Iodine oxidation of *o*-benzenedithiol reportedly yields a disulfide "$C_6H_4S_2$,"[3] but the product "was insoluble in ordinary organic solvents" and evidently was polymeric. At high dilution, we have obtained I and have established its identity by molecular weights (cryoscopic, ebullioscopic, x-ray), analysis, and absence of thiol.

o-Benzenedithiol[4] (12.50 g.) in 2.5 l. of benzene was added (68 hr.) with stirring under nitrogen to iodine (24.00 g.) in benzene (7.5 l.)-water (1 l.). Evaporation[5] of the mixture to 3 l. gave crop A (2.85 g., largely insoluble in molten camphor).

Concentration of the washed (aqueous bisulfite, water) and dried filtrate to 600 ml. gave 2.10 g. (17%) of crop B. Molecular weights of B were concentration-dependent; extrapolation to zero concentration gave 288 (Rast, camphor)[6] and 340 (ebullioscopic,[7] carbon disulfide); calcd., 280.4. When heated for 10 min. at 180° or for 12 hr. near 146°, I became insoluble in camphor; in contrast, it had a molecular weight (Rast) of 313–351 after 1–12 hr. at 120° and of 311 after irradiation for 1 hr. with ultraviolet light. The possibility of a rather specific temperature for polymerization seems unlikely, since differential thermal analysis[8] showed endotherms only at *ca.* 216° (probably the m.p.) and at 380°. Crop B when recrystallized from benzene (73%), carbon disulfide (47%), and chloroform (68%) gave I as small lemon yellow prisms of ill-defined m.p. (immersion at 145° and heating at 6°/min. gave m.p. *ca.* 215–230°). (*Anal.* Calcd. for $C_{12}H_8S_4$: C, 51.39; H, 2.88; S, 45.74. Found: C, 51.58; H, 3.05; S, 45.90.)

Evaporation of the filtrate from B to 75 ml. gave 1.21 g. of crop C, mol. wt. 513 (Rast). Molecular weights of recrystallized A, B, and C by x-ray diffraction were 280.1, assuming two molecules per unit cell of 586.4 Å³.

Another oxidation gave crop B (7% yield, m.p. *ca.* 210–218°), mol. wt. 281.5 (x-ray); stability at *ca.* 25° for 21 months is evidenced by absence of apparent change in the x-ray pattern. Ebullioscopic molecular weights were 297 (chloroform, also carbon disulfide), 342 (benzene); 207 (benzene),[9] 192 (chloroform);[9] the Rast mol. wt. was 323. No infrared absorption characteristic of a thiol was seen. Feigl's test[10] was negative in dioxane, although 2-mercaptobenzothiazole gave a strong test at less than 1/300 the concentration. After 16 hr. in refluxing benzene, the molecular weight was 700, showing extensive polymerization.

All x-ray patterns are believed to represent only one substance. I showed no damage during x-ray studies, which are being continued.

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Received July 28, 1961

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[3] P. C. Guha and M. N. Chakladar, *Quart. J. Ind. Chem. Soc.*, **2**, 318 (1925).

[4] Prepared essentially according to W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926).

[5] All evaporations effected below 25°.

[6] In high concentration, I polymerized readily. As the last crystal melted, solid began appearing and did not melt at 40° higher.

[7] Micro apparatus developed and kindly loaned by Prof. M. T. Bush.

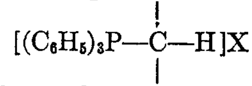
[8] Kindly performed by W. R. Adams, Redstone Division, Thiokol Chemical Corp.

[9] Clark Microanalytical Laboratory, Urbana, Ill.

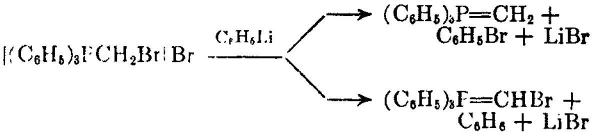
[10] F. Feigl, *Spot Tests. Vol. II. Organic Applications*, Elsevier Publishing Co., New York, 1954, p. 164.

The Action of Phenyllithium on Bromomethyl- and Iodomethyltriphenylphosphonium Halides[1]

Sir:

All known cases of triphenylphosphinealkylidene formation using organometallic reagents involve proton abstraction from the  $[(C_6H_5)_3P{-}\overset{|}{\underset{|}{C}}{-}H]X$ system.[2] Such behavior was observed by us also in the case of chloromethyltriphenylphosphonium bromide, only triphenylphosphinechloromethylene being formed when the phosphonium salt was treated with phenyllithium.[3]

We have investigated the reaction of bromomethyltriphenylphosphonium bromide[4] and iodomethyltriphenylphosphonium iodide[5] with phenyllithium in ether and subsequent Wittig reactions of the triphenylphosphinealkylidenes formed. In both cases a mixture of triphenylphosphinemethylene and the respective triphenylphosphinehalomethylene was formed. Thus the action of one molar equivalent of ethereal phenyllithium on bromomethyltriphenylphosphonium bromide gave an orange solution to which cyclohexanone was added subsequently. The usual procedure[2] for carrying out such Wittig reactions was followed,



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[1] Studies in Phosphinemethylene Chemistry, Part V. For Part IV see D. Seyferth and K. A. Brändle, *J. Am. Chem. Soc.*, **83**, 2055 (1961).

[2] For a review see U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

[3] D. Seyferth, S. O. Grim, and T. O. Read, *J. Am. Chem. Soc.*, **82**, 1510 (1960); *J. Am. Chem. Soc.*, **83**, 1617 (1961).

[4] Prepared by Dr. Erwin Hahn in these laboratories by the action of phosphorus tribromide in hot benzene on hydroxymethyltriphenylphosphonium bromide. An independent synthesis was reported recently by F. Ramirez *et al.*, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

and the following products were obtained in the yields given: benzene (59%); methylenecyclohexane (18%); bromobenzene (40%); and bromomethylenecyclohexane (46%).[6] Yields were determined *via* gas chromatography, using unreacted cyclohexanone present in the reaction mixture (determined independently as the 2,4-dinitrophenylhydrazone)[7] as a standard. The first three products were isolated also using preparative scale gas chromatography, and their identity was confirmed by comparison with authentic samples. A similar procedure using iodomethyltriphenylphosphonium iodide gave benzene (28%); methylenecyclohexane (30%); iodobenzene (70%); and iodomethylenecyclohexane[8] (26%). Similar results were obtained using other carbonyl compounds.

Thus, in contrast to the chloromethyltriphenylphosphonium salt, the bromomethyl- and iodomethyltriphenylphosphonium halides are attacked at the C—X bond as well as at the C—H bond by phenyllithium. The data presented show the C—X/C—H reaction ratio to be considerably greater for the iodomethylphosphonium halide. These results are in line with the known relative reactivity of carbon-halogen links toward organolithium reagents: C—Cl < C—Br < C—I.[9]

At present, this is the only Wittig-type procedure available as a general synthesis of vinylic bromides and iodides. Attempts are in progress to define conditions which will eliminate or at least minimize attack at the C—Br and C—I links in the bromomethyl- and iodomethylphosphonium salts. Details of these and other related experiments will be given at a later date.

Acknowledgment. The authors are grateful to the U. S. Army Research Office (Durham) for support of this work.

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Received September 15, 1961

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[5] Prepared by the reaction of methylene iodide and triphenylphosphine in warm benzene.

[6] n_D^{26} 1.5130. *Anal.* Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 48.29; H, 6.24.

[7] H. A. Iddles, A. W. Low, B. D. Rosen, and R. T. Hart, *Anal. Chem.*, **11**, 102 (1939).

[8] n_D^{25} 1.5623. *Anal.* Calcd. for $C_7H_{11}I$: C, 37.86; H, 4.99; I, 57.15. Found: C, 37.93; H, 5.20; I, 56.99.

[9] R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 342 (1951).