856. *Organophosphorus Compounds. Part III.* Reactions of the Alkali Derivatives of Dialkyl Phosphites.*

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A sodium dialkyl phosphite reacts with the dialkyl hydrogen phosphite to give the sodium alkyl hydrogen phosphite and the dialkyl alkylphosphonate.

Dimethyl phosphite, under the same conditions, gave sodium methyl methylphosphonate and disodium dimethylpyrophosphonate.

Phosphonic acids are often prepared by reaction of an alkali-metal dialkyl phosphite with an alkyl halide, the salts of diethyl and dibutyl phosphite having the advantage of being soluble in organic solvents.[1] A closer study of this reaction has shown that preparation of sodium dibutyl phosphite by reaction of dibutyl phosphite with metallic sodium is followed by a homogeneous disproportionation reaction between the sodium salt and the free phosphite ester:

$$(BuO)_2P(O)Na + (BuO)_2P(O)H \longrightarrow (BuO)_2P(O)Bu + (BuO)(NaO)P(O)H$$

Dibutyl butylphosphonate and sodium butyl hydrogen phosphite are formed. This secondary reaction proceeds at a significant rate above 60°; it lowers the yield of the dibutyl alkylphosphonates in the usual alkylation reaction and causes the alkylation products (dibutyl alkylphosphonates) to be contaminated, almost always, by dibutyl butylphosphonate.

Conditions have been found under which this reaction of a sodium dialkyl phosphite with the dialkyl hydrogen phosphite can be used for preparative purposes. Sodium alkyl hydrogen phosphites have been described by Nylén,[2] but the methods were tedious and the purity of the products was questionable. In fact, the present method shows that dialkyl phosphites can be used as alkylating agents in the same way as alkyl halides or sulphates.

Similar reactions have been observed by Petrov and his co-workers [3] and earlier by Hoffmann and Weiss [4] and by Kamai and Kukhtin; [5] trimethyl thiophosphite has also been reported to have methylating properties.[6]

Our method has given good results with diethyl, dipropyl, and dibutyl phosphite; separation of the products was easy. The dialkyl alkylphosphonates were identified by conversion into alkylphosphonyl dichlorides.[7] The sodium alkyl hydrogen phosphites were identified by analysis and infrared spectrum: the P–H,[8] P=O, and P–O–C frequencies were found at 2380, 1200—1220, and 980—1020 cm.$^{-1}$, respectively. The alkylphosphonyl dichlorides showed the P=O absorption at 1250—1300 cm.$^{-1}$; Corbridge [8] found that if the P=O bond participates in a hydrogen bridge, as in the above salts, which are partly associated, the frequency is somewhat lowered.

An unexpected reaction was observed when dimethyl phosphite was treated analogously. When an attempt was made to isolate its sodium salt (by evaporation of the methanol in which it had been prepared), an exothermic reaction set in, accompanied by evolution of dimethyl ether, and a solid mixture of salts remained which we did not succeed in resolving. It was converted in 50% yield into methylphosphonyl dichloride by successive acidification

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* Part II, *J.*, 1961, 241.

[1] Kosolapoff, *J. Amer. Chem. Soc.*, 1945, **67**, 1180.

[2] Nylén, *Svensk Kem. Tidskr.*, 1936, **48**, 2.

[3] Petrov, Bliznyuk, Korshanov, Maklayev, and Voronkov, *Zhur. obshchei Khim.*, 1959, **29**, 3407.

[4] Hoffmann and Weiss, *J. Amer. Chem. Soc.*, 1956, **79**, 4759.

[5] Ḳamai and Kukhtin, *Zhur. obshchei Khim.*, 1957, **27**, 949.

[6] Hilgetag and Teichmann, *J. prakt. Chem.*, 1959, **8**, 73, 90.

[7] Pelchowicz, *J.*, 1961, 238.

[8] Corbridge, *J. Appl. Chem.*, 1956, **6**, 456.

with alcoholic hydrogen chloride and treatment with phosphorus pentachloride. Thus, the above exothermic reaction must have been of the Arbuzov–Michaelis type, leading to the formation of a Me–P bond. The three possible products of this reaction which would be convertible into methylphosphonyl dichloride are methyl sodium methylphosphonate, Me·PO(OMe)(ONa), disodium methylphosphonate, $Me\cdot PO(ONa)_2$ and disodium dimethylpyrophosphonate, Me·PO(ONa)·O·PMeO(ONa);[9] only formation of the latter would explain the occurrence of dimethyl ether as a by-product. From the amount of dimethyl ether formed, it can be concluded that about 50% of the solid salt mixture consisted of disodium dimethylpyrophosphonate. Also, in the infrared spectrum of the salt mixture obtained from dimethyl phosphite and its sodium salt, the bands (900, 725 cm.$^{-1}$) characteristic of the P–O–P bond[10] have been observed.

EXPERIMENTAL

The following dialkyl hydrogen phosphites were prepared as described in the literature:[11-14] dimethyl, b. p. 69—73°/25 mm., 80%; diethyl, b. p. 82—86°/28 mm., 72%; dipropyl, b. p. 105—106°/15 mm., 86%. Dibutyl phosphite was a commercial product, b. p. 96—99°/2 mm.

For the preparation of the sodium salts, the appropriate sodium alkoxide is preferable to metallic sodium. For example, a solution of sodium (23 g.) in butanol (500 ml.) was cooled with ice–salt, and dibutyl phosphite (194 g.) added slowly with stirring. The excess of butanol was removed at 20 mm.; the sodium salt remained as colourless crystals (216 g.). In all cases yields were quantitative.

Reaction of Dibutyl Hydrogen Phosphite with its Sodium Salt.—Dibutyl hydrogen phosphite (194 g.) was added with stirring to a boiling solution of sodium dibutyl phosphite (216 g.) in toluene (400 ml.); heating was continued for a further 3 hr., then the toluene (from which a white precipitate had separated) was decanted and replaced by ether. The insoluble *sodium butyl hydrogen phosphite* (143 g., 90%) melted at 180—181° after recrystallisation from ethanol–acetone (Found: C, 29·7; H, 5·6. $C_4H_{10}NaO_3P$ requires C, 30·0; H, 6·3%). From the ethereal solution, dibutyl butylphosphonate (217 g., 87%), b. p. 102—120°/2 mm., was obtained by distillation.

For identification, the second product (125 g.) was added to phosphorus pentachloride (250 g.), and the mixture refluxed for 1 hr. Volatile material (butyl chloride and phosphorus oxychloride) was then removed, and the product distilled. Butylphosphonyl dichloride (49 g., 56%) had b. p. 102—103°/24 mm. (lit.,[15] 96—98°/15—16 mm., $d_4^{20\cdot5}$ 1·245, $n_D^{20\cdot5}$ 1·4655, $[M]_R$ 38·88 (calc., 37·99) (Found: C, 27·8; H, 4·8. $C_4H_9Cl_2OP$ requires C, 27·5; H, 5·2%).

Reaction of Dipropyl Hydrogen Phosphite with its Sodium Salt.—In the same way sodium dipropyl phosphite (188 g.) in benzene (200 ml.) and dipropyl hydrogen phosphite (166 g.) gave *sodium propyl hydrogen phosphite* (135 g., 92%), m. p. 196—197° (from acetone–ethanol) (Found: C, 24·5; H, 5·2. Calc. for $C_3H_8NaO_3P$: C, 24·7; H, 5·5%), and dipropyl propylphosphonate (176 g., 84%), b. p. 113—132°/24 mm. From the latter compound (104 g.) and phosphorus pentachloride (300 g.), propylphosphonyl dichloride (55 g., 68%), b. p. 90—91°/28 mm.,[16] 63—64·5°/10 mm., n_D^{27} 1·4540, d_4^{21} 1·298, $[M_R]$ 33·58 (calc., 33·37), was obtained (Found: C, 22·3; H, 3·5. Calc. for $C_3H_7Cl_2OP$: C, 22·4; H, 4·4%).

Reaction of Diethyl Hydrogen Phosphite with its Sodium Salt.—Sodium diethyl phosphite (160 g.) in toluene (100 ml.) with diethyl hydrogen phosphite (138 g.) gave *sodium ethyl hydrogen phosphite* (125 g., 94%), m. p. 182° (from ethanol–acetone) (Found: C, 18·0; H, 4·5. $C_2H_6NaO_3P$ requires C, 18·2; H, 4·6%), and diethyl ethylphosphonate (127 g., 77%), b. p. 89—97°/25 mm. The latter product (83 g.) with phosphorus pentachloride (250 g.) gave ethylphosphonyl dichloride (51 g., 70%), b. p. 74·5—75°/25 mm. (lit.,[17] 34°/3 mm.), d_4^{22} 1·368,

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[9] Pelchowicz, unpublished results.

[10] (*a*) Bergmann, Littauer, and Pinchas, *J.*, 1952, 847; (*b*) Harvey and Mayhood, *Canad. J. Chem.*, 1955, **33**, 1552.

[11] Nylén, *Ber.*, 1924, **57**, 1023.

[12] Arbuzov and Vinogradova, *Bull. Acad. Sci. U.S.S.R., Classe Sci. chim.*, 1947, 617 (*Chem. Abs.*, 1948, **42**, 5844).

[13] McCombie, Saunders, and Stacey, *J.*, 1945, 380.

[14] Ramaswami and Kirch, *J. Amer. Chem. Soc.*, 1953, **75**, 1763.

[15] Razumov, Mukhacheva, and Markovich, *Zhur. obshchei Khim.*, 1958, **28**, 194.

[16] Kabachniksh and Godovikov, *Doklady Akad. Nauk U.S.S.R.*, 1956, **110**, 217.

[17] Kinnear and Perren, *J.*, 1952, 3437.

n_D^{22} 1·4495, $[M_R]$ 28·83 (calc., 28·75) (Found: C, 16·0; H, 3·6. Calc. for $C_2H_5Cl_2OP$: C, 16·3; H, 3·4%).

Self-decomposition of Sodium Dimethyl Phosphite.—At −20°, dimethyl hydrogen phosphite (110 g.) was added to a solution of sodium (23 g.) in anhydrous methanol (400 ml.). Then the excess of methanol was removed *in vacuo* at $\not>$50°, a lively exothermic reaction setting in and a gas being liberated which was condensed at −78°. The reaction was moderated by cooling; when it had subsided, the product was slowly heated to 150°. Thus a white, water-soluble salt was obtained. The infrared spectrum (in a potassium bromide pellet) showed bands at 2940, 2410, 1310 1200b, 1080b, 1000, 900, 780, and 725 cm.$^{-1}$. The following assignments are made: 900 and 725, P–O–P; [10] 1000, P–O stretching in quinquevalent phosphorus compounds; [18] 1080, superposition of P–OH deformation and P=O in ionic compounds; [18] 1310 Me·P=O.[10b]

The low-temperature condensate was saturated with gaseous boron trifluoride, with cooling; the boron trifluoride complex, b. p. 127°, of dimethyl ether was obtained (lit.,[19] b. p. 127°). From 1 mole of dimethyl hydrogen phosphite, 10·7 g. of dimethyl ether have been obtained, corresponding to a 46·5% yield of disodium dimethylpyrophosphonate in the solid product.

The solid product was treated with an excess of methanolic hydrochloric acid, and the filtered solution concentrated *in vacuo*. The residual viscous oil was identified by adding it slowly to phosphorus pentachloride (400 g.); when the exothermic reaction had ceased, the product was refluxed for 2 hr., and volatile material (up to 108°) was removed. The residue (66 g., 50%) boiled at 163°, melted at 32°, and was identified as methylphosphonyl dichloride (lit.,[17] b. p. 162°, m. p. 33°).

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[18] Bellamy and Beecher, *J.*, 1952, 1701; 1953, 728.

[19] Beilstein's " Handbuch," Vol. I, p. 282; cf. McLaughlin and Tamres, *J. Amer. Chem. Soc.*, 1960, **82**, 5618.