448. *Methylenebisphosphonates and Related Compounds. Part I. Synthesis from Methylene Halides.*

By J. A. Cade.

Two established methods for preparing ethyl methylenebisphosphonates can be extended to allyl systems, but with limited success. Only one method gave a product suitable for the preparation of resins for complex formation with metals. The yield of saturated alkyl esters has been improved, and some new esters containing phosphorus are described.

INTEREST in compounds containing a P–C–P bridge has hitherto been small, but the possibility that such compounds could form complexes with metals initiated a search for new methods of obtaining them.

Organic phosphates and phosphonates,[1] in resin form, take up uranium selectively from solutions containing a few mg. per l. Adsorption is considered to involve a chelate complex (A). From analogy with the very stable uranyl pyrophosphate complex, for which a six-membered ring structure has been suggested,[2] it was considered [3] that diphosphonic acids $X(PO_3H_2)_2$ might give uranyl complexes (B) of enhanced stability.

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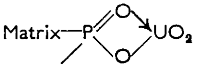
[1] Kennedy, *Chem. and Ind.*, 1956, 378; Kennedy and Davies, *Chem. and Ind.*, 1956, 378; A.E.R.E. Reports C/R 2329, C/R 2330, and unpublished work.

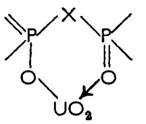
[2] Voegtlin and Hodge, " Pharmacology and Toxicology of Uranium Compounds," McGraw-Hill Co., New York, Vol. I, 1949.

[3] Kennedy and Lane, personal discussion.

Compounds of this type in which X = O, N, S, Sn, or C are known, but for durability of the resin it was desirable to have a carbon bridge, since in the other compounds hydrolysis affects the essential P–X–P bonds. This paper deals with application of the Michaelis–Becker and the Arbusov–Michaelis reaction[4] to give esters $CH_2(PO_3R_2)_2$ (R = allyl, to preserve continuity [1]). Yields were small, with formation of large amounts of undistillable residues and hazard of explosion during prolonged heating or at high temperatures, all due to a tendency for spontaneous polymerisation. The allyl esters, once isolated, could be redistilled with high recovery (>90%). The addition of a small quantity of quinol increased the yields of monomer.

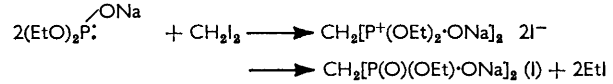
(A)





(B)

Sodium Diallyl Phosphite and Methylene Dihalide.—Nylen[5] showed that the main product (40% yield) from methylene di-iodide and sodium diethyl phosphite was symmetrical disodium diethyl methylenebisphosphonate (I), believed to be due to reaction of the dialkyl phosphite in the " enol " form:



$$2(EtO)_2\overset{\diagup ONa}{P{:}} + CH_2I_2 \longrightarrow CH_2[P^+(OEt)_2{\cdot}ONa]_2\ 2I^-$$
$$\longrightarrow CH_2[P(O)(OEt){\cdot}ONa]_2\ (I) + 2EtI$$

Sodium iodide, ethyl iodide, diethyl ethylphosphonate, and unchanged reactants were identified among the products but the required tetraethyl methylenebisphosphonate was not obtained. A reaction not involving elimination of alkyl groups could only be realised when a dihalide was used in which the halogen atoms are separated by at least three carbon atoms.

These observations have been corroborated by those for allyl systems. Methylene di-iodide or di-bromide with sodium diallyl phosphite gave allyl iodide, diallyl allylphosphonate, and disodium diallyl methylenebisphosphonate. It is unlikely that dealkylation occurs as depicted by Nylen. Neutral bisphosphonate is probably first formed, then dealkylated by halide ions, apparently with the aid of electron-delocalising substituents on the carbon atom attached directly to phosphorus in phosphonic acids.[6]

Attempts, by various techniques, to exclude moisture and free alcohol, and thus to prevent elimination of two alkyl residues, failed to give tetra-allyl methylenebisphosphonate.

Direct reaction of sodium with diallyl hydrogen phosphite in benzene or toluene was unsatisfactory for the preparation of sodium diallyl phosphite because a gel was deposited before all the sodium had dissolved. Addition of diallyl hydrogen phosphite to sodium allyloxide, followed by removal of allyl alcohol by repeated distillation with toluene, gave a very reactive product. When methylene dibromide was added to this, sodium bromide was precipitated immediately, but the reaction became uncontrollable after ¼ to ⅓ of an equivalent of methylene dibromide had been added, even at 0°. (Similar results were obtained with the chloride.) This could be prevented by addition of quinol, but reactivity was thus reduced and sodium bromide (equivalent in some experiments to 60—75% of the bromine in the system) was produced only after warming to 60° for some hours. In all experiments allyl bromide was produced, the main product being a viscous residue which could not be distilled or crystallised, but which in some cases contained derivatives of methylenebisphosphonic acid.

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[4] See Kosolapoff, " Organophosphorus Compounds," Wiley, New York, 1950, pp. 121, 123.

[5] Nylen, Diss., Uppsala, 1930, pp. 77—84.

[6] Cf., *e.g.*, the preparation of ethyl aryloxymethylphosphonic acid from sodium aryloxide and diethyl iodomethylphosphonate; McGuire and Shaw, *Chem. and Ind.*, 1953, 668; *J.*, 1955, 1756.

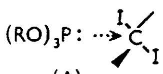
Attempts to obtain resins from some of these residues failed because the degree of polymerisation obtainable was insufficient to make them insoluble in water.

Trialkyl Phosphite and Methylene Dihalide.—There is controversy about application of the Arbusov–Michaelis reaction to methylene dihalides.

Arbusov and Kushkova [7] isolated only the monosubstitution product $(EtO)_2PO{\cdot}CH_2I$ from methylene di-iodide and triethyl phosphite, failed to obtain the tetraester bisphosphonate therefrom by use of sodium diethyl phosphite, but claimed that diethyl iodomethylphosphonate with potassium diethyl phosphite in 90% ethanol gave diethyl hydroxymethylphosphonate, which was the sole product from methylene di-iodide and potassium diethyl phosphite in ether. In contrast, Ford-Moore and Williams [8] obtained the bisphosphonate on using the di-iodide, though some halogenomethylphosphonate was also formed. Kosolapoff [9] found that when a 50% excess of phosphite is used the yield approaches 30%.

The reactivity of alkyl halides in this reaction is in the order $RI > RBr \gg RCl$, and decreases with increase in molecular weight. With methylene di-iodide, the by-product alkyl halide was produced in a one-phase reaction.[10] When trialkyl phosphite and an alkyl halide of sufficiently high boiling point were heated together, a temperature was attained at which reaction became self-ustaining. This temperature differed sufficiently among various halides used to be regarded as an approximate measure of the reactivity, which was found to be in the order $(EtO)_2PO{\cdot}CH_2Cl \ll (EtO)_2PO{\cdot}CH_2Br \sim (EtO)_2PO{\cdot}CH_2I < EtI > C_3H_5I \gg CH_2I_2$, with respect to triethyl or triallyl phosphite.

Gerrard and Green [11] have provided evidence that the reaction normally proceeds by two successive S_N2 steps. The low reactivity of methylene dihalide may therefore be attributed partly to impedance by the negative iodine atom to the in-line end-on approach of the phosphorus, necessitating a direction of attack requiring higher energy of activation (cf. A), and partly to the higher energy required to break the halogen–carbon bond when the latter atom is adjacent to another electron-withdrawing atom or group. The halogenomethylphosphonates are even less reactive, probably because of steric hinderance offered by the $(RO)_2P(O)$– group, in addition to the foregoing factors.



(A)

The low reactivity of these halides makes the unwanted isomerisation more likely when the reactants are mixed before heating, especially as the formation of low-boiling alkyl halide tends to prevent the threshold temperature for fast reaction in the main sequence being attained. The importance of removing the more reactive by-product halide as it is formed has been recognised by previous investigators,[8] including Kabachnik and Medved [12] who attempted to blow it out with air. The isomerisation can also be further controlled by adding the trialkyl phosphite to the inactive halide held at a high temperature, at a slower rate than that at which the simple active halide is removed. Thus when diethyl iodomethylphosphonate and an excess of triethyl phosphite were merely heated together, nearly 90% of the latter reappeared as isomer. If however the phosphite was added slowly to the phosphonate at *ca.* 200° so that the instantaneous concentrations of both ethyl iodide and phosphite were kept to a minimum, almost 60% conversion into bisphosphonate was achieved. By using an excess of hot methylene di-iodide (the excess could be recovered), the yield of iodomethylphosphonate itself was improved to 90% with respect to the triethyl phosphite used, by the same technique. This represents a three-fold increase in the efficiency of the preparation of the bisphosphonate. The two stages could not, however, be combined, for although there was an overall reduction in the amount of diethyl ethylphosphonate formed, its accumulation necessitated prolonging the addition

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[7] Arbusov and Kushkova, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 283; *Chem. Abs.*, 1936, **30**, 4813.
[8] Ford-Moore and Williams, *J.*, 1947, 1465.
[9] Kosolapoff, *J.*, 1955, 3092.
[10] Contrast Kosolapoff, *J. Amer. Chem. Soc.*, 1944, **66**, 1511.
[11] Gerrard and Green, *J.*, 1951, 2550.
[12] Kabachnik and Medved, *Isvest. Akad. Nauk S.S.S.R.*, 1950, 635; *Chem. Abs.*, 1951, **45**, 8444.

in order to keep up the temperature and so led to a considerable undistillable residue. Apparently more bisphosphonate was formed, but the amount isolated was again only about 30%. Diethyl bromomethylphosphonate was nearly as reactive as the iodo-ester; an advantage in using the former was that it could be prepared from bromomethylphosphonyl dibromide, without the use of triethyl phosphite. Diethyl chloromethylphosphonate was ineffective.

The modified method had very limited success with allyl esters, because the prolonged heating produced much residue. Adding triallyl phosphite to hot methylene di-iodide in excess gave diallyl iodomethylphosphonate in 41% yield, but the latter with triallyl phosphite above 190° gave unidentified unsaturated material boiling at 38°, and at higher temperatures violent decomposition was common. An optimum yield of only 12% of tetra-allyl methylenebisphosphonate was obtained by the Kosolapoff technique.

TABLE 1.

No.	Compound	Yield (%)	B. p./mm.	n_D	d_4
1	Triallyl phosphite [a]	90—92	34°/0·06	1·4589	0·999
2	Diallyl phosphite [b]	70—76	40°/0·07	1·4478	1·087
3	Diallyl allylphosphonate [c]	82	54°/0·08, 72°/0·45	1·4622	1·046
4	Diallyl chloromethylphosphonate [d]	60	83°/0·15	1·4665	1·175
5	Diallyl bromomethylphosphonate [d]	72	76°/0·1	1·4842	1·373
6	Diallyl iodomethylphosphonate	8; 41 [e]	102°/0·1	1·5015	1·552
7	Tetra-allyl methylenebisphosphonate	12	142°/0·1	1·4675	1·132
8	Diethyl bromomethylphosphonate [d]	82	121°/15, 56°/0·25	1·4595	1·432
9	Tetrabutyl methylenebisphosphonate [f]	45	150—155°/5 × 10^{-4} *	1·4455 †	1·041 †
10	Tetrabutyl ethylenebisphosphonate [f]	51	175—178°/5 × 10^{-4} *	1·4484, 1·4465 †	1·035

* Surface temperature during molecular distillation. † At 25°. Other values at 20°.

[a] Prepared by Ford-Moore and Williams's method.[8] [b] Toy and Cooper [17] give alternative physical constants; this ester was prepared by Gerrard's procedure [18] but at 25°. [c] From triallyl phosphite and excess of allyl iodide. An excess of the (low-boiling) iodide was used to avoid rise in temperature and possible violent decomposition. The ester was described by Kamai and Kukhtin [19] but the physical constants given by them (n_D^{20} 1·4600; d_4^{20} 1·005) lead to $[R_L]_D$ 55·1 (cf. Table 2). [d] Halogenomethylphosphonyl dichloride (1 equiv.) was added at −10° to sodium alkoxide (2 equiv.) prepared in excess of alcohol. Next morning the mixture was poured on ice and the oil which separated was extracted with methylene dichloride and worked up in the usual way. [e] Yields from Arbusov and Kushkova's method,[7] and the modification described in the Experimental section. [f] Prepared by the two-stage method used to obtain the tetraethyl ester as described in the Experimental section. The intermediate bromo-compounds were not purified. *Esters* 4—10 are new.

TABLE 2.

	Required (%)				Found (%)			
No.	C	H	P	$[R_L]_D$	C	H	P	$[R_L]_D$
1	53·5	7·5	15·3	55·33	53·6	7·4	15·3	55·32
2	44·5	6·85	19·1	39·32	45·25	7·05	19·2	39·17
3	53·5	7·5	15·3	53·33	52·95	7·4	15·3	53·17
4	39·9	5·75	14·7	49·3	39·9	5·75	14·2	49·66
5	33·0	4·7	12·15	52·2	32·95	4·8	12·4	53·16
6	27·85	4·0	10·25	57·41			10·4	57·4
7	46·4	6·6	18·4	82·26	46·65	6·8	18·1	82·5
8	26·0	5·2	13·4	43·76	25·9	5·4	13·35	44·16
9	51·0	9·6	15·5	102·54	50·85	9·6	16·1	102·54
10 *	52·2	9·4	14·95	107·19	50·35, 50·3	9·6, 9·6	14·4	107·25

* This ester is hygroscopic (cf. tetra*iso*propyl ethylenebisphosphonate [7]). Physical constants were determined in a dry-box, but weighings for the analyses were made in air; so the analytical results are low.

An attempt to obtain diallyl iodomethylphosphonate from the chloromethylphosphonate and sodium iodide in dry acetone gave allyl iodide as the only identifiable product.

The yields and properties of the new esters are in Tables 1 and 2. Calculated values of $[R_L]_D$ were obtained from Kabachnik's atomic constants [13] for phosphorus and oxygen and Vogel's values [14] for the organic residues.

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[13] Kabachnik, *Bull. Acad. Sci. U.S.S.R.*, 1948, 219; *Chem. Abs.*, 1948, **42**, 5736.

[14] Vogel, " Textbook of Practical Organic Chemistry," Longmans, London, 1948, p. 898.

Bulk or emulsion polymerisation of tetra-allyl methylenebisphosphonate produced a resin suitable for exchange columns (to be described elsewhere).

EXPERIMENTAL

Some analyses (C & H) were by Mr. R. A. D. Smith of Messrs. Albright and Wilson Ltd., Oldbury; phosphorus was determined as magnesium pyrophosphate.

Allyl alcohol was dried (K_2CO_3) and redistilled; Phosphorus trichloride was redistilled after being heated under reflux to expel dissolved hydrogen chloride. Diethylaniline was purified as described by Vogel.[14] Benzene, toluene, ether, and light petroleum were dried over phosphoric oxide, decanted, redistilled, and stored over sodium wire. Methylene dibromide was treated as was allyl alcohol, and the di-iodide was decolorised over mercury before redistillation under reduced pressure.

Diethyl chloromethylphosphonate was prepared from the acid chloride which was obtained from phosphorus trichloride and paraformaldehyde (cf. ref. 15).

Bromomethylphosphonyl Dibromide.[16]—To aluminium bromide (280 g., *ca.* 1 mol.) and phosphorus tribromide (272 g., 1 mol.) in a 1 l. flask fitted with a reflux condenser, methylene dibromide (500 c.c., excess) was added portionwise with cooling. The mixture was heated cautiously, then boiled for 2 hr. It became a homogeneous red liquid. The bulk (350 c.c.) of the methylene dibromide was removed by distillation. The residual syrup solidified in a desiccator; it was added in lumps to methylene dichloride (1·2 l.) at $-20°$ with stirring. It then disintegrated. Water (160 c.c., 8·5 mols.) was added dropwise while the mixture was kept at $-20°$. The precipitate was collected on sintered glass and washed twice with methylene dichloride (200 c.c.). The filtrate and washings were distilled to low bulk and degassed at the water pump, and the residue was distilled, the fraction (154—180 g., 50—60%), b. p. 130—138°/12—14 mm., being collected. Redistillation afforded pure bromomethylphosphonyl dibromide, b. p. 118—120°/7 mm., n_D^{20} 1·512.

Interaction of Sodium Diallyl Phosphite and Methylene Dihalide.—(*a*) Sodium (4·6 g., 2 mol.) was dissolved in allyl alcohol (100 c.c.) under reflux, and diallyl phosphite (32·4 g., 2 mols.) was added at 0°. Methylene di-iodide (26·8 g., 1 mol.) was added during 30 min. with stirring, and the solution then warmed at 60° for 2 hr. No precipitate was formed. The bulk of the alcohol was distilled off and residual volatile matter was removed at 60°/0·1 mm. and trapped at $-80°$. The combined distillate and trap contents were treated with water, and the insoluble material dried (Na_2SO_4) and distilled, giving allyl iodide (16 g.), b. p. 98—102° (*S*-thiuronium picrate m. p. and mixed m. p. 154—156°), and methylene di-iodide (4·2 g., 15·5% recovery; b. p. 79—82°/25 mm., d_4^{20} 3·32). The pasty residue (43 g.) was washed with 1 : 1 acetone–ether until free from iodide and recrystallised from methanol–ether, to give symmetrical *disodium diallyl methylenebisphosphonate* (15 g., 50%), m. p. 209—211° (Found: C, 27·8; H, 4·0; P, 21·35. $C_7H_{12}O_6P_2Na_2$ requires C, 28·0; H, 4·0; P, 20·6%). The acetone washings were treated with a large excess of water; distillation of the insoluble oil which separated gave diallyl allylphosphonate (6·5 g.), b. p. 75—78°/0·5 mm., n_D^{20} 1·4614.

(*b*) Sodium diallyl phosphite was prepared as described in (*a*) from sodium (4·6 g., 2 mols.) and diallyl hydrogen phosphite (32·4 g., 2 mols.) in allyl alcohol, after which the latter was removed at 20°/15 mm. To the dry product, toluene (200 c.c.) was added and then a portion (100 c.c.) was distilled. The process was repeated until the distillate was free from allyl alcohol. To the resulting solution, methylene dibromide (17·5 g., 1 mol.) was added in 30 min. with stirring at 0°. After about ¼—⅓ of the bromide had been added, a violet reaction set in. Sometimes the bisphosphonate was eventually obtained but the process was unreliable. Methylene dichloride gave similar results, and addition of quinol also did not give reliable reactions.

Separation of methylenebisphosphonic acid. Disodium diallyl methylenebisphosphonate (9 g.) was heated under reflux with constant-boiling hydrobromic acid (80 c.c.) for 3 hr. and the mixture was then distilled. From the distillate allyl bromide (3·8 g.) was obtained. The residual syrup was treated with more acid (50 c.c.) and sodium bromide (4·9 g., 75%) was filtered off. The filtrate was evaporated to small bulk, treated with absolute ethanol (50 c.c.),

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[15] Kabachnik and Shepeleva, *Isvest. Akad. Nauk S.S.S.R.*, 1951, 185; *Chem. Abs.*, 1951, **45**, 10,191.

[16] An example of the Kinnear–Perren reaction, *J.*, 1952, 3437; Cade, A.E.R.E. Report C/M 302.

[17] Toy and Cooper, *J. Amer. Chem. Soc.*, 1954, **76**, 2191.

[18] Gerrard, *J.*, 1940, 1464.

[19] Kamai and Kukhtin, *Doklady Akad. Nauk S.S.S.R.*, 1953, **89**, 309; *Chem. Abs.*, 1954, **48**, 7540.

filtered, and evaporated, this process being repeated until the residual syrup was free from bromide. The residue, after 5 days over phosphoric oxide, gave methylenebisphosphonic acid (1·5 g.), m. p. 191—198°. Recrystallisation from *tert.*-butyl alcohol gave the pure acid [5] (0·3 g.), m. p. 201°.

Interaction of Triethyl Phosphite and Methylene Di-iodide.—(*a*) The phosphite (425 g., 2·2 mols.) and the iodide (311 g., 1 mol.) were heated together under a column (10″) containing glass helices and a condenser set for distillation. Reaction set in at 148° and the temperature rose spontaneously to 200°. Liquid distilled and the temperature was held at 190—200° until the distillation ceased (20 min.). The residue gave, by repeated redistillation, diethyl ethylphosphonate (263·6 g., 62%), b. p. 43—45°/0·1 mm., n_{D}^{20} 1·4150, diethyl iodomethylphosphonate (56·3 g., 7·9%), b. p. 90—100°/0·2 mm., n_{D}^{20} 1·4816, tetraethyl methylenebisphosphonate (81·2 g., 22%), b. p. 122—128°/0·5 mm., n_{D}^{20} 1·4300, and mixed fractions and residues. The primary distillate was combined with the low-boiling forerun from the main products and, after treatment with dilute hydrochloric acid and drying, gave ethyl iodide (68·6 g.), b. p. 70—73°, a mixed fraction (18·9 g.), b. p. 134—140°, and recovered methylene di-iodide (45·8 g., 14·9%), b. p. 175—182°.

(*b*) The phosphite (183 g., 2·2 mols.) was added to the iodide (134 g., 1 mol.) at 185° which was refluxing half-way up the column. The rate of addition was adjusted so that distillation (70—110°) occurred steadily and the temperature increased, finally to 220°. Heating was continued for a further 10 min. The products were ethyl iodide (128 g., 82%), b. p. 70—73°, crude diethyl ethylphosphonate (27·5 g., 15%), b. p. 35—50°/0·1 mm., n_{D}^{20} 1·4200, a mixed fraction containing the iodomethylphosphonate (82 g.), b. p. 80—100°/0·1 mm., n_{D}^{20} 1·4680, bisphosphonate (42·5 g., 29·5%), b. p. 100—105°/0·1 mm., n_{D}^{20} 1·4311, and a residue (32·3 g.) (Found: P, 19·8. Calc. for $C_9H_{22}O_6P_2$: P, 21·5%).

(*c*) The foregoing procedure, with the phosphite (83 g., 1 mol.) and iodide (200 g., 1·5 mol.), gave ethyl iodide (74 g., 95%), methylene di-iodide (68 g., 34%), and diethyl iodomethylphosphonate (120 g., 90%), b. p. 96—99/0·5 mm., n_{D}^{20} 1·5002. The residue (11 g.) contained no iodine but pure bisphosphonate was not obtained from it.

Interaction of Triethyl Phosphite and Diethyl Iodomethylphosphonate.—(*a*) When the phosphite (33·2 g., 2 mols.) and phosphonate (27·8 g., 1 mol.) were heated to 160° ebullition began but no violent reaction. Heating was continued, eventually to 180° (15 min.) where liquid began to distil (b. p. 60—80°). When distillation ceased (15 min.) the temperature was 195° at which the reactants were held for 1 hr. The distillate was ethyl iodide (2 g.) contaminated with triethyl phosphite (odour). Distillation of the reaction mixture gave: (i) forerun (4·6 g.), b. p. 40—77°/10 mm., n_{D}^{20} 1·4128, containing triethyl phosphite; (ii) (15·8 g.), b. p. 77—83°/10 mm., n_{D}^{20} 1·4150; (iii) (9·0 g.), b. p. 34—50°/0·08 mm., n_{D}^{20} 1·4198; (iv) (10·1 g.), b. p. 50—98°/0·08 mm., n_{D}^{20} 1·4748; (v) (13·9 g.), b. p. 98—135°/0·08—0·35 mm. (decomp.), n_{D}^{20} 1·4600; and a residue (4·8 g.) which contained iodine. From fractions (iv) and (v) combined, the iodomethylphosphonate (13·5 g., 48·6%), b. p. 80—83/0·08 mm., n_{D}^{20} 1·4970, was obtained by refractionation. From the forerun of this distillation combined with fractions (i)—(iii), diethyl ethylphosphonate (29·0 g., 87·4%), b. p. 43—45°/0·08 mm., n_{D}^{20} 1·4166, was similarly obtained. Pure tetraethyl methylenebisphosphonate was not obtained from the residues.

(*b*) The phosphite (33·9 g., 1 mol.) was added to the phosphonate (37·6 g.) at 220° as described for the preparation of the latter. The final temperature was 240°. The product included ethyl iodide (17·6 g., 83·5%) and tetraethyl methylenebisphosphonate (23 g., 59%), b. p. 123—128°/0·5 mm., n_{D}^{20} 1·4297. Very little iodomethylphosphonate was recovered.

Interaction of Triethyl Phosphite with Other Diethyl Halogenomethylphosphonates.—(*a*) The phosphite (40 g., 1·25 mol.) was added in 1 hr. to diethyl bromomethylphosphonate (44 g., 1 mol.) at 220—235° as described for the preparation of diethyl iodomethylphosphonate. After the usual working up, the products were ethyl bromide (14·5 g., 70%), b. p. 35—38°; diethyl ethylphosphonate (19 g., 25%), b. p. 36—40°/0·1 mm., n_{D}^{20} 1·412; and tetraethyl methylenebisphosphonate (263 g., 48%), b. p. 122—124/0·5 mm., n_{D}^{20} 1·4308.

(*b*) The phosphite (60 g., 1·1 mol.) was added to heated diethyl chloromethylphosphonate (60 g., 1 mol.) at such a rate that the temperature never fell below 220°. The addition required 14 hr. and crude ethyl chloride (4 g.) collected in a trap (0°) following the distillation receiver. There was a phosphine-like odour towards the end of the addition. The mixture was heated for a further 2 hr. but no more liquid collected in the trap. Distillation afforded crude diethyl ethylphosphonate (36·1 g., 60%), b. p. 72—90°/12 mm., n_{D}^{20} 1·416, and a residue (40·8 g.) which decomposed on further heating. Methylenebisphosphonic acid was not obtained by hydrolysis of this residue.

Interaction of Triallyl Phosphite with Methylene Di-iodide.—(*a*) The phosphite (60·6 g., 3 mol.) and iodide (26·8 g., 1 mol.) were heated. Vigorous reaction set in at 130°, and liquid distilled. After 2 hours' heating at 170—185° distillation ceased. The products, worked up as in the corresponding experiments with triethyl phosphite, were allyl iodide (14·2 g., 42·25%), b. p. 98—102°, methylene di-iodide (7·5 g., 28%), b. p. 53°/11 mm., d_4^{20} 3·31, diallyl allylphosphonate (25·5 g., 40%), b. p. 75—79°/0·6 mm., n_D^{20} 1·4640, diallyl iodomethylphosphonate (12 g.), b. p. 95—106°/0·6 mm., n_D^{20} 1·4995, tetra-allyl methylenebisphosphonate (4·0 g., 8%), b. p. 138—140°/0·6 mm., n_D^{20} 1·4675, various mixed fractions, and a residue (18 g.). The maximum yield of tetraester obtained in this way was 12%. In one experiment 8% of the iodomethylphosphonate, b. p. 100—102°/0·5 mm., n_D^{20} 1·5004, was isolated when purified at the expense of other products.

(*b*) The phosphite (40·4 g., 1 mol.) and iodide (81 g., 1·5 mol.) gave, by the method described for the corresponding diethyl ester, diallyl iodomethylphosphonate (24·8 g., 41%), b. p. 65—67°/0·05 mm., n_D^{20} 1·5015.

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