[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Mercuration of Dialkyl Phosphonates[1,2]

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A number of dialkyl phosphonates have been mercurated with mercuric acetate and with a mixture of mercuric oxide and a mercuric salt. The derivatives obtained are characterized by a new bond, the phosphorus–mercury bond.

In recent years, many synthetic reactions involving the dialkyl esters of phosphonic acid have been developed which indicate that these compounds possess a reactive hydrogen atom somewhat similar in properties to an α-hydrogen atom in a ketone or the hydrogen atoms in a reactive methylene group. Among these reactions may be cited the addition of dialkyl phosphonates in the presence of a base to carbonyl groups[3] and unsaturated electrophilic compounds[4]; the formation of phosphorochloridates by direct reaction of dialkyl phosphonates with chlorine[5]; the Mannich-type reaction of dialkyl phosphonates with carbonyl compounds and amines[6]; and the formation of dialkyl alkylphosphonates from the sodium derivatives of the dialkyl phosphonates and alkyl halides.[7] That the dialkyl phosphonates can exist in a keto form containing a P–H bond is indicated by their infrared spectra[8]; thus, under suitable conditions the nucleophilic dialkoxyphosphinyl group should be available for reaction.

One such reaction which would be predicted on these grounds is direct mercuration with mercuric acetate, a reaction analogous to the direct mercuration of reactive methylene containing compounds.[9] As expected, mercuration of the dialkyl phosphonates took place quite readily. Indeed, mixing 0.05 mole quantities of diethyl phosphonate and mercuric acetate in an open beaker at room temperature results in a temperature rise to about 80°; this level of reactivity is considerably higher than that for the direct mercuration of aromatic compounds[10] and, in fact, it exceeds that for reactive methylene compounds; acetoacetic ester, for example, under the same conditions gives a temperature increase to only 36°. The structure of the resulting products is regarded as that of a dialkoxyphosphinylmercuric acetate, $(RO)_2P(O)Hg$-OAc, with the mercury atom bonded to the phosphorus, rather than the tautomeric form which might be expected to form from the dialkyl phosphite. This is inferred from the unusual solubility of these compounds in organic solvents and their specific melting points; a comparison of the infrared spectra of the dialkyl phosphonates[8] with the corresponding dialkoxyphosphinylmercuric acetates shows the characteristic P–H absorption at 4.2 μ to be lacking in the latter. As with other metal to phosphorus linkages such as P–Si,[11] P–Sn,[12] and P–As,[13] the P–Hg bond is relatively weak, free mercury being formed with a trace of alkali or on heating in the presence of solvents to as low as 70° in the case of the lower esters.

Conversion of the acetates to the corresponding halides is accomplished readily by conventional methods such as treatment with an alkali metal halide. However, it was found that the halides were obtained in higher yield and greater purity by proceeding directly from the dialkyl phosphonates by reaction with an equimolar mixture of mercuric oxide and the mercuric halide. This method is a modification of one used for the monomercuration of aliphatic ketones[14]; the mechanism of this reaction is under study. The over-all course of the reaction is

$$2(RO)_2P(O)H + HgX_2 + HgO \longrightarrow 2(RO)_2P(O)HgX + H_2O$$

These reactions are conducted in benzene as a solvent and the water removed by azeotropic distillation (the use of a solid drying agent is less satisfactory). In most cases, reaction is complete when the orange color of the mercuric oxide is discharged, and the rapidity of this color discharge indicates to some extent the relative ease of reaction. Yields of the iodides were lower than with the other halides, and it should be observed that although the red mercuric iodide color disappears immediately, the orange oxide color is never completely discharged.

The method is less practical than the conventional procedures when mercuric acetate is used, particularly since the acetates tend to decompose to free mercury in refluxing benzene. When Drierite is used as the dehydrating agent at 40°, mercuric acetate gives only an 11% yield of diethoxyphosphinylmercuric acetate.

Generally, the chlorides and bromides are more stable than the acetates to heat and alkali. The iodides, on the other hand, tend to decompose to an unidentified amorphous yellow material, even on standing in a dry atmosphere at room tempera-

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(1) The nomenclature in this paper follows that outlined in *Chem. Eng. News*, **30**, 4515 (1952).

(2) The opinions contained herein are the private ones of the writers and are not to be construed as official or reflecting the view of the Navy Department.

(3) V. S. Abramov, *Doklady Akad. Nauk S.S.S.R.*, **73**, 487 (1950).

(4) A. N. Pudovik, *Doklady Akad. Nauk S.S.S.R.*, **73**, 499 (1950); A. N. Pudovik and B. A. Arbusov, *ibid.*, **73**, 327 (1950); A. N. Pudovik and B. A. Arbusov, *Zhur. Obschei Khim.*, **21**, 382 (1951); B. Bochwic and J. Michalski, *Nature*, 1035 (1951).

(5) H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

(6) E. K. Fields, THIS JOURNAL, **74**, 1528 (1952).

(7) G. M. Kosolapoff, *ibid.*, **67**, 1180 (1945); P. Nylen, "Studien uber Organischenphosphorverbindungen," Uppsala, 1930.

(8) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(9) K. G. Naik and R. P. Patel, *J. Indian Chem. Soc.*, **9**, 185 (1932).

(10) K. A. Kobe and P. F. Lueth, Jr., *Ind. Eng. Chem.*, **34**, 309 (1942).

(11) B. A. Arbusov, *Doklady Akad. Nauk S.S.S.R.*, **59**, 43 (1948).

(12) B. A. Arbusov and A. N. Pudovik, *Zhur. Obschei Khim.*, **17**, 2158 (1947); B. A. Arbusov and N. P. Grechkin, *ibid.*, **17**, 2166 (1947); **20**, 107 (1950).

(13) G. Kamai and O. N. Belorossova, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 91 (1947); 198 (1950).

(14) A. A. Morton and H. P. Penner, THIS JOURNAL, **73**, 3300 (1951).

TABLE I

DIALKOXYPHOSPHINYLMERCURIC SALTS, $(RO)_2P(O)HgX$

R	X	M.p., °C.	Yield, %	Formula	Mercury, % Calcd.	Mercury, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
C_2H_5	$OCOCH_3$	106.8–107.6	83.3	$C_6H_{13}O_5HgP$	50.55	50.40	7.81	7.85
n-C_3H_7	$OCOCH_3$	86.3–87.2	87.0	$C_8H_{17}O_5HgP$	47.45	47.44	7.29	7.26
Iso-C_3H_7	$OCOCH_3$	146.2–146.8	94.8	$C_8H_{17}O_5HgP$	47.45	47.22	7.29	7.23
n-C_4H_9	$OCOCH_3$	80.5–81.0	86.6	$C_{10}H_{21}O_5HgP$	44.30	44.43	6.83	6.89
Iso-C_4H_9	$OCOCH_3$	116.0–116.6	92.5	$C_{10}H_{21}O_5HgP$	44.30	44.52	6.83	6.86
n-C_5H_{11}	$OCOCH_3$	72.5–73.5	77.0	$C_{12}H_{25}O_5HgP$	41.71	41.81	6.43	6.44
n-C_6H_{13}	$OCOCH_3$	73.9–74.6	80.0	$C_{14}H_{29}O_5HgP$	39.40	39.02	6.08	6.14
n-C_7H_{15}	$OCOCH_3$	83.2–84.0	92.5	$C_{16}H_{33}O_5HgP$	37.36	37.09	5.76	5.80
C_2H_5	Cl	104.0–104.5	59.3	$C_4H_{10}O_3ClHgP$	53.75	53.30	8.29	8.40
n-C_3H_7	Cl	80.0–81.5	61.4	$C_6H_{14}O_3ClHgP$	50.00	50.11	7.71	7.78
Iso-C_3H_7	Cl	114.6–115.2	73.3	$C_6H_{14}O_3ClHgP$	50.00	49.94	7.71	7.72
n-C_4H_9	Cl	91.0–92.0	27.4	$C_8H_{18}O_3ClHgP$	46.73	46.56	7.22	7.24
Iso-C_4H_9	Cl	118.8–119.2	61.9	$C_8H_{18}O_3ClHgP$	46.73	46.71	7.22	7.21
C_2H_5	Br	86.0–87.0	73.1	$C_4H_{10}O_3BrHgP$	48.04	48.30	7.41	7.34
n-C_3H_7	Br	70.0–70.4	66.4	$C_5H_{14}O_3BrHgP$	45.01	45.06	6.94	7.00
n-C_4H_9	Br	78.0–78.4	43.9	$C_8H_{18}O_3BrHgP$	42.35	42.32	6.54	6.57
C_2H_5	I	102.0–102.5	61.0	$C_4H_{10}O_3IHgP$	43.18	42.84	6.67	6.64
n-C_3H_7	I	75.2–76.0	49.1	$C_6H_{14}O_3IHgP$	40.71	39.98	6.28	6.22
n-C_4H_9	I	56.0–57.2	41.9	$C_8H_{18}O_3IHgP$	38.52	38.26	5.94	5.94
C_2H_5	SCN	124.2–124.6	94.0	$C_5H_{10}O_3SNHgP$	52.34	50.68	7.82	7.82

ture although they can be stored in the cold. Decomposition is more pronounced in the presence of traces of impurities. Both diethoxyphosphinylmercuric acetate and chloride can be recrystallized from water without apparent hydrolysis. These and the other derivatives reported here are characterized by their relatively high solubility in organic solvents; most may be recrystallized readily from hexane.

Fungicidal screening tests with *Aspergillus niger* and *Trichoderma* have indicated that both the acetates and halides generally have a level of inhibition near that of phenylmercuric chloride or pyridylmercuric acetate.

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Experimental[15]

Materials.—U.S.P. grade mercury salts were used throughout. With the exception of diethyl and di-*n*-butyl phosphonate, which were obtained from the Virginia-Carolina Chemical Corporation, the phosphonates were prepared by the conventional procedure from PCl_3, the alcohol, and triethylamine as the HCl acceptor.

Analysis.—Phosphorus was determined gravimetrically as ammonium phosphomolybdate following oxidation of the samples with sulfuric–nitric acid mixtures. Attempts to determine mercury from the same samples as the phosphorus gave inconsistent results. Mercury was determined by the reduction of the salts to free mercury with stannous chloride[16] in the case of the acetates, chlorides and bromides, and with ethanolamine[17] in the case of the iodides and thiocyanates followed by oxidation to mercuric nitrate and titration with potassium thiocyanate.

Diethoxyphosphinylmercuric Acetate. (a).—To a vigorously stirred suspension of mercuric acetate (350.5 g., 1.1 moles) in 500 ml. of dry toluene was added 138 g. (1.0 mole) of diethyl phosphonate at room temperature. The mixture was stirred for 2.5 hours, the temperature being maintained at 25° with an ice-bath. Filtration gave 3 g. of insoluble material. Removal of acetic acid as the toluene azeotrope was accomplished by distillation of the filtrate at 60 mm. pressure until the take-off temperature was 36° and 175 ml. of distillate was collected; distillation at higher temperatures resulted in the formation of considerable amounts of free mercury. After filtration, evaporation of the filtrate gave 330.0 g. (83.3% yield) of crude product. Recrystallization from toluene or benzene–ether mixture gave pure diethoxyphosphinylmercuric acetate, m.p. 106.8–107.6°.

Anal. Calcd. for $C_6H_{13}O_5PHg$: Hg, 50.55; P, 7.81. Found: Hg, 50.40; P, 7.85.

Solutions of the pure material may be heated to 60° without deposition of free mercury. It is soluble in alcohol, acetone, acetic acid, benzene and chloroform; moderately soluble in toluene and water; and almost insoluble in ether and petroleum hydrocarbons. The melting point of a sample recrystallized by the evaporation of an aqueous solution over a period of several days at room temperature was unchanged, indicating the rate of hydrolysis under these conditions to be quite slow. The addition of alkali, however, immediately results in the deposition of free mercury. Cryoscopic molecular weight determinations indicate the acetate to be monomeric in acetic acid, tetrameric in benzene.

(b).—The above compound can also be prepared by mixing equimolar amounts of mercuric acetate and the phosphonate without solvent. On mixing 0.05 mole each of these materials, a rapid temperature rise to 82° takes place, along with formation of a gray sludge of free mercury. The mixture is then taken up in benzene, filtered, and the filtrate added to a large quantity of hexane to precipitate the product. The yield of crude diethoxyphosphinylmercuric acetate is 78.6%, but the product is considerably less pure than that obtained by method (a).

(c).—A mixture of 13.8 g. (0.1 mole) diethyl phosphonate, 16.2 g. (0.05 mole) mercuric acetate, 10.9 g. (0.05 mole) mercuric oxide and 28 g. of Drierite in 150 ml. of toluene was stirred at 40° for 2.5 hours. After filtration of the inorganic salts, evaporation of the filtrate gave 4.2 g. (11% of theoretical) of diethoxyphosphinylmercuric acetate, m.p. 104–107°, identical with that obtained under method (a).

Other Dialkoxyphosphinylmercuric Acetates.—Method (a) given above was generally followed for the higher esters listed in Table I, except that ethylbenzene or *n*-octane was used as the solvent. The acetic acid was usually removed as the azeotrope at 40–50° under 40 mm. pressure. *n*-Octane is particularly well suited to this procedure, since the products are readily recrystallized from the hot solvent and are more stable to heat than the ethyl derivative; the azeotrope contains about 50% acetic acid at the working pressures. It should be noted that it is necessary to remove as much

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[15] Melting points were determined in glass capillaries with thermometers calibrated against National Bureau of Standards standard thermometers, but are otherwise uncorrected. Infrared spectra of diethoxy- and dibutoxyphosphinylmercuric acetate are available from the Naval Research Laboratory.

[16] J. N. Bartlett and W. M. McNabb, *Anal. Chem.*, **19**, 484 (1947).

[17] W. H. Rauscher, *ibid.*, **10**, 331 (1938).

acetic acid as possible since the crude acetates are very soluble in this material.

Dialkoxyphosphinylmercuric Chlorides and Bromides. (a) From the Acetates.—A solution of 0.74 g. (0.01 mole) of potassium chloride in 25 ml. of water was added to a solution of 3.96 g. (0.01 mole) diethoxyphosphinylmercuric acetate in 25 ml. of water and the clear mixture evaporated to about half its volume under an infrared lamp. After filtration from a small amount of free mercury, further concentration gave 1.9 g. (50.8% yield) of diethoxyphosphinylmercuric chloride, m.p. 85–95°. Two recrystallizations from water gave material having m.p. 104.0–104.5°.

Anal. Calcd. for $C_4H_{10}O_3ClPHg$: Hg, 53.75; P, 8.29. Found: Hg, 53.30; P, 8.40.

The bromide, iodide and thiocyanate were prepared similarly in 74.2, 88.4 and 94.0% yields, respectively; the latter two compounds were insoluble in water and the crudes were thus collected by filtration. This method is suited to water-soluble acetates only; the other acetates may be converted to the halides in acetone solution.

(b) **From the Dialkyl Phosphonates.**—Di-*n*-propoxyphosphinylmercuric bromide may be taken as a typical example of this procedure. A mixture of 8.3 g. (0.05 mole) di-*n*-propyl phosphonate, 5.4 g. (0.025 mole) mercuric oxide and 9.0 g. (0.025 mole) mercuric bromide in 50 ml. of dry benzene was refluxed three hours, water being continuously removed with a trap. Soon after the reflux period began, the orange mercuric oxide color changed to white. After cooling, 2.6 g. of inorganic material was removed by filtration; evaporation of the filtrate gave a sirup which crystallized readily upon the addition of petroleum ether. The yield was 14.8 g. (66.4%), m.p. 67–68.5°; two recrystallizations from hot hexane gave pure di-*n*-propoxyphosphinylmercuric bromide, m.p. 70.0–70.4°.

Anal. Calcd. for $C_6H_{14}O_3BrPHg$: Hg, 45.01; P, 6.94. Found: Hg, 45.06; P, 7.00.

The halides listed in Table I were prepared by this procedure. With the exception of the ethyl derivatives, they are soluble in hot hexane; all are soluble in ordinary organic solvents.

Di-*n*-propoxyphosphinylmercuric Iodide.—A mixture of 8.3 g. (0.05 mole) of di-*n*-propyl phosphonate, 5.4 g. (0.025 mole) of mercuric oxide and 11.35 g. (0.025 mole) of mercuric iodide in 50 ml. of dry benzene was refluxed 5 hours; due to excessive foaming, no attempt was made to collect the water formed in the reaction. The red iodide color was soon discharged, but the final precipitate had the appearance of mercuric oxide. After filtration of the inorganic salts, the filtrate was dried with Drierite and evaporated, during which a considerable quantity of an unidentified amorphous yellow material formed. The yellow mixture of solids was taken up in boiling hexane, filtered to remove the yellow material, and concentrated to give 12.1 g. (49.1%) of crude product, m.p. 74.6–75.6°; recrystallization from warm hexane yields pure di-*n*-propoxyphosphinylmercuric iodide, m.p. 75.2–76.0°.

Anal. Calcd. for $C_6H_{14}O_3IPHg$: Hg, 40.71; P, 6.28. Found: Hg, 39.98; P, 6.22.

The other iodides were prepared similarly.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Syntheses and Relative Dehydration Rates of Some Methyl-substituted 1-Phenylcyclohexanols[1]

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Eleven methyl-substituted 1-phenylcyclohexanols and the unsubstituted parent compound have been synthesized and arranged in the order of their dehydration rates in the presence of *p*-toluenesulfonic acid under identical conditions. Evidence is presented which demonstrates that carbon skeleton rearrangements do not occur during dehydration. Examination of the relative dehydration rates indicates that the presence of ortho or para methyl groups in the benzene ring tends to accelerate the dehydration rate, but methyl groups in the 2-, 4- or 6-positions of the cyclohexanol ring tend to slow the rate. A study of the ultraviolet absorption spectra of the phenylcyclohexenes reveals that methyl groups in either ring diminish the absorption band in the ultraviolet which is associated with conjugation of side-chain unsaturation with that of the aromatic ring; however, the aromatic methyl groups exert a more profound effect than alicyclic methyls. The observations of the effects of methyl substitution on the spectra of the phenylcyclohexenes can be explained in terms of steric interference by the methyls with the coplanarity of the ethylenic system with the aromatic ring. The effects of the methyl groups on the dehydration rates of the carbinols, on the other hand, are more complex, and a satisfactory interpretation cannot be given until more is known about the reaction mechanism, the stereochemistry of the carbinols and the position of the alicyclic double bond.

The apparent sluggishness of 1-(2,4-dimethylphenyl)-2,6-dimethylcyclohexanol in acid-promoted dehydration reactions[2,3] prompted a study of the relative dehydration rates of a series of methyl-substituted 1-phenylcyclohexanols. A detailed kinetic analysis of the reactions was not attempted during this study; the objective was to obtain enough reliable data to permit the carbinols to be arranged in the order of their decreasing ease of dehydration under the imposed conditions. The results of this study are presented here, and an account is also given of efforts to discover whether the substituent methyl groups affect the dehydration rates of the carbinols and the ultraviolet absorption spectra of their dehydration products, the methyl-substituted phenylcyclohexenes, in any related way.

Previous experience[2] indicated that in general methyl-substituted 1-phenylcyclohexanols should be prepared in better yield by treating the appropriate cyclohexanones with aryl lithium compounds than can be realized when the corresponding Grignard reagents are used. Accordingly, the aryl lithium compounds were employed exclusively in this work. The methyl-substituted cyclohexanones required for the syntheses were prepared by oxidizing the related methylcyclohexanols, which in turn were the hydrogenation products of methylphenols. The synthesis of 1-(2,4-dimethylphenyl)-2,4-dimethylcyclohexanol (VII) provides typical examples of the reactions used throughout the series.

The methyl-substituted 1-phenylcyclohexenes were prepared for spectral study by heating the corresponding cyclohexanols with anhydrous oxalic acid; in the rate determinations the dehydration catalyst was *p*-toluenesulfonic acid, and the reactions were carried out in glacial acetic acid

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[1] From the D.Sc. Thesis by Harold P. Landerl.

[2] R. B. Carlin, THIS JOURNAL, **67**, 928 (1945).

[3] R. B. Carlin and D. A. Constantine, *ibid.*, **69**, 50 (1947).