electrons available for the "donor-acceptor" pattern (compare with the UV spectrum of methyltriphenylphosphonium bromide, Fig. XV).

The inductive effect must have played a major role in the quaternization of compound (7). McEwen et al[58] found that the reaction rate for the reaction diphenyl-(methoxymethyl)-phosphine, $(C_6H_5)_2\ddot{P}\text{-}CH_2\text{-}\ddot{O}CH_3$, with benzyl bromide was too slow to measure under certain conditions (Table IV). But, for diphenyl(2-methoxyethyl)-phosphine, $(C_6H_5)_2\ddot{P}\text{-}CH_2CH_2\text{-}\ddot{O}CH_3$, or dipheynl(3-methoxypropyl)-phosphine, $(C_6H_5)_2\ddot{P}\text{-}CH_2CH_2CH_2\text{-}\ddot{O}CH_3$, the reactions were much faster, unaffected by the methoxy-group, since the through -chain inductive effects decreases as the length of chain increases.

Similarly, in compound (7), $(C_6H_5)_2\ddot{P}\text{-}CH_2\text{-}\ddot{N}(CH_3)_2$, the rate of alkylation at nitrogen is much greater than at phosphorus. Similar to the case with diphenyl(methoxy-methyl)-phosphine, it is possible that the inductive effect of nitrogen may slow the phosphorus alkylation rate.

It is to be expected that the nucleophilicity of a tertiary phosphine will be sharply decreased if the phosphine is α-substituted with a highly electronegative heteratom (Table VI)[60], the electronegativity of the $-CH_2\ddot{N}(CH_3)_2$ group that slows down the P-alkylation.

60. A. L. Allred, J. Inorg. Nucl. Chem., 17 215 (1961)

Table VI

element	electronegativity
O	3.44
N	3.04
C	2.55
P	2.19

Because steric factors are considerable with quaternization on nitrogen, lower steric requirements of the small size methyl groups favor N-quaternization,

Therefore, a combination of steric and inductive factors may be involved in the alkylation of compound (7), leading exclusively to N-alkylation. Issleib[61a, 61b] found that 2-aminoethylphosphines were alkylated on nitrogen with methyl groups on the nitrogen, but on phosphorus with ethyl groups on the nitrogen.

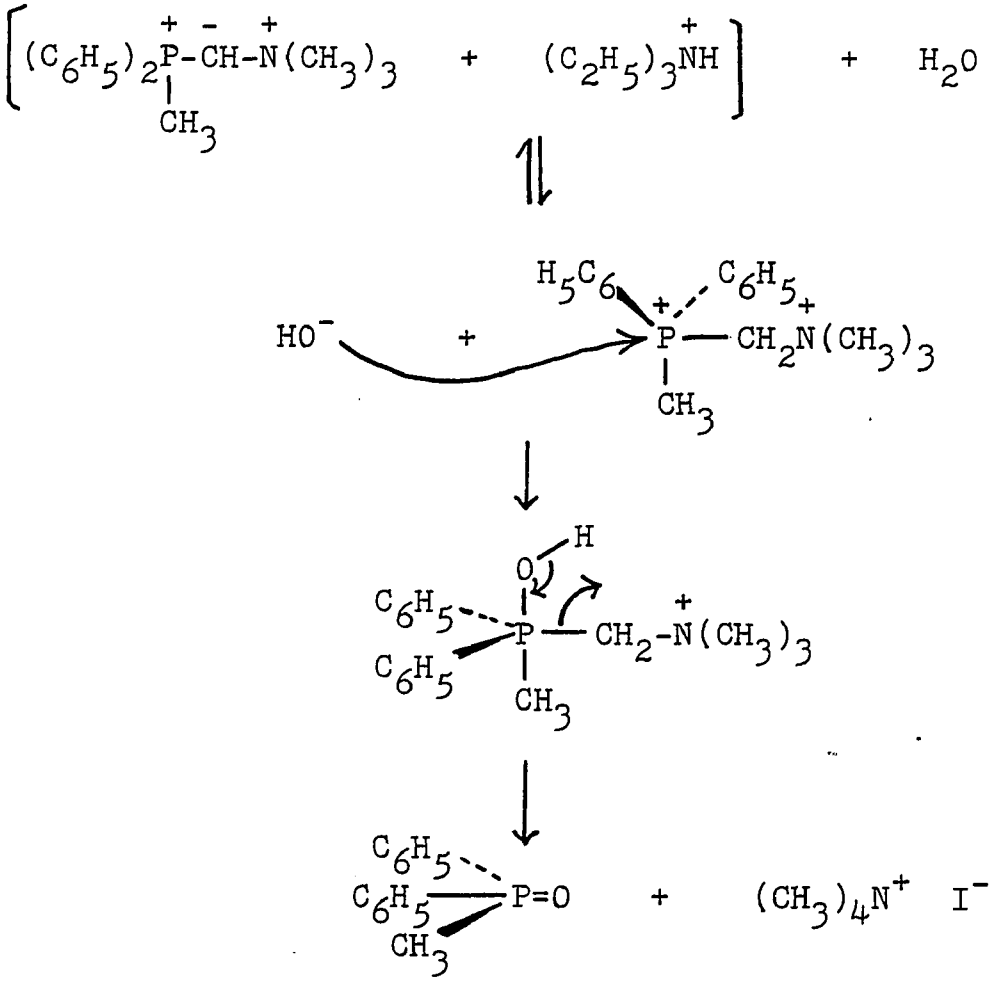
Methylene protons of compounds (9) and (14) underwent hydrogen-deuterium exchange, indicating that these are weakly acidic protons, and can be removed with base. With the intention of making nitrogen ylids from compounds (9) and (14), several bases have been employed. However, no such ylid has been isolated or trapped.

Treatment of compound (14) with triethylamine in ether gave on work up tetramethylammonium iodide and diphenylmethylphosphine oxide. A hydroxide-catalyzed hydrolysis of the phosphonium salt may have occurred, leading to the elimination of a tetramethylammonium ion (Scheme II).

In contrast, a stable ylid was obtained from the

treatment of a comparable bis-(triphenylphosphonium)-methylene ion with potassium carbonate[62].

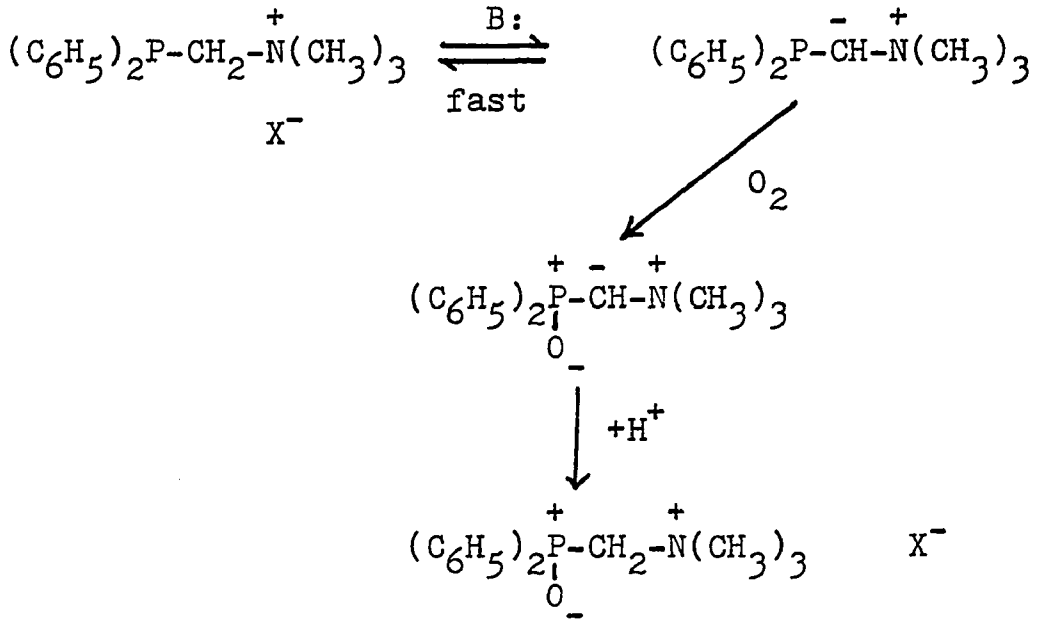
Scheme II



62. F. Ramirez, N. B. Desai and N. McKelvie, J. Am. Chem. Soc., 84 1745 (1962)
N. McKelvie, Ph.D. Thesis, Columbia U. (1961)
61a. K. Issleib and D. H. Haferburg, Z. Naturforsch (B) 20 916 (1965)
61b. K. Issleib and R. Rieschel, Chem. Ber., 100 2685 (1967)

Compund (9) is stable toward air and many acids and bases, under most circumstances. It is oxidized by air to the corresponding phosphine oxide only upon refluxing with sodium hydroxide aqueous solution. This is thought to be via formation of an ylid intermediate, followed by air oxidation of the phosphine (Scheme III).

Scheme III



However, water-soluble t-dimethylphosphines react with refluing sodium hydroxide solutions to give the phosphine oxides and hydrogen gas.[63] Compound (9) does notsimilarly form the oxide in the absence of oxygen.

63. S. M. Bloom, S. A. Buckler, R. F. Lambert and E. V. Merry, Chem. Commun. (J. Chem. Soc. D) 870-1 (1970)

Upon treatment of compound (9) with phenyllithium in ether solution, a nucleophilic displacement reaction at the methylene carbon was observed. Benzyldiphenylphosphine oxide was collected and identified, after the ether solution was exposed to air. The H-nmr spectrum of this gave a doublet at δ=3.86 (2H, J=12 Hz) assigned as methylene protons split by an adjacent quadrivalent phosphorus atom. Three groups of multiplets (Fig. XI) at δ=6.64-7.85 (15H) were assigned to (i) ortho-, (ii) meta-, and para-protons of the benzyl ring, and (iii) protons of the two phenyl rings. Some suggested mechanisms are via (a1) or (a2) a direct nucleophilic substitution at the methylene carbon, and/or (b) an ylid intermediate which decomposes to a carbene. Nucleophilic attack on the carbene could follow. (Scheme IV)

Reaction of compound (9) with sodium hydride in tetrahydrofuran followed by methyl iodide, led to the collection of either diphenylmethylphosphine oxide, after the reaction mixture was exposed to air, or dimethyldiphenylphosphonium iodide, when methyl iodide was in excess. Reaction of compound (9) with sodium hydride in N,N-dimethylformaldehyde gave sodium diphenylphosphinate. Sodium diphenylphosphinate was neutralized with concentrated hydrochloride acid, and crystallized from acidic aqueous solution, it was identified

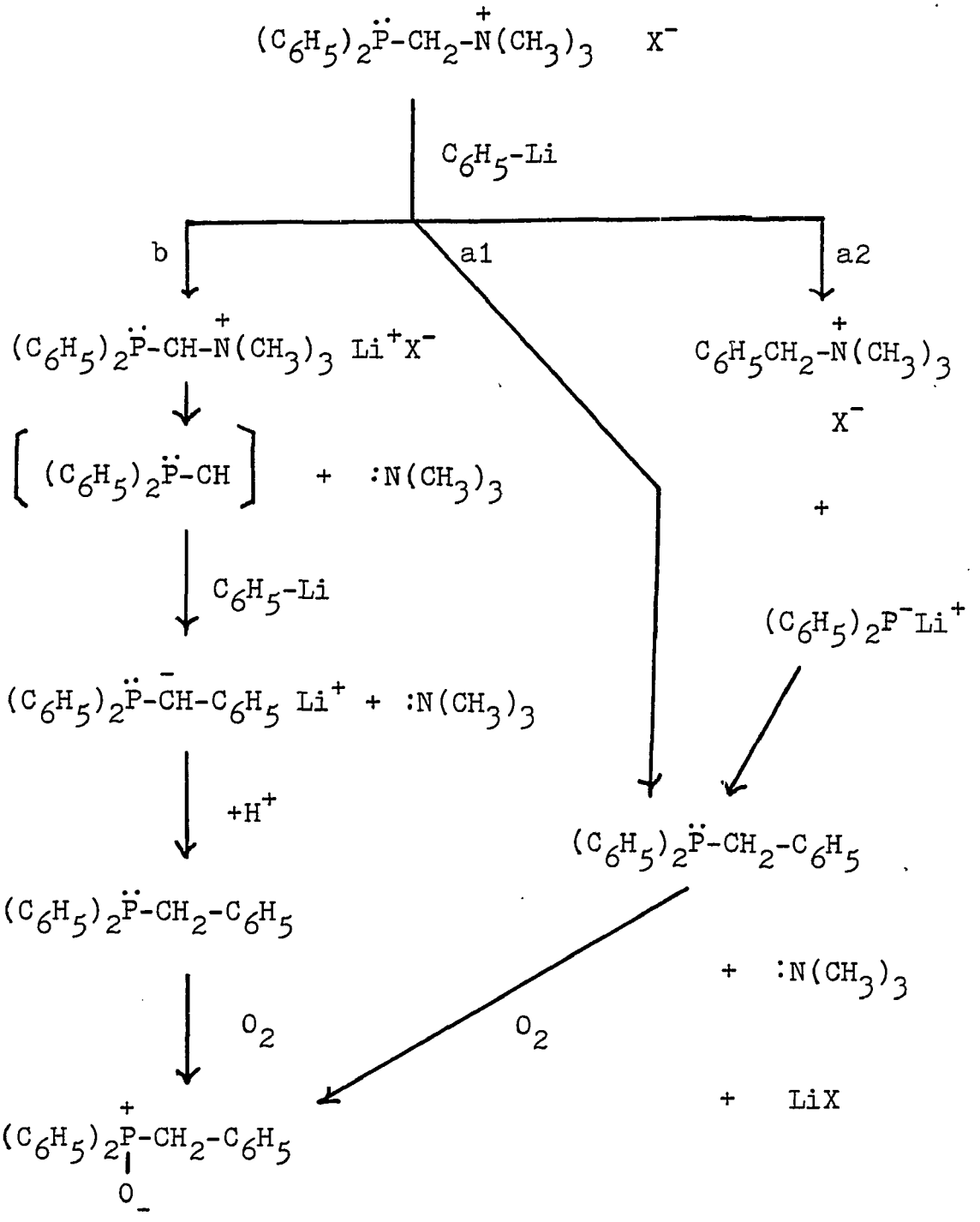
by mixed melting point determination.

One possible mechanism is that a phosphorus-methylene carbon bond was broken, as attacked by a hydride, into (a) trimethylaminomethylide, which on picking up a proton from diphenylphosphine, $(C_6H_5)_2\ddot{P}$-H, became tetramethylammonium iodide, or decomposed, and (b) diphenylphosphine followed by a intermolecular proton-transfer became diphenylphosphine, which in anhydrous THF can be methylated with methyl iodide, leading to the formation of diphenylmethylphosphine, and then be quaternized to became dimethyldiphenylphosphonium iodide. In rigorously dried DMF, the diphenylphosphide can be oxidized by the solvent (Scheme V).

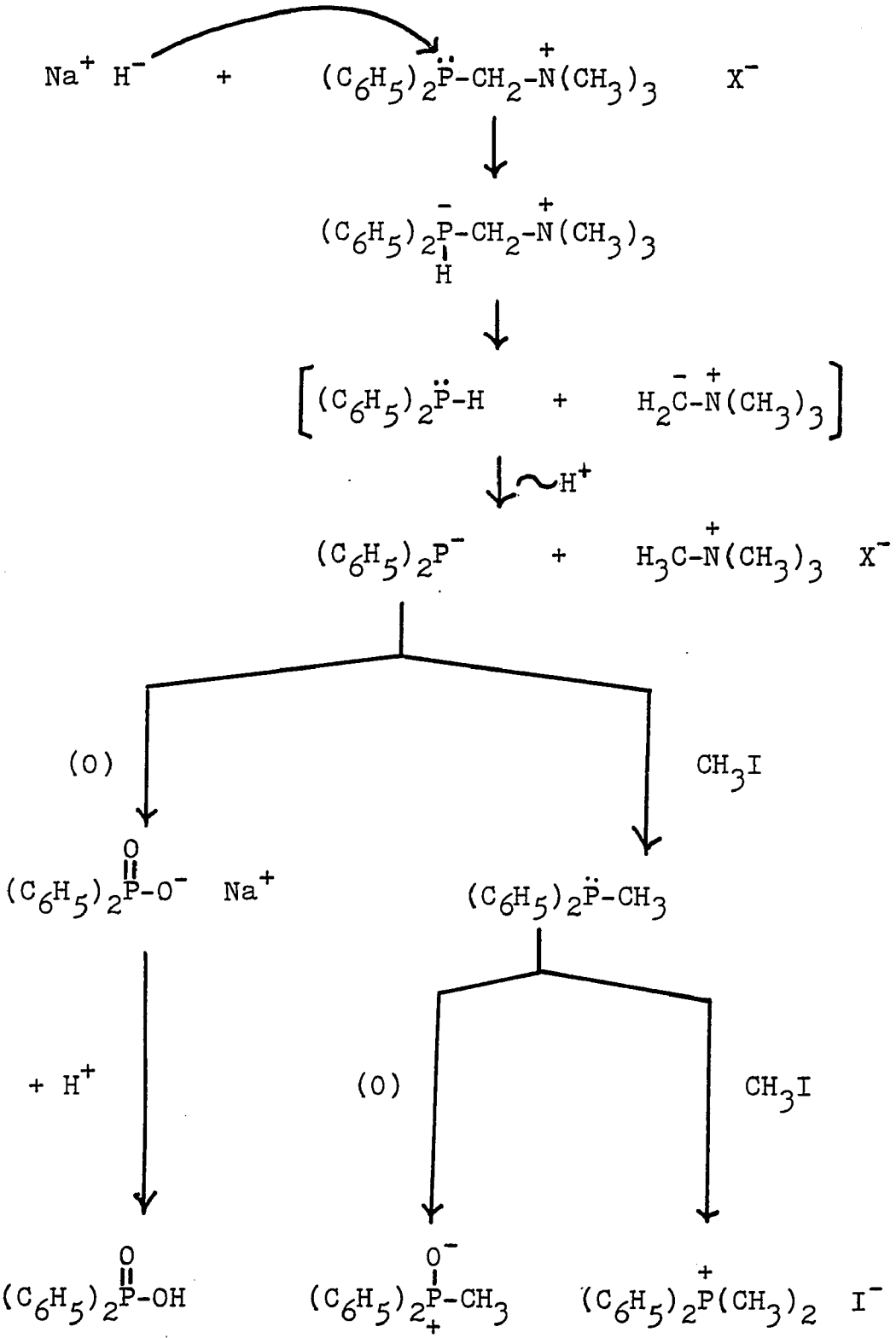
For a summary of reactions see Scheme VI.

The H-nmr spectral data of compounds is shown in Table VII.

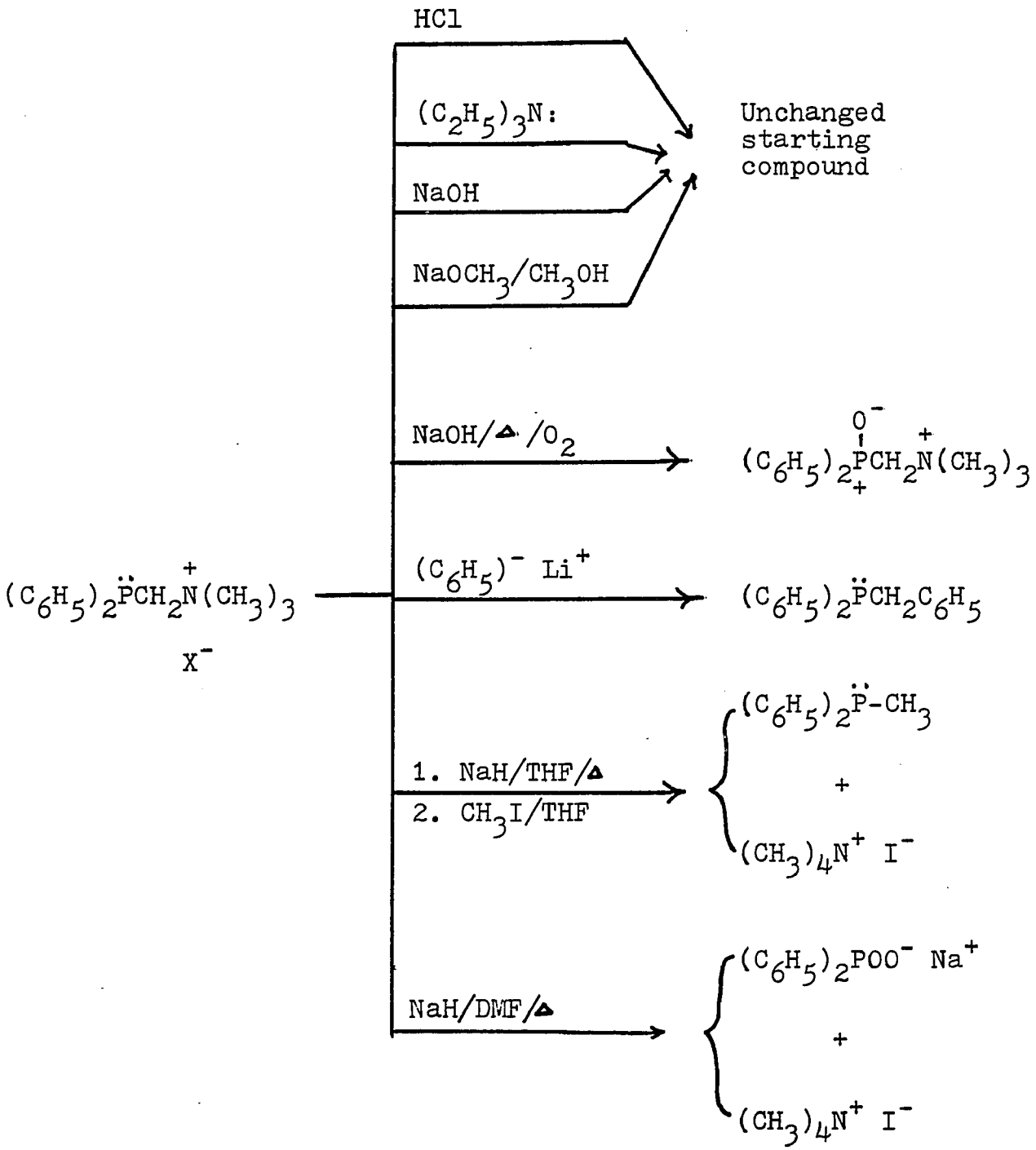
Scheme IV


$(C_6H_5)_2\ddot{P}-CH_2-\overset{+}{N}(CH_3)_3$ X^-
C_6H_5-Li
b
a1
a2
$(C_6H_5)_2\ddot{P}-CH-\overset{+}{N}(CH_3)_3$ Li^+X^-
$C_6H_5CH_2-\overset{+}{N}(CH_3)_3$ X^-
$\left[(C_6H_5)_2\ddot{P}-CH \right]$ + $:N(CH_3)_3$
+
C_6H_5-Li
$(C_6H_5)_2P^-Li^+$
$(C_6H_5)_2\ddot{P}-\bar{C}H-C_6H_5$ Li^+ + $:N(CH_3)_3$
$+H^+$
$(C_6H_5)_2\ddot{P}-CH_2-C_6H_5$
$(C_6H_5)_2\ddot{P}-CH_2-C_6H_5$
+ $:N(CH_3)_3$
O_2
O_2
+ LiX
$(C_6H_5)_2\overset{+}{P}(O^-)-CH_2-C_6H_5$

Scheme V


Na+ H−
+
(C6H5)2P-CH2-N(CH3)3 X−
(C6H5)2P-CH2-N(CH3)3
H
[(C6H5)2P-H + H2C-N(CH3)3]
~H+
(C6H5)2P− + H3C-N(CH3)3 X−
(O)
CH3I
(C6H5)2P-O− Na+
(C6H5)2P-CH3
+ H+
(O)
CH3I
(C6H5)2P-OH
(C6H5)2P-CH3
(C6H5)2P(CH3)2 I−

Scheme VI


HCl
$(C_2H_5)_3N$:
NaOH
$NaOCH_3/CH_3OH$
Unchanged starting compound
$NaOH/\Delta/O_2$
$(C_6H_5)_2\overset{\cdot\cdot}{P}CH_2\overset{+}{N}(CH_3)_3$ X^-
$(C_6H_5)^-$ Li^+
$(C_6H_5)_2\overset{\cdot\cdot}{P}CH_2C_6H_5$
1. NaH/THF/Δ
2. CH_3I/THF
$(C_6H_5)_2\overset{\cdot\cdot}{P}-CH_3$
+
$(CH_3)_4N^+$ I^-
NaH/DMF/Δ
$(C_6H_5)_2POO^-$ Na^+
+
$(CH_3)_4N^+$ I^-

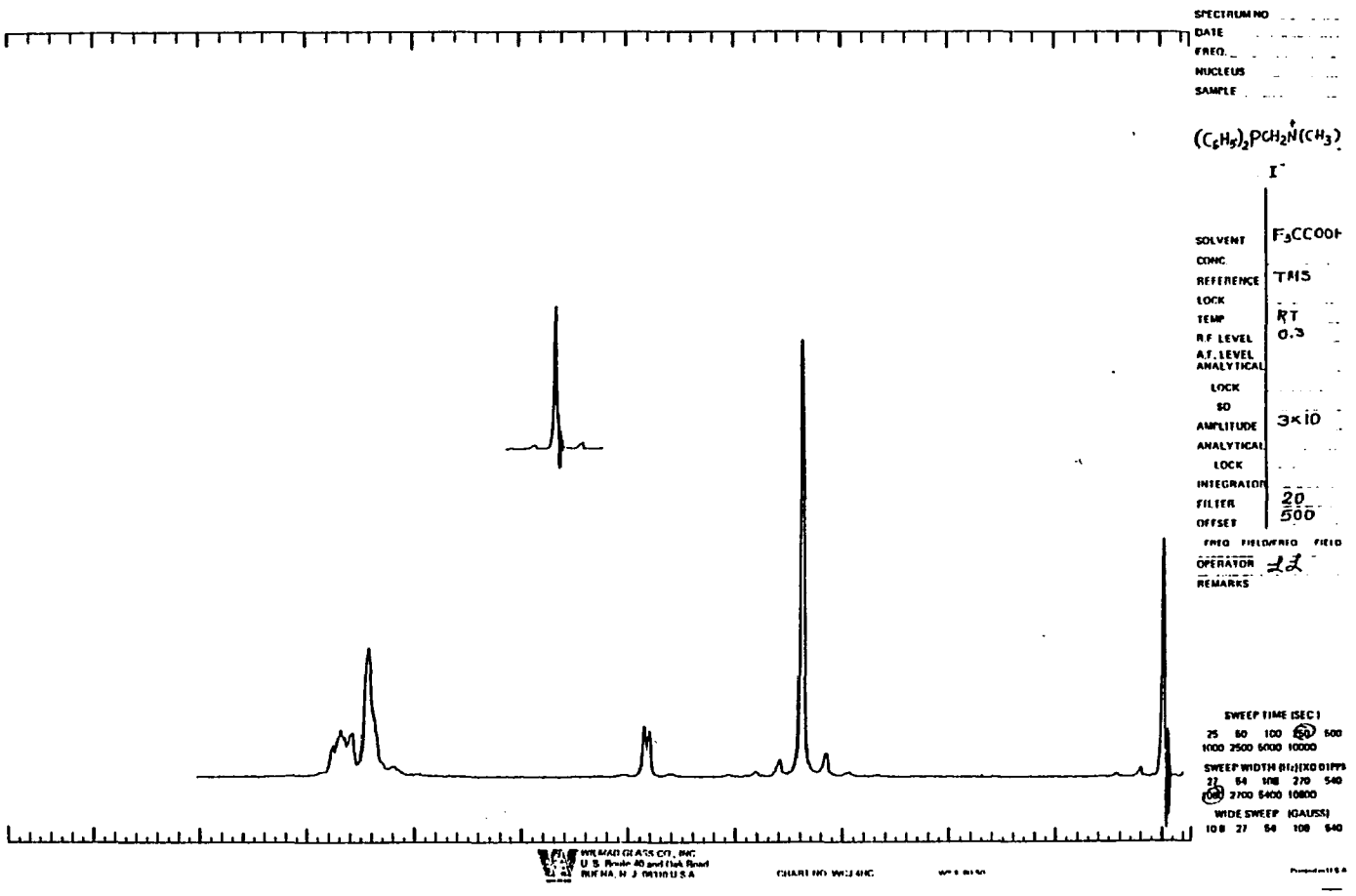


Fig. I. The H-nmr spectrum of diphenylphosphinomethyltrimethylammonium iodide (9), $(C_6H_5)_2P\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_3\ I^-$, in F_3CCOOH solution (TMS δ=0.00).

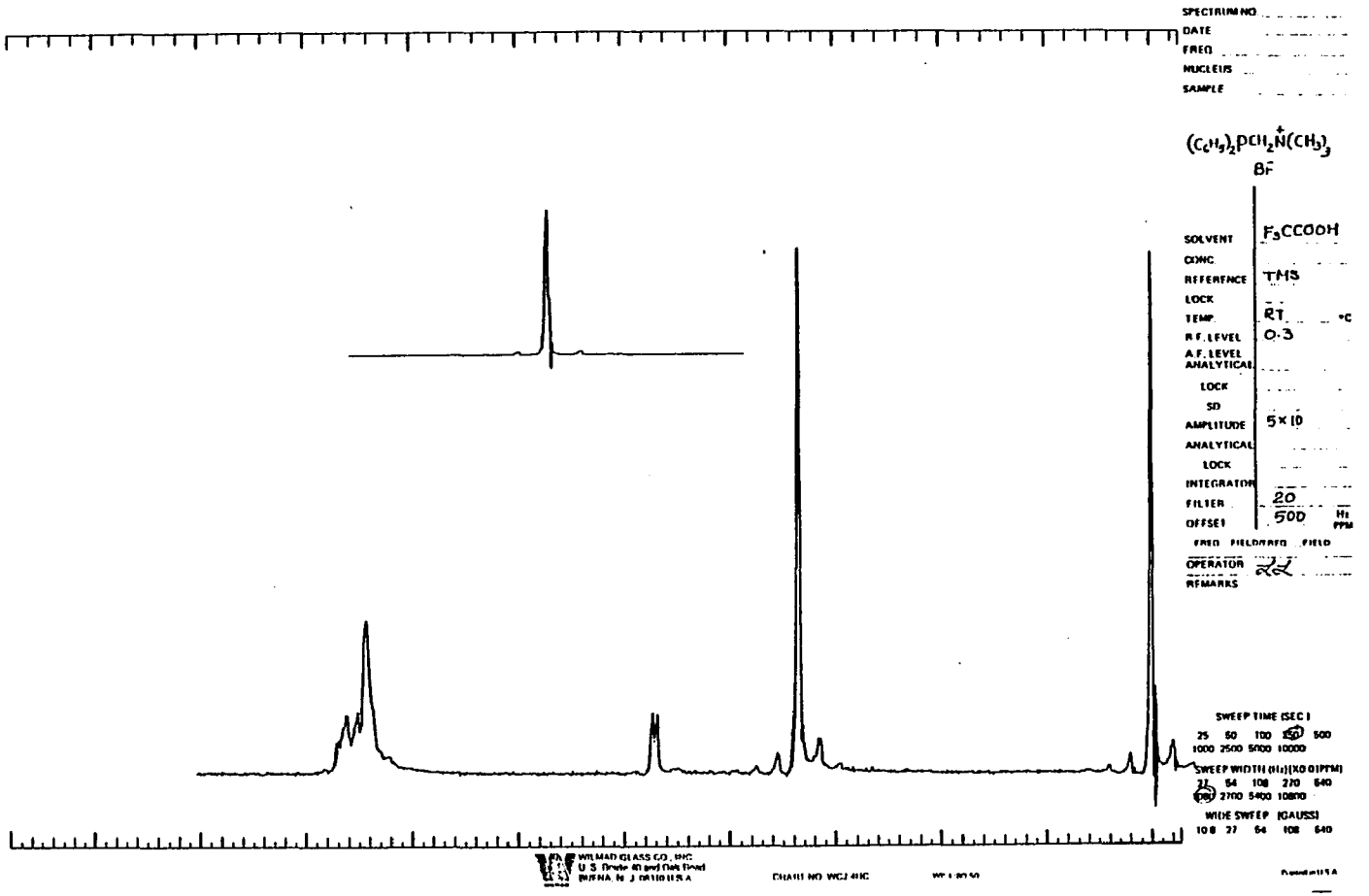


Fig. II. The H-nmr spectrum of diphenylphosphinomethyltrimethylammonium bromide (10), $(C_6H_5)_2P\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_3\ Br^-$, in F_3CCOOH solution (TMS δ=0.00).

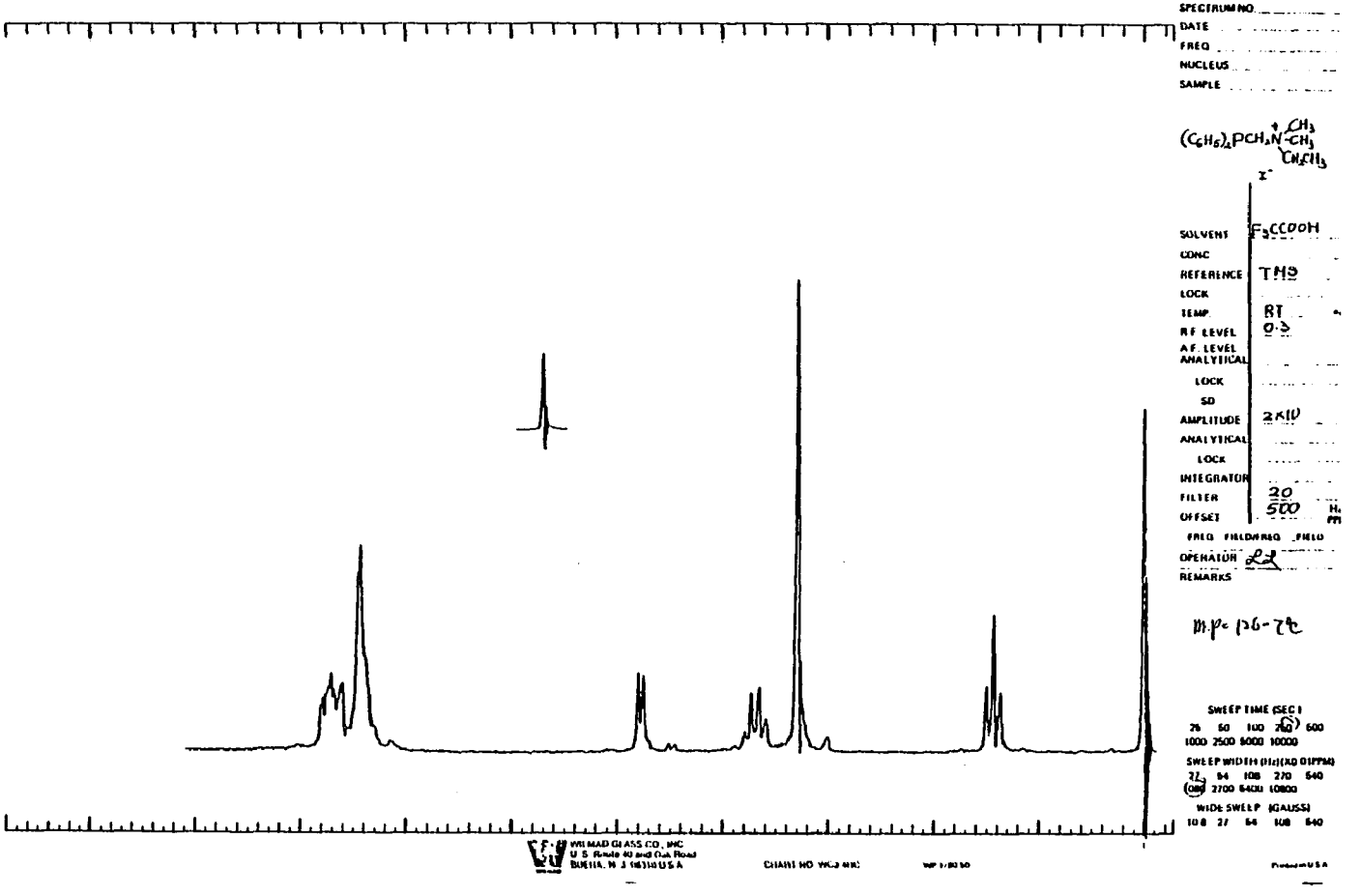


Fig. III. The H-nmr spectrum of diphenylphosphinomethyldimethylethylammonium iodide (11), $(C_6H_5)_2P\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_2\ I^-$, in F_3CCOOH solution (TMS δ=0.00).
C_2H_5

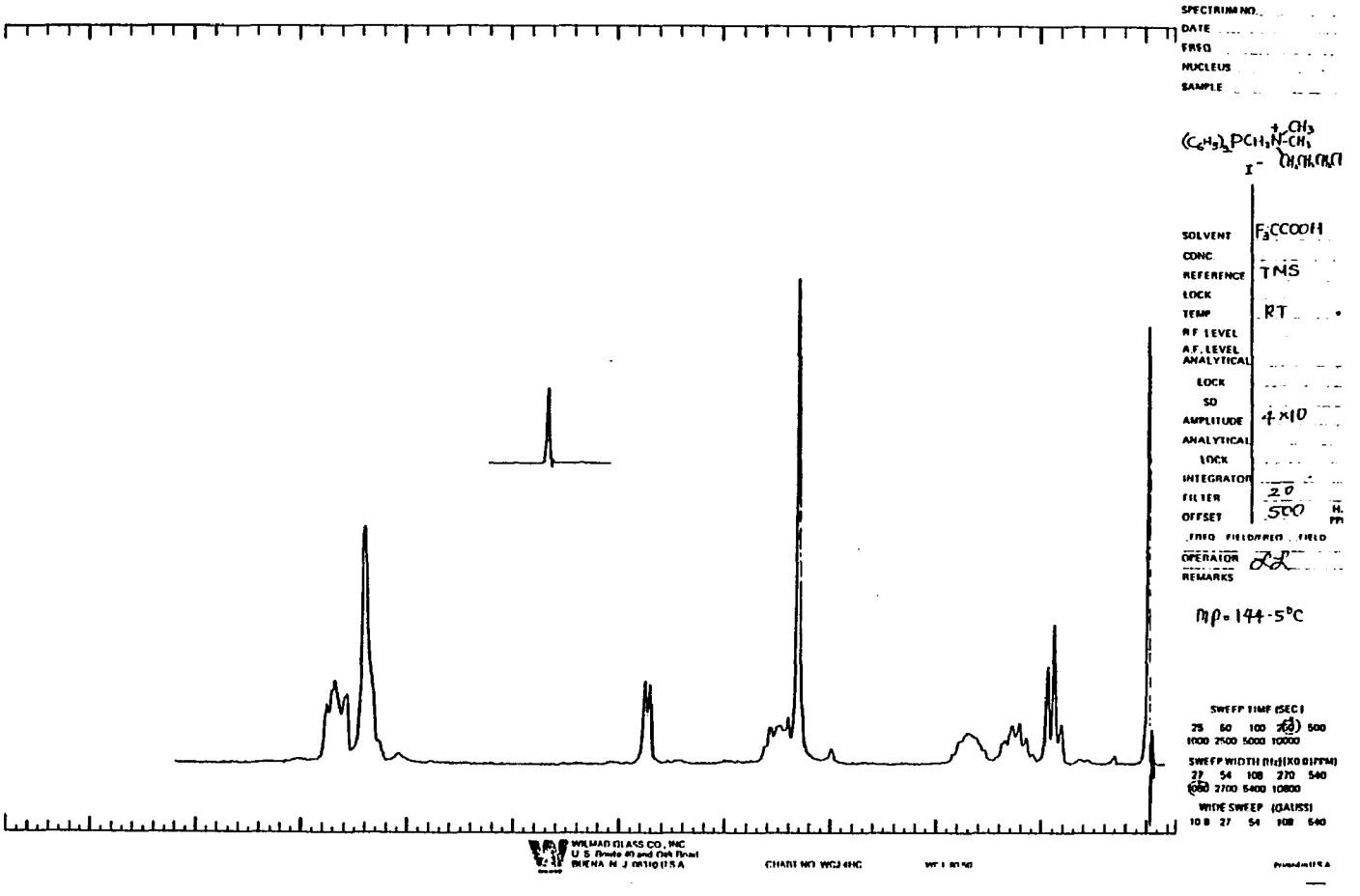


Fig. IV. The H-nmr spectrum of diphenylphosphinomethylbutyldimethylammonium iodide (12), $(C_6H_5)_2P\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_2CH_2CH_2CH_2CH_3\ I^-$, in F_3CCOOH solution (TMS δ=0.00).

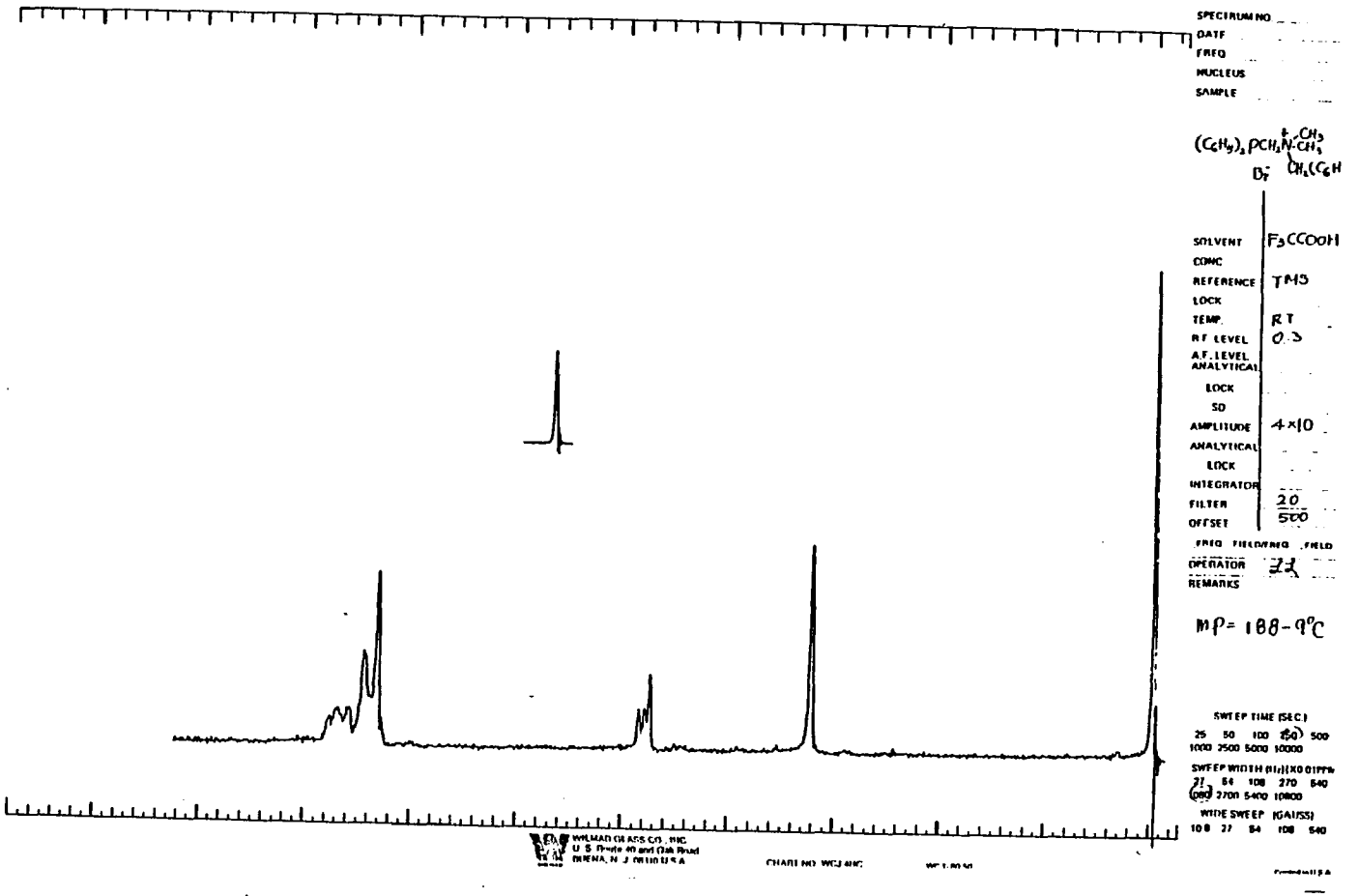


Fig. V. The H-nmr spectrum of diphenylphosphinomethylbenzyldimethylammonium bromide (13), $(C_6H_5)_2P\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_2CH_2C_6H_5\ Br^-$, in F_3CCOOH solution (TMS δ=0.00).

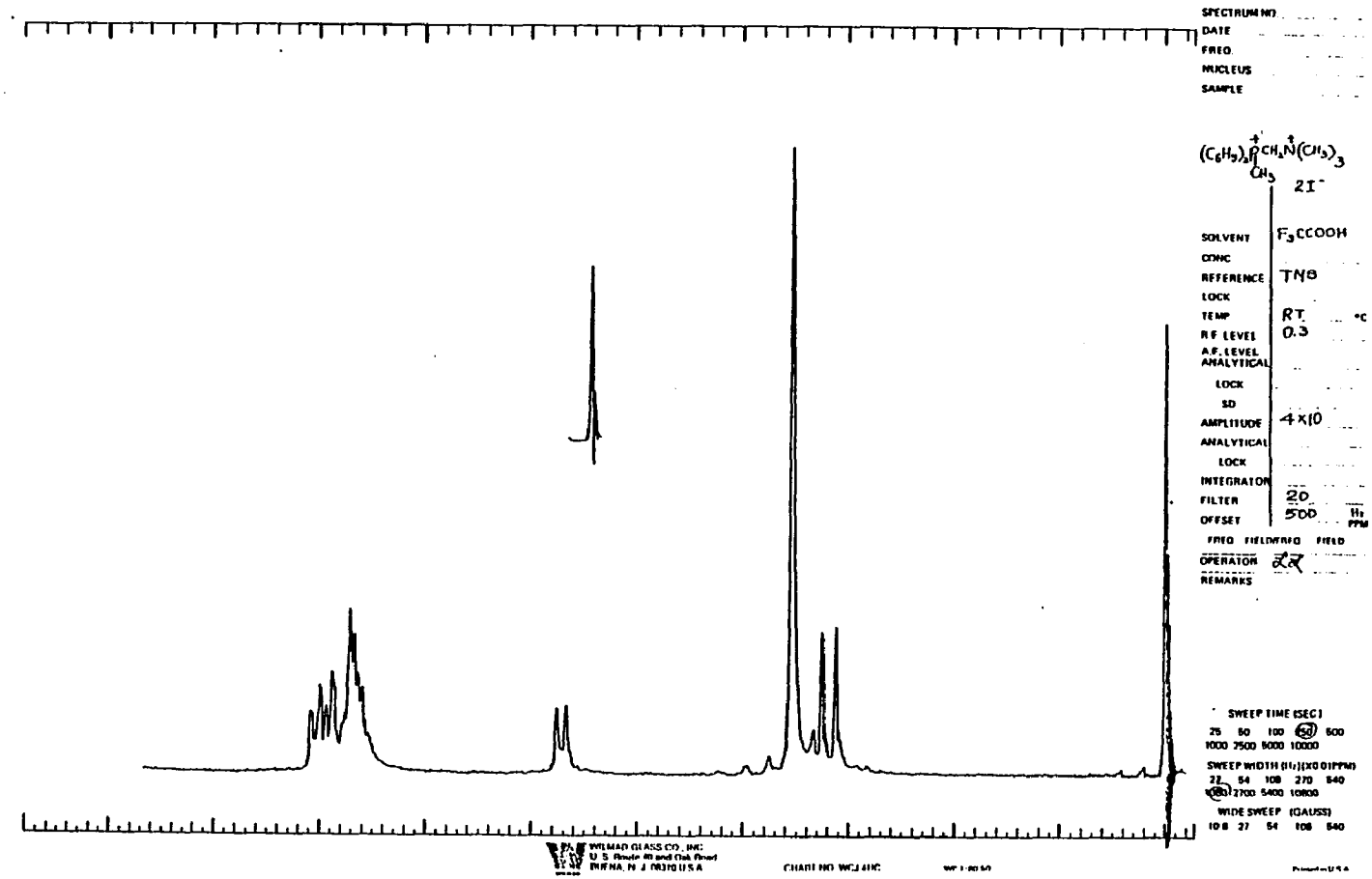


Fig. VI. The H-nmr spectrum of (diphenylmethylphosphonium-trimethylammonium)-methylene diiodide (14), $(C_6H_5)_2\overset{+}{P}(CH_3)CH_2\text{-}\overset{+}{N}(CH_3)_3\ 2I^-$ in F_3CCOOH solution (TMS δ=0.00)

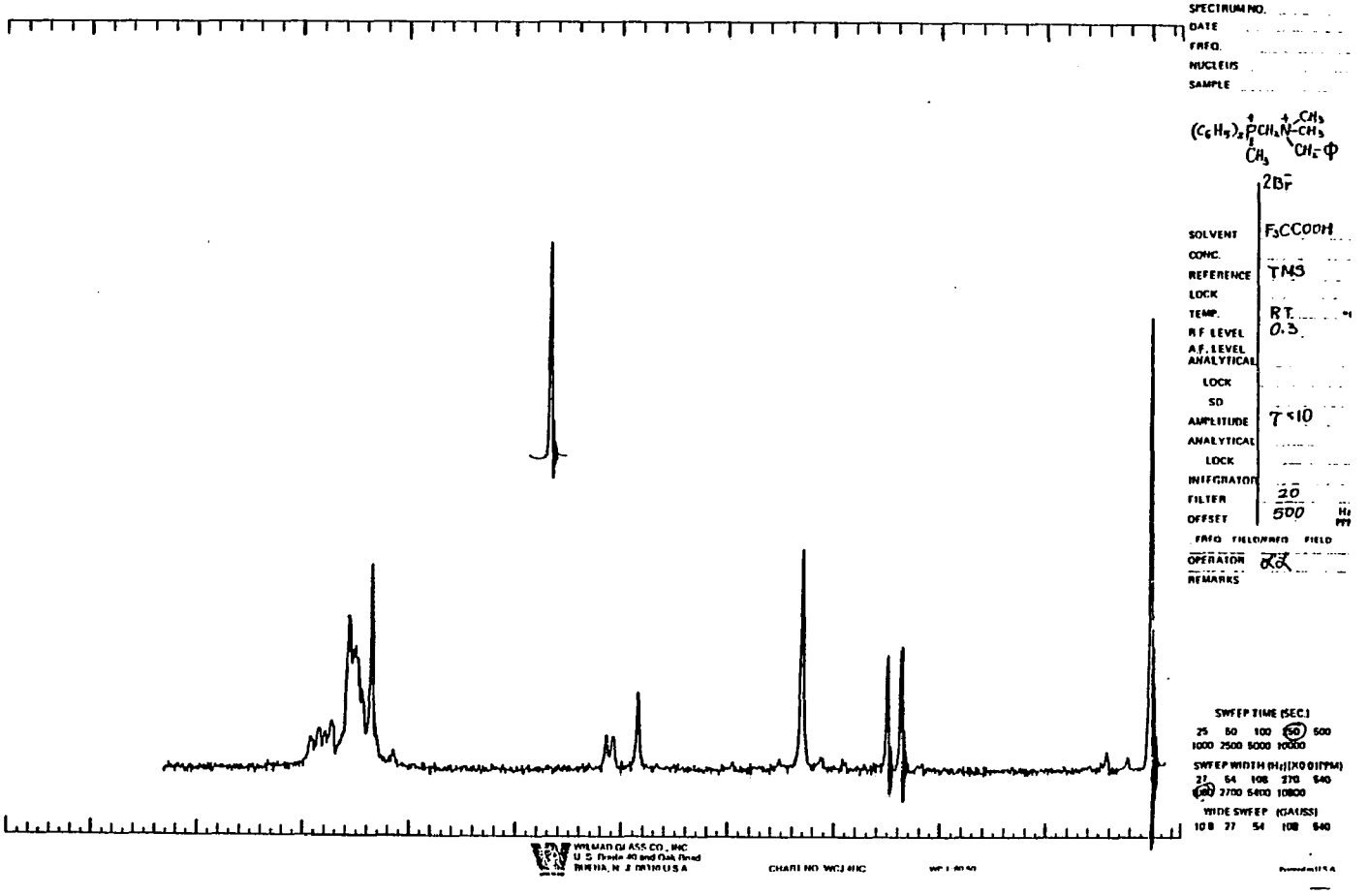


Fig. VII. The H-nmr spectrum of (diphenymethylphosphonium-benzyldimethyl-ammonium)-methylene dibromide (15), $(C_6H_5)_2\overset{+}{P}(CH_3)\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_2CH_2C_6H_5$ $2Br^-$ in F_3CCOOH solution (TMS δ=0.00).

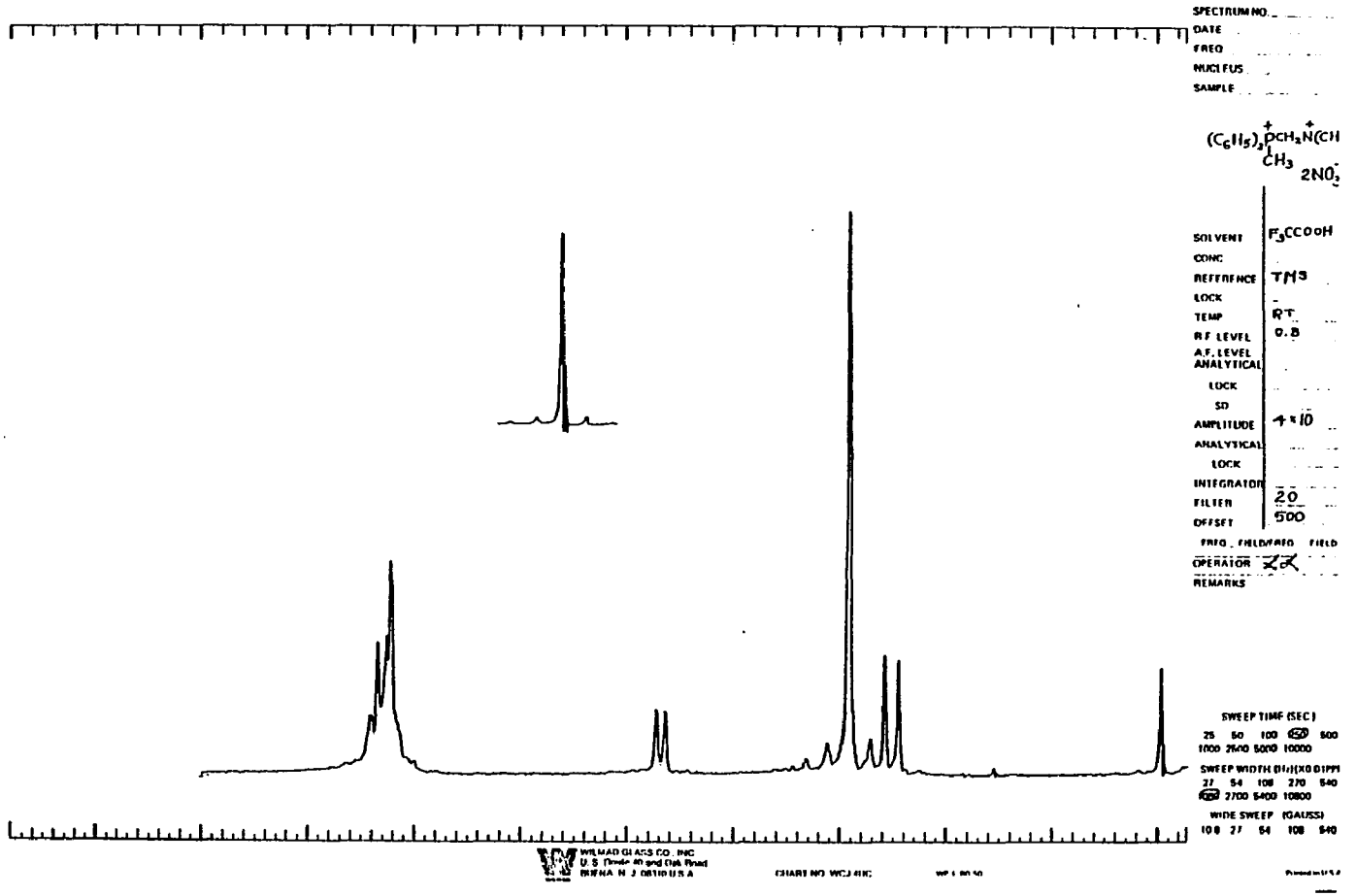


Fig. VIII. The H-nmr spectrum of (diphenylmethylphosphonium-trimethylammonium)-methylene dinitrate (16), $(C_6H_5)_2\overset{+}{P}(CH_3)CH_2\text{-}\overset{+}{N}(CH_3)_3$ 2 NO_3^- in F_3CCOOH solution (TMS δ=0.00).

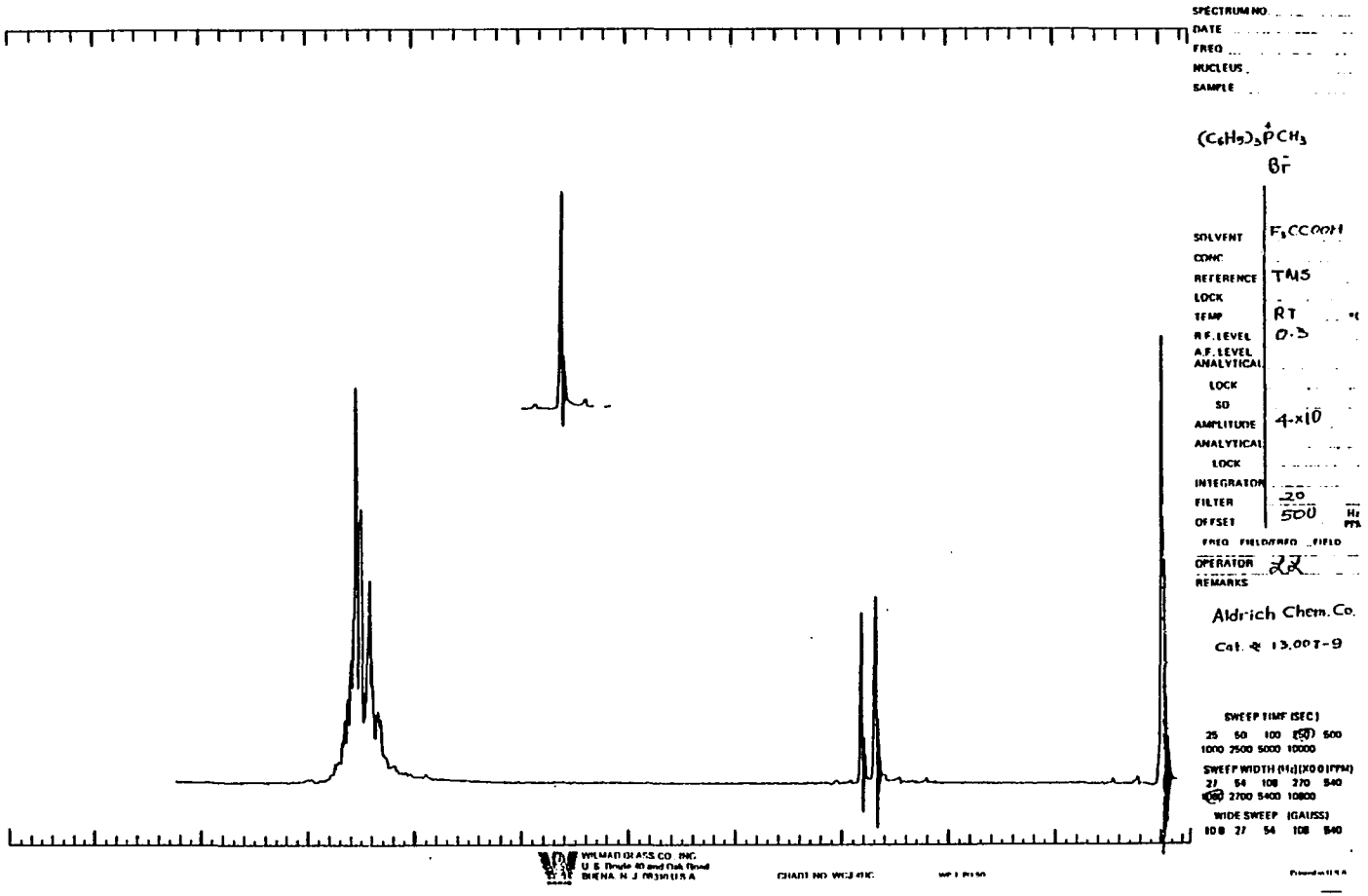


Fig. IX. The H-nmr spectrum of methyltriphenylphosphonium bromide, $(C_6H_5)_3\overset{+}{P}CH_3\ Br^-$, in F_3CCOOH solution (TMS δ=0.00).

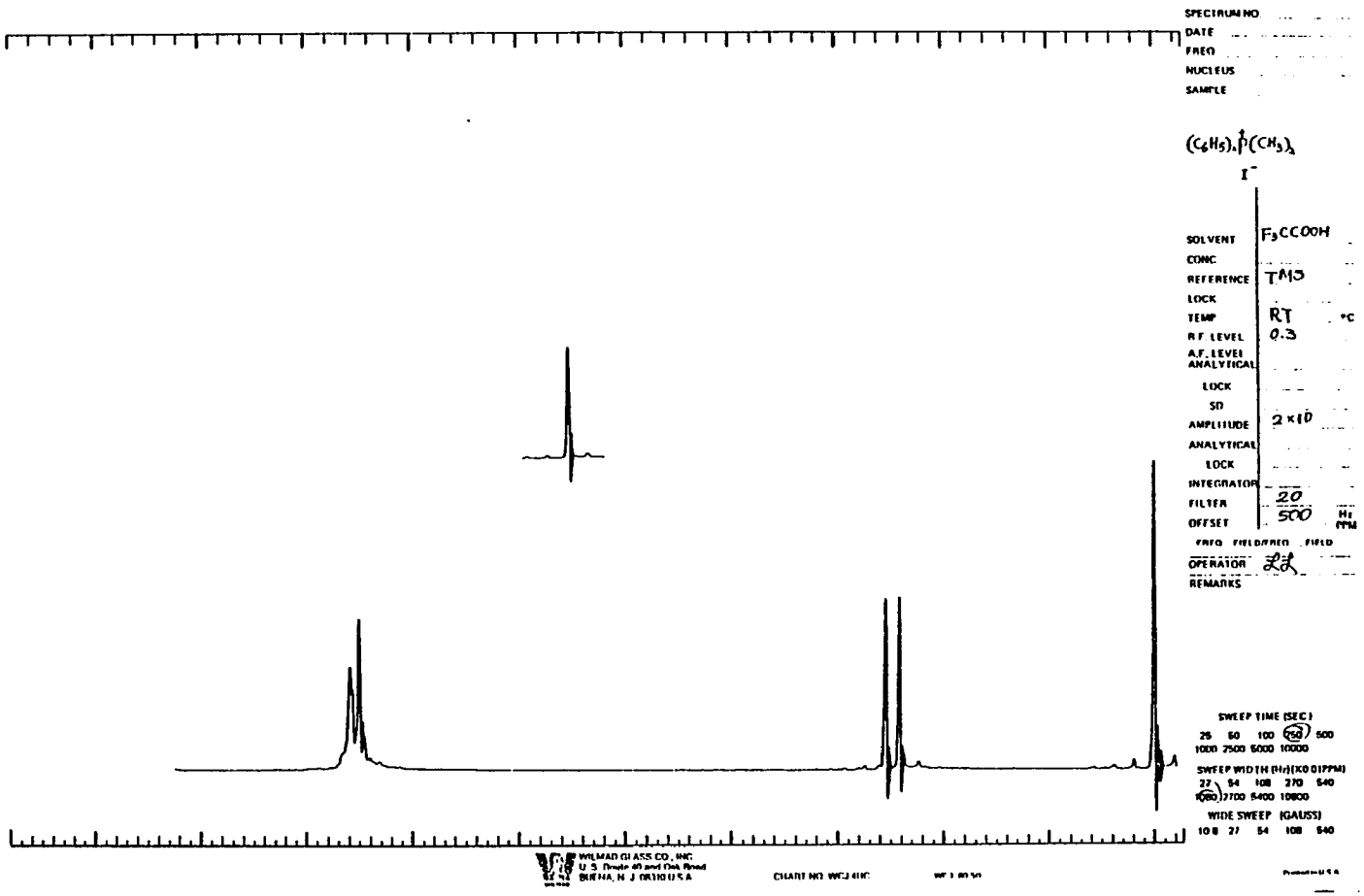


Fig. X. The H-nmr spectrum of dimethyldiphenylphosphonium iodide, $(C_6H_5)_2\overset{+}{P}(CH_3)_2$ I^-, in F_3CCOOH solution (TMS δ=0.00).

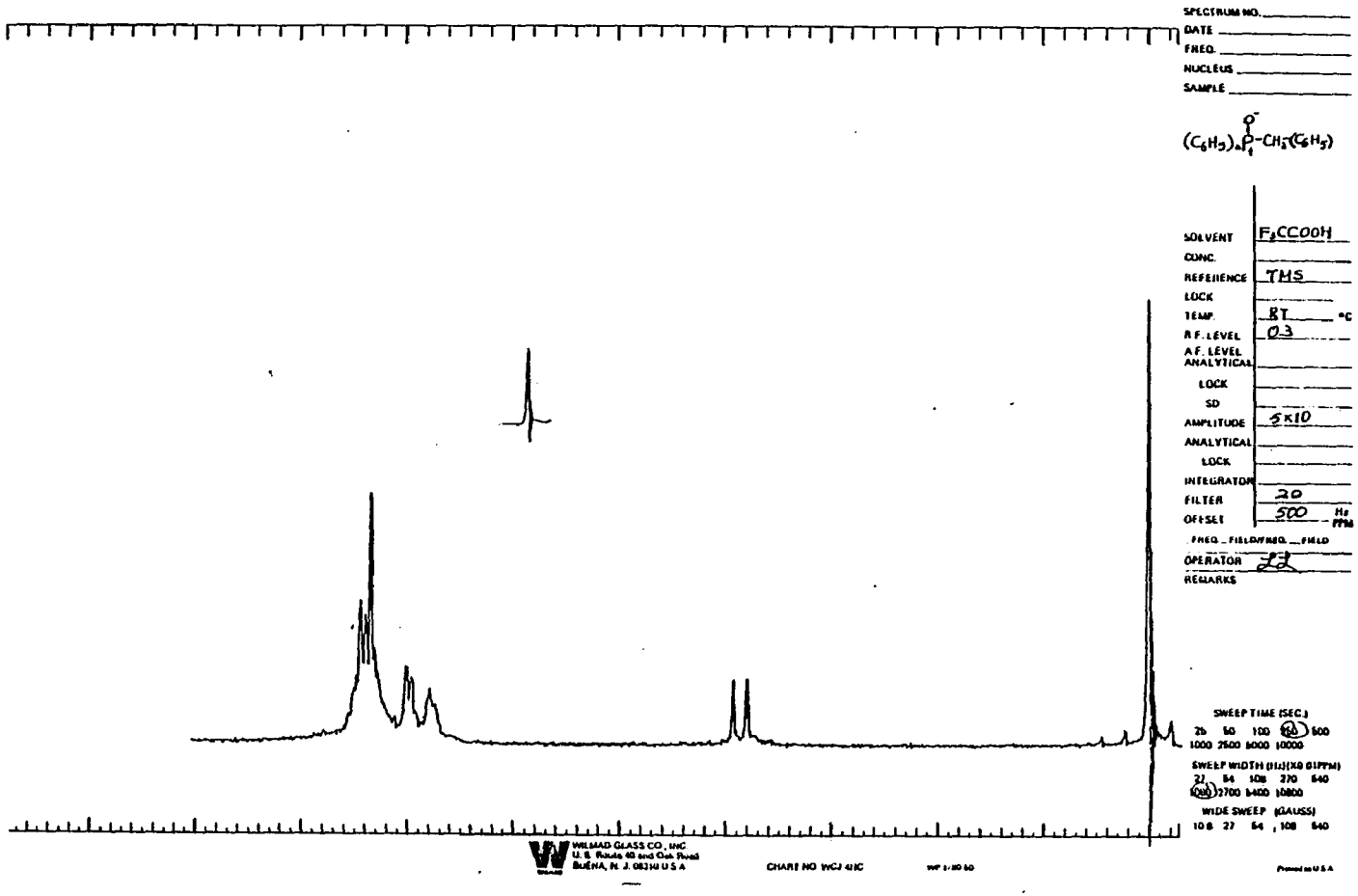


Fig. XI. The H-nmr spectrum of benzyldiphenylphosphine oxide, $(C_6H_5)_2P(O)-CH_2-C_6H_5$, in F_3CCOOH solution (TMS δ=0.00)

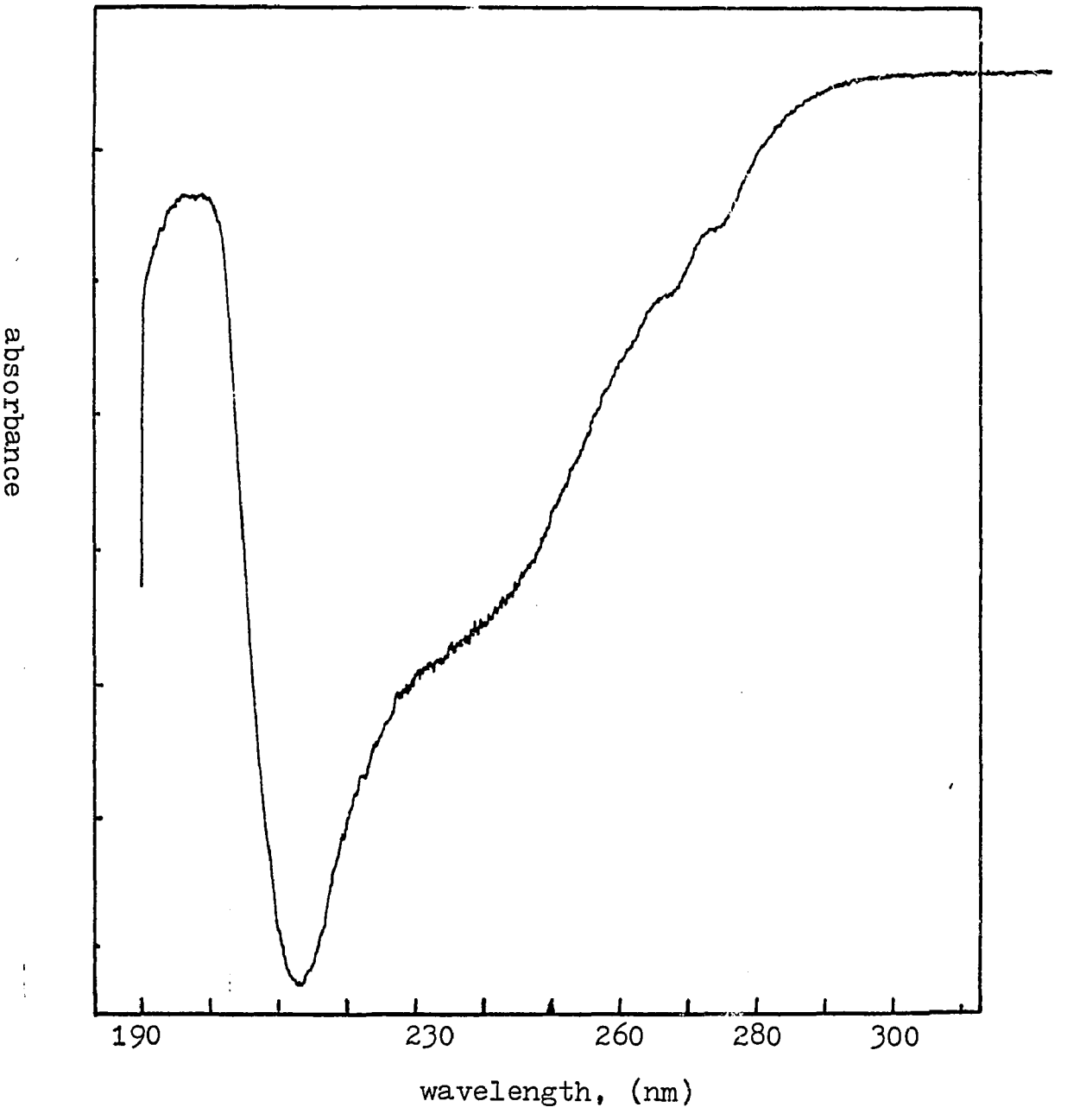


Fig. XII. The Ultraviolet absorption spectrum of diphenylphosphinomethyltrimethylammonium bromide (10), $(C_6H_5)_2P\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_3\ Br^-$, in methyl alcohol solution.

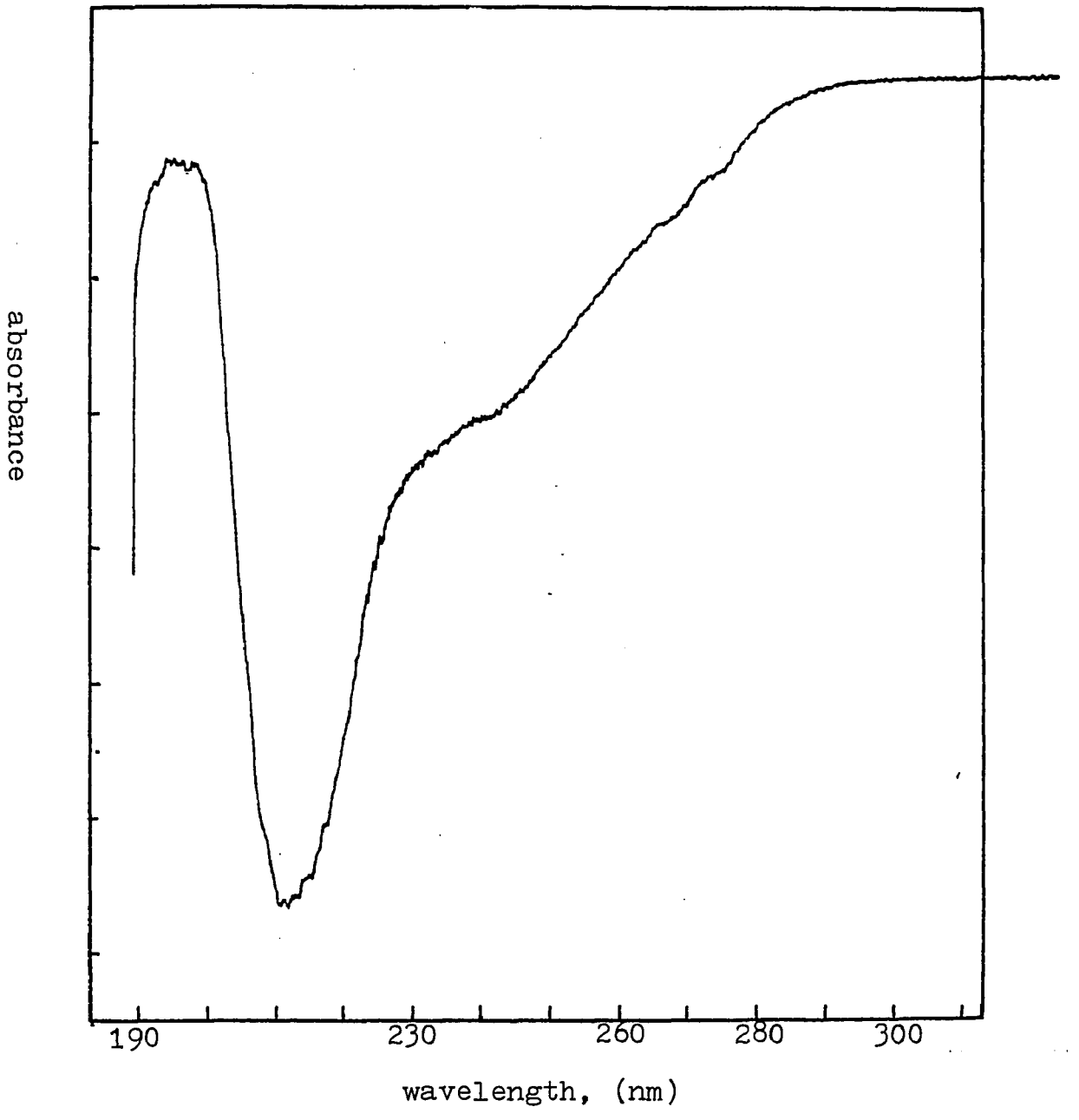


Fig. XIII. The Ultraviolet absorption spectrum of diphenylphosphinomethylbenzyldimethylammonium bromide (13), $(C_6H_5)_2P\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_2CH_2C_6H_5\ Br^-$, in methyl alcohol solution.

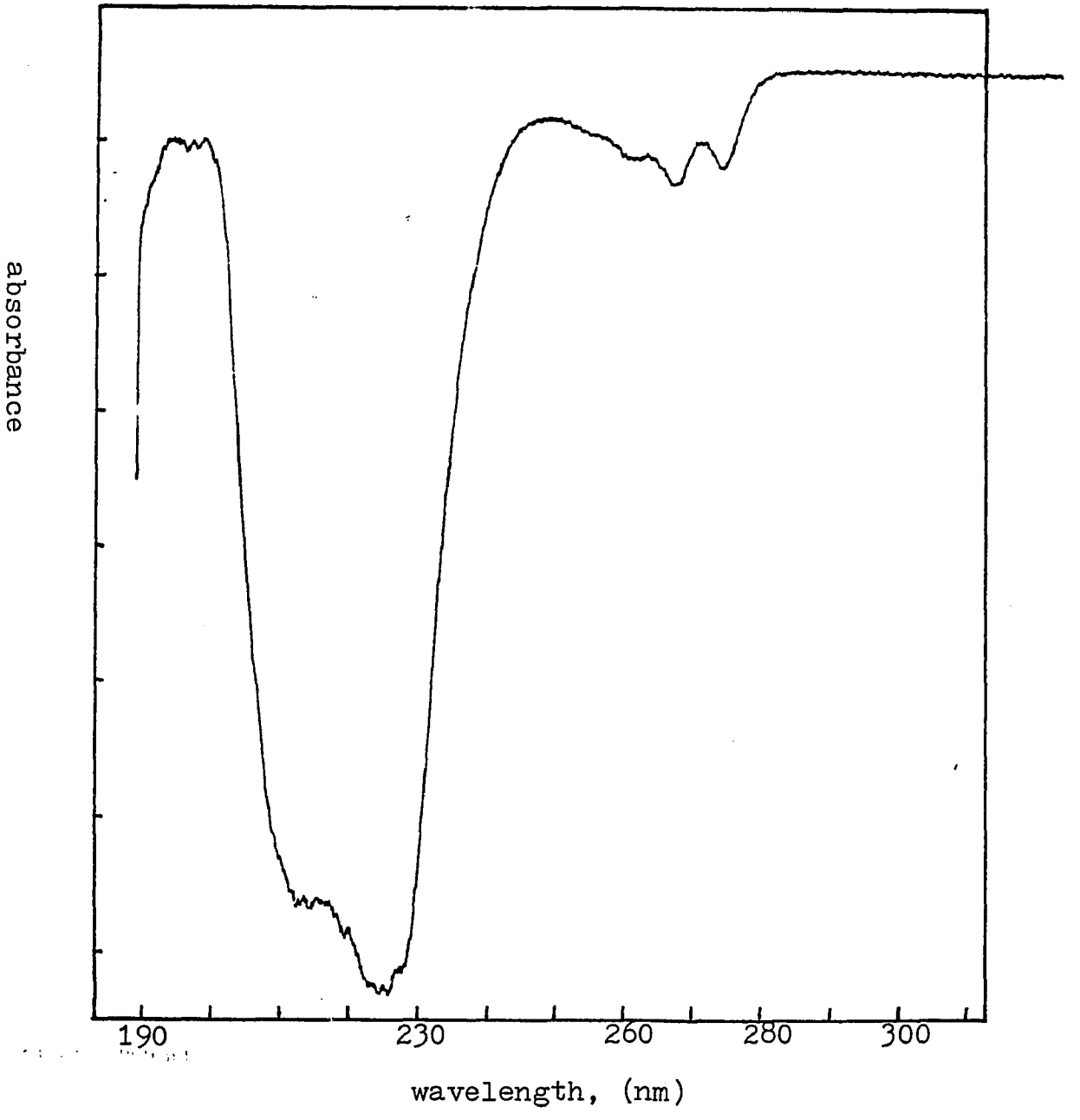


Fig. XV. The Ultraviolet absorption spectrum of methyltriphenylphosphonium bromide, $(C_6H_5)_3\overset{+}{P}CH_3\ Br^-$, in methyl alcohol solution.

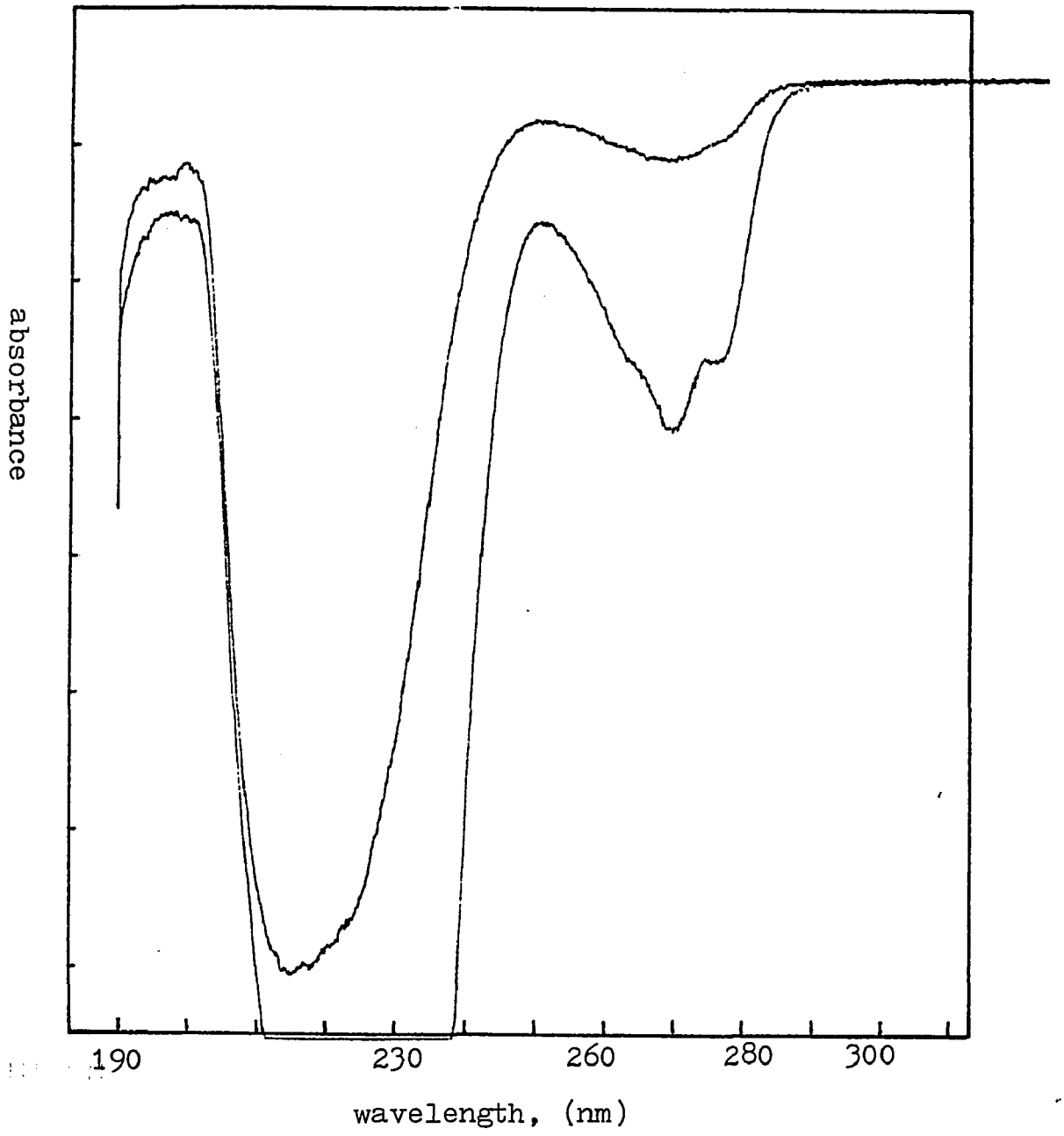


Fig. XIV. The Ultraviolet absorption spectrum of (diphenylmethylphosphonium-trimethylammonium)-methylene dinitrate, $(C_6H_5)_2\overset{+}{P}(CH_3)\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_3$ 2 NO_3^-, in methyl alcohol solution.

Table VII

H-nmr Spectra

compound	solvent	chemical shift, ppm, coupling constants, cps, number of protons
		(TMS δ=0.00)
$(C_2H_5O)_2\overset{O^-}{\underset{+}{P}}CH_2\overset{+}{N}(C_2H_5)_3\ Cl^-$	$CDCl_3$	1.20-1.46 (m, 15H) 3.07 (d, J=12, 2H) 3.28 (q, J=7, 6H) 3.99 (m, 4H)
$(C_2H_5O)\overset{O^-}{\underset{+}{P}}(H_5C_6)CH_2\overset{+}{N}(C_2H_5)_3\ Cl^-$	$CDCl_3$	1.24-1.60 (m, 12H) 2.76-3.20 (m, 2H) 3.32-3.64 (m, 6H) 3.88-4.40 (m, 2H) 7.44-7.92 (m, 5H)
$(C_6H_5)_2\overset{O^-}{\underset{+}{P}}CH_2N(C_2H_5)_2$	$CDCl_3$	0.90 (t, J=7, 6H) 2.70 (q, J=7, 4H) 3.26 (d, J=6, 2H) 7.53 (m, 6H) 7.93 (m, 4H)
$(C_6H_5)_2\overset{O^-}{\underset{+}{P}}CH_2\overset{+}{N}(C_2H_5)_2(CH_3)\ I^-$	$CDCl_3$	1.30 (t, J=7, 6H) 3.30 (s, 3H) 4.76 (d, J=12, 2H) 7.50-8.10 (m, 10H)
$(C_6H_5)_2\overset{O^-}{\underset{+}{P}}CH_2N(CH_3)_2$	$CDCl_3$	2.34 (s, 6H) 4.14 (d, J=6, 2H) 7.20-7.80 (m, 10H)
$(C_6H_5)_2\ddot{P}CH_2\overset{+}{N}(CH_3)_3\ {}^-OSO_2F$	$CDCl_3$	3.50 (s, 9H) 4.61 (s, 2H) 7.20-7.60 (m, 10H)
$(C_6H_5)_2\ddot{P}CH_2\overset{+}{N}(CH_3)_3\ I^-$	$CDCl_3$	3.66 (s, 9H) 4.82 (s, 2H) 7.64-8.08 (m, 10H)
	F_3CCOOH	3.38 (s, 9H) 4.84 (d, J=5, 2H) 7.30-7.82 (m, 10H) 10.64 (s, F_3CCOOH)

Table VII (cont.)

$(C_6H_5)_2\ddot{P}CH_2\overset{+}{N}(CH_3)_3$ Br^-	$CDCl_3$	3.50 (s, 9H) 4.70 (s, 2H) 7.24-7.76 (m, 10H)
	F_3CCOOH	3.33 (s, 9H) 4.72 (d, J=4, 2H) 7.30-7.74 (m, 10H) 10.70 (s, F_3CCOOH)
$(C_6H_5)_2\ddot{P}CH_2\overset{+}{N}(CH_3)_2$ I^- C_2H_5	$CDCl_3$	1.26 (t, J=6, 3H) 3.44 (s, 6H) 3.90 (q, J=6, 4H) 4.56 (s, 2H) 7.24-7.76 (m, 10H)
	F_3CCOOH	1.43 (t, J=7, 3H) 3.28 (s, 6H) 3.70 (q, J=7, 2H) 4.78 (d, J=5, 2H) 7.30-7.84 (m, 10H) 10.64 (s, F_3CCOOH)
$(C_6H_5)_2\ddot{P}CH_2\overset{+}{N}(CH_3)_2$ $^-OSO_2F$ C_2H_5	$CDCl_3$	1.24 (t, J=8, 3H) 3.20 (s, 6H) 3.64 (q, J=8, 2H) 4.28 (s, 2H) 7.36-7.72 (m, 10H)
$(C_6H_5)_2\ddot{P}-CH_2\overset{+}{N}(CH_3)_2$ I^- C_4H_9	F_3CCOOH	0.91 (t, J=5, 3H) 1.28 (m, 2H) 1.72 (m, 2H) 3.32 (s, 6H) 3.52 (m, 2H) 4.74 (d, J=5, 2H) 7.28-7.84 (m, 10H) 10.69 (s, F_3CCOOH)
$(C_6H_5)_2\ddot{P}CH_2\overset{+}{N}(CH_3)_2$ Br^- $CH_2C_6H_5$	F_3CCOOH	3.24 (s, 6H) 4.74-4.91 (m, 4H) 7.26-7.84 (m, 15H) 10.70 (s, F_3CCOOH)

Table VII (cont.)

$(C_6H_5)_2\overset{+}{P}(CH_3)CH_2\overset{+}{N}(CH_3)_3\ 2I^-$	F_3CCOOH	3.19 (d, J=15, 3H) 3.52 (s, 9H) 5.71 (d, J=9, 2H) 7.40-8.12 (m, 10H) 10.43 (s, F_3CCOOH)
$(C_6H_5)_2\overset{+}{P}(H_3C)CH_2\overset{+}{N}(CH_3)_2CH_2C_6H_5\ 2Br^-$	F_3CCOOH	2.42 (d, J=15, 3H) 3.90 (s, 6H) 4.84 (s, 2H) 5.10 (d, J=6, 2H) 7.24-7.99 (m, 15H) 10.67 (s, F_3CCOOH)
$(C_6H_5)_2\overset{+}{P}(CH_3)CH_2\overset{+}{N}(CH_3)_3\ 2\ NO_3^-$	D_2O	3.14 (d, J=15, 3H) 3.40 (s, 9H) 7.74-8.20 (m, 10H) 4.70 (s, DO-H)
	F_3CCOOH	2.52 (d, J=15, 3H) 2.94 (s, 9H) 4.70 (d, J=8, 2H) 7.10-7.50 (m, 10H) 10.63 (s, F_3CCOOH)
$(C_6H_5)_2\overset{+}{P}(CH_3)CD_2\overset{+}{N}(CH_3)_3\ 2\ I^-$	F_3CCOOH	2.72 (d, J=14, 3H) 3.12 (s, 9H) 7.00-7.56 (m, 10H) 10.63 (s, F_3CCOOH)
$(C_6H_5)_2\overset{O^-}{\underset{+}{P}}CH_2C_6H_5$	F_3CCOOH	3.86 (d, J=12, 2H) 6.64-7.58 (m, 15H) 10.86 (s, F_3CCOOH)
$(C_6H_5)_2\overset{O^-}{\underset{+}{P}}CH_2\overset{+}{N}(CH_3)_3\ I^-$	$CDCl_3$	3.57 (s, 9H) 5.04 (d, J=7, 2H) 7.50-7.70 (m, 4H) 8.00-8.24 (m, 6H)
$(C_6H_5)_2\overset{O^-}{\underset{+}{P}}CH_3$	F_3CCOOH	2.80 (d, J=13, 3H) 7.10-7.61 (m, 10H) 10.70 (s, F_3CCOOH)

Table VII (cont.)

$(C_6H_5)_3\overset{+}{P}CH_3$ Br^-	F_3CCOOH	2.73 (d, J=15, 3H) 7.30-7.54 (m, 15H) 10.60 (s, F_3CCOOH)
$(C_6H_5)_2\overset{+}{P}(CH_3)_2$ I^-	D_2O	2.66 (d, J=14, 6H) 7.50-8.00 (m, 10H) 3.34 (s, DOH)
	F_3CCOOH	2.48 (d, J=15, 6H) 7.40-7.50 (m, 10H) 10.54 (s, F_3CCOOH)
$(CH_3)_4N^+ I^-$	F_3CCOOH	3.13 (s) 10.24 (s, F_3CCOOH)
$(CH_3)_4N^+ Br^-$	D_2O	3.21 (s)[64] 4.54 (DOH)

64. Sadtler Standard Spectra, NMR # 6820

Conclusion

(i) Monoalkylation of N,N-dimethylaminomethyldiphenylphosphine (7) takes place entirely on nitrogen, with several different alkylating agents

(ii) The type compound (9), diphenylphosphinomethyltrimethylammonium iodide, is stable to either air oxidation or to prolonged refluxing with either concentrated hydrochloric acid or 10% sodium hydroxide solution under nitrogen. Slow deuterium exchange occurs on refluxing in $D_2O/NaOD$.

(iii) Base-catalyzed air oxidation of this compound leads to diphenylphosphinooxymethyltrimethylammonium iodide, $(C_6H_5)_2P(O)CH_2\overset{+}{N}(CH_3)_3\ I^-$.

(iv) Further alkylation gives a series of bis-(phosphonium-ammonium) salts. This is only possible with more reactive alkylating agents.

(v) These bis-salts exchange with neutral deuterium oxide extremely rapidly, without added base, at the methylene groups between P^+ and N^+. They are rapidly cleaved by dilute aqueous base.

(vi) A series of other quaternary ammonium salts, substituted at an α-carbon by various other phosphorus-containing groups, has been prepared.

EXPERIMENTAL

General

All chemicals and solvents used were of reagent-grade quality. Solvents used were freshly distilled before being used. Tetrahydrofuran and dried ether were dried over sodium metal and distilled over sodium before use. N,N-dimethylformaldehyde was dried over KOH-pellets and distilled over CaH_2 under nitrogen-atmosphere. Dimethylsulfoxide was dried over KOH-pellets and flask-to-flask tilled over CaH_2 under nitrogen-atmosphere. All air- and moisture-sensitive compounds were handled by glove-bag and/or vacuum take-off techniques. Proton magnetic resonance spectra were determined on a Jeol MH 100 spectrophotometer. Ultraviolet spectra were determined on a Perkin-Elmer UV 402 spectrophotometer. Infrared spectra were determined on a Perkin-Elmer 247 Grating Infrared spectrophotometer. All melting points were determined on a Thomas Hoover Capillary Melting Point Apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc..

N,N,N',N'-Tetraethyldiethylamino-methane (1).

21 ml (0.20 mole) of diethylamine and 8.23 g (0.10 mole) of 37% formalin solution were refluxed for one hour. The N,N,N',N'-tetraethyldiethylamine was distilled and collected as a colorless liquid at 164-5°C. The yield was 10.8 g (68%).

N,N-Diethylmethylene-iminium Chloride (2).

To an ice-cold solution of 7.9 g (0.05 mole) of compound (1) in 100 ml of absolute ether was added drop by drop of 3.92 g (0.05 mole) of dried acetyl chloride in 50 ml of dry ether under nitrogen-atmosphere for a period of 30 minutes. The reaction mixture was filtered in a nitrogen-filled glove-bag and 6.0 g (94%) of a very hygroscopic white compound (2) was collected.

Dietoxy Phosphonomethyltriethylammonium Chloride (3).

2.00 g (0.012 mole) of triethylphosphite was added to 1.22 g (0.01 mole) of compound (2) suspended in 100 ml of dry ether under nitrogen-atmosphere. The reaction was vigorous. The product was recrystallized from absolute ether-ethanol solution. 2.1 g (76%) of a very hygroscopic white compound (3) was collected. mp=120-2°C [48a]. The H-nmr spectrum of chloroform-d solution showed: a multiplet at δ=1.20-1.46 (15H); a doublet centered at δ=3.07 (2H, J=12 Hz);

a quartet centered at δ=3.28 (6H, J= 7Hz) and a multiplet centered at δ=3.99 (4H). A satisfactory analysis for this compound could not be obtained. Traces ofmoisture caused rapid formation of $(C_2H_5)_3\overset{+}{N}CH_2\bar{P}O_2(OH)\cdot xH_2O$.

Ethoxy Phenylphosphinomethyltriethylammonium Chloride (4).

2.4 g (0.012 mole) of diethyl phenylphosphite was added to 1.22 g (0.010 mole) of compound (2) suspended in 100 ml of dry ether under nitrogen-atmosphere. The product was recrystallized from absloute ether-ethanol solution. 2.0 g (65%) of a hygroscopic compound (4) was collected. mp=96-7°C. The H-nmr spectrum of chloroform-d solution showed a multiplet at δ=1.24-1.60 (12H); a multiplet at δ=2.76-3.20 (2H); a multiplet at δ=3.32-3.64 (6H); a multiplet at δ=3.88-4.40 (2H) and a multiplet at δ=7.44-7.92 (5H). A satisfactory analysis for this compound could not be ovtained. Trace of moisture caused rapid formation of $(C_2H_5)_3\overset{+}{N}CH_2\overset{+}{P}(\bar{O})_2(C_6H_5)\cdot xH_2O$.

N,N-Diethylaminomethyldiphenylphosphine Oxide (5) (or N,N-Dimethylaminomethyldiphenylphosphine Oxide.

2.30 g (0.010 mole) of ethoxy diphenylphosphine was added into 1.22 g (0.010 mole) of compound (2) (or N,N-dimethylmethylene-iminium chloride) suspended in 100 ml of dry ether under nitrogen-atmosphere. The product, compound (5), was recrystallized from absolute-ether-ethanol solution. The yield was 1.5 g (50%). mp=89-90°C. The H-nmr

spectrum of chloroform-d solution showed a triplet at δ=090 (6H, J=7Hz); a quartet at δ=2.70 (4H, J=7Hz); a doublet at δ=3.26 (2H, J=6Hz).

Anal. Caled. $C_{17}H_{22}NOP$: C, 71.06; H, 7.72; N, 4.87; O, 5.57; P, 10.78

Found: C, 70.94; H, 7.68;

Diphenylphosphinylmethyldiethylmethylammonium Iodide (6).

To 0.30 g of compound (2) in 50 ml of dry ether was added drop by drop 0.15 g of methyl iodide in 10 ml of dry ether solution. A white solid was formed, yielding 0.30 g of compound (6), mp=186-7°C. The H-nmr spectrum of chloroform-d solution showed a triplet centered at δ=1.30 (6H, J=7Hz); a singlet at δ=3.30 (3H); a multiplet centered at δ=3.84 (4H); a doublet centered at δ=4.76 (2H, J=12 Hz) and a multiplet centered at δ=7.80 (10H).

Anal. Caled. $C_{18}H_{25}NOPI$: C, 50.36; H, 5.87; N, 3.26; P, 7.22; O, 3.73; I, 29.56.

Found: C, 50.32; H, 5.93;

Diphenylphosphinomethyltrimethylammonium Fluorosulfonate (8).

2.10 g (8.56 mmole) of dimethylaminomethyldiphenylphosphine[52](7) in 50 ml of dry ether and excess of methyl fluorosulfonate (magic methyl) in 20 ml of dry ether was added under nitrogen-atmosphere, at varied temperature condition (-95°C, liquid N_2-CH_2Cl_2, to 36°C). The white precipitate was collected. The crude product was recrystallized from

ethanol-ether mixture solution, and was identified as compound (8), mp=203-4°C (dec.). The H-nmr spectrum of chloroform-d solution showed a singlet at δ=3.50 (9H); a singlet at δ=4.61 (2H) and a multiplet at δ=7.20-7.60 (10H). The ir-spectrum (in nujol) showed: 1069 cm^{-1}, 960 cm^{-1}, 910 cm^{-1}, 835 cm^{-1}, 755 cm^{-1}, 745 cm^{-1}, 722 cm^{-1} and 695 cm^{-1}.

Anal. Caled.: $C_{16}H_{21}PNO_3SF$: C, 53.77; H, 5.92; P, 8.67; N, 3.92; O, 13.43; S, 8.97; F, 5.32.

Found: C, 50.06; H, 5.62.

Diphenylphosphinomethyltrimethylammonium Iodide (9).

To a solution of 1.17 g (4.8 mmole) of compound (7) in 50 ml of dry ether, an excess of methyl iodide was added drop by drop under a nitrogen atmosphere for a period of 30 min. The reaction mixture was then stirred for 4 hours. A white precipitate was collected and recrystallized from ethanol-ether solution in quantitative yield, mp 206-7°C. This reaction has been repeated in dried dioxane, tetrahydrofuran, acetonitrile and methanol under several different temperatures conditions, but the results came out the same. The H-nmr spectrum of chloroform-d solution showed a singlet at δ=3.66 (9H); a singlet at δ=4.82 (2H) and a multiplet at δ=7.64-8.08 (10H). The ir spectrum (KBr-pellet) showed bands at: 3000 cm^{-1}, 1470 cm^{-1}(s), 1425 cm^{-1}

(s), 1400 cm^{-1}(s), 1300 cm^{-1}(s), 1275 cm^{-1}(m), 1220 cm^{-1} (w), 1192 cm^{-1}(m), 1155 cm^{-1}(m), 1106 cm^{-1}(m), 1094 cm^{-1} (s,s), 1068 cm^{-1}(s,s), 1009 cm^{-1}(w), 995 cm^{-1}(w), 955 cm^{-1} (s), 940 cm^{-1}(s), 904 cm^{-1}(s), 882 cm^{-1}(m), 832 cm^{-1}(s), 740 cm^{-1} and 720 cm^{-1} (s,s).

Anal. Caled.: $C_{16}H_{21}PNI$: C, 49.88; H, 5.50; P, 8.04; N, 9.64; I, 32.94

Found: C, 49.03; H, 5.67.

Diphenylphosphinomethyltrimethylammonium Bromide (10).

Methyl bromide gas was bubbled though a solution of 0.73 g (3.00 mmole) compound (7) in 50 ml of dry ether under nitrogen-atmosphere for 24 hours, (methanol and acetonitrile were also employed as solvents). The reaction mixture was filtered and a white solid was collected in quantitative yield. The crude product was recrystallized from isopropyl alcohol solution, mp=203-4°C. No bis-(phosphonium-ammonium) salts were produced, even when the reaction was run for 4 days in room temperature. The H-nmr spectrum of chloroform-d solution showed a singlet at δ=3.50 (9H); a singlet at δ=4.70 (2H) and a multiplet at δ=7.24-7.76 (10H). The ir spectrum was similar to of compound (9).

Anal. Caled.: $C_{16}H_{21}NPBr$: C, 56.81; H, 6.26; N, 4.14; P, 9.16; Br, 23.63

Found: C, 56.74; H, 6.33.

Diphenylphosphinomethyl dimethylethylammonium Iodide (11).

1.0 g (2.60 mmole) of compound (7) in 50 ml of methyl alcohol was refluxed with an excess of ethyl iodide (ethyl fluorosulfonate was also used as an ethylating agent) under nitrogen-atmosphere over night. Technical ether was added to the cold reaction mixture, and white precipitate was formed. The solid was collected and recrystallized from isopropyl alcohol solution, mp=126-7°C. The H-nmr spectrum in chloroform-d showed a triplet at δ=1.26 (3H, J=6Hz); a singlet at δ=3.44 (6H); a quartet centered at δ=3.90 (4H, J=6Hz); a singlet at δ=4.56 (2H) and a multiplet at δ=7.24 -7.76 (10H).

Anal. Caled.: $C_{17}H_{23}NPI$: C, 51.14; H, 5.80; N, 3.51; P, 7.76; I, 31.79.

Found: C, 51.05; H, 5.90.

Diphenylphosphinomethylbutyldimethylammonium Iodide (12).

1.0 g (2.6 mmole) of compound (7) and an excess of butyl iodide was refluxed in ethanol under a nitrogen-atmosphere for three days. Technical ether was added to the cold reaction mixture to precipitate out the crude product of compound (12). The compound (12) was recrystallized from isopropyl alcohol solution, mp= 144-5°C. The H-nmr spectrum in trifluoroacetic acid solution (TMS δ=0.0) showed a triplet centered at δ=0.91 (3H, J=5 Hz); a multiplet at δ=1.28 (2H); a multiplet at δ=1.72 (2H); a singlet at δ=3.32 (6H); a multiplet centered at δ=3.52 (2H); a

doublet centered at δ=4.74 (2H, J=5Hz); a multiplet centered at δ=7.28-7.84 (10H) and a singlet at δ=10.69 (F_3CCOOH).

Anal. Caled.: $C_{19}H_{27}PNI$: C, 53.40; H, 6.37; P, 7.25; N, 3.28; I, 29.70.

Found: C, 53.35; H, 6.15.

Diphenylphosphinomethylbenzyldimethylammonium Bromide (13).*

To a stirred solution of 1.0 g (2.6 mmole) of compound (7) in 50 ml of dry 30% benzene/hexane contained in a 100 ml three-necked round-bottom flask and maintained under nitrogen at room temperature was added a solution of an excess of benzyl bromide in 10 ml of dry benzene over a one hour period. The reaction mixture was stirred overnight. Colorless crystals which had formed were sepsrsted from the solution and washed with benzene. The crystals were recrystallized from methanol-ether (or from distilled water), mp=188-9°C. The H-nmr spectrum of a trifluoroacetic acid sol tion showed a singlet at δ=3.24 (6H); a multiplet centered at δ=4.82 (4H); a multiplet at δ=7.26-7.84 (15H) and a singlet at δ=10.70 (F_3CCOOH). The ir spectrum (KBr-pel- showed bands at 3000 cm^{-1}(s), 1600 cm^{-1}(s), 1420-1480 cm^{-1} (multi-bands, s,s), 1350 cm^{-1}(w), 1320 cm^{-1}(w), 1300 cm^{-1} (m), 1280 cm^{-1}(w), 1250 cm^{-1}(w), 1220 cm^{-1}(m), 1190 cm^{-1}(m), 1160 cm^{-1}(w), 1120 cm^{-1}(w), 1100-1075 cm^{-1}(multi, m), 1030 cm^{-1}(m), 1000 cm^{-1}(m), 995 cm^{-1}(m), 950 cm^{-1}(m), 850 cm^{-1}

* W. E. McEwen's procedure[54].

(b,s), 792 cm^{-1}(m), 750 cm^{-1}(s).

Anal. Caled.: $C_{22}H_{25}PNBr$: C, 63.77; H, 6.08; P, 7.48; N, 3.38; Br, 19.29.

Found: C, 63.50; H, 6.02.

(Diphenylmethylphosphonium-trimethylammonium)-methylene Diiodide (14).

2.00 g (5.20 mmole) of compound (9) was refluxed with a excess of methyl iodide solution in ethanol for 72 hours. Colorless crystals were formed in boiled ethanol. 1.65 g (61%) of compound (14) was collected and recrystallized from distilled water, mp=180-1°C. The H-nmr spectrum of trifluoroacetic acid solution showed a doublet centered at δ=3.19 (3H, J=15Hz); a singlet at δ=3.52 (9H); a doublet centered at δ=5.71 (2H, J=9Hz); a multiplet centered at δ=7.76 (10H) and a singlet at δ=10.40 (F_3CCOOH). The H-nmr spectrum of a hot deuterium oxide solution showed no methylene proton signal. The ir spectrum (KBr-pellet) showed: 3030 cm^{-1}(s), 2980-2800 cm^{-1}(s), 1600 cm^{-1}(m), 1495 cm^{-1}(s,s), 1450 cm^{-1}(s,s), 1430 cm^{-1}(s), 1415cm^{-1} (s), 1355 cm^{-1}(s), 1335 cm^{-1}(s), 1172 cm^{-1}(m), 1120 cm^{-1} (b, s), 1005 cm^{-1}(m), 985 cm^{-1}(s), 940 cm^{-1}(b,s), 915 cm^{-1} (b,s), 860 cm^{-1}(b,s), 800 cm^{-1}(s), 740 cm^{-1}(b,s), 715 cm^{-1} and 685 cm^{-1}(b,s) .

Anal. Caled.: $C_{17}H_{24}PNI_2$: C, 38.73; H, 4.59; P, 5.87; N, 2.66; I, 48.15.

Found: C, 38.85; H, 4.64.

(Diphenylmethylphosphonium-benzyldimethylammonium)-methylene Dibromide (15).

2.00 g (4.83 mmole) of compound (13) and excess of methyl iodide were refluxed in ethanol solution for 72 hours. Technical ether was added into the cold reaction mixture, white precipitates were formed. The crude product was recrystallized from ethanol-ether, mp=177-8°C. The H-nmr spectrum of trifluoroacetic acid solution showed a doublet centered at δ=2.42 (3H, J=15Hz); a singlet at δ=4.84 (3H); a doublet centered at δ=5.10 (2H, J=6Hz); a multiplet at δ=7.24-7.99 (15H) and a singlet at δ=10.67 (F_3CCOOH).

Anal. Caled. $C_{23}H_{28}PNBr_2$: C, 54.24; H, 5.54; P, 6.08; N, 2.75; Br, 31.38.

Found: C, 55.05; H, 5.38;

(Diphenylmethylphosphonium-trimethylammonium)-methylene Dinitrate (16).

2.00 g (3.80 mmole) of compound (14) was stirred with 1.28 g (7.53 mmole) of silver nitrate solution for one hour. The reaction mixture was filtered through a glass-filter-pad. The filtrate was boiled about 1 ml, white solids were formed in quantitative yield. The crude product was recrystallized from isopropyl alcohol, mp=194-5°C. The H-nmr spectrum of trifluoroacetic acid showed a doublet centered at δ=2.52 (3H, J=15Hz); a singlet at δ=2.94 (9H);

a doublet centered at δ=4.70 (2H, J=8Hz) and a multiplet at δ=7.10-7.50 (10H), and a singlet at δ=10.63 (F_3CCOOH).

Anal. Caled. $C_{17}H_{24}PO_6N_3$: C, 51.38; H, 6.09; N, 7.80; P. 10.56; O, 24.16.

Found: C, 51.26; H, 6.23;

Methylation of N,N-dimethylaminophosphine Oxide.

2.0 g (7.6 mmole) of N,N-dimethylaminophosphine oxide (an air oxidation product of N,N-dimethylaminophosphine) and a excess of methyl iodide in 50 ml of methanol were stirred for four hours. Technical ether was added, white crystals were formed. The crude product was recrystallized from isopropyl alcohol, mp=200-1°C. The H-nmr of chloroform-d solution showed a singlet at δ=3.57 (9H); a doublet centered at δ=5.40 (2H, J=7Hz) and two groups of multiplets at δ=7.50-7.70 and δ=8.00-8.24 (10H). The ir spectrum (KBr-pellet) showed: 3080 cm^{-1}(m), 3030 cm^{-1}, 2870 cm^{-1} (s), 2790-2830 cm^{-1}(b,s), 1600 cm^{-1}(m), 1495 cm^{-1}(s), 1485 cm^{-1}(s), 1446 cm^{-1}(s), 1430 cm^{-1}(m), 1355 cm^{-1}(w), 1340 cm^{-1} (w), 1330 cm^{-1}(w), 1290 cm^{-1}(w), 1195 cm^{-1}(s), 1170 cm^{-1}(m), 1105 cm^{-1}(s), 1130 cm^{-1}(s), 1080 cm^{-1}(m), 1035 cm^{-1}(w), 1005 cm^{-1}(m), 965 cm^{-1}(m), 955 cm^{-1}(m), 940 cm^{-1}(m), 850 cm^{-1}(s), 785 cm^{-1}(s), 760 cm^{-1}(s), 735 cm^{-1}(s), 715 cm^{-1} (s), 690 cm^{-1}(s).

Anal. Caled. $C_{16}H_{21}PNO$: C, 47.89; H, 5.28: N,3.49; P, 7.72 O, 3.99; I, 31.63.

Found: C, 47.80; H, 5.34;

Hydrogen-deuterium Exchange of Compound (14).

1.00 g (1.90 mmole) of compound (14) was boiled with the minimum amount of neutral deuterium oxide in a small test tube, for two minutes. White needle crystals were formed upon cooling, 100% yield. mp=173-4°C. The H-nmr spectrum of a trifluoroacetic acid solution showed a doublet centered at δ=2.72 (3H, J=14Hz); a singlet at δ=3.12 (9H); and a multiplet at δ=7.00-7.56 (10H). The ir spectrum (KBr-pellet) showed: 3020 cm^{-1}(m), 2940 cm^{-1}(s), 2880 cm^{-1}(m), 2170 cm^{-1}(sharp, $P^+-CD_2-N^+$), 1590 cm^{-1}(m), 1490 cm^{-1}(m), 1445 cm^{-1}(s), 1440 cm^{-1}(s), 1418 cm^{-1}(m), 1408 cm^{-1}(m), 1350 cm^{-1}(m), 1358 cm^{-1}(w), 1246 cm^{-1}(w), 1165 cm^{-1}(w), 1110 cm^{-1}(b,s, P^+-CH_3), 996 cm^{-1}(m), 964 cm^{-1}(m), 925 cm^{-1}(s), 905 cm^{-1}(s), 886 cm^{-1}(m), 868 cm^{-1}(m), 800 cm^{-1}(m), 750 cm^{-1}(s), 730 cm^{-1}(s), 700 cm^{-1}(m) and 675 cm^{-1}(s).

Anal. Caled.: $C_{17}H_{22}D_2PNI_2$: C, 38.58; H, 4.19; D, 0.76; P, 5.85; N, 2.65; I, 47.96.

Found: C, 38.73; H, 4.37.

Hydrogen-deuterium Exchange of Compound (9).

1.00 g (2.60 mmole) of compound (9) was boiled with NaOD in deuterium oxide solution under N_2-atmosphere overnight. A white crystalline compound was formed, mp=205-7°C. The H-nmr spectrum of a trifluoroacetic acid solution showed no methylene protons. The ir spectrum showed a absortion band at 2200 cm^{-1} (characteristic C-D stretch).

Anal. Caled. $C_{16}H_{19}D_2NPI$: C, 49.62; H, 4.95; D, 1.04; N, 3.62; P, 8.00; I, 32.77.

Found: C, 49.72; H, 5.02

Reaction of Compound (9) with Sodium Hydroxide (and Other Bases).

1.0 g (2.60 mmole) of compound (9) was refluxed in a 50 ml deoxygenated sodium hydroxide solution (triethylamine in dry ether, sodium methoxide in methanol) under nitrogen-atmosphere overnight. Crystalline white needles were formed upon cooling, in quantitative yield. The crystalline material was found to be compound (9) by identity of H-nmr, ir spectra and mixed melting determination. The oxide of compound (9) was collected when the reaction was carried out in the air. The H-nmr and ir spectra were the same as for compound (17).

Reaction of Compound (9)with Phenyllithium in ether.

5 mmole of phenyllithium[65](prepared from 0.80 g of bromobenzene reacted with excess of Li-wire in 50 ml of dry ether) was added drop by drop into 1.93 g (5 mmole) of compound (9) which was suspended in 50 ml of absolute ether under nitrogen-atmosphere for a 30 min period. The reaction mixture were then stirred for one more hour after the addition of phenyllithium was completed. It was quenched with D_2O. Crystalline white needles were formed and isolated from the ether layer when it was

exposed to air, in 20% yield. This crystalline compound was recrystallized from ethanol-ether, and was identified as benzyldiphenylphosphine oxide, mp=190-1°C (lit. mp= 192-3°C)[66]. The H-nmr spectrum of a trifluoroacetic acid solution showed a doublet centered at δ=3.86 (2H, J=14Hz) and a multiplet at δ=6.64-7.85 (15H) (Fig. XI). The mass spectrum showed a peak at 292 (40%), a peak at 201 (100%), $(C_6H_5)_2P^+=O$, and another significant peak at 291 (36%). A white crystalline compound was isolated from aqueous layer, recrystallized from isopropanol, and identified as tetramethylammonium iodide by H-nmr and ir spectra.

Reaction of Compound (9) with Sodium Hydride in THF.

1.0 g (2.6 mmole) of compound (9) and 0.06 g (2.5 m mole) of NaH were refluxed in dry THF under nitrogen-atmosphere for an hour. 0.40 g of methyl iodide in THF was then added to the reaction mixture. On filtration, tetramethylammonium iodide was isolated and identified from the solid. A white solid was precipitated from THF when the solution was exposed to air. This compound was recrystallized from isopropanol-ether, mp=109-110°C. It was identified as diphenylmethylphosphine oxide by its H-nmr and ir spectra. The H-nmr spectrum of chloroform-d solution showed a doublet centered at δ=3.30 (3H, J=14 Hz) and a multiplet centered at δ=7.90 (10H). The infrared

65. H. Gilman and L. S. Miller, Org. Reaction 6 353 (1955)
66. M. Epstein and S. A. Buckler, Tetrahedron 18 1231 (1962)

spectrum (KBr-pellet) showed 3100-2850 cm^{-1}(broad),1600 cm^{-1}(m), 1495 cm^{-1}(m), 1456 cm^{-1}(s), 1430 cm^{-1}(s), 1400 cm^{-1}(m), 1346 cm^{-1}(m), 1338 cm^{-1}(s), 1322 cm^{-1}(s), 1170 cm^{-1}(s), 1115 cm^{-1}(s), 1078 cm^{-1}(s), 1002 cm^{-1}(s), 890 cm^{-1} 865 cm^{-1}(s), 778 cm^{-1}(s), 744 cm^{-1}(s,b), 690 cm^{-1}(s).

Reaction of Compound (9) with Sodium Hydride in DMF.

1.0 g (2.6 mmole) of compound (9) and 0,06 g (2.5 mmole) of NaH were refluxed in a dry DMF solution under nitrogen atmosphere for an hour. A 0.40 g of methyl iodide in DMF solution was added to the reaction mixture. The reaction mixture was filtered. The solid was dissolved in water and neutralized with concentrated HCl solution. Crystalline colorless needles were formed. This compound was purified by repeated acid-base neutralization, and identified as diphenylphosphinic acid, mp=190-1^{o}C (lit. mp=192-1^{o}C)[67], by mixed melting point determination.

Reaction of Compound (9) with Sodium Hydride in DMSO.

To a solution of 1.0 g (2.6 mmole) of compound (9) in 50 ml of dry DMSO was added 2.5 mmole (ca) of methylsulfinylcarbanion[62, 63] drop by drop under nitrogen-atmosphere at room temperature for a 30 min period. The reaction mixture was stirred at 60^{o}C for 2 hours. It was quenched with

67. G.M. Kosolapoff and R. F. Struck, J. Chem. Soc. 3950 (1959)

D_2O. The solvent was distilled off under reduced pressure, brown solid was collected. This solid was dissolved in water, and neutrallized with concentrated HCl, crystalline colorless needles were formed. It was identified as diphenylphosphinic acid by its H-nmr and ir spectra and mixed melting point determination. After evaporating the acidic aqueous solution, tetramethylammonium iodide was isolated.

Reaction of Compound (14) with Bases.

The reactions were ran under a nitrogen-atmosphere, all solvents were dried and deoxygenated. The products were obtained in quantitative yield, and were identified as diphenylphosphine oxide and tetrameehylammonium iodide by their H-nmr and ir spectra.

De-oxygenation of Compound (6).

A solution of phosphine oxide in acetonitrile (or benzene) was refluxed with an excess of Si_2Cl_6 (or $H\text{-}SiCl_3$) for 10 minutes (and longer). THF was added to the solution to precipitate out the corresponding phosphino-ammonium salt. The ir spectrum showed an absorption band around 1210 cm^{-1} indicating that the P-O bond had not been removed. The melting point was unchanged.