

55. *The Thermal Decomposition of Dialkyl Alkylphosphonates:  
A New Route to Alkylphosphonic Acids.*

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Di-n-butyl ethylphosphonate decomposes under reflux to give ethylphosphonic acid in 99% yield and but-1-ene. The esters  $n\text{-C}_6\text{H}_{13}\cdot\text{PO}(\text{OR})_2$ , where R = Et, Pr<sup>n</sup>, Pr<sup>i</sup>, Bu<sup>n</sup>, or Bu<sup>s</sup>, similarly give the corresponding olefins and n-hexylphosphonic acid; the ease of decomposition and the purity of the acid obtained increase in the order (R =) Et < Pr<sup>n</sup> < Pr<sup>i</sup> < Bu<sup>s</sup>.

Dimethyl n-hexylphosphonate decomposes more slowly on similar heating, to give mainly hex-1-ene, along with methanol, dimethyl methylphosphonate, and unidentified substances. It is suggested that hex-1-ene is eliminated from a hexyloxy-group after interchange of methyl and hexyl groups in the original phosphonate.

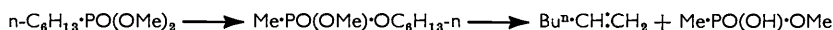
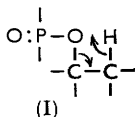
DURING a study of the thermal decomposition of a range of organophosphorus compounds we found that when di-n-butyl ethylphosphonate was heated under reflux in nitrogen but-1-ene was evolved (88% of the theoretical amount being collected in a cold trap), and almost pure ethylphosphonic acid was left in 99% yield. A little butan-1-ol was also formed.

Similar heating of di-n-butyl n-hexylphosphonate gave but-1-ene, along with a little butan-1-ol, the reaction being faster than with the corresponding ethylphosphonate, probably because of the higher boiling temperature of the ester. The n-hexylphosphonic acid formed, however, was not pure (but was obtained so by one recrystallization) presumably because of simultaneous and subsequent reactions, particularly, we suspect, formation of derivatives of anhydrides of phosphonic acid.

It was to be expected that the n-hexylphosphonic acid formed would be purer the milder the conditions for olefin-formation. It was found that the ease of reaction and the purity of the acid formed from the esters  $n\text{-C}_6\text{H}_{13}\cdot\text{PO}(\text{OR})_2$  increased in the order (R =) Et < Pr<sup>n</sup> < Pr<sup>i</sup> < Bu<sup>s</sup>, that is, with increased branching in the alkyl group and increased

methyl substitution on the olefin formed. The olefin evolved from the di-*n*-butyl compound was shown by its infrared spectrum to be a mixture of but-1-ene and *trans*- and *cis*-but-2-ene. The results accord with results in thermal decompositions of phosphates,<sup>1,2</sup> and of acetate, xanthate, and other esters.<sup>3</sup>

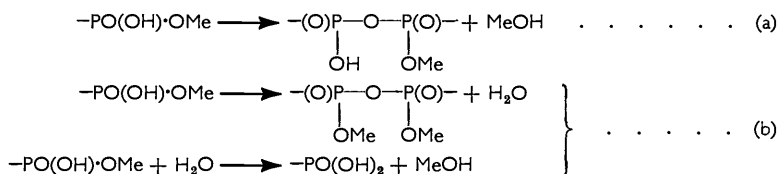
The reactions presumably involve *cis*- $\beta$ -elimination [cf. (I)] (for a consideration of analogous eliminations involving alkyl phosphates see ref. 2). It was thus of interest to examine the behaviour of dimethyl *n*-hexylphosphonate, in which such  $\beta$ -elimination cannot occur. This compound decomposed much more slowly than those mentioned above, but in 20 hours' heating hex-1-ene was obtained in 45% yield, and methanol and dimethyl methylphosphonate in 11% and 10% yield, respectively. The formation of hex-1-ene might involve a free-radical process which would be the reverse of the well-known addition of dialkyl phosphites to olefins (while no dimethyl phosphite was found in the products, it might be destroyed under the severe conditions employed, one of the possible products being dimethyl methylphosphonate formed by disproportionation). However, we suggest, instead, that the evolution of hex-1-ene follows a rearrangement in which *n*-hexyl and methyl groups are interchanged, the interchange possibly taking place through a step which could be regarded as a reversal of a Michaelis-Arbuzov rearrangement, *e.g.*:



Dimethyl methylphosphonate would then be formed by disproportionation of the methyl hydrogen methylphosphonate, but if the alkyl-interchange were intermolecular it could be formed directly:



The formation of methanol is probably linked with formation of condensed acids, as in processes of types (a) and (b), which could be expected to occur in the complex acid residues at the high temperatures involved:



The high-boiling residue from the reaction could not be identified but its infrared spectrum was consistent with the presence of P-O-P bonds.

The thermal decomposition of suitable esters represents a new method of making organophosphonic acids, which might have value for thermally stable acids, particularly in cases in which the conventional hydrolysis gives trouble either because of the hydrolytic instability of the acid or because of the difficulty of removing all water from it. The value of the new method is enhanced by the commercial availability of suitable di- and tri-alkyl phosphites from which dialkyl organophosphonates can be readily prepared.

#### EXPERIMENTAL

*Di-n-butyl Alkylphosphonates.*—The Arbuzov reaction, as used by Kosolapoff,<sup>4</sup> was used to make di-*n*-butyl ethylphosphonate, b. p. 138–140°/17 mm.,  $n_D^{20}$  1.4282, in 77% yield; di-*n*-butyl *n*-hexylphosphonate, b. p. 183–185°/20 mm.,  $n_D^{20}$  1.4333–1.4355, in 60% yield; *di-n-propyl n-hexylphosphonate*, b. p. 109–110°/0.5 mm.,  $n_D^{20}$  1.4362 (Found: C, 57.55; H, 11.1.

<sup>1</sup> Lecocq and Todd, *J.*, 1954, 2381; Gamrath, Hatton, and Weesner, *Ind. Eng. Chem.*, 1954, **46**, 208.

<sup>2</sup> Baumgarten and Setterquist, *J. Amer. Chem. Soc.*, 1957, **79**, 2605.

<sup>3</sup> DePuy and King, *Chem. Rev.*, 1960, **60**, 431.

<sup>4</sup> Kosolapoff, *J. Amer. Chem. Soc.*, 1945, **67**, 1180.

$C_{12}H_{27}O_3P$  requires C, 57.55; H, 10.9%), in 55% yield; *di-isopropyl n-hexylphosphonate*, b. p. 111.5—113°/2.0 mm.,  $n_D^{20}$  1.4328 (Found: C, 57.4; H, 10.9%), in 55% yield; and *di-s-butyl n-hexylphosphonate* b. p. 125—128°/1.0 mm.,  $n_D^{20}$  1.4335 (Found: C, 61.0; H, 11.1.  $C_{14}H_{31}O_3P$  requires C, 61.0; H, 11.0%), in 36% yield.

*Dimethyl n-Hexylphosphonate*.—A mixture of trimethyl phosphite (62 g., 0.50 mole) and n-hexyl bromide (82.5 g., 0.50 mole) was boiled under reflux until the liquid temperature rose from ca. 105° to 180°. Fractionation gave *dimethyl n-hexylphosphonate*, b. p. 121—123°/10 mm.,  $n_D^{20}$  1.4276 (39.2 g., 49%) (Found: C, 49.5; H, 10.2.  $C_8H_{19}O_3P$  requires C, 49.5; H, 9.9%). The distillation temperature fluctuated within the range 121—123°/10 mm. during the fractionation and occasionally fell briefly to 118°/10 mm., suggesting that some decomposition was occurring.

*Thermal Decompositions*.—The phosphonates were decomposed by boiling them under reflux in Pyrex glass flasks in a slow stream of nitrogen, the heating being adjusted to maintain steady boiling. (An inert atmosphere may be unnecessary, but the gas stream serves also to carry away volatile liquids which would otherwise lower the temperature of the reaction medium.) The outlet from the reflux condenser led to a trap cooled in ethanol-solid carbon dioxide, and thence *via* sulphuric acid bubblers to the air. (Inefficient trapping led to loss of olefins, and the yields reported below must be regarded as minimum values.) A thermometer recorded the temperature of the boiling liquid, which gives a rough guide to the progress of the decomposition.

(a) *Di-n-butyl ethylphosphonate*. The phosphonate (80 g., 0.36 mole) was heated for 9 hr., at which time violent spurting occurred as each drop of reflux fell on to the liquid in the flask. The temperature of the liquid at various times was as follows:

Time (hr.) .....	1	2	4	5	7	8	9
Temp. ....	256°	260°	252°	235°	196°	235°	306°

After 5 hr., 24.1 g. of liquid had collected in the cold trap, and this had increased to 35.9 g. after 9 hr. It was found to consist of but-1-ene (35.6 g., 88%) (identified by its infrared spectrum and by conversion into 1,2-dibromobutane) and butanol (0.3 g.) (identified by its smell and its infrared spectrum).

The residue in the flask crystallized. After traces of butan-1-ol, detectable by its smell, had been removed in a vacuum, the solid had m. p. 61° and was shown to be ethylphosphonic acid<sup>5</sup> (39.2 g., 99%) (Found: C, 21.6; H, 6.25; P, 27.6. Calc. for  $C_2H_7O_3P$ : C, 21.8; H, 6.4; P, 28.1%).

(b) *Di-n-butyl n-hexylphosphonate*. This phosphonate (10 g.) decomposed more rapidly; the liquid temperature fell from 280° after  $\frac{1}{2}$  hr. to 265° after 1 hr. and then rose to over 360° after 1 $\frac{1}{2}$  hr. at which time heating was stopped. The liquid (5.0 g.) in the cold trap was shown to be mainly but-1-ene (theor., 4.04 g.), along with some higher-boiling material which probably included butan-1-ol and possibly water. The residue (5.0 g.) in the flask, which had a smell resembling that of phosphine, solidified, and recrystallization from light petroleum gave n-hexylphosphonic acid, m. p. 104—105°, identified by its infrared spectrum and by mixed m. p. with an authentic sample, m. p. 104.5—106° (cf. ref. 6), obtained by acid hydrolysis of di-n-butyl n-hexylphosphonate.

(c) *Comparative study of di-ethyl, -n-propyl, -isopropyl, and -s-butyl n-hexylphosphonate*. With the diethyl compound (10 g.), the liquid temperature had to be raised to 340° before reaction was apparent, and the temperature was maintained at about this level for 6 hr., during which time ethylene was evolved and some liquid which was not examined collected in the cold trap. The residue gave a wax on cooling, and after two recrystallizations n-hexylphosphonic acid of m. p. 104—105° was obtained in 30% yield.

With the di-n-propyl compound gas evolution was observed when the liquid temperature reached 240°, and heating was continued for 2 $\frac{1}{2}$  hr. until the liquid temperature reached 360°. The loss of weight corresponded to qualitative evolution of propene (some of which was collected and identified), but the residue had m. p. ca. 45—50°. One recrystallization gave n-hexylphosphonic acid, m. p. 104—105°, in 75% yield.

<sup>5</sup> Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons Inc., New York, 1950, p. 149.

<sup>6</sup> Ref. 5, p. 150.

With the di-isopropyl compound, gas evolution appeared to start when the liquid temperature reached 210–220° (after 10 min.), and was violent when it reached 260° (after 15 min.). The temperature then fell rapidly to 220°, and after 25 min. gas evolution had ceased and the temperature began to rise, reaching 275° in 25 min. Propene was collected in 88% yield, although the loss of weight was that expected for quantitative evolution of the gas. The residue melted at 78–81°, and one recrystallization gave *n*-hexylphosphonic acid, *m. p.* 104–105°, in 83% yield.

With the di-*s*-butyl compound, gas evolution was apparent after 5 minutes' heating, when the liquid temperature had reached *ca.* 240°, and was vigorous after 8 min., when the temperature had reached 255°. The temperature fell to 210° (after 12 min.), and gas evolution had ceased after 17 min., when the temperature had risen to 220°. The loss in weight was that expected for quantitative evolution of butene, which was collected in 85% yield, and shown by means of its infrared spectrum to be a mixture of but-1-ene and *trans*- and *cis*-but-2-ene. The residue melted at 86–88°, and one recrystallization gave *n*-hexylphosphonic acid, *m. p.* 104·5°, in 90% yield.

(d) *Dimethyl n-hexylphosphonate.* When the phosphonate (38·7 g., 0·20 mole) was boiled little change was apparent for several hours, the liquid temperature falling from 240° to 235° during 3 hr. and then rising again to reach 240° after 14 hr. Decomposition then seemed to become faster, and the temperature fell to 218° after 16 hr., and to 191° after 21 hr., at which time heating was stopped. The contents of the cold trap consisted of two layers. When they were allowed to warm, a volatile liquid (1·3 g.) boiled out: it was not identified, but a band at 4·23–4·32  $\mu$  in the infrared spectrum was consistent with the presence of a P–H bond.

The remaining contents of the cold trap were distilled to give an azeotrope (4·6 g.) of hex-1-ene and methanol, *b. p.* 48·5°. Hex-1-ene (2·7 g.) and methanol (0·7 g.) were isolated after addition of water to the mixture. From the known composition of the azeotrope<sup>7</sup> it was calculated that 3·2 g. of hex-1-ene and 1·4 g. (11%) of methanol were present.

The residue in the reaction flask was fractionated to give hex-1-ene (4·3 g.), *b. p.* 63–64°,  $n_D^{20}$  1·3875, intermediate fractions boiling from 70°/760 mm. to 110°/10 mm., some slightly impure dimethyl *n*-hexylphosphonate (0·8 g., 2%), *b. p.* 120–124°/10 mm.,  $n_D^{20}$  1·4158, and material of *b. p.* 274–318°/0·5–0·6 mm. (15·4 g.) (acid equiv. by titration against sodium hydroxide, 139) (Found: C, 31·6; H, 6·9; P, 16·2%) which was not identified but whose infrared spectrum was consistent with the presence of P–OH, P=O, P–Me, P–O–Alkyl, and P–O–P bonds. It slowly solidified in a vacuum desiccator to a solid of *m. p.* 122–132°.

The intermediate fractions mentioned above were refractionated to give dimethyl methylphosphonate (1·62 g., 10%), *b. p.* 65°/10 mm.,  $n_D^{20}$  1·4140 (Found: C, 29·3; H, 7·6. Calc. for C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>P: C, 29·1; H, 7·3%). No dimethyl phosphite, which has *b. p.* 55–56°/10 mm., was detected.

The total yield of hex-1-ene was 7·5 g. (45%). Its identity was confirmed by means of its infrared spectrum, which, however, contained two very small additional peaks at 8·5 and 10·38  $\mu$  which might have arisen from the presence of traces of other olefins.

We thank Joseph Crosfield and Sons, Ltd., for the award of a research scholarship (to B. F. D.).

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[Received, June 9th, 1961.]

<sup>7</sup> "Azeotropic Data," Advances in Chemistry Series No. 6, Amer. Chem. Soc., Washington, 1952, p. 30.