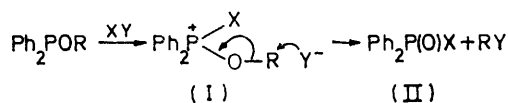


Factors in the Formation of Isomerically and Optically Pure Alkyl Halides. Part IX.¹ Reactions of (1-Substituted n-Alkyl) Diphenylphosphinites with Hydrogen Halides and with Halogens

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1-Substituted n-alkyl chlorides and bromides are obtained in high yield, and with no detectable rearrangement, by the interaction of the corresponding alkyl diphenylphosphinites with hydrogen halides or with halogens at 0–20 °C. A slight tendency to the formation of rearrangement products is shown in the iodide systems, although products of at least 99.5% purity are obtainable if the reaction time is restricted. Optically active 2-chloro-octane is readily obtained with no loss in optical purity, although the bromide and iodide are liable to undergo some racemization after their initial formation.

As part of an investigation into the uses of esters of trivalent phosphorus in the preparation of alkyl halides,^{2–5} the reactions of a number of (1-substituted n-alkyl) diphenylphosphinites with hydrogen halides and with halogens have been examined. It is thought that the reactions involve quasi-phosphonium intermediates (I), which subsequently undergo dealkylation by halide ion.



X = H or Y; Y = Cl, Br, or I

From the reactions with hydrogen halides the phosphorus-containing product (II; X = H) was not isolated as such but yielded the disproportionation products, diphenylphosphine and diphenylphosphinic acid;⁶ the direct interaction of chlorodiphenylphosphine with an alcohol also presumably proceeds *via* dealkylation of the diphenylphosphinite by hydrogen chloride. From reactions with chlorine or bromine, the corresponding diphenylphosphinic halide (II; X = Cl or Br) was obtained.

Reactions of the diphenylphosphinites with hydrogen halides thus afforded the 1-substituted n-alkyl halides (R = 1-methylbutyl, 1-ethylpropyl, 1-methylheptyl; Y = Cl or Br), and also 2-iodo-octane, with no detectable rearrangement, provided the reaction was not prolonged. Reactions with the halogens (Cl₂, Br₂, or I₂) likewise gave 2-halogeno-octanes with no detectable isomeric impurities. In the dealkylations of 1-methylbutyl and 1-ethylpropyl diphenylphosphinites by hydrogen iodide, small amounts of rearrangement appeared to be un-

avoidable and were probably due to more rapid product isomerization and/or olefin–hydrogen halide addition reactions, in these systems. With a short reaction time, however, the extent of rearrangement was no more than 0.5%.

In view of the enantiomeric purity of the 2-chloro-octane^{5,7} formed by the reaction of either hydrogen chloride or chlorine with (–)-1-methylheptyl diphenylphosphinite (Table 1), the dealkylation step is thought to occur by an S_N2 mechanism. 2-Bromo-octane was also formed initially with no loss in rotatory power^{5,7} in the hydrogen bromide system. This was demonstrated by immediately quenching the reaction mixture after the addition of hydrogen bromide was complete, although the yield obtained by this procedure was poor. Such loss in rotatory power as was observed for 2-bromo-octane after a longer reaction period, or for 2-iodo-octane, is probably due to racemization of the first-formed product by halide exchange;⁸ this did not entail accompanying rearrangement.

The reactions are potentially useful for the preparations of secondary alkyl halides (especially the chlorides or bromides), and afford higher yields (based on the starting alcohol), than are obtained by dealkylation of the corresponding trialkyl phosphites, from which only one alkyl group is available for alkyl halide formation.²

EXPERIMENTAL

Pentan-2-ol and pentan-3-ol were dried (BaO) and distilled; their purities were assessed by g.l.c. on polyethylene glycol 400. Octan-2-ol was resolved as described.^{9,10} Chlorodiphenylphosphine (Aldrich) was redistilled; b.p. 127° at 0.5 mmHg, n_D²⁰ 1.6334 (Found: Cl, 16.0. Calc. for C₁₂H₁₀ClP: Cl, 16.1%). Anhydrous hydrogen halides were obtained from cylinders (The Matheson Co.). Alkyl

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halides were analysed by described methods,^{9,11} the lower limits of detection of isomeric impurities being *ca.* 0.1% (C₅ halides) and *ca.* 0.5% (C₈ halides). Optically active 2-chloro-octane and 2-bromo-octane were purified, without loss of rotatory power, in a 4 ft × 5/8 in preparative g.l.c. column, containing 10% polyethylene glycol 400 on 85–100 mesh Celite at 50° (N₂ flow-rate 200 ml min⁻¹). The

nites.—The esters were prepared as described previously for the *s*-butyl ester.⁴ Pentan-2-ol (12.4 g) gave 1-methylbutyl diphenylphosphinite (17.5 g, 0.51 mol. equiv.), b.p. 120–121° at 0.15 mmHg, *n*_D²⁰ 1.5661 (Found: C, 75.7; H, 7.7; P, 11.3. C₁₇H₂₁OP requires C, 75.0; H, 7.9; P, 11.4%) (³¹P δ -106 p.p.m.). Pentan-3-ol (31.2 g) gave 1-ethylpropyl diphenylphosphinite (70.5 g, 0.77 mol. equiv.), b.p.

TABLE 1

Reactions of (+)- or (-)-1-methylheptyl diphenylphosphinite with hydrogen halides and halogens

Ph ₂ PO·CHMe·[CH ₂] ₅ Me	From ROH of α _D ²⁰ b	HX or X ₂		Further reaction time at 20° (h)	Me[CH ₂] ₅ ·CHXMe ^a			
		g	mol. equiv.		mol. equiv. ^c	α _D ²⁰ b, d	α _D ²⁰ (corr.) b, e	
9.3	+6.85°	HCl	2.2	2.0	1.0	0.68 f	-26.36° g	-30.86°
20.6	-6.56	Cl ₂	4.5	1.0	0	0.73 f, h	+25.77 i	+31.51
14.8	+6.85	HBr	4.3	1.1	1.0	0.78 j	-34.81 j	-40.76
10.6	+7.80	HBr	2.45	0.9	0	0.24 k	-42.74 i	-43.95
20.3	+6.85	Br ₂	11.0	1.1	24	0.59 f, m	-33.06 n	-38.71
16.4	-6.56	HI	6.7	1.0	0	0.27°	+32.64°	+39.90
19.6 p	+3.33	I ₂ q	15.8	1.0	6	0.77 r	-9.15 r	-22.04

^a All products isomerically pure. ^b *l* 1 dm. ^c Total yield by g.l.c. of trap condensate or first distillate. ^d After purification by preparative g.l.c. or distillation, as indicated. ^e Calculated for optically pure octan-2-ol, α_D²⁰ ± 8.02° (*l* 1).¹⁰ ^f Isolated by procedure (A) (see Experimental section). ^g After prep. g.l.c.; 2 ml gave 1.6 g, *n*_D²⁰ 1.4262 (Found: Cl, 23.9. Calc. for C₈H₁₇Cl: Cl, 23.9%). ^h Residue from similar experiment gave diphenylphosphinic chloride¹³ (0.1 mol. equiv.), b.p. 148–149° at 0.05 mmHg, *n*_D²⁰ 1.5999 (Found: Cl, 14.9; P, 12.9. Calc. for C₁₂H₁₀ClOP: Cl, 15.0; P, 13.1%). ⁱ After prep. g.l.c.; 2 ml gave 1.1 g, *n*_D²⁰ 1.4265 (Found: Cl, 23.9%). ^j After distillation; 5.3 g gave (i) 1.6 g, b.p. 83–84° at 18 mmHg, *n*_D²⁰ 1.4497 (Found: Br, 41.0. Calc. for C₈H₁₇Br: Br, 41.5%); (ii) 1.5 g, b.p. 88° at 20 mmHg, *n*_D²⁰ 1.4500. ^k Procedure (B): first distillate (2.6 g), b.p. 80–84° at 19 mmHg, *n*_D²⁰ 1.4402, containing 2-bromo-octane (60%) and octan-2-ol (40%). ^l After prep. g.l.c., *n*_D²⁰ 1.4496 (Found: Br, 41.4%). ^m First distillate (7.4 g), b.p. 32–35° at 0.5 mmHg, *n*_D²⁰ 1.4507, α_D²⁰ -32.34°. Residue from similar experiment gave diphenylphosphinic bromide¹⁴ (0.51 mol. equiv.), b.p. 160–166° at 0.05 mmHg, *n*_D²⁰ 1.6373 (Found: Br, 28.3; P, 10.6. Calc. for C₁₂H₁₀BrOP: Br, 28.5; P, 11.0%). ⁿ After distillation; 7.4 g gave 6.7 g, b.p. 30° at 0.5 mmHg, *n*_D²⁰ 1.4507 (Found: Br, 41.5%). ^o Procedure (B) including extraction with ether and treatment with Na₂S₂O₃ solution. Main fraction from first distillation, b.p. 48–49° at 0.5 mmHg, *n*_D²⁰ 1.4832 (Found: I, 52.4. Calc. for C₈H₁₇I: I, 52.9%). ^p In CH₂Cl₂ (50 ml). ^q Dissolved or suspended in CH₂Cl₂ (400 ml). ^r Procedure (B), including washes with NaOH and NaHSO₃ solutions. First distillate was pure 2-iodo-octane (11.5 g), b.p. 40–41° at 0.5 mmHg, *n*_D²⁰ 1.4874 (Found: I, 52.6%).

TABLE 2

Reactions of 1-methylbutyl and 1-ethylpropyl diphenylphosphinites with hydrogen halides

Ph ₂ POR	HX		Further reaction time at 20° (h)	RX Isolated ^a							
	R	g		X	g	mol. equiv.	b.p. (°C)	<i>n</i> _D ²⁰	X(%)	Composition (%)	
MePr ^c CH	11.3	Cl	2.0	1.3	0.25	0.69	90–96	1.4065	32.9 ^b	100	0
	30.6	Cl	9.2	2.2	19.20	0.61	90–95	1.4072	33.0 ^b	94	6
	12.4	Br	4.2	1.1	0.33	0.67	116–117	1.4404	52.9 ^c	100	0
	16.6	I	8.0	1.0	18.0	0.66	21 at 0.3 mmHg	1.4949	63.8 ^d	98	2
Et ₂ CH	24.4	Cl	4.4	1.3	0.25	0.61 ^e	96–97	1.4102	33.1 ^b	0	100
	25.0	Br	8.3	1.1	2.0	0.56	118	1.4448	52.8 ^c	0	100
	18.0	I	8.7	1.0	0.25	0.53	144–145	1.4493	63.2 ^d	0.5	99.5

^a Procedure (A) (see Experimental section). ^b Calc. for C₈H₁₇Cl: Cl, 33.3%. ^c Calc. for C₈H₁₇Br: Br, 53.0%. ^d Calc. for C₈H₁₇I: I, 64.1%. ^e The white semi-solid residue (17.7 g) was distilled to give diphenylphosphine (3.0 g), b.p. 117–118° at 0.3 mmHg, *n*_D²⁰ 1.6260 (Found: P, 16.0. Calc. for C₁₂H₁₁P: P, 16.7%) [³¹P δ -42.3 p.p.m. (d, *J*_{PH} 221 Hz)], identification confirmed by i.r. spectrum. Recrystallization of the final residue from aqueous ethanol gave diphenylphosphinic acid (10 g), m.p. 191° (Found: P, 14.2. Calc. for C₁₂H₂₁O₂P: P, 14.2%).

bromide underwent some racemization in the column at 100°. Optical rotations were measured for samples in thermostatted cells at 20°, with a Perkin-Elmer 141 photoelectric polarimeter.

Preparations of (1-Substituted *n*-Alkyl) Diphenylphosphi-

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150° at 1.0 mmHg, *n*_D²⁰ 1.5683 (Found: C, 75.0; H, 7.8; P, 11.3%) (³¹P δ -107 p.p.m.). (+)-Octan-2-ol (8.1 g), α_D²⁰ +6.85° (*l* 1), gave 1-methylheptyl diphenylphosphinite¹² (10.3 g, 0.53 mol. equiv.), b.p. 140° at 0.1 mmHg, *n*_D²⁰ 1.5484, α_D²⁰ +25.58° (*l* 1) (Found: P, 9.6. Calc. for

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$C_{20}H_{27}OP$: P, 9.9%). Other batches of optically active ester were made similarly.

Reactions of Diphenylphosphinites with Hydrogen Halides or Halogens.—The diphenylphosphinite was cooled to 0° . Gaseous reactants (hydrogen halides or chlorine) were passed in slowly (0.25—1 h), with stirring. Bromine was added dropwise with vigorous agitation (1 h). Iodine (in CH_2Cl_2) was added quickly to the diphenylphosphinite (in CH_2Cl_2) at 20° . After the specified time (Tables 1 and 2), one of two procedures was followed: (A) volatile products were removed under reduced pressure at 20° , trapped (-80°), washed, and dried (K_2CO_3); (B) ice-cold water was added to the product at 0° , the organic layer then being separated, washed, and dried (K_2CO_3). Products from the 1-methylbutyl and 1-ethylpropyl systems were then distilled and analysed (Table 2). Those from (+)- or

(-)-1-methylheptyl systems were purified by preparative g.l.c. or distillation as indicated (Table 1).

Reaction of Chlorodiphenylphosphine with (+)-Octan-2-ol.—Chlorodiphenylphosphine (18.0 g, 0.0816 mol) was added dropwise with shaking (20 min) to octan-2-ol (10.7 g, 0.0823 mol), $\alpha_D^{20} + 6.75^\circ$ (l 1), at 0° . Volatile products (11.9 g) were removed at 0.1 mmHg, trapped (-80°), washed, dried (K_2CO_3), and distilled to give: (i) material (1.9 g) of b.p. $36-61^\circ$; (ii) material (9.5 g) of b.p. $61-69.5^\circ$ at 15 mmHg containing 2-chloro-octane (9.4 g, 0.0633 mol) and octene (0.1 g). A quantity (2 ml) was purified by preparative g.l.c. to give 2-chloro-octane (1.4 g) (Found: Cl, 24.0%), n_D^{20} 1.4264, $\alpha_D^{20} - 25.84^\circ$ (l 1), $\alpha_D^{20} - 30.70^\circ$ (l 1) corrected for optically pure octan-2-ol.

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