							Borate recovered:			
No.	Butyl borate.	Weight, g.	HX.	Time of passage, hours.	Temp.	Yield of RX, g. (and b. p.).	g.	b. p. (mm.).	n_D.	Found: B, %.
1	*n*-	9·1	HCl	8	35°	none	9·0	112°/12	1·4107 (20°)	4·7
2	*sec.*-	5·1	HCl	12 30	120 15	none	4·9	84°/15	1·3968 (20°)	4·8
3	*iso*-	2·54	HCl	13 30	115 20	none	2·24	96°/14	1·4059 (16°)	(no residue)
4	*tert.*-	2·38	HCl	$\frac{1}{2}$	15	2·4 (51°)	(Residue of boric acid, 0·63 g., 98%)			
5	*n*-	5·5	HBr	15	18	none	5·4	116°/18	1·4115 (18°)	—
6	,,	2·25	HBr	7	115	1·4 (97—100°)	1·35	114°/14	1·4111 (20°)	4·7
7	*sec.*-	2·65	HBr	60	20	4·0 (88—90°)	(Residue, 0·8 g. containing boric acid, 0·65 g.)			
8	*iso*-	2·50	HBr	72	20	none	2·42	96°/14	1·4062 (16°)	—
9	,,	3·80	HBr	16 30	115 20	1·7 (86—89°)	2·27	96°/15	1·4042 (21°)	—
10	*n*-	5·7	HI	$\frac{3}{4}$	18	1·0 (43°/18 mm.)	4·7	114°/18	1·4108 (20°)	—
11	,,	5·5	HI	4	50	12·7 (130°) *	—	—	—	—
12	*sec.*-	1·8	HI	2	20	2·4 (117—119°)	(Residue containing boric acid, 0·46 g., 96%)			

* Found: I, 69·6. Calc. for C_4H_9I: I, 69·1%.

(Found: Cl, 38·3. Calc. for C_4H_9Cl: Cl, 38·4%). The alkyl bromide in expt. 6 was shaken with lead carbonate, and it then had b. p. 99—100°, n_D^{20} 1·4361. In expt. 9 the alkyl bromide was shaken with lead carbonate before redistillation; it had n_D^{23} 1·4328. There was a primary residue (0·30 g.) of boric acid. In expt. 12, primary distillation afforded a liquid, b. p. 105—120°, and a residue of boric acid (0·46 g., 96%). The liquid was shaken with solid sodium thiosulphate and then redistilled; it had b. p. 117—119°, n_D^{20} 1·4945. Tri*iso*butyl borate (2·65 g.) and hydrogen iodide (12 hours at 20°) afforded unchanged borate (1·32 g., 50%), b. p. 96—97°/14 mm., n_D^{16} 1·4061, but the other material was not identified with certainty.

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568. *Mechanism of the Formation of Dialkyl Alkylphosphonates.*

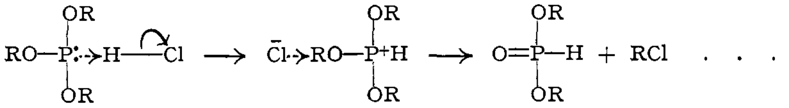
By W. GERRARD and W. J. GREEN.

Interaction of tri-2-octyl phosphite, from (+)-octan-2-ol, and ethyl iodide gave (—)-2-iodo-octane, a result which indicates an intermolecular, end-on, three-centre dealkylation of $EtP(OR)_3^+$ by I^-. Results from the interaction of the same phosphite and acetyl halides indicate the same process: $Ac{\cdot}P(OR)_3^+ + Cl^-$ (or Br^-) $\longrightarrow$ (—)-2-chloro- and (—)-2-bromo-octane. (+)-2-Iodo-octane was readily, (+)-2-bromo- and (+)-2-chloro-octane were much more slowly, racemised when heated with triethyl phosphite. Observations on (+)-1-halogeno-1-phenylethanes and on tri-1-phenylethyl phosphite are also described. Ethyl dichlorophosphinite did not undergo any clear interaction with ethyl iodide. Overall reaction sequences leading to the formation of alkyl- and acyl-phosphonates are discussed.

BY heating triphenyl phosphite with methyl iodide Michaelis and Kähne (*Ber.*, 1898, **31**, 1048) obtained the crystalline compound $PMe(OPh)_3I$, which was easily decomposed by water, according to the equation: $PMe(OPh)_3I + H_2O = Me{\cdot}PO(OPh)_2 + HI + Ph{\cdot}OH$. Landauer and Rydon (*Chem. and Ind.*, 1951, 313) used an alcohol instead of water, and gave an unexpected general method for preparing alkyl iodides. In the preparation of, *e.g.*, diethyl ethylphosphonate by the interaction of triethyl phosphite and ethyl iodide the formation of a similar type of intermediate compound has been assumed, but the compound has not been isolated (Arbusov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 687). The equation given is $P(OEt)_3 + EtI \longrightarrow PEt(OEt)_3I \longrightarrow EtPO(OEt)_2 + EtI$, and Kosolapoff ("Organophosphorus Compounds," Wiley, New York, 1950) summarises the situation thus: "If the radicals OR [in $Alk{\cdot}P(OR)_3I$] are aliphatic, the intermediate complex breaks down spontaneously, and it is necessary only to distil the mixture to obtain the final product."

The general findings with respect to the nature of the alkyl halide are : ease of reaction is in the order iodide > bromide > chloride, and primary > secondary. Kosolapoff (*op cit.*, and *J. Amer. Chem. Soc.*, 1944, **66**, 109) measured the rate of evolution of ethyl bromide when triethyl phosphite and a bromide such as *n*-butyl bromide were heated together. He concluded that the overall reaction must consist of at least two stages : formation of the intermediate addition compound, followed by its thermal decomposition. Ford-Moore and Williams (*J.*, 1947, 1465) showed that triethyl phosphite and *n*-hexyl bromide (or higher homologues) reacted smoothly and gave mainly ethyl bromide and diethyl alkylphosphonate. With *n*-butyl bromide and *iso*amyl bromide, the reaction was sluggish, and a considerable amount of diethyl ethylphosphonate was formed, because the by-product ethyl bromide had an opportunity to react on its own account. No reaction took place between triethyl phosphite and secondary bromides such as 2-bromo-octane.

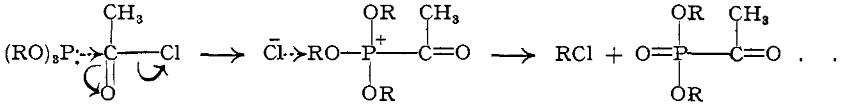
We now offer a contribution to the elucidation of the complete sequence of mechanism by considering the dealkylation part of the overall process. Gerrard showed (*J.*, 1944, 85) that 2-chloro-octane was produced by an inversion mechanism during the ready dealkylation of tri-2-octyl phosphite by hydrogen chloride. The postulated scheme is depicted in (1), and although it is conceivable that the production of the ions could entail two stages [the formation of $(RO)_3P{:}HCl$, or $HP(OR)_3Cl$, followed by a S_N1 ionisation] yet it appears certain that dealkylation is not intramolecular; rather is it a process entailing an end-on approach of an anion, the electron affinity of the oxygen atom being increased by the positive charge and thereby encouraging alkyl–oxygen fission. In a general way this picture has long been favoured in the study of the Walden inversion (Lewis, " Valence," Chem. Catalogue, New York, 1923; Kenyon and Phillips, *Trans. Faraday Soc.*, 1930, **26**, 451; Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1252). Removal of a second alkyl group by hydrogen chloride is very slow, indicating a less facile mechanism not involving a reactive lone pair of electrons on the phosphorus atom.



$$\mathrm{RO{-}\overset{OR}{\underset{OR}{P}}{:}\!\cdots\!\!>H{-}Cl} \longrightarrow \mathrm{\bar{C}l\cdots\!\!>RO{-}\overset{OR}{\underset{OR}{P}}{}^{+}H} \longrightarrow \mathrm{O{=}\overset{OR}{\underset{OR}{P}}{-}H} + \mathrm{RCl} \quad . \; . \; . \quad (1)$$

Tri-2-octyl phosphite with ethyl iodide at 95—105° afforded 2-iodo-octane, entailing an inversion of configuration. If ethyl iodide is written for hydrogen chloride, scheme (1) will serve to account for this result. There was an experimental complication in that the initially optically pure halide underwent recemisation, probably owing to iodine anionic exchange. When (+)-2-iodo-octane and triethyl phosphite were heated together at 95—105°, the former was quickly racemised, and we attribute this to anionic exchange, $I^- \dashrightarrow R - I \longrightarrow I - R + I^-$, the iodine anions being produced in small concentration by a slow interaction between the phosphite and 2-iodo-octane. The period of heating being increased, the amount of 2-iodo-octane recovered became smaller, and an appreciable amount of diethyl ethylphosphonate was isolated, this having been formed by the ethyl iodide produced by the iodine-anion cycle initiated by the primary interaction between 2-iodo-octane and triethyl phosphite. (+)-2-Bromo- and (+)-2-chloro-octane underwent slow racemisation when heated with triethyl phosphite.

The halogeno-octane formed by the interaction of tri-2-octyl phosphite and the appropriate acetyl halide had also the inverted configuration, and scheme (2) may represent the sequence.



$$\mathrm{(RO)_3P{:}\!\cdots\!\!>\overset{CH_3}{\underset{O}{\overset{|}{C}\,\Vert}}{-}Cl} \longrightarrow \mathrm{\bar{C}l\cdots\!\!>RO{-}\overset{OR}{\underset{OR}{\overset{+}{P}}}{-}\overset{CH_3}{C}{=}O} \longrightarrow \mathrm{RCl} + \mathrm{O{=}\overset{OR}{\underset{OR}{P}}{-}\overset{CH_3}{C}{=}O} \quad . \; . \quad (2)$$

Whereas (+)-1 chloro- and 1-bromo-1-phenylethane were slowly racemised when heated with triethyl phosphite, the 1-halogeno-1-phenylethane obtained by interaction of tri-1-phenylethyl phosphite and severally ethyl bromide and acetyl chloride was largely racemised. Furthermore, a considerable amount of styrene was produced in this system. The high degree of reactivity of the central carbon atom in the 1-phenylethyl structure dominates the situation here as it does in many other systems.

Just as ethyl dichlorophosphinite undergoes no more than an extremely slow dealkylation by the action of hydrogen chloride, so most of it was recovered after being heated at 70° for 12·5 hours with ethyl iodide. These observations are in accord with the postulations that the lone pair of electrons on the phosphorus atom are rendered much less available by the electron attraction of the two chlorine atoms.

EXPERIMENTAL.

Rotary powers are for $l = 1$ dm.

Interaction of Tri-2-octyl Phosphite and Ethyl Iodide.—Tri-2-octyl phosphite [9·85 g.; b. p. 162°/2 mm., n_D^{18} 1·4470, α_D^{19} −1·5°; from (+)-ROH, α_D^{20} +7·15°] (Found: C, 68·2; H, 12·1; P, 7·3. Calc. for $C_{24}H_{51}O_3P$: C, 68·8; H, 12·3; P, 7·4%) (cf. Gerrard, *J.*, 1944, 85) was heated at 95—105° with ethyl iodide (3·7 g.) for 4·5 hours. Distillation gave (−)-2-iodo-octane (2·60 g.), b. p. 97°/22 mm., 39—40°/0·5 mm., α_D^{20} −34·4°, and (+)-*di-2-octyl ethylphosphonate* (5·97 g.), b. p. 148°/2 mm., $\alpha_D^{17\cdot5}$ +14·16°, n_D^{18} 1·4402 (Found: C, 64·6; H, 11·6; P, 9·3. $C_{18}H_{39}O_3P$ requires C, 64·7; H, 11·8; P, 9·4%). When heating was for 4 hours, the 2-iodo-octane had α_D^{20} −46·0°.

Results for different times of heating are as follows, the other products being unchanged phosphite and the ethylphosphonate:

α_D^{20} for ROH used	$P(OR)_3$, g.	Time of heating (hours)	Yield of RI, g.	I in RI, % *	α_D^{20}
+7·15°	9·85	4·5	2·6	51·0	−34·4°
+7·15	9·85	4	2·3	51·2	−46·0
+8·0	8·36	2	1·67	51·4	−59·3
+8·0	8·36	12	2·65	52·2	−22·2

* Calc.: I = 52·9%.

Racemisation of (+)-2-Iodo-octane in the Presence of Triethyl Phosphite.—When triethyl phosphite (3·5 g., 1 mol.; b. p. 50—51°/15 mm., n_D^{20} 1·4139) (Found: C, 43·3; H, 9·05; P, 18·8. Calc. for $C_6H_{15}O_3P$: C, 43·4; H, 9·1; P, 18·7%) and 2-iodo-octane (5 g., 1 mol.; α_D^{18} +33·6°) were heated together at 100—105° for 8 hours, unchanged triethyl phosphite (2·1 g.), b. p. 51—52°/12·5 mm., and racemised 2-iodo-octane (4·0 g.), b. p. 87—89°/12 mm., α_D^{20} 0·0°, were obtained. Results of other experiments are recorded in the table.

Triethyl phosphite,		Time of heating (hours)	2-Iodo-octane,			
			taken		recovered	
taken, g.	recovered, g.		g.	α_D^{20}	g.	α_D^{20}
1·76	1·70	8	2·5	+33·8°	1·90	0°
1·75	1·52	2·75	2·5	+33·8	2·42	+0·32
1·75	1·62	1·0	2·51	+33·8	2·4	+5·2

After a mixture of triethyl phosphite (3·5 g., 1 mol.) and 2-iodo-octane (0·05 g., 0·01 mol.) had been heated at 100—105° for 8 hours, unchanged triester (2·9 g.), b. p. 47—48°/10 mm., and a fraction (0·2 g.), b. p. 50°/1 mm., probably diethyl ethylphosphonate, were isolated. When a mixture of the triester (3·5 g., 1 mol.) and 2-iodo-octane (0·25 g., 0·05 mol.) was heated at 100—105° for 82 hours, unchanged triethyl phosphite (1·76 g.), b. p. 50—52°/14 mm., and diethyl ethylphosphonate (0·5 g.), b. p. 50°/1 mm., n_D^{20} 1·4165 (Found: C, 43·2; H, 9·2; P, 19·5. Calc. for $C_8H_{15}O_3P$: C, 43·9; H, 9·1; P, 18·7%), were isolated.

Triethyl Phosphite and (−)-2-Chloro- and (−)-2-Bromo-octane.—The triester (3·25 g., 1 mol.; n_D^{15} 1·4170) and (−)-2-chloro-octane (2·9 g.; α_D^{20} −29·7°) were heated at 95—105° for 12 hours. The triester (3·0 g.), b. p. 48—50°/12 mm., n_D^{19} 1·4177, and (−)-2-chloro-octane (2·2 g.), b. p. 57°/12 mm., α_D^{20} −25·0°, n_D^{19} 1·4250 (Found: Cl, 24·4. Calc. for $C_8H_{17}Cl$: Cl, 23·9%), were recovered.

The triester (4·10 g., 1 mol.) and (−)-2-bromo-octane (4·77 g., 1 mol.; α_D^{21} −38·4°) were heated at 95—105° for 12 hours. The triester (3·8 g.), b. p. 51—53°/15 mm., n_D^{17} 1·4175, and (−)-2-bromo-octane (4·54 g.), b. p. 72·5—73°/14 mm., α_D^{20} −35·8°, n_D^{19} 1·4451 (Found: Br, 41·2. Calc. for $C_8H_{17}Br$: Br, 41·4%), were recovered. There was a residue (0·3 g.).

Tri-2-octyl Phosphite and Acetyl Halides.—The triester (12·5 g., 1 mol.; from alcohol, α_D^{20} +8·0°) and acetyl chloride (2·35 g., 1 mol.) were heated at 95—105° for 12·5 hours. No acetyl chloride remained, and from the mixture (−)-2-chloro-octane (4·26 g.), b. p. 57°/13 mm., α_D^{20} −29·64°, n_D^{20} 1·4272 (Found: Cl, 24·2%), and an undistillable residue were obtained.

The same triester (12·5 g., 1 mol.) and acetyl bromide (3·68 g., 1 mol.), heated at 95—105° for 6 hours, afforded (−)-2-bromo-octane (5·33 g.), b. p. 72°/13 mm., α_D^{18} −37·6°, n_D^{19} 1·4495 (Found: Br, 41·4%). There was an undistillable residue (8·8 g.).

Ths phosphite (7·77 g., 1 mol.) and acetyl bromide (2·28 g., 1 mol.), when heated at 95—105° for 12 hours, gave (−)-2-bromo-octane (3·32 g.), b. p. 76·5°/14 mm., α_D^{18} −39·3°, n_D^{18} 1·4480 (Found: Br, 41·3%), and an undistillable residue (5·23 g.).

Interaction of Tri-1-phenylethyl Phosphite and Ethyl Bromide.—The phosphite (Gerrard, *loc. cit.*) (13·1 g., 1 mol.; α_D^{20} +48·0°; from alcohol, α_D^{20} +24·1°) and ethyl bromide (3·5 g., 1 mol.) were heated for 95—105° for 12 hours. Violent refluxing occurred after 2 hours, believed to be due to the formation of styrene. At the end there was a gum and a supernatant liquid which was decanted and distilled. Styrene (3·45 g.), b. p. 39·5—40°/15 mm., n_D^{16} 1·5490 (Heilbron and Bunbury, "Dictionary of Organic Compounds," quote n_D^{20} 1·5462) (which gave the dibromide, m. p. 71—72°), and 1-bromo-1-phenylethane (3·8 g.), b. p. 88·5—89°/15 mm., α_D^{20} +0·8°, n_D^{18} 1·5612 (Found: Br, 43·0. Calc. for C_8H_9Br: Br, 43·3%).

Interaction of Tri-1-phenylethyl Phosphite and Acetyl Chloride.—The phosphite (Gerrard, *loc. cit.*) (10·4 g., 1 mol.; α_D^{20} +48·0°) and acetyl chloride (2·1 g., 1 mol.) were heated at 95—105°. After 30 minutes, a white gummy solid had separated, so heating was discontinued. Distillation of the clear supernatant liquid afforded styrene (0·65 g.), b. p. 35°/14 mm., n_D^{22} 1·5458, 1-chloro-1-phenylethane (6·12 g.), b. p. 76·5°/13 mm., α_D^{18} −20·64°, n_D^{20} 1·5300 (Found : Cl, 25·0. Calc. for C_8H_9Cl : Cl, 25·2%), and an undistillable residue (1·1 g.).

Triethyl Phosphite and (+)-1-*Halogeno*-1-*phenylethane*.—The triester (6·75 g., 1 mol.; n_D^{15} 1·4170) and (+)-1-chloro-1-phenylethane (5·74 g., 1 mol.; α_D^{20} +10·48°) were heated at 95—105° for 13 hours. Unchanged phosphite (5·2 g.), b. p. 48·5—50·5°/13 mm., n_D^{16} 1·4130, and the chloride (5·7 g.) b. p. 74·5—76°/14 mm., α_D^{20} +8·9°, n_D^{17} 1·5290 (Found : Cl, 25·0. Calc. for C_8H_9Cl : Cl, 25·2%), were recovered.

The same triester (8·5 g., 1 mol.; n_D^{15} 1·4170) and (−)-1-bromo-1-phenylethane (9·4 g., 1 mol.; α_D^{22} −17·48°) were heated at 95—105° for 12·5 hours. Distillation then gave unchanged phosphite (5·29 g.), b. p. 50—51°/14 mm., n_D^{18} 1·4151, the bromide (6·47 g.), b. p. 87·5—88·5°/14 mm., α_D^{20} 0·0°, n_D^{20} 1·5230 (Found : Br, 42·9. Calc. for C_8H_9Br : Br, 43·3%), and a fraction (1·97 g.), b. p. 105—106°/0·4 mm., $\alpha_D^{16\cdot5}$ +0·92°, n_D^{16} 1·4961 (Found : C, 59·1; H, 8·0; P, 12·6. *Diethyl* 1-*phenylethylphosphonate*, $C_{12}H_{19}O_3P$, requires C, 59·5; H, 7·9; P, 12·8%).

Triethyl Phosphite and (+)-1-*Chloro*-1-*phenylpropane*.—(+)-1-Chloro-1-phenylpropane (α_D^{16} +53·2°) was heated with triethyl phosphite at 100—105° for 15 hours. The initial mixture of triester (1·66 g., 1 mol.) and alkyl chloride (1·69 g., 1 mol.) had α_D^{20} +24·8°. The rotary powers after the mixture had been heated for specified times were : 15 minutes, α_D^{22} +24·8°; 50 minutes, +25·2°; 2 hours, +25·0°; 6·5 hours, +25·4°; and 15 hours, 25·7°.

On distillation, unchanged triethyl phosphite (0·8 g.), b. p. 47·5°/10 mm., and 1-chloro-1-phenylpropane (1·6 g.), b. p. 46—47°/2 mm., α_D^{24} +41·1°, were isolated. It appears that the concentration of chlorine anion was very small throughout although the slowness of the chlorine-anion exchange process accounts in some measure for the slowness of the racemisation. Octan-2-ol was resolved by Kenyon's method (*J.*, 1922, **121**, 2540), and 1-phenylethanol by that of Houssa and Kenyon (*J.*, 1930, 2260).

THE NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON, N.7. [*Received, June* 26*th*, 1951.]

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569. *Butadienes and Related Compounds. Part I. Conversion of Asymmetric Di-*(p-*alkoxyphenyl*)*ethylenes on Bromination into the Corresponding* 1 : 1 : 4 : 4-*Tetralkoxyphenylbuta*-1 : 3-*dienes.*

By WADIE TADROS and GAMIL AZIZ.

1 : 1 : 4 : 4-Tetralkoxyphenylbuta-1 : 3-dienes are prepared by bromination of the *as*-di-(*p*-alkoxyphenyl)ethylenes, heating the di-*p*-alkoxyphenylvinyl chloride or bromide alone, or heating a mixture of the vinyl bromide and *as*-di-(*p*-alkoxyphenyl)ethylenes. The rôles played by temperature, concentration, and mineral acids are demonstrated. The structure of the butadienes is confirmed by ozonolysis.

IT has been shown [Robson, Schönberg, and Fahim, *Nature*, 1938, **142**, 292; Schönberg, Robson, Tadros, and Fahim, *J.*, 1940, 1327; Schönberg, Robson, and Tadros, *Nature*, 1942, **150**, 22 (Tadros's name was inadvertently omitted from this publication); Tadros and Schönberg, *J.*, 1943, 394; Tadros and Robson, *Nature*, 1947, **160**, 20; Tadros, Farahat, and Robson, *J.*, 1949, 439) that the replacement of the ethylene hydrogen atom in triarylethylenes by halogen was accompanied by a considerable increase in œstrogenic activity. It was hoped that testing the *as*-di-(*p*-alkoxyphenyl)ethylenes and their halogeno-derivatives might throw light on the relation between structure and œstrogenic activity. Tested on groups of 5 ovariectomised mice (average weight, 25 g.), *as*-di-*p*-methoxyphenylethylene and di-*p*-methoxyphenylvinyl bromide (5 mg. in 0·4 c.c. of sesame oil, injected subcutaneously in 4 doses on 2 days) showed practically no activity.

The *as*-diarylethylenes required by us as intermediates were prepared by treating the diaryl ketones with methylmagnesium iodide (cf. Pfeiffer and Wizinger, *Annalen*, 1928, **461**, 132). The required *as*-diarylvinyl bromides were prepared from the diarylethylenes by treatment with one molecular proportion of bromine in acetic acid, chloroform, carbon tetrachloride, or ether, the solutions being warmed only sufficiently to effect dissolution (otherwise the butadienes may be formed) (cf. Pfeiffer and Wizinger, *loc. cit.*; Bergmann and Szmuszkowicz, *J. Amer. Chem. Soc.*, 1947, **69**, 1777).

Bergmann and Szmuszkowicz (*loc. cit.*), by treatment of *as*-di-*p*-methoxyphenylethylene with two atomic proportions of bromine in acetic acid, obtained a compound, m. p. 206—207°, shown later (Bergmann, Szmuszkowicz, and Dimant, *ibid.*, 1949, **71**, 2968) to be 1 : 1 : 4 : 4-