*Anal.* Calcd. for $C_{15}H_{16}O_2$ : C, 79.0; H, 7.03; OH, 14.9. Found: C, 78.8; H, 7.02; OH, 15.3.

Infrared data were consistent with the proposed structure and showed a predominance of *meta* substitution.

*Acknowledgment.* The authors are indebted to Mr. L. Boros and Mr. R. B. Smith for infrared interpretations and to Mr. J. V. Pustinger for NMR interpretations.

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## Synthesis of N-Substituted Aminophosphonium Halides by Alkylation Reactions

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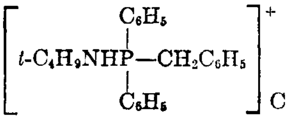
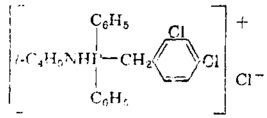
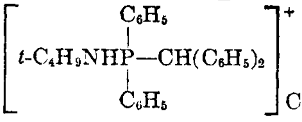
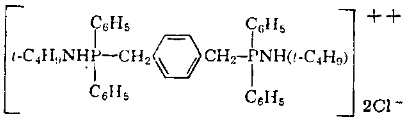
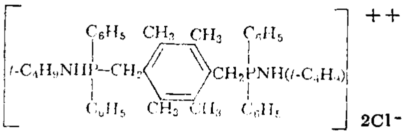
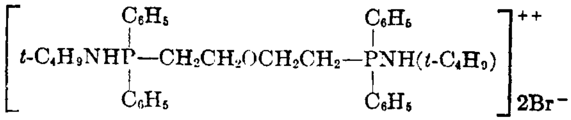
The preparation of trisubstituted aminophosphonium chlorides by the reaction of chloramine with tertiary phosphines, first established in our laboratory,[1] has been extended to additional compounds with alkyl,[2,3] alkenyl,[3] and aralkyl[3] substitutions on the phosphorus atom. The variety of *N*-substitutions in aminophosphonium chlorides by this mode of synthesis is, however, limited at present by the availability of only a few *N*-substituted chloramines.

A promising alternative approach to the *N*-substituted aminophosphonium halides was suggested by the relatively simple quaternization of tertiary phosphines by organic halides.[4] By the use of this method we have been able to synthesize easily mono- and diquaternary aminophosphonium halides with *N*-substitutions by the interaction of *N*-substituted aminophosphines with alkyl halides and dihalides. Solvents of the polar type such as dimethylformamide are useful in promoting this reaction.

The following *t*-butylaminodiphenylphosphonium chlorides were prepared by this method: *P*-benzyl-, *P*-(2,4-dichlorobenzyl)-, *P*-benzhydryl-, *P*-(*p*-xylylene)bis-, and *P*-(*p*-tetramethylxylylene)bis-(*t*-butylaminodiphenylphosphonium) chloride. Using a similar reaction with $\beta,\beta'$-dibromodiethyl ether,

TABLE I

SOME MONO- AND DIQUATERNARY AMINOPHOSPHONIUM HALIDES

| Formula | Yield, % | M.P. | C, % Calcd. Found | H, % Calcd. Found | Cl, % Calcd. Found |
|---|---|---|---|---|---|
|  $[t\text{-}C_4H_9NHP(C_6H_5)_2\text{—}CH_2C_6H_5]^+ Cl^-$ | 48 | 247° dec. | 71.95<br>71.72 | 7.09<br>6.98 | 9.23<br>9.15 |
|  | 46 | 271° dec. | 61.01<br>60.96 | 5.57<br>5.58 | 23.49<br>23.64 |
|  $[t\text{-}C_4H_9NHP(C_6H_5)_2\text{—}CH(C_6H_5)_2]^+ Cl^-$ | 50 | 247° dec. | 75.72<br>75.68 | 6.79<br>6.92 | 7.71<br>7.95 |
|  $\cdot H_2O$ | 80 | 269° dec. | 67.69<br>67.60 | 7.10<br>7.13 | 9.99<br>9.70 |
|  $\cdot 2H_2O$ | 52 | 295° dec. | 67.42<br>67.46 | 7.97<br>7.86 | 9.05<br>9.19 |
|  $[t\text{-}C_4H_9NHP(C_6H_5)_2\text{—}CH_2CH_2OCH_2CH_2\text{—}P(C_6H_5)_2NH(t\text{-}C_4H_9)]^{++} 2Br^-$ | 50 | 278° dec. | 57.92<br>57.86 | 6.48<br>6.39 | (Br)21.41 (N)3.75 (P)8.30<br>21.69 3.98 8.50 |

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[1] H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

[2] R. Appel and A. Hauss, *Ber.*, **93**, 405 (1960).

[3] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *J. Org. Chem.*, *in press.*

[4] R. N. McDonald and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 4669 (1960).

P-(β,β'-ethyl ether) bis(*t*-butylaminodiphenylphosphonium)bromide was prepared. In this latter case benzene was used as solvent.

To ascertain whether the quaternization occurs on the phosphorus or on the nitrogen atom, *P*-benzyl(*t*-butylamino)diphenylphosphonium chloride was subjected to alkaline hydrolysis. Only *t*-butylamine and benzyldiphenylphosphine oxide were isolated from the hydrolysis product. It is thus evident that the quaternization occurs on the phosphorus atom.

The alkaline hydrolysis of mono- and diquaternary aminophosphonium halides offers a convenient method for the preparation of mono- and ditertiary phosphine oxides.

### EXPERIMENTAL[5]

*Materials.* The preparation of *t*-butylaminodiphenylphosphine was carried out by the method previously described[6] except that dry benzene rather than ethyl ether was used as solvent. A yield of 80% is obtained by this procedure. The organic halides were used as received from the following sources: benzyl chloride and 2,4-dichlorobenzylchloride from Heyden Newport Chemical Corp., chlorodiphenylmethane from Distillation Products Industries, *p*-xylylene dichloride from Pennsalt Chemicals Corp., bis(chloromethyl)durene from Humble Oil and Refining Co., and β,β'-dibromodiethyl ether from Matheson, Coleman and Bell. Dimethylformamide (b.p. 152.6–153.5°) from Fischer Scientific Co. was used as received.

*Procedure.* As an example of the procedure used in the aralkylation of *t*-butylaminodiphenylphosphine the following description of the synthesis of *P*-(xylylene)bis(*t*-butylaminodiphenylphosphonium chloride) is given:

A solution of 8.8 g. (0.05 mole) of *p*-xylylene dichloride and 25.7 g. (0.10 mole) of *t*-butylaminodiphenylphosphine in 150 ml. of dimethylformamide was stirred at reflux for 4 hr. The mixture was then allowed to cool to room temperature and the colorless crystalline product was filtered, washed twice with ethyl ether and dried. The product weighed 28.0 g. (81% yield) and melted at 264° dec. An analytical sample was recrystallized from an ethyl ether-ethanol mixture to give colorless, salt-like crystals which melted at 269° dec. The compound is soluble in water. The use of ethyl ether and benzene for the reaction described lowers the yield considerably.

The diquaternary aminophosphonium salts tend to crystallize as hydrates as has been reported for the synthesis of diphosphonium salts.[4]

The physical properties, analytical data, and yields for the various aminophosphonium salts synthesized in this investigation are listed in Table I.

A characteristic of all the spectra of these aminophosphonium salts is an intense band at 1120 cm.$^{-1}$ and two moderately strong bands between 940 and 820 cm.$^{-1}$ A strong band also appears near 720 cm.$^{-1}$ in common with other aryl-substituted phosphonium compounds where the phosphorus atom is functioning as an electron donor.[7]

The alkaline hydrolysis of *P*-benzyl(*t*-butylamino)diphenylphosphonium chloride was carried out as follows:

A mixture of 3.8 g. (0.01 mole) of *P*-benzyl(*t*-butylamino)-diphenylphosphonium chloride and 2.0 g. of potassium hydroxide in 30 ml. of water was stirred at reflux for 1 hr. The amine was collected in a water trap. The crystalline residue was filtered and dried. It crystallized from aqueous ethanol as fine, colorless needles (m.p. 191–193°). The melting point agrees with that reported for benzyldiphenylphosphine oxide.[8] The product weighed 2.6 g. and represents a 86% yield based on the aminophosphonium chloride used.

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[5] All melting and boiling points are uncorrected. Microanalyses were done by Galbraith Laboratories, Knoxville, Tenn.

[6] H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

[7] J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **80**, 2120 (1960).

[8] G. M. Kosolapoff, *Organophosphorus Compounds*, Wiley, New York, 1950, p. 116.

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## Reaction of Trinitromethyl Compounds with Potassium Iodide

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*Received May 10, 1961*

In a recent report from this laboratory the preparation of potassium 1,1,3-trinitropropane (I) by the reduction of 1,1,1,3-tetranitropropane with potassium iodide in methanol was described.[1] Since the product was important to a proof of structure, we wish now to establish that the preparative reaction was unambiguous and to record some further examples of this convenient method for the conversion of trinitromethyl compounds to salts of the corresponding 1,1-dinitro derivatives (1-nitroalkyl-1-nitronates).

$$RC(NO_2)_3 + 2\,KI \longrightarrow RC(NO_2)_2^{-}K^{+} + KNO_2 + I_2$$

The closest reported analogies to these reactions of which we are aware involve the potassium iodide reductions of tetranitromethane to potassium nitroform[2] and of 1-bromo-1,1-dinitroalkanes to the corresponding 1-nitro-1-nitronate salts.[3]

Attempts to convert 2,2,2-trinitroethanol to potassium 2,2-dinitroethanol by this method were unsuccessful. The only product isolated under a variety of conditions was potassium nitroform,

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[1] M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *J. Org. Chem., in press.*

[2] C. Krauz and J. Stepanek, *Chem. Obzor.*, **12**, 81 (1937); *Chem. Abstr.*, **31**, 6138 (1937).

[3] K. Klager, *Anal. Chem.*, **23**, 534 (1951); J. Meisenheimer, *Ber.*, **36**, 434 (1903).

[4] S. S. Novikov, I. S. Korsakova, and N. N. Bulatova, *Zhur. Obshchei Khim.*, **29**, 3659 (1959).