mechanism with 1-bromoadamantane through the corresponding unsaturated compound with a double bond at the bridgehead (in violation of Bredt's rule) have been unsuccessful. The only reaction so far observed has been halogen–metal exchange.

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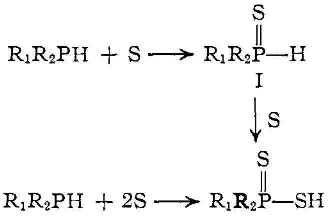
SECONDARY PHOSPHINE SULFIDES

Sir:

We wish to report the preparation of a new class of compounds, secondary phosphine sulfides $R_1R_2P(S)H$ (I), by the oxidation of secondary phosphines with elemental sulfur. Oxidation of secondary phosphines to the corresponding dithiophosphinic acids (II) has long been known,[1] but the addition of only one atom of sulfur to secondary phosphines has not been accomplished previously.



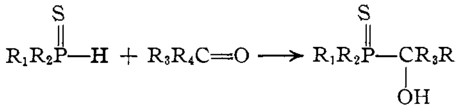
$$\begin{array}{c} R_1R_2PH + S \longrightarrow R_1R_2\overset{S}{\overset{\|}{P}}-H \\ \text{I} \\ \big\downarrow S \\ R_1R_2PH + 2S \longrightarrow R_1R_2\overset{S}{\overset{\|}{P}}-SH \end{array}$$

II

Successful control of the process is effected by the addition under nitrogen of one equivalent of sulfur to a solution of a secondary phosphine in an inert solvent, such as benzene or carbon tetrachloride. Disappearance of the sulfur signals completion of the reaction, whereupon the product is obtained in a fair state of purity by removing the solvent under reduced pressure. Further purification of liquid products by distillation is accompanied by decomposition which reduces the yield of purified material considerably. By this method there were obtained: di-*n*-butylphosphine sulfide (100% crude yield, 36% distilled, b.p. 122–125° (1.5 mm.); *anal.* Calcd. for $C_8H_{19}PS$: P, 17.38; S, 17.99. Found: P, 17.69; S, 18.00), di-isobutylphosphine sulfide (65% yield, m.p. 61–62° from ligroin; *anal.* Calcd. for $C_8H_{19}PS$: C, 53.89; H, 10.74; S, 17.99. Found: C, 53.89; H, 11.06; S, 18.29), cyclohexyl-2-cyanoethylphosphine sulfide (liquid, 56% yield; *anal.* Calcd. for $C_9H_{16}NPS$: P, 15.39; S, 15.93. Found: P, 15.42; S, 16.01), bis-(2-carbethoxyethyl)-phosphine sulfide (liquid, 82% yield; *anal.* Calcd. for $C_{10}H_{19}PO_4S$: C, 45.10; H, 7.19; P, 11.63. Found: C, 45.26; H, 7.19; P, 11.88), 2,4,6-triisopropyl-3,5-dioxa-1-phosphacyclohexane-1-sulfide (57% distilled yield, b.p. 107–112° (1.5 mm.), m.p. 37°; *anal.* Calcd. for $C_{12}H_{25}PO_2S$: C, 54.52; H, 9.53; P, 11.72; S, 12.13. Found C, 54.03; H, 9.48; P, 11.44; S, 11.78), and diphenylphosphine sulfide (100% yield, m.p. 95–97° from acetonitrile; *anal.* Calcd. for $C_{12}H_{11}PS$: C, 66.03; H, 5.08; P, 14.19; S, 14.69. Found: C, 65.93; H, 5.23; P, 14.47; S, 14.78).

Spectral analyses[2] indicate that secondary phosphine sulfides exist in the thiono, rather than the thiolo, form. A characteristic P–H absorption band of weak to medium intensity is exhibited in the infrared at 2320 ± 10 cm.$^{-1}$ (half intensity band width of 35 wave numbers) together with a P=S (CsBr disc) at 600 cm.$^{-1}$ (alkyl) or 640 cm.$^{-1}$ (aryl). Nuclear magnetic resonance spectra in the phosphorus region show a doublet centered near -22 p.p.m. (relative to 85% H_3PO_4) with an average splitting of 28 p.p.m. which is consistent with the proposed structure.

Secondary phosphine sulfides have been further characterized by base-catalyzed addition of aldehydes and ketones to form α-hydroxy-substituted tertiary phosphine sulfides (III). Typical examples



$$R_1R_2\overset{S}{\overset{\|}{P}}-H + R_3R_4C{=}O \longrightarrow R_1R_2\overset{S}{\overset{\|}{P}}-\underset{\underset{OH}{|}}{C}R_3R_4$$

III

are di-*n*-butyl-α-hydroxybenzylphosphine sulfide (75% yield; m.p. 54–55° from heptane; *anal.* Calcd. for $C_{15}H_{25}POS$: C, 63.35; H, 8.86; S, 11.27. Found: C, 63.56; H, 8.98; S, 11.49), bis-(2-cyanoethyl)-1-hydroxy-1-methylethylphosphine sulfide (70% yield; m.p. 113–115° from benzene; *anal.* Calcd. for $C_9H_{15}N_2OPS$: C, 46.94; H, 6.57; S, 13.93. Found: C, 46.92; H, 6.51; S, 13.88), and diphenyl-1-hydroxy-1-methylethylphosphine sulfide (75% yield, m.p. 118–120° from benzene; *anal.* Calcd. for $C_{15}H_{17}OPS$: C, 65.19; H, 6.20; S, 11.60. Found: C, 65.11; H, 6.99; S, 11.25).

In addition, secondary phosphine sulfides can be oxidized by elemental sulfur to the corresponding dithiophosphinic acids (II). Details of this reaction and the carbonyl addition will be presented in a broader study of the chemistry of the secondary phosphine sulfides.

[1] A. W. Hofmann and F. Mahla, *Ber.*, **25**, 2436 (1892); L. Malatesta and R. Pizzotti, *Gazz. Chim. Ital.*, **76**, 167 (1946).

[2] We are indebted to N. B. Colthup for the infrared spectral data, and to J. E. Lancaster for the n.m.r. results.

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ARYLSULFUR TRIFLUORIDES AND PENTAFLUORIDES

Sir:

We wish to report the first synthesis of arylsulfur pentafluorides and the first general syntheses of arylsulfur trifluorides.

Perfluoroalkylsulfur trifluorides and pentafluorides are known derivatives of sulfur tetrafluoride and hexafluoride, respectively, prepared in general, by oxidative fluorination reactions.[1] Although other sulfur hexafluoride derivatives such as S_2F_{10},[1b]

[1] (a) Lovelace, Rausch and Postelnek, "Aliphatic Fluorine Compounds," Chapter 13, Reinhold Publishing Corp., New York, N. Y., 1958; (b) Special Publication No. 12, "Chemical Society Symposia, Bristol, 1958," The Chemical Society, Burlington House, W. I., London, 1958, p. 317–327.

SF_5OF[1b] and SF_5Cl[2] are known, efforts to prepare alkyl- and arylsulfur pentafluorides have been unsuccessful.[1b,3] The only alkyl- or arylsulfur trifluoride known is 2,4-dinitrophenylsulfur trifluoride, prepared by Chamberlain and Kharasch[4] by the reaction of fluorine with the corresponding disulfide in anhydrous hydrogen fluoride solution.

We have found that phenylsulfur trifluoride is obtained in 50 to 60% yield by the exothermic reaction of silver difluoride with a solution of phenyl disulfide in a "Freon" solvent, 1,1,2-trichloro-1,2,2-trifluoroethane. Phenylsulfur trifluoride is a colorless liquid, b.p. 60° (5 mm.), that is hydrolyzed rapidly by water to benzenesulfinic acid and slowly attacks "Pyrex" glass.

$$(C_6H_5S)_2 + 6AgF_2 \longrightarrow 2C_6H_5SF_3 + 6AgF$$

Anal. Calcd. for $C_6H_5F_3S$: F, 34.3; S, 19.3. Found: F, 33.5; S, 19.9.

Phenylsulfur trifluoride fluorinates carbonyl compounds: for example, benzaldehyde is converted to benzal fluoride (80%) by being heated with phenylsulfur trifluoride for 5 minutes at 100°.[5]

$$C_6H_5SF_3 + C_6H_5\overset{\overset{O}{\|}}{C}H \longrightarrow C_6H_5\overset{\overset{O}{\|}}{S}F + C_6H_5CHF_2$$

Substituted arylsulfur trifluorides, $XC_6H_4SF_3$, where $X = NO_2$ or CH_3, are prepared in a similar manner.

When phenylsulfur trifluoride is heated gradually to 130° with silver difluoride in a reactor made of copper or Teflon [polytetrafluoroethylene], phenylsulfur pentafluoride is obtained in about 10% yield. Phenylsulfur pentafluoride is a colorless liquid, b.p. 149°, $n^{25}D$ 1.4290, that is comparable in thermal and hydrolytic stability to benzotrifluoride.

$$C_6H_5SF_3 + 2AgF_2 \longrightarrow C_6H_5SF_5 + 2AgF$$

Anal. Calcd. for $C_6H_5F_5S$: C, 35.3; H, 2.47; F, 46.5; S, 15.7. Found: C, 35.5; H, 2.74; F, 46.7; S, 15.6.

The n.m.r. (fluorine and proton), infrared and ultraviolet spectra are consistent with the structure $C_6H_5SF_5$. The compound is hydrolyzed slowly to benzenesulfonyl fluoride by heating at 100° with 100% sulfuric acid. *m*- and *p*-nitrophenylsulfur pentafluorides are also prepared (15–30% yield) by heating the corresponding disulfide with silver difluoride, first in the "Freon" solvent, CCl_2FCClF_2, and then at 130° in a copper reactor with fittings of "Teflon." Anilines substituted by a sulfur pentafluoride group in the *meta*- or *para*-position are prepared by catalytic hydrogenation of the corresponding nitro derivatives, and react in the manner typical of anilines; thus, they can be acylated or diazotized.

The above series of arylsulfur trifluorides and pentafluorides are unique in providing key compounds necessary for determination of the properties of the SF_3 and SF_5 groups in comparisons with other substituents. Thus, we have determined that the sulfur pentafluoride group is strongly electron-withdrawing and is *meta*-directing to electrophilic substitution.

A detailed report of the method of synthesis and chemistry of the arylsulfur trifluorides and pentafluorides, as well as quantitative measurements on the inductive and resonance effects of the sulfur pentafluoride group, will be published in the near future. We are indebted to Drs. B. C. McKusick and T. L. Cairns for helpful discussions and suggestions during the course of the work.

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RECEIVED JULY 18, 1960

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(2) H. L. Roberts and N. H. Ray, *J. Chem. Soc.*, 665 (1960).

(3) H. J. Emeleus and H. G. Heal, *ibid.* 1126 (1946).

(4) D. L. Chamberlain and N. Kharasch, THIS JOURNAL, **77**, 1041 (1955).

(5) The use of SF_4 for fluorination of carbonyl compounds is described by W. R. Hasek, W. C. Smith and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

THE SYNTHESIS OF PHENYLATED AZIRIDINONES[1]

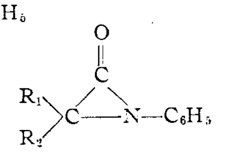
Sir:

This communication describes the preparation of a new class of cyclic amides, α-lactams, previously postulated as an intermediate in the sodamide-promoted conversion of α-chloro-α-phenylacetanilide (Ia) into α-anilinophenylacetamide[2] (II). Ia(λ_{max}^{EtOH} 247–250 mμ (4.19); λ_{max}^{KBr} (cm.$^{-1}$) 3306, 3150, 1667) was caused to react with sodium hydride in a manner described[2] (this time with a *complete* exclusion of oxygen from the reacting system), giving two compounds: (1) 2,5-diketo-1,3,4,6,-tetraphenylpiperazine (12% yield), and (2) 1,3-diphenyl-2-aziridinone, IIIa, (78–85% yield) as colorless crystals, (sintering at 115°) melting at 145–150° (dec.) (λ_{max}^{EtOH} 243–247 mμ (4.02); $\lambda_{max}^{CHCl_3}$ (cm.$^{-1}$) 1720, 1704, 1689; *anal.* found for $C_{14}H_{11}ON$: C, 79.9: H, 5.6; N, 6.4; mol. wt., 212 (ebullioscopic, benzene).[3] Alkaline hydrolysis of IIIa was slow even at 78°, consuming approximately 0.4 equivalent of alkali on being refluxed with 0.1 *N* ethanolic potassium hydroxide during six hours. However, ammonolysis of IIIa by means of sodamide in liquid ammonia provided II as the only isolable product.

$$R_1R_2ClCCONHC_6H_5 \xrightarrow[-H_2,\ -NaCl]{NaH}$$

I

Ia and IIIa, $R_1 = H$; $R_2 = C_6H_5$



III

Ib and IIIb, $R_1 = R_2 = C_6H_5$

α-Chloro-α,α-diphenylacetanilide[4] (Ib, m.p. 86°, λ_{max}^{EtOH} 245 mμ (4.24)) was brought to reaction

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(1) May otherwise be termed α-lactams or *azacyclopropanones*, the above systematic name, illustrating a carbonyl containing derivative of aziridine (otherwise termed ethyleneimine) is to be preferred. See Patterson and Capell "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940.

(2) S. Sarel and A. Greenberger, *J. Org. Chem.*, **23**, 330 (1958).

(3) Measurements were taken with a Gallenkamp semimicro ebuliometer, No. 7665K.

(4) H. Klinger, *Ann.*, **389**, 253 (1912).