previous workers[3] have claimed that thiophene and iron pentacarbonyl afford the π-complex thiophene-iron dicarbonyl, described as a pale red solid with a melting point of 51° and characterized by carbon, hydrogen and oxygen analysis. However, although the literature describes numerous well authenticated π-complexes involving iron tricarbonyl groups, similar complexes of iron dicarbonyl groups are rare.

(3) R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chemistry and Industry*, 1592 (1958).

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EVIDENCE FOR CYCLOPENTYNE AS A REACTION INTERMEDIATE IN THE COUPLING OF PHENYLLITHIUM WITH 1-CHLOROCYCLOPENTENE[1]

Sir:

Evidence has been presented previously for the intervention of benzyne[2,3] and cyclohexyne[4] as intermediates in nucleophilic substitution reactions of phenyl and cyclohexenyl halides, respectively. In studies designed to determine the minimum ring size for operation of the elimination–addition mechanism, we have now found that an entity with the symmetry properties of *cyclopentyne* must be involved in the formation of 1-phenylcyclopentene from 1-chlorocyclopentene-1-^{14}C and phenyllithium. The occurrence of cyclopentyne as a reaction intermediate was suggested some time ago. Favorskii proposed that tris-trimethylenebenzene, formed by the action of sodium in ether on 1,2-dibromocyclopentane, arose from the trimerization of cyclopentyne.[5] Very recently Wittig[6] appears to have trapped cyclopentyne as a Diels–Alder adduct in a similar reaction.

The general plan of attack was similar to that employed previously[4] with 1-chlorocyclohexene-2-^{14}C, except that the degradation scheme and controls were more nearly complete.

Our starting material was adipic-1,6-$^{14}C_2$ acid.[7] The preparation of 1-phenylcyclopentene-x-^{14}C from this material as well as the degradative schemes and ^{14}C analyses for 1-phenylcyclopentene-x-^{14}C and 1-chlorocyclopentene-1-^{14}C are summarized in Fig. 1. Clearly, the reaction of phenyllithium with 1-chlorocyclopentene-1-^{14}C proceeds with rearrangement, and the extent of formation of 1-phenylcyclopentene-1-^{14}C is almost exactly that which would be expected for cyclopentyne (I) as an intermediate. The 14.9% of 1-phenylcyclopentene-5-^{14}C formed in the reaction most probably arises from a phenyllithium-induced allylic rearrangement of the double bond of the first-formed 1-phenylcyclopentene-2-^{14}C (III). The starting chloride, 1-chlorocyclopentene-1-^{14}C, had 97.3% of the ^{14}C in the 1-position.

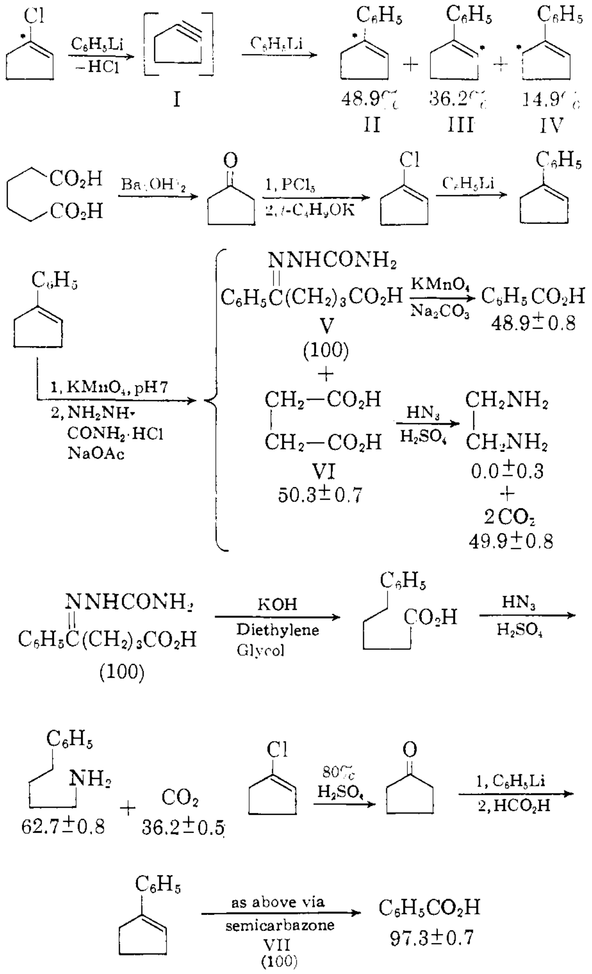

Fig. 1.—Degradative schemes for 1-phenylcyclopentene-x-^{14}C and 1-chlorocyclopentene-1-^{14}C. Specific activities for key compounds: 5-phenyl-5-oxopentanoic-x-^{14}C acid semicarbazone (V), 2.331 ± 0.002 μc./mmole; succinic-x-^{14}C acid, diluted (VI), 0.470 ± 0.002 μc./mmole; 5-phenyl-5-oxopentanoic-5-^{14}C acid semicarbazone, diluted (VII), 1.150 ± 0.004 μc./mmole. The figures under the formulas represent the found percentages of ^{14}C content relative to the corresponding key compounds from which they were derived.

Our attempts to extend this type of study to halides with still smaller rings so far have been unsuccessful. 1-Bromocyclobutene does indeed react with phenyllithium, but the only reaction products that have been isolated are phenylacetylene and cyclobutene. The mechanism of the unusual fragmentation reaction that affords phenylacetylene is not yet known. Efforts to induce substitution by way of the elimination-addition

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(1) Supported in part by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the Donors of this Fund.

(2) (a) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, THIS JOURNAL, **75**, 3290 (1953); (b) J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and D. A. Semenow, *ibid.*, **78**, 601 (1956); (c) E. F. Jenny and J. D. Roberts, *Helv. chim. acta*, **38**, 1248 (1955).

(3) *Cf.* the recent review of R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(4) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **1**, 343 (1957).

(5) A. E. Favorskii, *J. Gen. Chem.* (*U. S. S. R.*), **6**, 720 (1936).

(6) G. Wittig, A. Krebs and R. Pohlke, *Angew. Chem.*, **72**, 324 (1960).

(7) Supplied by Merck and Company, Limited.

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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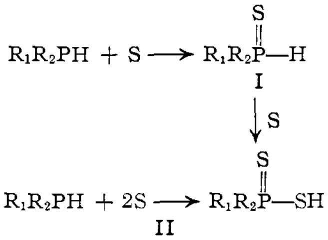
SECONDARY PHOSPHINE SULFIDES

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.

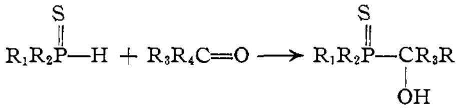


$$\begin{array}{c} R_1R_2PH + S \longrightarrow R_1R_2\overset{S}{\overset{\|}{P}}{-}H \\ \text{I} \\ \big\downarrow S \\ R_1R_2PH + 2S \longrightarrow R_1R_2\overset{S}{\overset{\|}{P}}{-}SH \\ \text{II} \end{array}$$

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.

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(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]

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(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.