489. *Experiments on the Interaction of Hydroxy-compounds and Phosphorus and Thionyl Halides in the Absence and in the Presence of Tertiary Bases. Part VI.*

By Marianne C. Berlak and William Gerrard.

To elucidate further the mechanism of replacement of a hydroxyl group by halogen, we have examined the reaction of phosphorus tri-iodide with various alcohols in carbon disulphide solution. The experiments were conducted at temperatures below 15—20°, no attempt being made to force subsequent reactions on the system. Yields of iodide were determined for different molecular proportions of reagents and for different reaction times. (+)-Butan-2-ol and (+)-octan-2-ol afforded the respective (—)-iodides, with inversion and little or no loss in rotatory power, and an interesting effect of branching is revealed by low yields of *iso*propyl and *iso*butyl iodide.

Addition of the tri-iodide (0·34 mol.) to the alcohol (1 mol.) and pyridine (1 mol.) gave pyridine hydriodide and no alkyl iodide, but the latter product was formed on further addition of tri-iodide. Evidence that dialkyl hydrogen phosphites, $(RO)_2P\cdot OH$, interact much more readily with hydrogen iodide than with hydrogen chloride or hydrogen bromide is provided.

In the table are recorded the yields of iodide resulting from the interaction of alcohols and phosphorus tri-iodide dissolved in carbon disulphide. The influence of a change in molecular proportions of the reagents, and the influence of the time for which the reagents were allowed to remain in contact were in some measure studied. Temperatures, however, were in the main kept below 15—20°, and no attempt was made to force subsequent reactions on the system by the use of higher temperatures. The solvent was used in order to avoid heterogeneity and thus to ensure a more reliable basis for comparison with the phosphorus trichloride- and phosphorus tribromide–alcohol systems (Gerrard, *J.*, **1944**, 85; **1945**, 848).

Alcohol, 1 mol.	PI_3, mols.	Time, hours.	Yield of RI, %.	B. p.	I, %, in RI. Found.	I, %, in RI. Calc.	Weight of residue containing phosphorus, as wt.-% of alcohol.
1. Pr^nOH	0·33	24	40	100—102°	74·1	74·7	10
2. Pr^iOH	0·33	24	20	85— 89	—	—	9
	0·33	72	21	87— 88	74·3	74·7	—
	1·0	24	18	87— 89	74·1	74·7	—
3. Bu^nOH	0·33	24	43	126—128	68·0	69·0	20
	0·33	72	61	126—129	68·0	—	9
	0·33	2·5 (b. p.)	48	127—129	68·5	—	2
	1·0	24	56	127—128	68·4	—	4
	1·0	72	56	128—129	68·5	—	—
4, Bu^sOH	*a* 0·33	24	60	115—118	67·9	69·0	12
	0·33	72	58	117—118	68·2	—	—
	c 1·0	24	61	116—117	68·2	—	—
5. Bu^iOH	*a* 0·33	24	20	112—115	67·8	69·0	—
	b 0·33	74	20	115—116	69·0	—	—
	c 1·0	24	17	115—117	68·0	—	—
6. $Bu^s{\cdot}CH_2{\cdot}OH$	*a* 0·33	24	48	140—143	60·1	64·1	—
	b 0·33	68	44	142—143	63·2	—	—
	1·0	24	45	143—144	63·0	—	15
7. $CHPr^n_2{\cdot}OH$	0·33	24	74	81°/21 mm.	55·5	56·1	—
	1·0	24	80	77— 78°/20 mm.	55·7	—	—
8. n-$C_8H_{17}{\cdot}OH$	0·33	24	42	103—105°/15 mm.	50·9	52·9	—
	1·0	24	56	108°/18 mm.	52·8	—	—
9. n-$C_6H_{13}{\cdot}CHMe{\cdot}OH$	*a* 0·33	24	36	90— 92°/16 mm.	41·8	52·9	—
	b 0·66	24	66	89— 90°/15 mm.	50·0	—	—
	c 0·66	72	66	87— 88°/14 mm.	50·0	—	—
	d 1·0	24	75	90°/15 mm.	52·6	—	—

4 (*a*) RI, a_D^{21} +21·0°; from ROH, a_D^{21} −4·3°. (*c*) RI, a_D^{22} +20·6°; from ROH, a_D^{21} −4·3°.

5 (*a*) Also distillate (20%), b. p. 133—140°/24 mm. [Found: I, 5·7; P, 14·0. Calc. for $(RO)_2PHO$: P, 16·0%]. (*b*) Also distillate (50%), b. p. 124—126°/15 mm. (Found: P, 13·9%). (*c*) Also distillate (30%), b. p. 126—128°/22 mm. (Found: I, 2·4; P, 15·6%).

6 (*a*) Also distillate (12%), b. p. 160°/17 mm. (decomp.) [Found: P, 11·8. Calc. for $(RO)_2PHO$: P, 13·9%]. (*b*) Residue (10%) (Found: P, 12·5%).

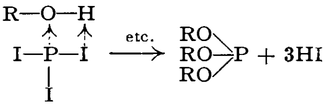
9 (*a*) RI + ROH, a_D^{16} −39·0°; from ROH, a_D^{16} +7·8°. Almost identical results were obtained after 48 and 72 hours. (*b*) RI, a_D^{16} −57·4°; from ROH, a_D^{16} +7·8°. (*c*) RI, a_D^{16} −57·0°; from ROH, a_D^{16} +7·8°. (*d*) RI, a_D^{16} −59·5°; from ROH, a_D^{16} +7·8°.

(In all rotations, l = 1 dm.)

An increase in the molecular proportion of the tri-iodide from 0·33 to 1·0 mol., or in the time (from 24 to 72 hours) during which the reagents were in contact, did not markedly increase the yield in most of examples studied. From this it appears that the iodide is formed during the early part of the first 24-hour period, and a fine-scale study of this system is now being made.

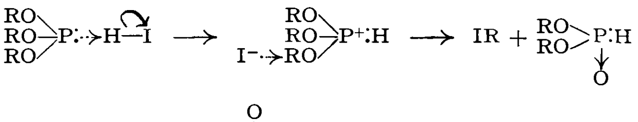
An interesting feature is the low yield of *iso*propyl and *iso*butyl iodide. These are probably produced by a comparatively quick reaction which stops when the material concerned in the final attachment of the iodine atom has been exhausted, whereas in the other examples a second reaction can proceed beyond the first.

By analogy with the trichloride and tribromide systems (Gerrard, *loc. cit.*) it may be supposed that the phosphite, $(RO)_3P$, is built up by successive broadside, four-centre approaches (1), but is rapidly attacked by hydrogen iodide, the latter reaction involving the lone pair of electrons on the phosphorus atom (2):



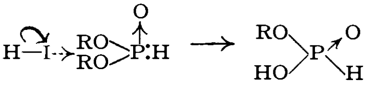
$$\mathrm{R{-}O{-}H} + \mathrm{I{-}PI{-}I} \xrightarrow{\text{etc.}} \mathrm{(RO)_3P + 3HI}$$

. . . . (1)



$$\mathrm{(RO)_3P{:}\cdots{>}H{-}I} \longrightarrow \mathrm{I^-\cdots{>}(RO)_3P^+{:}H} \longrightarrow \mathrm{IR} + \mathrm{(RO)_2P(\rightarrow O){:}H}$$

. . . . (2)



$$\mathrm{H{-}I\cdots{>}(RO)_2P(\rightarrow O){:}H} \longrightarrow \mathrm{(RO)(HO)P(\rightarrow O)H}$$

. . . . (3)

We believe that the dialkyl hydrogen phosphite, $(RO)_2PHO$, is available for further interaction with hydrogen iodide by a mechanism (3), which is not only different but proceeds much less readily. With hydrogen bromide, the mechanism (3) proceeds even less readily, and with hydrogen chloride still less so. It might be in the reluctance to replacement of the second alkyl group (reaction 3) that propan-2-ol and 2-methylpropan-2-ol differ from the other alcohols examined.

That the final attachment of the iodine atom is by an end-on approach (as in 2 and 3) is evident from the fact that (—)-2-iodobutane and (—)-2-iodo-octane were obtained from the respective (+)-alcohols with little or no loss in rotatory power, and the signs of rotation show that the iodides were produced by inversion (cf. Kenyon and Phillips, *Trans. Faraday Soc.*, 1930, **26**, 451; Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1196, 1201, 1208, 1243, 1252).

It will be seen that phosphorus tri-iodide can function instead of hydrogen iodide according to mechanism (3), because the hydrogen phosphite prepared from (—)-octan-2-ol interacted with the tri-iodide at room temperature to yield (+)-2-iodo-octane, $\alpha_{\rm D}^{24}$ +62·6° (l = 1 dm.), in 69% yield, this value probably representing full activity.

The influence of pyridine in the tri-iodide system is essentially the same as in the trichloride and tribromide systems, in that the broad-side approach (1) is greatly facilitated and halogen is precipitated as pyridine hydrohalide. The tri-iodide behaved differently in so far as it produced alkyl halide when it was added to the reaction mixture in amounts greater than 0·33 mol. for each mol. of alcohol and base.

EXPERIMENTAL.

(For all rotations, l = 1 dm., unless otherwise stated.)

Interaction of Phosphorus Tri-iodide and Alcohols in Carbon Disulphide Solution.—A solution of phosphorus tri-iodide (280 g. per l.) was prepared by the addition of the calculated amount of white phosphorus to a solution of iodine in carbon disulphide. Calculated amounts of this solution and of the alcohol were mixed at —10°, and the resulting solution was allowed to stand at room temperature for the time stated, after which it was washed with water and then dilute aqueous sodium carbonate, and finally dried (Na_2SO_4). Carbon disulphide was removed and the product was distilled. Results are recorded in the table.

Interaction of Phosphorus Tri-iodide and Alcohols in the Presence of Pyridine.—(+)-Octan-2-ol (6·5 g., 1 mol.; $\alpha_{\rm D}^{16}$ +7·8°) and pyridine (3·95 g., 1 mol.) in carbon disulphide (50 c.c.) were cooled to —10°. A precipitate formed during the dropwise addition of a solution of phosphorus tri-iodide (6·9 g., 0·33 mol.) in carbon disulphide. After 4 hours at 15°, the precipitate (9·3 g. Calc. for C_5H_5N,HI: 10·3 g.) was separated, and to the filtrate at —10° phosphorus tri-iodide (13·8 g., 0·66 mol.; in carbon disulphide) was added. After 66 hours at 15°, the mixture was washed as described above. (—)-2-Iodo-octane (7·78 g.), b. p. 98—100°/18 mm., $\alpha_{\rm D}^{18}$ —56·8° (Found: I, 51·0%), was obtained. There was no residue.

Butan-1-ol (7·4 g., 1 mol.), pyridine (7·9 g., 1 mol.), and carbon disulphide (50 c.c.) were mixed and cooled to —10°. Dropwise addition of phosphorus tri-iodide (13·7 g., 0·33 g.) in the same solvent caused a steady precipitation of pyridine hydriodide (17·9 g. Calc.: 20·7 g.) (Found: I, 60·0; C_5H_5N, 38·0. Calc.: I, 61·2; C_5H_5N, 38·3%). After being at 15° for 2 hours, the mixture was filtered, and the filtrate was washed and dried as usual. The residue (6·8 g.) remaining when the solvent was evaporated afforded a distillate, b. p. 145—150°/20 mm. [Found: P, 13·3. Calc. for $(RO)_3P$: P, 12·4%], but there was much decomposition.

The tri-iodide (20·6 g., 0·33 mol.; in carbon disulphide) was added to a solution of butan-1-ol (11·1 g., 1 mol.) and pyridine (11·83 g., 1 mol.) in carbon disulphide (100 c.c.) as before. Without filtration, a further quantity of tri-iodide (0·66 mol.) was added, and the mixture was set aside for 66 hours at 15°. From the washed and dried organic solution, *n*-butyl iodide (6·9 g.), b. p. 126—127° (Found: I, 68·4%), and 3·90 g. of undistillable residue [Found: I, 0; P, 15·7. Calc. for $(RO)_2$ POH: P, 16·0%] were obtained.

Octan-1-ol (13 g., 1 mol.), pyridine (1 mol.), and phosphorus tri-iodide (0·33 mol.), by the same prodedure, afforded pyridine hydriodide (85%) (Found: I, 60·7; C_5H_5N, 37·0%), and by the further addition of tri-iodide (0·66 mol.) *n*-octyl iodide (14·1 g.), b. p. 103—104°/15 mm. (Found: I, 52·9. Calc. for $C_8H_{17}I$: I, 52·9%), and 1·2 g. of residue were obtained.

Interaction of Phosphorous Esters and Hydrogen Iodide.—Through (—)-dimethylhexylcarbinyl hydrogen phosphite (4·6 g.; $\alpha_{\rm D}^{22}$ —12·6°), cooled at —10°, dry hydrogen iodide was passed for 1 hour, although absorption appeared to cease after 45 minutes. After 18 hours at 15°, the mixture was treated with ice and a dilute solution of sodium carbonate, and extracted with ether. From the dried ethereal extract, (+)-2-iodo-octane (5·93 g.), b. p. 101—102/23 mm., $\alpha_{\rm D}^{20}$ +45·8° (Found: I, 51·9%), and 0·4 g. of residue were obtained.

Hydrogen iodide was passed into di-*n*-butyl hydrogen phosphite (6·5 g.) at —10° for 50 minutes, absorption appearing complete after 30 minutes. After a further 30 minutes at —10°, the mixture was treated with ice and a dilute solution of sodium carbonate as previously described. *n*-Butyl iodide (2·65 g.), b. p. 127—130° (Found: I, 68·0%), and the hydrogen phosphite (2·03 g.), b. p. 130—131°/23 mm. [Found: P, 16·1. Calc. for $(RO)_2PHO$: P, 16·0%], were obtained from the ethereal solution. The sodium carbonate extract, on acidification with dilute sulphuric acid, afforded the dihydrogen phosphite (1·2 g.) [Found: P, 21·0. Calc. for $C_4H_9O{\cdot}P(OH)_2$: P, 22·5%] as an undistilled residue.

When the hydrogen iodide was passed into di-*n*-butyl hydrogen phosphite without external cooling, the temperature rose from 19° to 23°, absorption appearing complete after 30 minutes. Although the temperature was raised to 40°, no more absorption occurred. By the procedure described above, *n*-butyl iodide (5·3 g.), b. p. 127—130° (Found : I, 68·2%), 0·26 g. of residue, and, from the sodium carbonate extract, the dihydrogen phosphite (1·5 g.) (Found : P, 21·9) were obtained.

The authors gratefully acknowledge receipt of a grant from the Research Fund of the Chemical Society.

THE NORTHERN POLYTECHNIC, HOLLOWAY, LONDON, N.7. [*Received, May 6th*, 1949.]