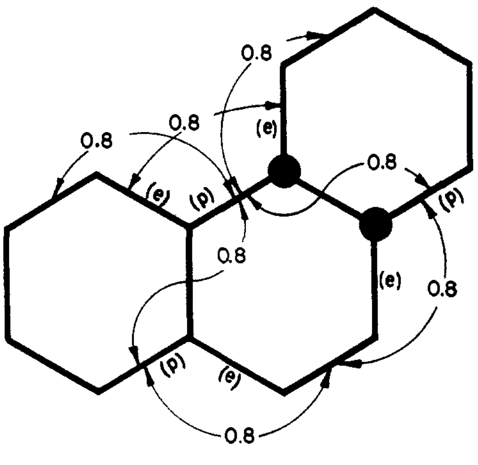
parameter, the energy differences for the *cis–syn–cis* isomer becomes *ca.* $2 \times 0.8 + 4.8 = 6.4$ kcal.

The most stable of the perhydrophenanthrenes, the *trans–anti–trans* isomer, differs from the *trans–syn–trans* perhydroanthracene by one *skew* interaction between the bonds forming the angle of the three rings, or by 0.8 kcal. (see Fig. 3). The *trans–anti–cis* and *cis–syn–trans* isomers both have one additional *cis*-decalin interaction making the total energy difference 3.2 kcal. The case of the *cis–anti–cis* isomer is of particular interest since the earlier method of analysis[3] did not distinguish between the form with 1,2-(p) (p) substituents on the central cyclohexane ring (as shown in Fig. 3) and the form with 1,4-(p) (p) substituents (Fig. 4).



cis-anti-cis, E = 5.6 kcal.

Fig. 4.

In the former the angular skew interaction is eliminated, and the energy difference is defined simply by two *cis*-decalin interactions, or 4.8 kcal. just as in the *cis–anti–cis*-perhydroanthracene. In the latter conformation, the angular *skew* interaction is operative producing an 0.8 kcal. increment or a total difference of 5.6 kcal. The former conformation, therefore, is the more stable.

The *cis–syn–cis*-perhydrophenanthrene has a 1,3-(p) (p) interaction of the type considered above in the *cis–syn–cis*-perhydroanthracene. If the parameter 4.8 kcal. is invoked for this interaction the total energy difference becomes 7.2 kcal. It is difficult to estimate the energy difference of *trans–syn–trans*-perhydrophenanthrene. In addition to the boat conformation for the central ring,[3] the bonds forming the angle define an eclipsed conformation giving rise to an interaction of the type shown in Fig. 5. The contribution of this interaction is not easily evaluated; however, the total energy difference of the *trans–syn–trans* form should be greater than 5.6 kcal.

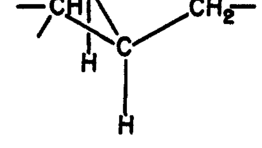


Fig. 5.

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The Chemistry of Aliphatic Phosphonic Acids. I. Alkylation of Methanediphosphonic Acid[1]

BY GENNADY M. KOSOLAPOFF

RECEIVED OCTOBER 30, 1952

Some time ago we reported a study of the alkylation at the central carbon atom of trialkyl phosphonoacetates, *i.e.*, compounds of the general type $(RO)_2P(O)CH_2CO_2R$.[2]

The phosphonoacetates can be regarded as partial phosphorus-bearing analogs of dialkyl malonates. The ready alkylation and dialkylation of the former showed very nicely the active methylene character of the central group in these esters, but the question still remained as to the source of the active methylene character, for this could have originated solely in the carboxylic end of the molecule.

In order to resolve this question we investigated the possibility of alkylation of tetraalkyl methanediphosphonates, *i.e.*, esters of the general type $(RO)_2P(O)CH_2P(O)(OR)_2$, which can be regarded as the true phosphorus analogs of the malonates. A few minor points relative to the preparation of the tetraethyl esters were clarified and it was established that esters higher than tetraethyl cannot be very satisfactory model substances, owing to very high boiling points. Since the purification of the reaction products centers exclusively in the fractionation procedures, the use of very high-boiling materials is undesirable. The sensitivity of the methyl esters to hydrolysis made such esters equally undesirable.

It was found that tetraethyl methanediphosphonate reacts readily with potassium in inert solvent, the reaction being quite exothermic. The resulting potassio derivative alkylates moderately readily with *n*-butyl bromide yielding the corresponding tetraethyl pentane-1,1-diphosphonate, which was characterized and hydrolyzed to the free acid which was also characterized. The rather unsatisfactory yields of the products effectively precluded the extension of the work to dialkylation reactions. However, the monoalkylation was demonstrated beyond doubt. The behavior of the mixture indicated that a considerable portion of the ester undergoing alkylation suffers ester-cleavage with subsequent formation of partial sodium salts. Such reactions have been noted for other esters of phosphonic acids[3] and present a serious problem to be solved in respect to satisfactory isolation of such substances.

The activity of the hydrogen in the methylene group of the diphosphonate can be attributed to

[1] Presented at the Southeastern Regional Meeting, October, 1952.

[2] G. M. Kosolapoff and J. S. Powell, THIS JOURNAL, **72**, 4198 (1950). See the bibliography in this paper for earlier references.

[3] V. S. Abramov and M. N. Morozova, *Zhur. Obshchei Khim.*, **22**, 257 (1952).

one of the two possible causes. One of these can be the operation of the inductive effect of the two $PO(OR)_2$ groups attached to the methylene group. The other cause can be the partial double bond character of the P(O) linkage, which would permit the formation of an enolic structure involving the methylene group as well as the P(O) group, in a manner analogous to that customarily formulated for the sodio malonates and to which is usually attributed the stability and the ease of formation of such enolates. The very readiness of the reaction of the ester with potassium seems to argue for the latter explanation. Obviously if one assumes the completely semi-polar character of the P(O) linkages the formulation of the enol becomes impossible. Naturally, our observation is not the terminal solution of the true nature of the P(O) link, which has eluded such a solution after numerous experimental approaches.

The methylene activity in the diphosphonates has been made a starting point for further studies of alkylation of ordinary esters of aliphatic phosphonic acids, which coupled with a study of dipole moments of the compounds involved, may be expected to throw more light on the problem. The results of this work will be reported at a later date.

Experimental Part

Tetraethyl Methanediphosphonate.—This ester has been prepared earlier by Ford-Moore and Williams[4a] and by Schwarzenbach and Zurc.[4b] The method used by the former group was the most convenient for our purpose and the following description gives the details which were omitted by the previous workers in their synthesis in publication. Freshly distilled methylene iodide (103 g., b.p. 85–86° at 35 mm.) was rapidly added to 200 g. of triethyl phosphite (kindly supplied by the Virginia-Carolina Chemical Company; the product was redistilled before use) in a 500-ml. round-bottom flask, which was attached to a 16-inch Vigreux column. The mixture was heated rapidly to 160° by means of a pre-heated oil-bath. The colorless mixture acquired a dark brown-violet color which persisted for some 10 minutes, after which a vigorous reaction set in, with rapid evolution of ethyl iodide, which was collected in a cooled receiver. The reaction and the distillation were complete within 20 minutes, when the bath was heated to 170° for 10 minutes without causing any further change. Approximately 88 g. of ethyl iodide was collected for a 72.5% yield.

The reaction mixture was distilled under reduced pressure through a short fractionating column and gave, after redistillation, three fractions, as follows. The first fraction of 89 g. was composed in main of diethyl ethanephosphonate, b.p. up to 100° (mostly 98–100°) at 30 mm. The second fraction, which boiled at 95–135° at 0.5–0.4 mm. weighed 91 g. and was composed mainly (63 g.) of diethyl iodomethanephosphonate, b.p. 100° at 0.5 mm., 59% yield. The third fraction consisting of tetraethyl methanediphosphonate boiled at 135–137° at 0.4 mm. and weighed 20 g., for an 18% yield.

A somewhat smaller excess of triethyl phosphite (88 g. treated with 54 g. of methylene iodide) gave 31 g. of diethyl iodomethanephosphonate and 10 g. of tetraethyl methanediphosphonate. The large excess of the phosphite is quite essential for securing an appreciable yield of the disubstituted derivative.

Attempts to improve the yield of the latter by heating the isolated iodomethane derivative with triethyl phosphite were of dubious value, for the products were composed largely of diethyl ethanephosphonate and the iodomethane derivative, with only very small amounts of the diphosphonate. This result is in accord with the known sluggishness of the halogen in halomethanephosphonates. It also indicates that the Arbuzov–Michaelis reaction with dihalides essentially completes itself in the initial stage, at least with methylene iodide, and is not a true two-step reaction.

Alkylation of the Diphosphonate.—The diphosphonate (20 g.) was diluted with one volume of dry xylene and the solution was added over a 15-minute period to 2.7 g. of sliced potassium suspended in 250 ml. of dry xylene. The reaction evolved an appreciable amount of heat and resulted in an initial formation of a light flocculent precipitate which was largely dissipated after two hours required for completion of the reaction. The mixture was gently heated for the last few minutes to facilitate the reaction. (If the mixture is heated and the metal is kept in molten state, the addition of the diphosphonate causes a very vigorous reaction and the evolved gas causes severe foaming.)

The mixture was then treated with 20 g. (excess) of *n*-butyl bromide and was stirred for three hours without any visible change. The flask was then heated cautiously to the reflux temperature and the heating was continued for 3.5 hr. at which time a definite precipitate of potassium bromide formed. This was filtered off and the filtrate was fractionated, yielding 14 g. of unreacted ester and 5 g. of diethyl pentane-1,1-diphosphonate, a colorless viscous liquid, b.p. 147–149° at 0.3 mm., n^{20}_{D} 1.4428. This was hydrolyzed by refluxing overnight with 50 ml. of concentrated hydrochloric acid and evaporation to dryness with an infrared lamp. The product was recrystallized twice from water by repeated evaporation to remove any residual hydrochloric acid. The extremely hygroscopic pentane-1,1-diphosphonic acid was obtained in the form of waxy colorless needles which, after drying in high vacuum at 100°, soften at 143° and melt at 163–165°. The product gave a sharp depression of mixed melting point with methanediphosphonic acid.

Analytical.—The acid was titrated electrometrically to *p*H 5 according to Schwarzenbach.[4b] Calcd. for $BuCH(PO_3H_2)_2$: P, 26.7; equiv. wt., 116. Found: P, 26.5, 26.5; equiv. wt., 114, 114.5.

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[4] (a) A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1465 (1947); (b) G. Schwarzenbach and J. Zurc, *Monatsh.*, **81**, 202 (1950).

The Growth and Analysis of Barium Oxide Crystals Containing a Stoichiometric Excess of Barium[1]

BY GEORGE G. LIBOWITZ

RECEIVED OCTOBER 6, 1952

In studying the possible existence of a suboxide of barium, Schriel[2] obtained small crystallites of barium oxide by dissolving BaO in molten barium metal. These crystallites were colored deep red, and contained a stoichiometric excess of barium in the crystal lattice. Schriel's analysis of these crystals showed that they contained from 0.6 to 1.3% excess barium. As a result of the present work, these values were shown to be too high due to the presence of microscopic globules of free barium metal which were found embedded in these crystals. Because of the interest in barium oxide as a semiconductor, large crystals of this red barium oxide were desired, as well as an accurate method of determining the excess barium in the crystal lattice. By the method described below, crystals as large as 2 mm. thick by 1 cm.^{2} have been grown at this Laboratory.

Experimental

Growth of Barium Oxide Crystals.—A mixture of 60% barium metal chips and 40% barium oxide was put into a steel crucible, 1.25 in. in diameter and 4 in. long, so that only half the crucible was filled. The crucible was covered, and the lower half placed into a molybdenum wire wound furnace. The entire system was evacuated to a pressure of less than 10^{-4} mm. and heated at about 900° for 60–80

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[1] This work has been supported by the Office of Naval Research.

[2] M. Schriel, *Z. anorg. Chem.*, **231**, 313 (1937).