Properties and Reactions of Mesomeric Phosphonium Salts[1]

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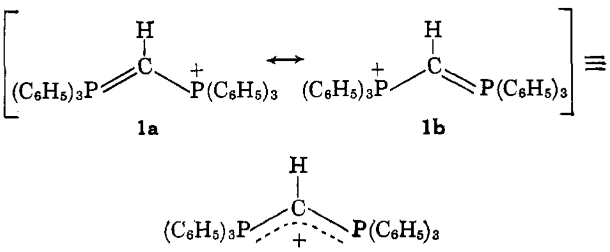
The triphenylphosphonium methylenetriphenylphosphorane cation (**1**) has been shown to be mesomeric. A number of salts possessing this stable cation have been synthesized, including the inner salt triphenylphosphoniumtriphenylboronyl methylenetriphenylphosphorane (**11**). The photochromism of triphenylphosphonium methylenetriphenylphosphorane tetraphenylboron (**12**) is described.

Recent investigations[2-4] of the reaction of triphenylphosphine with methylene bromide have led to the discovery of stable salts possessing the triphenylphosphonium methylenetriphenylphosphorane cation (**1a–c**).


1a **1b** **1c**

A number of new salts of this type have been prepared and the previously assumed mesomeric nature of the cation has been confirmed.

The essential precursor in the synthesis work was methylenebis(triphenylphosphonium bromide) (**2**) which was prepared by the reaction of triphenylphosphine with methylene bromide or bromomethyltriphenylphosphonium bromide (**3**) in molten triphenylphosphate. The corresponding diphosphonium chloride (**4**) and iodide (**5**) could then be prepared by metathesis reactions of **2**. These acidic salts were easily dehydrohalogenated with aqueous bases or *n*-butyllithium in hexane to produce triphenylphosphonium methylenetriphenylphosphorane salts. Triphenylphosphonium methylenetriphenylphosphorane chloride (**7**) was also prepared by the reaction of hexaphenylcarbodiphosphorane[2,5] (**8**) with hydrochloric acid. Metathesis of triphenylphosphonium methylenetriphenylphosphorane bromide (**6**) gave an alternate route to the iodide (**9**). The bromide (**6**) and chloride (**7**) formed stable complexes with ferric chloride. The iodide (**9**) gave a triiodide complex (**10**) on reaction with iodine. Scheme I summarizes these reaction paths.

Both physical and chemical evidence indicate that the triphenylphosphonium methylenetriphenylphosphorane cation is better represented by the symmetrical mesomeric structure **1c** than by an ylide form. The phosphorus atoms in the cation were shown to be equivalent by the presence of a single P^{31} n.m.r. absorption (Table I). Additionally, the single, nonaromatic proton absorption appeared as a triplet, the nature of which indicated that the phosphorus environments were identical. The stability suggested by the mesomeric structure **1c** was reflected in the relative inertness of the cation towards reaction with hot aqueous carbonate, benzyl bromide, or acetone.

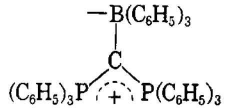
Table I

N.m.r. Spectral Data

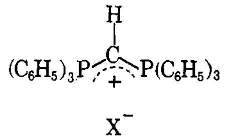
Compound	Chemical shifts (p.p.m.)[a]			
		H^1		
	P^{31}	Aromatic	Nonaromatic	B^{11}
2	−18.4[b]	7.3–8.2 (m)[c,d]	6.75 (t)[e]	
3	−24.0	7.8–8.8 (m)	6.22 (d)	
6	−21.2	7.7–8.2 (m)	2.00 (t)	
9	−21.1	7.8–8.2 (m)	2.00 (t)	
11	−20.9	7.5–8.1 (m) 7.0–7.4 (m)		19.0[f]
12	−20.8	7.1–8.1 (m)	1.80 (t)	25.0

[a] Reference standards were 85% phosphoric acid, tetramethyl silane, and triethylborate. [b] P^{31} spectra of **3**, **6**, **9**, and **12** in chloroform (10–20 wt. %), **2** in 80% methanol–water (10 wt. %), and **11** in methylene chloride (11 wt. %). [c] H^1 spectra of **3**, **6**, **9**, and **12** (5–10 wt. %) and **11** (saturated solution) in deuteriochloroform, **2** in methanol (20 wt. %). [d] m = multiplet, t = triplet, and d = doublet. [e] Nonaromatic, J_{HP} = 16 c.p.s. for **2**, 6 c.p.s. for **3**, **6**, **9**, and **12**. [f] B^{11} spectrum of **11** in methylene chloride (13 wt. %), **12** in chloroform (17 wt. %).

Replacement of the single nonaromatic proton in **1c** by the triphenyl boron group resulted in the formation of the mesomeric inner salt[6] triphenylphosphoniumtriphenylboronyl methylenetriphenylphosphorane (**11**).


11

Compound **11** was synthesized by the addition of triphenylboron to hexaphenylcarbodiphosphorane (**8**). Triphenylphosphonium methylenetriphenylphosphorane tetraphenylboron (**12**), fluoborate (**13**), and borohydride[4] (**14**) were prepared from **6** by metathesis reactions for comparison with the inner salt (**11**).


12, X = $B(C_6H_5)_4$
13, X = BF_4
14, X = BH_4

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[1] This work was sponsored in part by the Office of Naval Research, 1961.

[2] F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

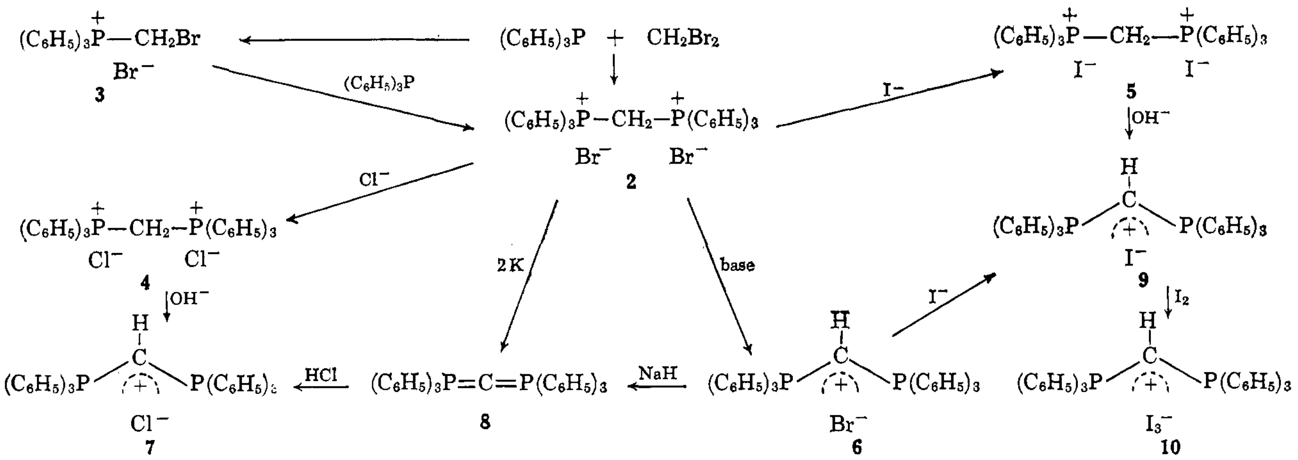
[3] C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *ibid.*, **84**, 4349 (1962).

[4] J. S. Driscoll and C. N. Matthews, *Chem. Ind.* (London), 1282 (1963).

[5] Hexaphenylcarbodiphosphorane (**8**) is triboluminescent. When crystals of **8** are crushed in a dry, nitrogen atmosphere, a green-white light flash is emitted from the compound.

[6] The synthesis of the nonmesomeric inner salt $(C_6H_5)_3\overset{+}{P}-CH_2-\overset{-}{B}(C_6H_5)_3$ has been reported by D. Seyferth and S. O. Grim [*J. Am. Chem. Soc.*, **83**, 1613 (1961)].

SCHEME I



The inner salt (**11**) had a phosphorus n.m.r. spectrum characteristic of the mesomeric cation. The nonaromatic absorption, corresponding to the lone proton on the central carbon atom of **12**, was not observed in the proton spectrum of **11**. The B^{11} absorption of the inner salt indicated that an unsymmetrical tetravalent boron atom was covalently bonded to the mesomeric phosphonium system. The very broad B^{11} absorption of **11** (half-peak width 5 p.p.m.) contrasted markedly with the sharp B^{11} absorption of **12** (half-peak width 0.9 p.p.m.). The broadening is probably due to quadruple relaxation effects present in **11**, but absent in **12** with its symmetrical boron anion.[7]

During the structural studies on the boron-containing salts, it was observed that the tetraphenylboron derivative (**12**) was markedly photochromic. The white, crystalline solid became orange-red when exposed to an ultraviolet lamp, sunlight, or an incandescent bulb, the rate of change being most rapid with the first source and slowest with the last. As has been found in numerous other photochromic systems, **12** exhibited a color change only in the solid state.[8]

The appearance of color was accompanied by the formation of a radical species with an electron paramagnetic resonance (e.p.r.) g value of 2.0065. No hyperfine structure was present in the solid state e.p.r. spectrum (Fig. 1).

The white and colored forms of **12** had identical infrared spectra. The ultraviolet spectra of the two forms were quantitatively the same.

Crystal form appeared to be important in the photochromic phenomenon, since samples of **12** which were melted and resolidified were not photochromic. Although no change was observed in the infrared spectrum of a sample of **12** after melting, a 2° increase in the melting point of the resolidified sample indicated a possible polymorphic change.

Upon removal of the radiation source, the sample color faded from orange-red to yellow over a 24-hr. period. While samples faded at approximately the same rate in air or nitrogen, evacuated samples faded at a much slower rate. Relative to the rate at room temperature, the decoloration was very rapid at 190° and greatly slowed at −70°.

While **12** showed the most dramatic light-induced color change, compounds **9**, **14**, **2**, **11**, **4**, **3**, **5**, **13**, and **7** were also photochromic. They are listed in the order of decreasing rate of color formation. Compounds **6** and **10** had no apparent photochromic properties.

Experimental[9]

Materials.—n-Butyllithium (Foote Mineral Co.) was used as a 15% solution in hexane. Sodium hydride (Metal Hydrides) was used as a 50% dispersion in mineral oil. Triphenylboron (Aldrich) and nitrogen gas were used as obtained. Diglyme (dimethyl ether of diethylene glycol) was distilled from sodium hydride directly into reaction vessels.

Spectra.—Infrared spectra were determined in potassium bromide pellets with a Perkin-Elmer Model 21 spectrophotometer. The spectra of the methylenebis(triphenylphosphonium halides) were essentially identical. Characteristic absorption bands occurred at 2600 (m),[10] 1105 (s), and 815 (s) cm.$^{-1}$. Absorptions characteristic of triphenylphosphonium methylenetriphenylphosphorane compounds were a triplet at 1227 (s), 1182 (m), and 1157 (w), a doublet at 1100 (s) and 1073 (w), and a triplet at 1027 (w), 1008 (m), and 989 (s) cm.$^{-1}$.

Ultraviolet spectra were determined in solution with a Cary Model 14A recording spectrophotometer.

Proton n.m.r. spectra were determined with a Varian Model A-60 spectrometer at 60 Mc. P^{31} and B^{11} spectra were determined with a Varian Model V-4300-2 high resolution n.m.r. spectrometer at 16.2 and 12.8 Mc., respectively.

E.p.r. spectra were determined with a Varian 4500 spectrometer at 9.525 kMc. The magnetic field sweep covered the range 50–4000 gauss. The resonance of diphenylpicrylhydrazyl was observed at 3396 gauss.

Irradiation Experiments.—The sample prepared for the e.p.r. study was irradiated in a quartz tube with a Hanovia UVS-250 lamp at a distance of 15 cm.

The qualitative photochromism studies were carried out in a horizontal, water-cooled (21°), quartz reflux condenser with a Hanovia lamp, Model 30600, at a distance of 4 cm. in a nitrogen atmosphere. There was no apparent difference between quartz and Pyrex containers with respect to the rate of color formation or fading.

Bromomethyltriphenylphosphonium Bromide (3).—A stirred solution of triphenylphosphine (1049 g., 4.0 moles), methylene bromide (347.8 g., 2.0 moles), and toluene (2000 ml.) was heated at reflux for 24 hr. under nitrogen. The resulting suspension was filtered and the solid was dried at 80° (20 mm.) to yield 572.1 g. of tan crystals, m.p. 221–237°. The product was dissolved in methanol, reprecipitated with ethyl acetate, filtered, and washed with ether to give 335 g. (38%) of white needles, m.p. 236.5–241.5°, lit.[2] m.p. 240–241°, $\lambda_{\max}^{\mathrm{EtOH}}$ 228 mμ (ϵ 27,200).

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[7] N^{14} quadrupole broadening in unsymmetrical ammonium compounds has been demonstrated by R. A. Ogg and J. D. Ray [*J. Chem. Phys.*, **26**, 1339 (1957)].

[8] G. H. Brown and W. G. Shaw, *Rev. Pure Appl. Chem.*, **11**, 2 (1961).

[9] Melting points are corrected. Microanalyses were performed by Schwarzkopf Laboratory, Woodside, N. Y.

[10] The letters s, m, and w refer to strong, medium, and weak, respectively.

The infrared spectrum of the product was identical with that of an authentic sample of **3** prepared by the method of Ramirez.[2]

Methylenebis(triphenylphosphonium bromide) (2). Method A.—Methylene bromide (17.4 g., 0.1 mole) was added to a stirred solution of triphenylphosphine (52.4 g., 0.2 mole) in 125 g. of triphenyl phosphate at 86° in an atmosphere of nitrogen. The ensuing mixture was heated at 98–110° for 22.5 hr. and then at 145–150° for an additional 5 hr. Benzene (200 ml.) was added to the stirred slurry at 80–100°, and the mixture was filtered to yield a tan solid. After a benzene wash, the solid (62.5 g.) was twice taken up in warm methanol, reprecipitated with ethyl acetate, and dried at 80° (20 mm.) to yield white needles of **2** monohydrate (26.5 g., 36%), m.p. 311.5–314.5°.

Anal. Calcd. for $C_{37}H_{32}Br_2P_2 \cdot H_2O$: H_2O, 2.51. Found: H_2O, 2.36 (Karl Fischer).

The infrared spectrum of the hydrate was identical with that of an anhydrous reference sample prepared by the method of Ramirez[2] except that an additional band was present at 3400 cm.$^{-1}$ (H_2O). The reference sample, dried at 100° (0.1 mm.), m.p. 310–310.5°, lit.[2] m.p. 308–310°, had the correct elemental analysis. The monohydrate was dehydrated at 100° (0.1 mm.). Small amounts of impurities apparently cause large variations in the melting point of **2**.

Method B.—Triphenylphosphine (5.24 g., 20 mmoles), bromomethyltriphenylphosphonium bromide (8.72 g., 20 mmoles), and 25.0 g. of triphenyl phosphate were stirred under nitrogen at 135–140° for 5 hr. The mixture, which was cooled to room temperature, stirred with 80 ml. of benzene, and allowed to stand for 18 hr., gave 12.6 g. of a hygroscopic solid. Upon solution in methanol and reprecipitation with ethyl acetate, 6.18 g. (43%) of **2** monohydrate, m.p. 303–308°, was obtained. The product was identified by its infrared spectrum.

Methylenebis(triphenylphosphonium chloride) Monohydrate (4).—A chloride ion-exchange resin (Rohm and Haas Amberlist-XN-1002, 50 g.) was placed in a 21.6 × 2.5 cm. column. It was treated successively with 200 ml. of methanol, 21 g. of HCl in 140 ml. of methanol, and 300 ml. of methanol. A solution of 3.58 g. (50 mmoles) of methylenebis(triphenylphosphonium bromide) in 20 ml. of methanol was placed on the column and eluted with 300 ml. of methanol. Removal of the solvent gave a viscous oil which after trituration with ethyl acetate yielded a solid, 2.64 g., m.p. 232–239°. This material was dissolved in 10 ml. of methanol and reprecipitated with 70 ml. of ethyl acetate. The product was dried at 55° (0.1 mm.) to give 2.15 g. (68%) of the white monohydrate, m.p. 239.5–246° (shrinking at 224°). Drying at 100° (0.1 mm.) caused dehydrochlorination.

Anal. Calcd. for $C_{37}H_{32}Cl_2P_2 \cdot H_2O$: C, 70.82; H, 5.46; Cl, (total), 11.30; Cl (ionic), 11.30; P, 9.87; H_2O, 2.89. Found: C, 70.43; H, 6.39; Cl (total), 11.27; Cl (ionic), 11.36; P, 9.49; H_2O, 2.29.

Methylenebis(triphenylphosphonium iodide) (5).—A solution of methylenebis(triphenylphosphonium bromide) (3.49 g., 5 mmoles) in deaerated methanol (30 ml.) was added to a stirred solution of potassium iodide (8.3 g., 50 mmoles) in deaerated methanol (80 ml.). Crystals began to separate immediately. The mixture was stirred for 30 min. and filtered to yield 3.85 g. of product, m.p. 304–311° dec. The solid was recrystallized from methanol under nitrogen to yield 2.27 g. (58%) of pale yellow needles, m.p. 301–307° dec. Two further recrystallizations from methanol under nitrogen raised the melting point to 306–311° dec.

Anal. Calcd. for $C_{37}H_{32}I_2P_2$: C, 55.44; H, 4.05; I, 32.48; P, 7.82. Found: C, 55.48; H, 4.25; I, 32.43; P, 7.85.

Hexaphenylcarbodiphosphorane (8).—Upon addition of 2.0 g. (3 mmoles) of triphenylphosphonium methylenetriphenylphosphorane bromide to a mixture of sodium hydride in mineral oil (0.15 g., 3 mmoles) and diglyme (50 ml.), slow gas evolution resulted. The temperature was raised to reflux over a 20-min. period, during which time the suspension color changed from light green to yellow. The reaction was stopped after 30 min., when gas evolution had ceased. The hot solution was filtered in a dry nitrogen atmosphere. A small amount of starting material precipitated from the yellow filtrates and was filtered. The filtrates were evaporated *in vacuo* to a moist solid. Nitrogen was reintroduced into the apparatus. The yellow solid was washed with 50 ml. of anhydrous ether to yield 0.67 g. (42%) of hexaphenylcarbodiphosphorane, m.p. 196–203°. This material was similar to a reference sample (m.p. 198–201°) prepared using potassium metal as the base, lit.[2] m.p. 208–210°.

Triphenylphosphonium Methylenetriphenylphosphorane Bromide (6).—To a stirred suspension of 17.5 g. (25 mmoles) of methylenebis(triphenylphosphonium bromide) in 600 ml. of anhydrous ether under a nitrogen atmosphere was slowly added 15.0 ml. (25 mmoles) of *n*-butyllithium in hexane. A buff-colored suspension formed, becoming creamy white after 2 hr. of stirring. A white solid (17 g.) was filtered from the colorless ether filtrate and was extracted several times with a mixture of methylene chloride and water. The combined methylene chloride portions were washed with water and dried over anhydrous magnesium sulfate, to give a pale yellow solution. Evaporation yielded a white solid (13 g.) which was recrystallized twice from methylene chloride–ethyl acetate to give 10 g. (65%) of fine white crystals, m.p. 272–274°, λ_{max}^{EtOH} 268 mμ (ε 7900). The infrared spectrum of this compound was identical with that of a reference sample[2,3] prepared by the use of aqueous sodium carbonate as base.

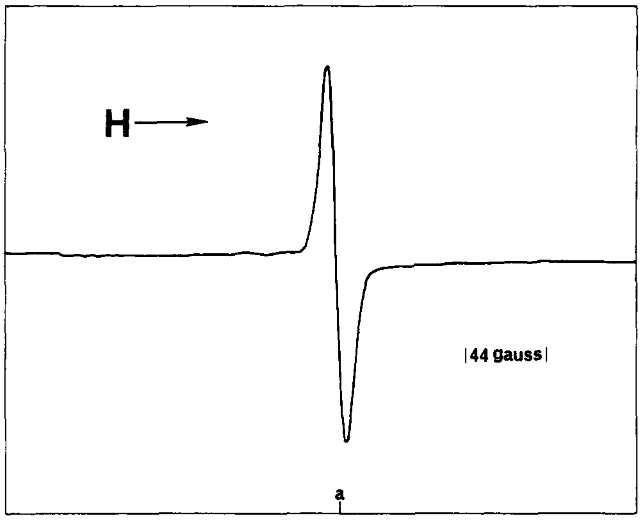

Fig. 1.—E.p.r. spectrum of triphenylphosphonium methylenetriphenylphosphorane tetraphenylboron (**12**) after ultraviolet irradiation; a, diphenylpicrylhydrazyl absorption position.

Triphenylphosphonium Methylenetriphenylphosphorane Bromide–Ferric Chloride Complex.—To a suspension of anhydrous ferric chloride (3.12 g., 19.3 mmoles) in 400 ml. of methylene chloride was added 11.9 g. (19.3 mmoles) of triphenylphosphonium methylenetriphenylphosphorane bromide in a dry nitrogen atmosphere. The mixture was stirred for 18 hr. and filtered to remove a small amount of orange solid. The filtrate was evaporated *in vacuo* to give a red-gold solid, m.p. 220–224°. The solid was extracted with 25 ml. of absolute ethanol, filtered, and dried (70° at 15 mm.) to yield 13.8 g. (91%) of the product, m.p. 228–229°. Recrystallization of the complex from ethanol gave red-gold needles, m.p. 230–230.5°.

Anal. Calcd. for $C_{37}H_{31}BrCl_3FeP_2$: C, 56.99; H, 4.01; Br, 10.25; Cl, 13.64; Fe, 7.16; P, 7.94. Found: C, 57.23; H, 4.34; Br, 10.19; Cl, 13.89; Fe, 6.60; P, 8.12.

Triphenylphosphonium Methylenetriphenylphosphorane Chloride (7). Method A.—Small pieces of potassium (1.75 g., 45 mmoles) were added to 100 ml. of dry diglyme and the mixture was heated to 150°. Methylenebis(triphenylphosphonium bromide) (14.0 g., 20 mmoles) was quickly added. The solution slowly turned orange during a 1-hr. reflux period. The solution was filtered while hot in a dry, nitrogen atmosphere. Hydrochloric acid (0.1 *N*, 150 ml.) was added to the orange filtrate containing hexaphenylcarbodiphosphorane. An immediate decoloration of the solution took place. The colorless solution was extracted with 100 ml. of chloroform. The chloroform layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to yield 6.05 g. of a white solid, m.p. 224–230°. The solid was extracted with 150 ml. of hot ethyl acetate, washed with 100 ml. of ether, and extracted with 100 ml. of hot benzene to yield 3.9 g. of white solid, m.p. 224–235° (positive Beilstein test). This material was thoroughly mixed with 100 ml. of water, filtered, and dried to yield 1.03 g. (14%) of the white product, m.p. 267–272°. Recrystallization from methylene chloride–ether raised the melting point to 274–276°.

Anal. Calcd. for $C_{37}H_{31}ClP_2$: C, 77.55; H, 5.45; Cl, 6.91; P, 10.89. Found: C, 77.69; H, 5.48; Cl, 6.81; P, 10.84.

Method B.—To a stirred solution of 1.38 g. (13 mmoles) of sodium carbonate in 15 ml. of water, was added 1.38 g. (2.3 mmoles) of methylenebis (triphenylphosphonium chloride) monohydrate. The suspension was refluxed for 2.5 hr., and the oily mixture cooled to room temperature. The resulting crystals were filtered and washed with water to give 1.24 g. of crude product, m.p. 266–268°. Reprecipitation from methylene chloride–hexane gave raised m.p. 271.5–273° and yielded 0.96 g. (75%) of a white solid which had an infrared spectrum identical with that of the product of method A. A mixture melting point showed no depression.

Triphenylphosphonium Methylenetriphenylphosphorane Chloride–Ferric Chloride Complex.[11] **Method A.**—A mixture of methylene chloride (85.0 g., 1.0 mole) and triphenylphosphine (262.0 g., 1.0 mole) was heated with agitation for 6 hr. at 160° in a 316 stainless steel pressure vessel. After cooling, the viscous green material was partially extracted from the bomb with 850 ml. of hot methanol to give a suspension of red-gold needles in a green solution. The residual green tar was completely removed from the bomb by the addition of 360 ml. of hot methylene chloride to yield a green solution. Evaporation of the solution gave a mixture of red-gold crystals and a green solid. The green solid was extracted from the red-gold crystals with six 50-ml. portions of methanol. The two crops of red-gold crystals were combined yielding 51.9 g. (70 mmoles) of the complex, m.p. 238–239°. Recrystallization from methanol did not change the melting point.

Anal. Calcd. for $C_{37}H_{31}Cl_4FeP_2$: C, 60.44; H, 4.25; Cl, 19.29; Fe, 6.92; P, 8.42. Found: C, 60.77; H, 4.43; Cl, 19.10; Fe, 7.06; P, 8.27.

Method B.—Ferric chloride was stirred with triphenylphosphonium methylenetriphenylphosphorane chloride in methylene chloride. Filtration and evaporation of the solvent gave light gold-colored crystals. Recrystallization from absolute ethanol gave gold-colored crystals, m.p. 237.5–238.5°, which gave no melting point depression when mixed with the material from method A.

Triphenylphosphonium Methylenetriphenylphosphorane Iodide (**9**). **Method A.**—To a solution of 8.50 g. (51.2 mmoles) of potassium iodide in 125 ml. of absolute methanol was added 3.00 g. (4.87 mmoles) of triphenylphosphonium methylenetriphenylphosphorane bromide.

The solution was refluxed for 2 hr. and cooled to room temperature. Water (2.5 l.) was added and the resulting white precipitate was filtered in the dark. After drying at 25° (0.5 mm.), 3.1 g. (96%) of light yellow solid, m.p. 252–254°, was obtained. This compound showed a positive Beilstein test and a depressed melting point (250–259°) with starting material. Reprecipitation from methylene chloride–hexane gave light yellow crystals, m.p. 253–254°, λ_{max}^{EtOH} 268 mμ (ε 7775).

Anal. Calcd. for $C_{37}H_{31}IP_2$: C, 66.87; H, 4.70; I, 19.10; P, 9.32. Found: C, 67.19; H, 4.69; I, 18.97; P, 9.41.

Method B.—Methylenebis(triphenylphosphonium iodide) (0.93 g., 1.2 mmoles) was added to a solution of sodium carbonate (0.71 g., 6.7 mmoles) in 10 ml. of water and the suspension was stirred under reflux for 3 hr. The oily mixture was cooled to room temperature. Filtration yielded 0.72 g. of pale yellow solid, m.p. 250–254°. Recrystallization from methanol gave 0.36 g. (45%) of pale yellow crystals, m.p. 252–255°. A mixture melting point with an authentic sample was not depressed. The infrared spectrum of the sample was identical with the product of method A.

Triphenylphosphonium Methylenetriphenylphosphorane Triiodide (**10**).—A solution of 12.0 g. (18.1 mmoles) of triphenylphosphonium methylenetriphenylphosphorane iodide in 150 ml. of chloroform was added dropwise to a stirred solution of 4.59 g. (18.1 mmoles) of iodine in 450 ml. of chloroform during a 12-min. period. The reaction mixture gradually changed from a purple to a dark brown color. The solution was stirred for an additional 30 min., then evaporated *in vacuo* to yield 15.4 g. of brown solid. The solid was extracted with 500 ml. of hot methanol, leaving 12.9 g. (77%), of brown product, m.p. (color change at 174°) 193–196°. Recrystallization from methanol gave brown needles, m.p. 199–199.5°.

Anal. Calcd. for $C_{37}H_{31}I_3P_2$: C, 48.39; H, 3.40; I, 41.46; P, 6.75. Found: C, 48.47; H, 3.56; I, 41.38; P, 7.01.

Triphenylphosphoniumtriphenylboronyl Methylenetriphenylphosphorane (**11**).—Hexaphenylcarbodiphosphorane was prepared from triphenylphosphonium methylenetriphenylphosphorane bromide (17.3 g., 28 mmoles) and 1.40 g. (36 mmoles) of potassium in 150 ml. of dry diglyme.[2] The yellow-orange solution was filtered while hot in a dry nitrogen atmosphere. To the stirred filtrates at reflux (under nitrogen) was slowly added a solution of 7.5 g. (32 mmoles) of triphenylboron in 150 ml. of dry diglyme. During the 4.5-hr. reflux period, the orange turbid solution became brown. The solvent was removed at reduced pressure, 5 ml. of methanol was added to the residue, and the resulting buff-colored solid was filtered. After extracting this material with boiling ether for 30 min., 3.2 g. (17%) of the inner salt, m.p. 241–248° (negative Beilstein test), was obtained. Recrystallization in the presence of activated charcoal from methylene chloride–ethyl acetate gave off-white crystals, m.p. 254–256°, $\lambda_{max}^{CH_3CN}$ 267 mμ (ε 9440).

Anal. Calcd. for $C_{55}H_{45}BP_2$: C, 84.83; H, 5.82; B, 1.39; P, 7.96; mol. wt., 779. Found: C, 85.12; H, 5.88; B, 1.46; P, 7.42; 7.79; mol. wt., 725.

Triphenylphosphonium Methylenetriphenylphosphorane Tetraphenylboron (**12**).—To 175 ml. of hot distilled water was added 12.7 g. (20.6 mmoles) of triphenylphosphonium methylenetriphenylphosphorane bromide and 7.0 g. (20.5 mmoles) of sodium tetraphenylboron. The suspension was refluxed for 4 hr., cooled to room temperature, and filtered. The resulting white powder was dissolved in 150 ml. of methylene chloride and the solution was dried over magnesium sulfate. Removal of the solvent under reduced pressure gave a white solid which was dried at 25° (0.1 mm.) to yield 18.4 g. of product, m.p. 200–205°. One recrystallization from acetone–ether in the presence of activated charcoal gave 13.6 g. (78%) of white crystals, m.p. 205–208°, $\lambda_{max}^{CH_3CN}$ 267 mμ (ε 10,800).

Anal. Calcd. for $C_{61}H_{51}BP_2$: C, 85.50; H, 6.00; B, 1.26; P, 7.23. Found: C, 85.33; H, 6.09; B, 0.97; P, 7.40.

Triphenylphosphonium Methylenetriphenylphosphorane Fluoborate (**13**). **Method A.**[12]—To a stirred mixture of 8.76 g. (12.5 mmoles) of methylenebis(triphenylphosphonium bromide) in 300 ml. of dry ether under a nitrogen atmosphere at 0°, was slowly added 7.5 ml. of *n*-butyllithium in hexane (12.5 mmoles). Boron trifluoride etherate (36.0 g., 250 mmoles) was added dropwise to the suspension. An additional 12.5 mmoles of *n*-butyllithium was then added, and the white suspension was warmed to room temperature and stirred for an additional 3 hr. The mixture yielded 10.5 g. of white solid which was dissolved in 500 ml. of a 2:3 methylene chloride–water mixture. The organic layer was separated and dried over magnesium sulfate. Evaporation of the filtrates *in vacuo* gave white crystals (6.5 g. 83%). Recrystallization from absolute ethanol gave white needles, m.p. 259.5–260.5°, λ_{max}^{EtOH} 267 mμ (ε 7360).

Anal. Calcd. for $C_{37}H_{31}BF_4P_2$: C, 71.17; H, 5.00; B, 1.73; F, 12.17; P, 9.92. Found: C, 71.52; H, 5.55; B, 1.51; F, 11.98; P, 10.04.

Method B.—To a solution of 3.56 g. (32.4 mmoles) of sodium fluoroborate in 75 ml. of water was added 2.00 g. (3.24 mmoles) of triphenylphosphonium methylenetriphenylphosphorane bromide. The mixture was refluxed for 65 min. and filtered hot. The resulting solid, 1.94 g. (96%), m.p. 242.5–250°, showed a negative Beilstein test and a melting point depression with starting material. Recrystallization from absolute ethanol produced white needles, m.p. 256–257°, which showed no melting point depression on admixture with the product from method A.

Triphenylphosphonium Methylenetriphenylphosphorane Borohydride (**14**).—Triphenylphosphonium methylenetriphenylphosphorane bromide (10.0 g., 16 mmoles) was added to a stirred, freshly prepared solution of 6.35 g. (170 mmoles) of sodium borohydride in 500 ml. of methanol. After 5 min., the clear solution was added to 3 l. of distilled water, resulting in the precipitation of the product. The suspension was stirred for 5 min. and filtered. The white solid was washed with 250 ml. of distilled water and dried at 80° (15 mm.). The white powder,

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[11] The acidic diphosphonium salt (4-anhydrous), a proposed intermediate in this reaction, apparently attacked the stainless steel reactor to produce ferric chloride and **7** which combined to form a complex.

[12] This unexpected synthesis of **13** occurred during an attempt to prepare the boron trifluoride analog of **11**.

8.46 g. (96%), m.p. 210–211° dec., was recrystallized from ethanol–ether to give white needles, m.p. 211–211.5° dec., $\lambda_{\max}^{\text{EtOH}}$ 267 mμ (ε 7840).

Anal. Calcd. for $C_{37}H_{35}BP_2$: C, 80.44; H, 6.39; B, 1.96; P, 11.21. Found: C, 80.87; H, 6.34; B, 1.67; P, 11.26.

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Reactions of 3-Bromooxindoles. The Synthesis of 3-Methyleneoxindole[1]

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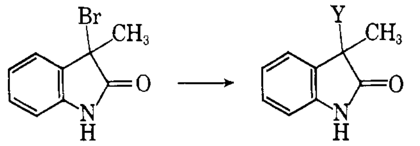
3-Alkyl-3-bromooxindoles underwent facile replacement of the halogen by nucleophiles, including alkoxide, hydroxide, and thiophenoxide ions, and piperidine. With 3-bromooxindole-3-propionic and butyric acids lactone formation took place in the presence of base, but oxindole-3-acetic acid underwent decarboxylation and dehydrobromination to 3-methyleneoxindole. The last compound readily underwent conjugate addition with thiophenol and amines. From hydrolysis of 3-bromooxindole-3-butyric acid in acidic media, the free dioxindole acid was obtained rather than the lactone. Some lactone was obtained from dioxindole-3-propionic acid, but again lactonization under acidic conditions did not take place readily. Attempts to hydrolyze 3-bromooxindole-3-acetic acid to dioxindole-3-acetic acid, under acidic conditions, were unsuccessful. The ultraviolet, infrared, and proton magnetic resonance spectra of a variety of oxindoles and dioxindoles are tabulated and discussed.

In a previous paper a convenient one-step synthesis of 3-bromooxindoles by reaction of the corresponding indoles with N-bromosuccinimide (NBS) was described.[2] The ready accessibility of the 3-bromooxindoles by this new method has led to a study of some aspects of their chemistry, with particular attention to the reactions of the 3-bromooxindole-3-alkanoic acids,[3] and some of the compounds derived therefrom.

Although the 3-bromooxindoles are stable crystalline compounds, the bromine, activated by the adjacent phenyl and carbonyl groups, is very reactive. A precipitate is formed with alcoholic silver nitrate within 3 sec. at room temperature, and replacement of the halogen by nucleophilic agents occurs with ease.[4] Substitution has been effected by nucleophiles of the oxygen, sulfur, and nitrogen series, as shown in eq. 1. 3-Methyldioxindole was also prepared in one over-all step from skatole by addition of sodium bicarbonate to the reaction mixture after formation of I, and treatment of 3-methyloxindole with bromine followed by hydrolysis *in situ* gave 5-bromo-3-methyldioxindole. Structures of the products (II) were confirmed by n.m.r., which showed in all cases a singlet of the proper intensity for the 3-methyl group (Table II). No evidence was found for the presence of the isomeric 3-methylene derivatives, such as 3-(phenylthiomethyl)oxindole (XIII), which could conceivably have been formed by elimination, followed by addition of the nucleophile to the resulting conjugated system (X). In the one case for which both isomers were available (IIc and XIII), they were readily distinguishable by n.m.r. and by the reactivity of isomer XIII towards base (see below).



(1)

I

IIa, Y = OH
b, Y = OCH_3
c, Y = SC_6H_5
d, Y = NC_5H_{10}

Intramolecular nucleophilic displacement by carboxylate ion in the side chain at the 3-position was also observed. In basic solution both 3-bromooxindole-3-propionic acid (IIIa) and 3-bromooxindole-3-butyric acid (IIIb) underwent ring closure to the corresponding lactones (IV). Reference has been made in the previous paper[2] to the direct conversion of indole-3-propionic acid to the lactone IVa by reaction with NBS in the presence of sodium bicarbonate and to the formation of the closely related lactone of α-acetamidodioxindole-3-propionic acid under similar conditions. Since basic conditions promote 3-bromination of an oxindole, reaction of an indole with NBS in a basic hydrolytic medium might serve as a general synthetic route to dioxindoles, similar to the reactions of hypochlorite and lysergic acid derivatives.[2,5,6]

In contrast to the facile lactonization effected by base, hydrolysis of the 3-bromooxindole-3-alkanoic acids (IIIa and IIIb) under acidic conditions, which repress ionization of the carboxyl group, led to the corresponding dioxindole-3-alkanoic acids (VI). Although some lactone was formed along with the dioxindole in the propionic acid case, dioxindole-3-butyric acid was the sole product (76% yield) from IIIb. The reluctance of the dioxindole acids to undergo ring closure was further demonstrated by the following reactions. The dioxindolebutyric acid (VIb) was recovered unchanged after (1) 1 hr. in refluxing 0.05 *M* hydrochloric acid, (2) 30 min. in refluxing glacial acetic acid, or (3) 1 hr. in acetic anhydride at 60°. Ring closure was effected by re-

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[1] Presented in part before the Organic Division of the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

[2] R. L. Hinman and C. P. Bauman, *J. Org. Chem.*, **29**, 1206 (1964).

[3] Other methods for preparing 3-bromooxindoles are mentioned in ref. 2. It should be noted in addition that replacement of the dioxindole hydroxyl by reagents such as thionyl chloride is apparently a satisfactory route to 3-halooxindoles [J. M. Bruce and F. K. Sutcliffe, *J. Chem. Soc.*, 4789 (1957); see also P. L. Julian, E. W. Meyer, and H. C. Printy "Heterocyclic Compounds," Vol. III, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1952, p. 247], which has not been used extensively.

[4] A few examples of hydrolysis of 3-halooxindoles have been reported, including the conversion of 3,3-dihalooxindoles to isatin derivatives [E. Fisher and O. Hess, *Ber.*, **17**, 559 (1884); A Michaelis, *ibid.*, **30**, 2811 (1897)] and replacement of the 3-halogen by alkoxide as reported by Bruce and Sutcliffe[3] for 3-chloro-3-phenyloxindole.

[5] F. Troxler and A. Hofmann, *Helv. Chim. Acta*, **42**, 793 (1959).

[6] The previous paper[2] should be consulted for a discussion of the effect of the medium on the mode of bromination of oxindoles.