[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Mercuration of Dialkyl Phosphonates. II. Bis-(dialkoxyphosphinyl)-mercury

BY DAVID L. VENEZKY AND ROBERT B. FOX

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A series of bis-(dialkoxyphosphinyl)-mercury esters has been prepared by the mercuration of dialkyl phosphonates with mercuric oxide.

It was shown recently that the mercuration of dialkyl phosphonates produces dialkoxyphosphinylmercuric salts.[1] The halides were prepared directly from the dialkyl phosphonates by reaction with an equimolar mixture of mercuric oxide and mercuric halide. A mechanism proposed for this reaction[2] was the slow reaction of the dialkyl phosphonate with mercuric oxide to form bis-(dialkoxyphosphinyl)-mercury, followed by the rapid disproportionation between bis-(dialkoxyphosphinyl)-mercury and the mercuric halide to yield the corresponding dialkoxyphosphinylmercuric salt. This

$$2(RO)_2P(O)H + HgO \xrightarrow{\text{slow}} [(RO)_2P(O)]_2Hg + H_2O$$

$$[(RO)_2P(O)]_2Hg + HgX_2 \xrightarrow{\text{fast}} 2(RO)_2P(O)HgX$$

mechanism is corroborated by the isolation of the intermediate bis-(dialkoxyphosphinyl)-mercury esters and by their reaction with mercuric halides to produce dialkoxyphosphinylmercuric salts.

The bis-(dialkoxyphosphinyl)-mercury esters were prepared by refluxing a benzene solution of the dialkyl phosphonate in the presence of mercuric oxide. To prevent the thermal decomposition of the product, the reflux temperature was maintained below 50° by heating the system under a reduced pressure of 200 mm. The water produced during the reaction was removed continuously by azeotropic distillation until no more water was collected. After removal of the solvent at reduced pressure, the viscous oil or solid residue was purified by recrystallization or chromatographic methods using several percolations through activated alumina. In place of benzene, cyclohexene may be used as the solvent. Diethyl ether, *n*-hexane or excess dialkyl phosphonate also may be used as the solvent without azeotropic removal of the water produced during the reaction. The mercuration is catalyzed by acids such as *p*-toluenesulfonic acid, whereas bases such as triethylamine have little effect on the rate of the reaction. When impure dialkyl phosphonate is used, the reaction is vigorous but can be inhibited by addition of base which probably neutralizes the acid present.

The bis-(dialkoxyphosphinyl)-mercury derivatives range from solids to viscous liquids (Table I). All of the esters appear to be somewhat hygroscopic. Those esters that are soluble in water are stable in aqueous solutions at room temperature for several weeks before depositing free mercury. In boiling water, mercury deposition is immediate. The esters are soluble in most organic solvents and the methyl, ethyl and propyl esters are extremely soluble in water. Since the methyl and ethyl esters tend to decompose on storage at room temperature, they are best stored in a cold, dry place. The compounds are decomposed by heat, free mercury and tetraalkyl hypophosphate being formed in all instances.[3]

Fungicidal screening tests with *Aspergillus niger* and *Trichoderma* have indicated that the derivatives have a level of inhibition less than that of phenylmercuric chloride or pyridylmercuric acetate.

Experimental[4]

Materials.—C.P. grade yellow mercuric oxide was used throughout. With the exception of dimethyl, diethyl and di-*n*-butyl phosphonate, which were obtained from the Virginia–Carolina Chemical Corporation, the phosphonates were prepared by the conventional procedure from phosphorus trichloride and the alcohol with triethylamine as the hydrogen chloride acceptor. Adsorption alumina, 200 mesh, was heated overnight at 210° before use in the chromatographic purifications.

Analysis.—Mercury was determined by the reduction of the compounds to free mercury with ethanolamine[5] followed by oxidation to mercuric nitrate and titration with potassium thiocyanate. Phosphorus was determined gravimetrically as ammonium phosphomolybdate.

Bis-(dimethoxyphosphinyl)-mercury. Method A.—To a vigorously stirred solution of dimethyl phosphonate (50 g., 0.45 mole) in 75 ml. of dried benzene, was added 49.0 g. (0.23 mole) of mercuric oxide at room temperature, followed by an additional 50 ml. of benzene after the oxide addition was complete. The pressure was reduced to 200 mm. and the reaction mixture refluxed at 40–45°. The water produced by the reaction was removed as the benzene azeotrope and collected in a Dean–Stark trap. Although some unreacted mercuric oxide remained, the reaction was considered complete when no more water was collected in the trap. The product precipitated from the benzene solution on cooling. After one recrystallization from benzene, 78.9 g. (83% yield) of bis-(dimethoxyphosphinyl)-mercury was obtained. Three recrystallizations from hot benzene gave a product having m.p. 121.6–123.0°.

Anal. Calcd. for $C_4H_{12}O_6P_2Hg$: Hg, 47.81; P, 14.80; mol. wt., 419. Found: Hg, 47.48; P, 14.64; mol. wt., 396 (Rast Method).

Generally the other esters were prepared by this method. The *n*-butyl, isobutyl and the *n*-propyl esters were purified by percolating the reaction mixtures through a wet-packed column of activated alumina. The resulting crude product was further purified by two percolations in *n*-hexane solution.

Bis-(diethoxyphosphinyl)-mercury. Method B.—To a solution of technical diethyl phosphonate (138.1 g., 1.0 mole) in 150 ml. of absolute ether was added 108.3 g. (0.50 mole) of mercuric oxide portionwise. After one-half of the mercuric oxide had been added, the solution refluxed vigorously and the orange color immediately discharged. When the initial reaction had subsided, the remaining mercuric oxide was added and the mixture refluxed six hours. The turbid gray mixture was allowed to settle overnight. The insoluble material, 1.6 g. of a mixture of free mercury and unreacted oxide, was filtered from the reaction mixture before the solvent was removed under reduced pressure. In

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(1) R. B. Fox and D. L. Venezky, THIS JOURNAL, **75**, 3967 (1953).

(2) R. B. Fox and D. L. Venezky, presented before the 124th Meeting of The American Chemical Society, Chicago, Illinois, 1953.

(3) David L. Venezky, presented before the 126th Meeting of the American Chemical Society, New York, N. Y., 1954.

(4) All melting points are corrected. Infrared spectra of the bis-(dialkoxyphosphinyl)-mercury esters are available from the Naval Research Laboratory.

(5) W. H. Rauscher, *Anal. Chem.*, **19**, 481 (1947).

Table I

Bis-(dialkoxyphosphinyl)-mercury, $[(RO)_2P(O)]_2Hg$

R	M.p., °C.	Yield, %	Formula	Mercury, % Calcd.	Mercury, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
CH_3	121.6–123.0	83	$C_4H_{12}O_6HgP_2$	47.81	47.48	14.80	14.64
CH_3CH_2	56.8–58.2	91	$C_8H_{20}O_6HgP_2$	42.16	41.76	13.05	12.89
n-C_3H_7	35.6–36.8[a]	80	$C_{12}H_{28}O_6HgP_2$	37.70	36.46	11.67	11.62
i-C_3H_7	124.4–125.0	81	$C_{12}H_{28}O_6HgP_2$	37.70	37.22	11.67	11.70
n-C_4H_9	25.0–27.2[b]	92	$C_{16}H_{36}O_6HgP_2$	34.10	33.51	10.54	10.43
i-C_4H_9	132.0–133.5	88	$C_{16}H_{36}O_6HgP_2$	34.10	31.88	10.54	10.55

[a] Super-cooled liquid, $n^{20}D$ 1.5062. [b] Super-cooled liquid, $n^{20}D$ 1.4991.

the cold trap, 6.7 g. (0.37 mole) of water was isolated. The gray plates formed after removal of the low boiling materials were recrystallized three times from petroleum ether to give 216.1 g. (91.2% yield) of bis-(diethoxyphosphinyl)-mercury, m.p. 56.8–58.2°.

Anal. Calcd. for $C_8H_{20}O_6P_2Hg$: C, 20.24; H, 4.25; P, 13.05; Hg, 42.25; mol. wt., 474. Found: C, 20.32, 20.27; H, 4.74, 4.72; P, 12.90, 12.87; Hg, 42.25, mol. wt., 486 (Rast Method).

The Effect of Acid and Base on the Synthesis.—A vigorously stirred mixture of redistilled[6] diethyl phosphonate (0.1 mole), mercuric oxide (0.05 mole) and 100 ml. of dried benzene was refluxed for three hours under a reduced pressure of 200 mm. The quantities of recovered mercuric oxide, water collected and crude bis-(diethoxyphosphinyl)-mercury are given in Table II for the following runs using the above quantities and conditions: (1) with acid and base absent, (2) with triethylamine (0.7 g., 0.007 mole), and (3) with p-toluenesulfonic acid (1 g., 0.006 mole). It is evident from these results that acid is the best catalyst for the reaction.

Table II

Effect of Catalyst

Catalyst	Moles	Water collected, mole	Mercuric oxide recovd., mole	Yield of crude product, mole
None		None	0.050	None
Triethylamine	0.007	Trace	.036	None
p-Toluenesulfonic acid	.006	0.039	.006	0.046

Reaction of Mercuric Chloride with Bis-(dialkoxyphosphinyl)-mercury.—Bis-(diethoxyphosphinyl)-mercury (4.7 g., 0.01 mole) was dissolved in 20 ml. of dried benzene, and 2.7 g. (0.01 mole) of mercuric chloride was added. The mixture was refluxed 15 minutes and allowed to cool to room temperature. An unidentified fine crystalline material (0.5 g., m.p. 145° dec.) was filtered from the benzene solution and 5.9 g. (78.6% yield) of crude diethoxyphosphinylmercuric chloride was obtained in two crops from the filtrate. Recrystallization first from carbon tetrachloride and then from water gave a product melting at 103–104°. A mixed melting point with the product previously reported[1] showed no depression.

Washington, D. C.

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[6] These runs were made under rigorously dry conditions, since a brief exposure of the phosphonates to atmospheric moisture results in the formation of traces of acidic hydrolysis products.

[Contribution No. 1975 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology]

Coördination of Silver Ion with Unsaturated Compounds. VII. 3-Hexyne[1]

By W. Smith Dorsey and Howard J. Lucas[2]

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The value of the argentation constant of 3-hexyne, as determined by a distribution method, is smaller than those of alkenes and greater than those of aromatic hydrocarbons. Oxygen must be rigorously excluded.

The coördination of the olefinic double bond with silver ion has been fairly well investigated.[3–5] Although a number of complexes of acetylene with silver and cuprous salts have been known for a long time, acetylene and propyne are not the proper types of substances for investigating coördination of the acetylenic triple bond because an acidic hydrogen atom on a triply bound carbon atom can be replaced by a metal atom. 3-Hexyne is the simplest symmetrical non-acidic alkyne having a convenient boiling point. Failure of others[6] to observe complexing of dialkylacetylenes may be due to the limitations of visual methods when only slight changes in solubility are involved.

Method.—The distribution method of the earlier papers[3] was followed and the immiscible solvents were water and carbon tetrachloride. The mutual solubilities of the two solvents are low, and the extent to which the hexyne–silver nitrate complex dissolves in carbon tetrachloride is so small that its presence in solution could not be detected. The presence of oxygen even in low concentration was very troublesome. It was only after 99.9% pure nitrogen became available[7] that satisfactory analyses became the rule.

Materials.—The 3-hexyne was in part supplied by H. Lemaire of these laboratories (synthesized by the method of Bried and Hennion),[8] b.p. 80.0–80.6° (746 mm.), $n^{25}D$

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[1] Previous paper of this series, unnumbered, R. E. Kofahl and H. J. Lucas, This Journal, **76**, 3931 (1954).

[2] To whom requests for reprints should be sent.

[3] F. R. Hepner, K. N. Trueblood and H. J. Lucas, This Journal, **74**, 1333 (1952). Herein are cited a number of references.

[4] R. N. Keller, *Chem. Revs.*, **28**, 229 (1941).

[5] J. Chatt, "Cationic Polymerizations," edited by P. H. Plesch, W. Heffer and Sons, Ltd., Cambridge, Eng., 1953, pp. 41–48; G. Salomon, *ibid.*, pp. 57–64.

[6] H. J. Taufen, M. J. Murray and F. C. Cleveland, This Journal, **63**, 3500 (1941).

[7] From Linde Air Products Company.

[8] E. A. Bried and G. F. Hennion, This Journal, **59**, 1310 (1937).