Synthesis and Cleavage Reactions of Some Dibenzophosphole Derivatives

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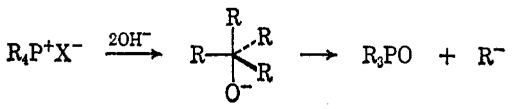
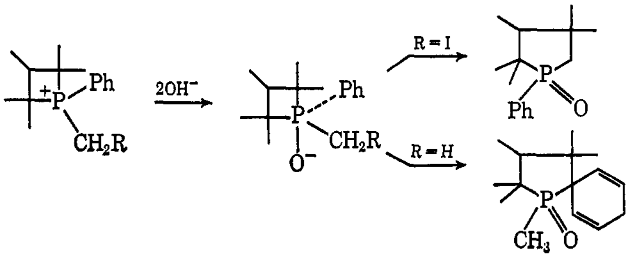
Several heterocyclic phosphine oxides and phosphonium salts have been prepared and cleaved with sodium hydroxide. Cleavage of 5-benzyl-5-phenyldibenzophospholium chloride (III) and 5-benzyl-5-methyldibenzophospholium iodide (VI) gave 5-phenyldibenzophosphole 5-oxide (II) and 5-methyldibenzophosphole 5-oxide, respectively. In these cases, the cleavage of the benzyl group appears to proceed from a position not colinear with the phosphorus-oxygen bond in the trigonal-bipyramidal intermediate. Cleavage of 5-phenyldibenzophosphole 5-oxide (II) and 5-benzyldibenzophosphole 5-oxide (V) led to exclusive ring opening for II and preferential ring opening for V. The unexpected instability of the heterocyclic ring in V suggests that this cleavage reaction does not proceed *via* a trigonal-bipyramidal intermediate but through a mechanism similar to that of an SN2 reaction.

There has been considerable interest in recent years in the cleavage of various bonds in heterocyclic phosphorus compounds. The generalizations concerning both the rate and direction of cleavage for acyclic systems are often altered for cyclic compounds. Westheimer[1] has explained how ring strain can enhance the rate of hydrolysis of cyclic phosphate esters even when ring opening does not occur. This increased rate is attributed to relief of strain in going from a tetrahedral phosphorus atom to a trigonal-bipyramidal intermediate. Similarly, trigonal-bipyramidal intermediates have been proposed for the cleavage of phosphonium salts with hydroxide ion. Kinetic data,[2] which show the reaction to be first order in phosphonium salt and second order in hydroxide ion, are consistent with Scheme I. It has been shown that the carbanion is lost from the apical position colinear with the phosphorus-oxygen bond by noting that cleavage of methylethylphenylbenzylphosphonium iodide proceeds with inversion of configuration at phosphorus.[3] There appear to be two rules governing the cleavage of phosphonium salts: (1) the group that is lost is the one that is capable of forming the most stable carbanion,[4] and (2) the group is lost from the apical position of the trigonal-bipyramidal intermediate. For acyclic compounds, both conditions can always be met. Two reported ring expansions[5] of four-membered phosphetanium salts indicate that the requirement that cleavage should occur at the apical position is important. In these cases, because of ring strain, the ring must occupy equatorial-axial positions in the intermediate. In each case ring expansion occurs with cleavage of the ring from the apical position even though this means formation of the least stable carbanion. This is illustrated in Scheme II. More recently,[6] it has been shown that, when R = phenyl, the benzyl group cleaves with retention of configuration at phosphorus. This shows that, when the difference in carbanion stabilities is great enough, then the group may be lost from a position not colinear with the phosphorus-oxygen bond.

SCHEME I



SCHEME II



For several years we have been studying the cleavage of the carbon-phosphorus bond in compounds in which the phosphorus atom is a member of a heterocyclic system. The present paper describes the preparation and cleavage of several phosphine oxides and phosphonium salts of the 5-dibenzophosphole ring system. The method of preparation is shown in Scheme III. Tetraphenylphosphonium bromide was prepared by the method of Horner and coworkers[7] and converted into 5-phenyldibenzophosphole (I) with lithium diethylamide.[8,9] Cleavage of I with lithium to form the lithium phosphide and phenyllithium has been reported by Britt and Kaiser.[10] Our reaction scheme from I to IV is analogous to a reported method[11] for conversion of triphenylphosphine into diphenylbenzylphosphine. Compounds III, V, and VI have not been previously

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[1] F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

[2] M. Zanger, C. A. VanderWerf, and W. E. McEwen, *J. Amer. Chem. Soc.*, **81**, 3806 (1959).

[3] A. Bladé-Font, C. A. VanderWerf, and W. E. McEwen, *ibid.*, **82**, 2396 (1960).

[4] For a summary, see D. W. Allen, I. T. Millar, and F. G. Mann, *J. Chem. Soc., C*, 1872 (1967).

[5] S. E. Fishwick, J. Flint, W. Hawes, and S. Trippett, *Chem. Commun.*, 1113 (1967).

[6] W. Hawes and S. Trippett, *ibid.*, 295 (1968).

[7] L. Horner, G. Mummeathey, M. Moser, and P. Beck, *Chem. Ber.*, **99**, 2782 (1966).

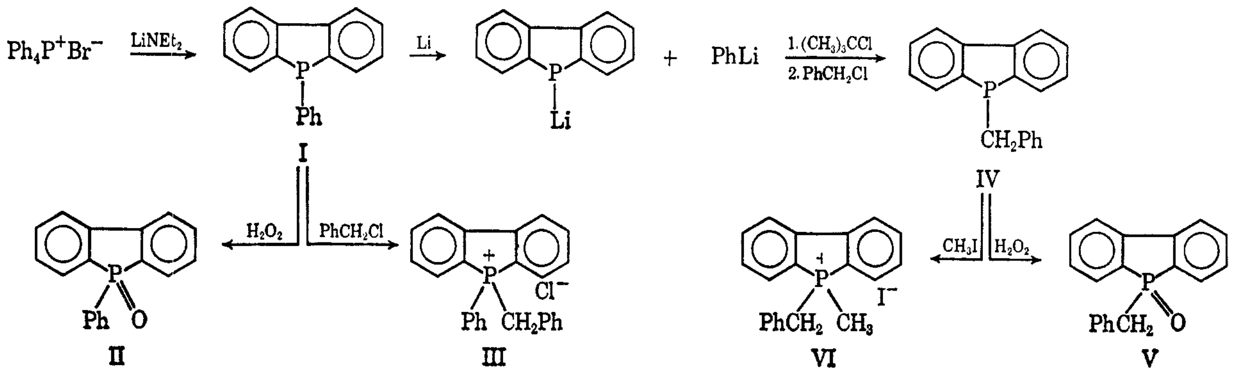
[8] H. Hoffman, *ibid.*, **95**, 2563 (1962).

[9] We have found that this reaction proceeds in the same way with the phosphonium chloride, but, when the iodide is used, only triphenylphosphine is formed. An attempt to extend this reaction to the preparation of 5-phenyldibenzoarsole and 5-phenyldibenzostibole by treatment of tetraphenylarsonium chloride and tetraphenylstibonium bromide with lithium diethylamide led to triphenylarsine and triphenylstibine, respectively.

[10] A. D. Britt and E. T. Kaiser, *J. Org. Chem.*, **31**, 112 (1966).

[11] A. M. Aguiar, J. Beisler, and A. Mills, *ibid.*, **27**, 1001 (1962).

Scheme III

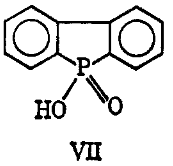


described. Compound IV, prepared by another procedure, was reported during the course of this work.[12]

Horner and coworkers[13] have shown that the fusion of a tertiary phosphine oxide with sodium hydroxide leads to cleavage of a carbon–phosphorus bond. Their

$$\mathrm{R_2R'PO + NaOH \longrightarrow RR'PO_2Na + RH}$$

findings indicate that the group that is preferentially cleaved is the one which can form the more stable carbanion. Thus, benzyl is cleaved more readily than phenyl, while phenyl is cleaved in preference to tolyl or alkyl. These results suggested to us that it should be possible to prepare heterocyclic phosphinic acids by the preferential cleavage of the exocyclic carbon–phosphorus bond present in an appropriate heterocyclic phosphine oxide. However, when 5-benzyldibenzophosphole 5-oxide (V) was allowed to react with sodium hydroxide at 200°, we isolated from the reaction mixture a 55% yield of 2-biphenylylbenzylphosphinic acid and only 23% 5-hydroxy-5 H-dibenzophosphole 5-oxide (VII).



VII

This result was especially surprising, since it had previously been reported[13] that the fusion of sodium hydroxide with diphenylbenzylphosphine oxide leads to exclusive cleavage of the benzyl group; and we have confirmed this finding. When 5-phenyldibenzophosphole 5-oxide (II) was allowed to react with fused sodium hydroxide, only 2-biphenylylphenylphosphinic acid could be isolated from the reaction mixture. The fact that the ring is preferentially cleaved in the case of II is, perhaps, not unexpected, since the substituted biphenylyl carbanion is probably more stable than the phenyl anion. It is surprising, however, that there is no cleavage at all of the exocyclic carbon–phosphorus bond.

The unexpected instability of the dibenzophosphole 5-oxide ring system prompted us to investigate the alkaline cleavage of the dibenzophospholium salts III and VI. When these compounds were allowed to react with an aqueous acetone solution of sodium hydroxide, only the benzyl–phosphorus bond was cleaved.[14–16] Thus, III gave a quantitative yield of 5-phenyldibenzophosphole 5-oxide (II), and VI gave a 90% yield of 5-methyldibenzophosphole 5-oxide. Since the ring strain in both the dibenzophosphole 5-oxide and the dibenzophospholium systems should be comparable, it seems reasonable to conclude that fundamentally different mechanisms must be involved in the alkaline cleavage of the two classes of compounds.

The cleavage of the benzyl–phosphorus bond in the dibenzophospholium salts probably proceeds *via* a trigonal–bipyramidal intermediate such as is illustrated in Scheme I. However, the leaving benzyl carbanion probably does not occupy a position colinear with the phosphorus and oxygen atoms in this intermediate for the following reason. If the benzyl group did occupy such a position, then the carbon–phosphorus bonds of the heterocyclic ring would have to occupy diequatorial positions, and this situation would mean an appreciable increase in ring strain in going from the phospholium salt to the trigonal–bipyramidal intermediate. On the other hand, formation of a trigonal–bipyramidal intermediate with the ring in an equatorial–apical conformation[17] results in a decrease in strain energy and in placing the benzyl–phosphorus bond at right angles to the phosphorus–oxygen bond. The benzyl group in this intermediate leaves as a carbanion, and the heterocyclic ring is not opened. As we have previously mentioned, other workers[6] have obtained similar results with the four-membered benzylphosphetanium system.[18]

We would like to propose that the cleavage of the ring in 5-benzyldibenzophosphole 5-oxide (V) by means of fused sodium hydroxide does not involve a trigonal-bipyramidal intermediate. If this reaction did proceed through such an intermediate, structures VIII–X should be considered. The formation of VIII, in which the ring occupies equatorial–apical positions, would mean some decrease in ring strain and would presumably be followed by benzyl group cleavage (as is observed

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[12] E. M. Richards and J. C. Tebby, *Chem. Commun.*, 957 (1967).

[13] L. Horner, H. Hoffman, and H. G. Wippel, *Chem. Ber.*, **91**, 64 (1958).

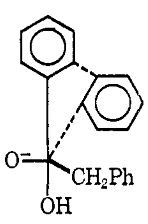
[14] Only ring opening has been previously observed[4,12,15,16] when dibenzophospholium salts were subjected to cleavage reactions; in each of these cases, ring opening resulted in formation of the most stable carbanion.

[15] E. Zbiral, *Tetrahedron Lett.*, 1649 (1964).

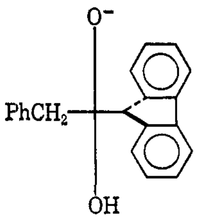
[16] D. W. Allen and I. T. Millar, *Chem. Ind.* (London), 2178 (1967).

[17] D. Hellwinkel [*Chem. Ber.*, **99**, 3628 (1966)] has presented evidence that the equatorial–apical conformation is definitely preferred in certain stable pentacovalent 5-dibenzophosphole derivatives.

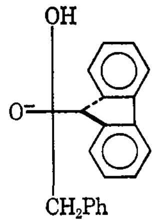
[18] Our results may be in contrast to a preliminary report[12] which indicates that the benzyl group does not migrate during ring expansion of the 5-dibenzophosphole ring system.



VIII



IX



X

with the benzyl-substituted dibenzophospholium salts). However, cleavage of the exocyclic carbon–phosphorus bond is *not* the main reaction observed when the 5-oxide V is fused with sodium hydroxide, and thus there must be some factor that inhibits the formation of VIII. It seems reasonable to suggest that the rate of formation of VIII is relatively slow because of the coulombic repulsion between the approaching hydroxide ion and the oxide oxygen atom. The existence of the trigonal-bipyramidal intermediates IX[19] or X, in both of which the ring occupies diequatorial positions, appears unlikely since there would be severe ring strain in these structures; in addition, the formation of X would involve serious coulombic repulsion. It seems probable, therefore, that the cleavage of the ring in the 5-oxide V does not proceed through a trigonal-bipyramidal intermediate. The transition state leading to ring cleavage may resemble IX and may involve the concurrent cleavage of a ring carbon–phosphorus bond and the formation of a second phosphorus–oxygen bond.

Experimental Section[20]

5-Phenyldibenzophosphole (I).—Tetraphenylphosphonium bromide was prepared in 55% yield by the method of Horner and coworkers[7] and converted into I in 62% yield by treatment with lithium diethylamide.[8] The phosphole was shown (melting point, mixture melting point, and ir spectrum) to be identical with an authentic sample prepared by another procedure.[21]

5-Benzyldibenzophosphole (IV).—5-Phenyldibenzophosphole (I, 0.0245 mol) was dissolved in 75 ml of dried tetrahydrofuran (THF) and small pieces of lithium wire (0.050 g-atom) were added. The mixture was stirred and refluxed under nitrogen for 3 hr and then cooled. *t*-Butyl chloride (0.0245 mol) in 10 ml of THF was then added dropwise with stirring. After the addition, the solution was refluxed for 10 min and then allowed to cool to room temperature. Benzyl chloride (0.025 mol) was then added dropwise with stirring. During the addition, the deep red solution changed to almost colorless. The solution was refluxed for 15 min after the addition, and then water was added. Ethyl ether (75 ml) was added, and the organic layer separated. The solvent was stripped and the residue was vacuum distilled. The product, 5.1 g, bp 165–170° (~10 μ) [lit. bp 162° (30 μ),[12] bp 175–180° (0.2 mm)[22]], was collected as a liquid which later solidified. The yield after recrystallization from methanol was 3.9 g (62%): mp 76–78°; nmr τ 6.98 (s, 2, CH$_2$P), 2.1–3.2 (m, 13, aromatic H).

Anal. Calcd for $C_{19}H_{15}P$: C, 83.20; H, 5.51; P, 11.29. Found: C, 83.01; H, 5.32; P, 11.14.

5-Benzyldibenzophosphole was prepared earlier[22] in this laboratory from *o,o'*-dilithiobiphenyl and benzylphosphonous dichloride[23] by a procedure similar to that of Wittig and Maercker.[24] The ir spectra of both samples were identical.

5-Benzyldibenzophosphole 5-Oxide (V).—5-Benzyldibenzophole (3.3 g) was dissolved in 30 ml of acetone and treated dropwise with 25 ml of 3% hydrogen peroxide. The solution was stirred for 1 hr after the addition, and the acetone evaporated. The reaction mixture, containing an insoluble viscous material, was extracted twice with 25-ml portions of benzene. The extracts were combined and dried with sodium sulfate. The product was then precipitated from the benzene solution by addition of petroleum ether. Recrystallization from a benzene–petroleum ether (bp 65–110°) mixture gave 3.3 g (95%) of the pure product: mp 139–141°; nmr τ 6.64 (d, J_{P-H} = 15.4 cps, 2, CH$_2$P), 2.2–3.1 (m, 13, aromatic H).

Anal. Calcd for $C_{19}H_{15}OP$: C, 78.61; H, 5.21; P, 10.67. Found: C, 78.55; H, 5.15; P, 10.45.

5-Phenyldibenzophosphole 5-Oxide (II).—Compound II was prepared from 5-phenyldibenzophosphole (I) by the method used for 5-benzyldibenzophosphole 5-oxide (V): yield 94%; mp 163–166° (lit.[21] mp 165–167°). The ir spectrum was identical with that of an authentic sample.[21]

Diphenylbenzylphosphine Oxide.—Diphenylbenzylphosphine was prepared from lithium diphenylphosphide and benzyl chloride by a procedure similar to that described for 5-benzyldibenzophosphole: bp 185–190° (0.75 mm); nmr τ 6.70 (s, 2, CH$_2$P), 2.4–3.2 (m, 15, aromatic H). The phosphine was oxidized by the procedure described for 5-benzyldibenzophosphole 5-oxide: yield, based on triphenylphosphine, 60%; mp 186–189° (lit.[11] mp 191–192°); nmr τ 6.37 (d, J_{P-H} = 14.6 cps, 2, CH$_2$P), 2.2–2.9 (m, 15, aromatic H).

5-Benzyl-5-phenyldibenzophospholium Chloride (III).—5-Phenyldibenzophosphole (2.0 g) was added to a large excess of benzyl chloride (20 ml) in a flask equipped with a reflux condenser. The mixture was slowly refluxed for 2 hr. The phosphonium salt, which crystallized on cooling, was collected and washed with 200 ml of ether: yield 2.8 g (94%); mp 303–306° dec.

Anal. Calcd for $C_{25}H_{20}ClP$: C, 77.62; H, 5.21; P, 8.01. Found: C, 77.60; H, 5.23; P, 8.18.

5-Benzyl-5-methyldibenzophospholium Iodide (VI).—A large excess of methyl iodide (25 ml) was added to 5-benzyldibenzophosphole (6.0 g) in a flask equipped with a reflux condenser. A vigorous reaction immediately followed the addition. The mixture was allowed to sit for 2 hr. The phosphonium salt was removed by filtration, washed with ether, and then recrystallized from an acetone–ethanol mixture: yield 6.0 g (99%); mp 239–242°; nmr τ 6.98 (d, J_{P-H} = 14.6 cps, 3, CH$_3$P), 4.63 (d, J_{P-H} = 16.6 cps, 2, CH$_2$P), 2.3–2.9 (m, 13, aromatic H).

Anal. Calcd for $C_{20}H_{18}IP$: C, 57.70; H, 4.36; P, 7.44. Found: C, 57.58; H, 4.44; P, 7.68.

Cleavage of 5-Benzyldibenzophosphole 5-Oxide (V).—The phosphine oxide V (0.0069 mol) was thoroughly mixed with finely powdered sodium hydroxide (0.014 mol) in a 25-ml pear-shaped flask fitted with a condenser. The flask was slowly heated to 200° and maintained between 200 and 210° for 30 min. During this time 0.12 ml of toluene (confirmed by ir and nmr) distilled. After cooling, the contents of the flask were dissolved in 75 ml of water, treated with charcoal, cooled, and acidified to yield 1.85 g of solid, mp 149–155°. This solid was recrystallized twice from ethanol to yield 1.17 g (55%) of 2-biphenylylbenzylphosphinic acid: mp 168–170°; nmr τ 7.12 (d, J_{P-H} = 15.6 cps, 2, CH$_2$P), 2.4–3.3 (m, 14, aromatic H). The acid was identified by analysis and by comparison of its melting point, mixture melting point, and ir spectrum with those of an authentic sample prepared as described below. The mother liquors from the above recrystallizations were combined to yield a solid, which, after two recrystallizations from ethanol, gave 0.34 g (23%) of 5-hydroxy-5H-dibenzophosphole 5-oxide (VII), mp 245–250°

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[19] Conformation IX is favored by the fact that both oxygen atoms occupy apical positions. In general, the more electronegative groups tend to occupy these positions in a trigonal-bipyramidal molecule.[1] However, it seems unlikely that this factor can counterbalance the large amount of ring strain in IX.

[20] Melting points were taken with a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 521 spectrophotometer. Nmr spectra were taken with either a Varian HA-100 or Varian T-60 instrument; deuteriochloroform was used as a solvent with tetramethylsilane as an internal standard. Elemental analyses were performed by Galbraith Laboratories.

[21] J. B. Levy, G. O. Doak, and L. D. Freedman, *J. Org. Chem.*, **30**, 660 (1965).

[22] C. N. Bean, Masters Thesis, North Carolina State University, Raleigh, N. C., 1965.

[23] P. J. Slota, Jr., Ph.D. Thesis, Temple University, Philadelphia, Pa., 1954.

[24] G. Wittig and A. Maercker, *Chem. Ber.*, **97**, 747 (1964).

(lit.[25] mp 253–257°); the acid was identified by comparison with an authentic sample.[26]

2-Biphenylylbenzylphosphinic Acid.—Thus compound was prepared[22] from 2-biphenyldiazonium tetrafluoroborate and benzylphosphonous dichloride by the method of Freedman and Doak:[27] yield 21%; mp 168–170°.

Anal. Calcd for $C_{19}H_{17}O_2P$: C, 74.02; H, 5.56; P, 10.05. Found: C, 74.20; H, 5.73; P, 9.62.

Cleavage of 5-Phenyldibenzophosphole 5-Oxide (II).—This compound (2.0 g) was cleaved by the procedure described for 5-benzyldibenzophosphole 5-oxide. 2-Biphenylylphenylphosphinic acid, 1.6 g (75%), mp 173–176° (lit.[28] mp 180–181°), was isolated and shown to be identical (mixture melting point and ir) with an authentic sample (see below). About 0.3 g (15%) of the phosphine oxide II was recovered from the reaction mixture.

2-Biphenylylphenylphosphinic Acid.—This compound was prepared from 2-biphenyldiazonium tetrafluoroborate and phenylphosphonous dichloride by the usual method:[27] yield 18%; mp 177–179° (lit.[28] mp 180–181°).

Cleavage of 5-Benzyl-5-phenyldibenzophospholium Chloride (III).—The phospholium salt III (1.4 g) was dissolved in 40 ml of a 1:1 acetone–water mixture. Sodium hydroxide (9 ml of a 20% solution) was added, and the mixture was allowed to sit for 24 hr. The acetone was evaporated and the aqueous mixture was extracted with two 15-ml portions of chloroform. The extracts were combined and stripped leaving 5-phenyldibenzophosphole 5-oxide (II): yield 1.0 g (100%); mp 162–165°. The compound was identical with the sample prepared above.

Cleavage of 5-Benzyl-5-methyldibenzophospholium Iodide (VI).—The phospholium salt VI (2.8 g) was cleaved by the procedure described for 5-benzyl-5-phenyldibenzophospholium chloride (III). 5-Methyldibenzophosphole 5-oxide was obtained as a hemihydrate after recrystallization from benzene–petroleum ether: yield 1.3 g (90%); mp 89–91°; nmr τ 8.21 (d, J_{P-H} = 13.6 cps, 3, CH_3P), 7.42 (s, 1, H_2O), 2.0–2.8 (m, 8, aromatic H). The ir spectrum showed the O–H stretching at 3470 and 3520 cm^{-1}. The water could be removed by heating the hemihydrate for 2 hr *in vacuo* over phosphorus pentoxide; the loss of water was demonstrated by an appropriate weight loss, the disappearance of the O–H stretching in the ir, and of the τ 7.42 peak in the nmr spectrum.

Anal. Calcd for $C_{13}H_{11}OP \cdot 0.5H_2O$: C, 70.00; H, 5.42; P, 13.88. Found: C, 70.45; H, 5.57; P, 14.01.

The compound was identical (melting point, mixture melting point, and ir) with an authentic sample prepared by the procedure given below.

5-Methyldibenzophosphole 5-Oxide.—5-Methyldibenzophosphole was prepared from 5-phenyldibenzophosphole (0.029 mol) and methyl iodide (0.029 mol) by the procedure described for 5-benzyldibenzophosphole (IV): yield 44%; bp 110° (10 μ) [lit.[4] bp 103° (0.2 mm)]; nmr τ 8.69 (s, 3, CH_3P), 2.3–2.8 (m, 8, aromatic H).

Anal. Calcd for $C_{13}H_{11}P$: C, 78.77; H, 5.60. Found: C, 78.60; H, 5.73.

The phosphine was oxidized with hydrogen peroxide to the phosphine oxide hemihydrate (70%), mp 88–90°.

Registry No.—III, 19190-36-4; IV, 19190-37-5; V, 19190-38-6; VI, 19190-39-7; 5-methyldibenzophosphole 5-oxide, 19190-40-0.

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[25] L. D. Freedman and G. O. Doak, *J. Org. Chem.*, **21**, 238 (1956).

[26] G. O. Doak, L. D. Freedman, and J. B. Levy, *ibid.*, **29**, 2382 (1964).

[27] L. D. Freedman and G. O. Doak, *J. Amer. Chem. Soc.*, **74**, 2884 (1952).

[28] I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 2133 (1961).

Some Novel Sulfonamides. The Chlorosulfonation of Aryl Alkyl Sulfides

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The chlorosulfonation of three methylthio-substituted benzenes has been investigated. With two of the compounds, the reaction proved satisfactory for preparation of sulfonamide derivatives. In the more favorable case, 2,4-dimethylthioacetanilide readily gave a crystalline sulfonyl chloride. Subsequent oxidation gave the corresponding disulfones. Various tetrasubstituted compounds were readily characterized by bands for isolated aromatic hydrogens in their proton magnetic resonance (pmr) spectra. Lack of splitting in these bands along with the facile substitution in the presence of the two methylthio-directing groups favors assignment of a 1,2,4,5-substitution pattern for these compounds. Analysis of the pmr spectra provides a rough correlation of chemical-shift parameters for the sulfonyl and methylthio substituents.

A study of some sulfonation reactions with simple alkyl aryl sulfides has shown participation by the sulfur as a sulfonium group in attack on the aromatic ring to give diarylalkylsulfonium salts. This reaction occurs with methyl *p*-tolyl sulfide at 20°. When the ring is somewhat deactivated, as with methyl *p*-chlorophenyl sulfide, some sulfonation is observed and this occurs *ortho* to the methylthio group.[1] An earlier study of the substitution of methyl phenyl sulfide reports that both bromination and sulfonation occur primarily in the *para* position.[2]

In work directed toward the preparation of new sulfonamides, chlorosulfonation of highly reactive methylthio-substituted benzenes was utilized. In addition to using cold chlorosulfonic acid, use of chloroform as a cosolvent in the two-phase procedure of Huntress and Carten[3] for characterization of aryl alkyl ethers was also used. This procedure was found to give better results than without the use of a cosolvent in the one case in which it was tried.

m-Methylthioacetanilide[4] was prepared and further characterized by oxidation with perbenzoic acid to the sulfone[4] (Scheme I). It was also chlorosulfonated followed by treatment with ammonia to give a new

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[1] F. Krollpfeiffer and W. Hahn, *Chem. Ber.*, **86**, 1049 (1953).

[2] T. Van Hove, *Bull. Sci. Acad. Roy. Belg.*, **12**, (5), 929 (1926); *Chem. Abstr.*, **21**, 2256 (1927).

[3] E. H. Huntress and F. H. Carten, *J. Amer. Chem. Soc.*, **62**, 511, 603 (1940).

[4] (a) Th. Zinke and J. Müller, *Ber.*, **46**, 775 (1913); (b) H. Gilman and G. A. Martin, *J. Amer. Chem. Soc.*, **74**, 5317 (1952).