

Aluminium Chloride-catalysed Reactions of 1-Alkyl-3,5-di-t-butylbenzenes with Phosphorus Trichloride. Migration of a t-Butyl Group to the Phosphorus Atom

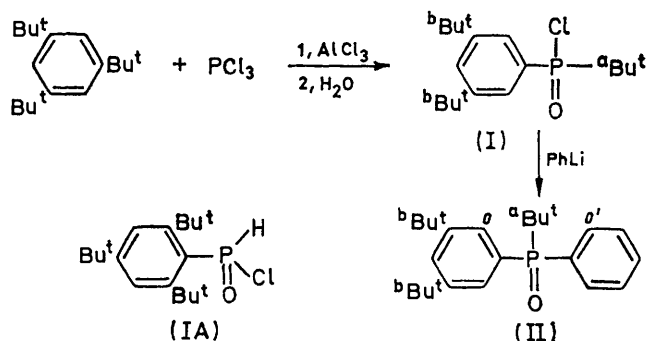
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Aluminium chloride-catalysed reactions of 1-alkyl-3,5-di-t-butylbenzenes with phosphorus trichloride gave (3-alkyl-5-t-butylphenyl)-t-butylphosphinic chlorides (alkyl = Bu^t, Me, or Pr^t) after hydrolysis. The previous identification of 2,4,6-tri-t-butylphenylphosphinic chloride as the product obtained from tri-t-butylbenzene has thus been shown to be incorrect. The reaction proceeds by migration of one t-butyl group from the benzene ring to the phosphorus atom.

DURING an investigation of sterically hindered organophosphorus compounds, a new type of rearrangement of a t-butyl group from a benzene ring to a phosphorus atom has been found.¹ The Friedel-Crafts reaction of 1,3,5-tri-t-butylbenzene with phosphorus trichloride gave, after hydrolysis, crystalline material of m.p. 132.5–133.5°, in 86% yield. This product was originally² identified as 2,4,6-tri-t-butylphenylphosphinic chloride (IA), m.p. 133–134°, but the following spectral evidence indicates that it was in fact (3,5-di-t-butylphenyl)-t-butylphosphinic chloride (I).

The i.r. spectrum had no absorption band in the P–H stretching region (2240–2460 cm⁻¹), but showed a strong band at 815 cm⁻¹ (P–Bu^t).³ The ¹H n.m.r. spectrum (C₆D₆; 100 MHz) showed that one of the three t-butyl groups was directly attached to the phosphorus atom, on the basis of the large coupling constant (18.3 Hz) which may be assigned to *J*_{PCCH}^a. Analysis of the phenyl signals and ¹H n.m.r. spectra measured

at a variety of magnetic fields in different solvents also confirmed the revised structure (I) (see Experimental section). The ³¹P n.m.r. signal (C₆D₆) at δ –71



p.p.m. (from 85% phosphoric acid) indicated that the compound was of the type R₂P(O)Cl (δ –30 to –90 p.p.m.).^{3,4}

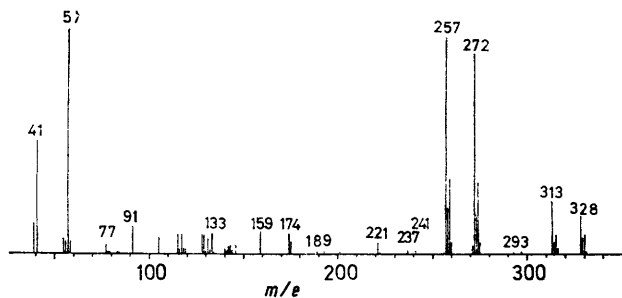
¹ M. Yoshifuji, I. Fujishima, R. Okazaki, and N. Inamoto, *Chem. and Ind.*, 1970, 625.

² A. G. Cook, *J. Org. Chem.*, 1965, **30**, 1262.

³ P. C. Crofts and D. M. Parker, *J. Chem. Soc. (C)*, 1970, 332.

⁴ M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 1; M. Yoshifuji, *J. Synthetic Org. Chem., Japan*, 1970, **28**, 177.

The mass spectrum also confirmed the structure (I) (Figure), and suggested a ready loss of isobutene from



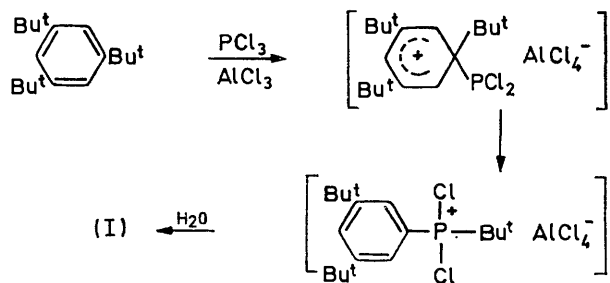
Mass spectrum of 3,5-di-t-butylphenyl-t-butylphosphinic chloride

a *P*-Bu^t group by a McLafferty rearrangement involving a five-membered ring.³ Loss of a methyl radical is the preferred fragmentation process for Ar-Bu^t groups. A metastable ion peak was observed at *m/e* 243, which indicated a unimolecular loss of a methyl radical from the fragment ion produced by the loss of isobutene from the molecular ion.

The resistance of the chloride to hydrolysis, which has been discussed by Cook,² can be explained in terms of steric hindrance by the *t*-butyl group attached to the phosphorus atom. Furthermore, the reaction of compound (I) with phenyl-lithium in ether gave (3,5-di-*t*-butylphenylphenyl)-*t*-butylphosphine oxide (II), similarly identified by means of its i.r., n.m.r., and mass spectra (see Experimental section).

Bergmann *et al.*⁵ have reported some aluminium chloride-catalysed reactions of *p*-bromophenyl *p*-halogenophenyl sulphides with phosphorus trichloride, which were very similar to the present reaction in that the bromo-substituted carbon on the phenyl ring was attacked by the phosphorus trichloride-aluminium chloride system.

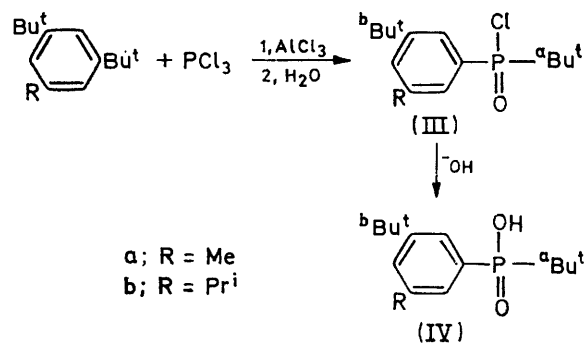
The formation of the rearranged product (I) instead of (IA) suggests that the reaction proceeds by an intramolecular rearrangement of the *t*-butyl group or by an S_Ni reaction by the PCl₂ group.



Brooks and Bunton⁶ have recently reported the aluminium chloride-catalysed reaction of *t*-butylbenzene with phosphorus trichloride, and suggested an intermolecular mechanism for the formation of *t*-butyl-*p*-*t*-butylphenylphosphinic (20%) and *t*-butylphenyl-

phosphinic (1%) acids. Intermolecular migration of a *t*-butyl group is also considered as one probable mechanism for the present reaction, but we do not have convincing evidence which indicates that the intermolecular migration is favoured over the intramolecular one.

The Friedel-Crafts reactions of 3,5-di-*t*-butyl-toluene and -cumene with phosphorus trichloride catalysed by anhydrous aluminium chloride followed by hydrolysis similarly gave (3-methyl-5-*t*-butylphenyl)-*t*-butylphosphinic (IIIa) and (3-isopropyl-5-*t*-butylphenyl)-*t*-butylphosphinic (IIIb) chlorides in 75 and 78% yield, respectively. Although good analyses were not obtained, no impurity could be detected by g.l.c. The coupling constants (18.7 and 19.2 Hz, respectively) obtained by the analysis of the *t*-butyl signals indicated that migration of a *t*-butyl group to the phosphorus atom had occurred. Alkaline hydrolysis of the phosphinic chlorides (III) gave the corresponding phosphinic acids (IV) which were identified by means of i.r., n.m.r., and mass spectra.



EXPERIMENTAL

¹H N.m.r. spectra were measured with Varian HA100 and T60 and JEOL JNM-4H-100, JNM-C-60H, and JNM-3H-60 spectrometers with tetramethylsilane as internal standard at room temperature (sx = sextet, sp = septet). The ³¹P n.m.r. spectrum was recorded on a Hitachi R-20-R-204-P spectrometer with 85% phosphoric acid as external standard. I.r. spectra were taken with Hitachi EPI-G2 and Hitachi-Perkin-Elmer 225 spectrometers.

Reaction of 1,3,5-Tri-t-butylbenzene⁷ with Phosphorus Trichloride.—The procedure was that of Cook.² (3,5-Di-*t*-butylphenyl)-*t*-butylphosphinic chloride (I) was obtained in 86% yield, m.p. 132.5–133.5° (lit.,² 133–134° for the so-called 2,4,6-tri-*t*-butylphenylphosphinic chloride) (Found: C, 65.9; H, 9.1; Cl, 11.0. C₁₈H₃₀ClOP requires C, 65.7; H, 9.2; Cl, 10.8%), *v*_{max.} (KBr) 1230 (P=O) and 815 cm⁻¹ (P-Bu^t), δ (60 MHz; CCl₄) 1.22 (9H, d, *J*_{PH}^a 18 Hz, 3 × Me^a), 1.38 (18H, s, 6 × Me^b), and 7.4–7.8 (3H, m, ArH), δ (60 MHz; C₆D₆) 1.18 (9H, d, *J*_{PH}^a 18 Hz, 3 × Me^a), 1.22 (18H, s, 6 × Me^b), 7.7 (1H, s, *p*-H), and 8.0 (2H, d, *J*_{PH}^a 13 Hz, 2 × *o*-H), δ (100 MHz; CDCl₃) 1.25 (9H, d, *J*_{PH}^a 18.7 Hz, 3 × Me^a), 1.36 (18H, s, 6 × Me^b), 7.6–7.8 (3H, m, ArH), δ (100 MHz; C₆D₆) 1.14 (9H, d, *J*_{PH}^a 18.3 Hz, 3 × Me^a), 1.19 (18H, s, 6 × Me^b), 7.61

⁶ R. Brooks and C. A. Bunton, *J. Org. Chem.*, 1970, **35**, 2642.

⁷ E. E. Betts and L. R. C. Barclay, *Canad. J. Chem.*, 1955, **33**, 1768.

⁵ I. Granoth, A. Kalir, Z. Pelah, and E. D. Bergmann, *Chem. Comm.*, 1969, 260.

(1H, sx, J_{HOHP} 1.8, J_{PHP} 1.2 Hz, *p*-H), and 7.93 p.p.m. (2H, q, J_{PHO} 12.5 Hz, $2 \times o$ -H), δ ^{31}P (C_6H_6) -71 p.p.m. (m), *m/e* 328 (M^+ , 20%), 313 (M^+ - CH_3 ; 24), 272 (M^+ - 83), 257 (M^+ - C_4H_8 - CH_3 ; 98), 189 ($\text{Bu}_2\text{C}_6\text{H}_3^+$; d 57 (C_4H_9^+ , 100), m^* 243 (272 \rightarrow 257) (see Figure).

o,o'-Di-t-butylphenylphenyl-t-butylphosphine Oxide.—The phosphinic chloride (I) (12.0 g, 36.5 mmol) in ether (150 ml) was added drop by drop to ethereal phenyl-lithium [freshly prepared from lithium (1 g, 0.144 g-atom) and bromobenzene (9.52 g, 60.6 mmol)] under nitrogen. The mixture was stirred overnight at 35°, and then heated at 50° for 1 h, cooled, poured into ice-water, and extracted with ether. The extracts were washed with water, dried (MgSO_4), and evaporated. The crystalline material thus obtained was recrystallised from benzene-light petroleum to give the pure oxide (II) (9 g, 24.3 mmol; 67%), m.p. 159–161° (Found: C, 77.5; H, 9.5. $\text{C}_{24}\text{H}_{36}\text{OP}$ requires C, 77.8; H, 9.5%), ν_{max} (KBr) 1173 (P=O) and 817 cm^{-1} (P-Bu^t), δ (100 MHz; CDCl_3) 1.24 (9H, d, J_{PHa} 14.6 Hz, $3 \times \text{Me}^a$), 1.34 (18H, s, $6 \times \text{Me}^b$), 7.36–7.54 (3H, m, $2 \times m'$ -H and *p'*-H), 7.58 (1H, sx, J_{HOHP} 1.9, J_{PHP} 1.2 Hz, *p*-H), 7.81 (2H q, J_{PHO} 11.0 Hz, $2 \times o$ -H), and 7.88–8.09 (2H, m, $2 \times o'$ -H), δ (100 MHz; C_6D_6) 1.23 (18H, s, $6 \times \text{Me}^b$), 1.25 (9H, d, J_{PHa} 14.3 Hz, $3 \times \text{Me}^a$), 7.0–7.2 (3H, m, $2 \times m'$ -H and *p'*-H), 7.61 (1H, sx, J_{PHP} 1.5, J_{HOHP} 2.0 Hz, *p*-H), 8.14 (2H, q, J_{PHO} 10.5 Hz, $2 \times o$ -H), and 8.1–8.3 p.p.m. (2H, m, $2 \times o'$ -H); irradiation at δ 7.61 p.p.m. (*p*-H) collapsed the pair of doublets of *o*-H (δ 8.14 p.p.m.) to one doublet (J_{PHO} 10.5 Hz), and decoupling of the multiplet of *o'*-H (δ 8.1–8.3 p.p.m.) partially collapsed the signals at δ 7.0–7.2 p.p.m., *m/e* 370 (M^+ ; 2%), 355 (M^+ - CH_3 ; 2), 314 (M^+ - C_4H_8 ; 55), 299 (M^+ - CH_3 - C_4H_8 ; 13), 125 (PhPOH^+ ; 20), 91 (C_7H_7^+ ; 10), and 57 (C_4H_9^+ ; 100), m^* 285 (314 \rightarrow 299).

Reaction of 3,5-Di-t-butyltoluene with Phosphorus Trichloride.—The reaction of 3,5-di-t-butyltoluene⁸ (17.3 g, 0.085 mol) with phosphorus trichloride (30 ml, 0.34 mol) in the presence of anhydrous aluminium chloride (16.7 g, 0.125 mol) was carried out similarly. After hydrolysis, distillation gave (3-methyl-5-t-butylphenyl)-t-butylphosphinic chloride (IIIa), b.p. 120–128° at 0.2 mmHg; it became semi-solid (18.3 g, 0.064 mol; 75%) on being left for a long time; ν_{max} (KBr) 1230 (P=O) and 810 cm^{-1} (P-Bu^t), δ (60 MHz; CDCl_3) 1.27 (9H, d, J_{PHa} 18.7 Hz, $3 \times \text{Me}^a$) and 1.34 p.p.m. (9H, s, $3 \times \text{Me}^b$). The chloride (1.61 g, 5.61 mmol) and sodium hydroxide (5 g) were dissolved in 50% ethanol (50 ml), and were refluxed for 3 h.

After almost all the ethanol was removed, the residue was acidified with hydrochloric acid, and crystallisation from ethanol-water gave the acid (IVa) (1.4 g, 5.22 mmol; 93%), m.p. 190–191.5° (Found: C, 67.0; H, 9.6. $\text{C}_{15}\text{H}_{25}\text{O}_2\text{P}$ requires C, 67.1; H, 9.4%), ν_{max} (KBr) 2700, 2300, 1700, and 950 (P-O-H), 1170 (P=O), and 820 cm^{-1} (P-Bu^t), δ (100 MHz; CDCl_3) 1.05 (9H, d, J_{PHa} 16 Hz, $3 \times \text{Me}^a$), 1.30 (9H, s, $3 \times \text{Me}^b$), 2.57 (3H, s, ArMe), 7.0–7.9 (3H, m, ArH), and 10.53 p.p.m. (1H, s, OH), *m/e* 268 (M^+ ; 18%), 212 (M^+ - C_4H_8 ; 80), 197 (M^+ - C_4H_8 - CH_3 ; 100), 133 ($\text{MePrC}_6\text{H}_3^+$; 10), and 56 (C_4H_9^+ ; 30), m^* 183 (212 \rightarrow 197).

Reaction of 3,5-Di-t-butylcumene with Phosphorus Trichloride.—The reaction of 3,5-di-t-butylcumene⁹ (4.9 g, 21 mmol) with phosphorus trichloride (7.5 ml, 86 mmol) in the presence of anhydrous aluminium chloride (4.2 g, 31 mmol) was carried out in a similar manner. After hydrolysis, the oil obtained was chromatographed on silica gel, eluted with ether, and then distilled, b.p. 136–137° at 0.4 mmHg (5.2 g, 16 mmol, 78%). Attempts to crystallise the syrupy phosphinic chloride (IIIb) were unsuccessful; ν_{max} (neat) 1230 (P=O) and 815 cm^{-1} (P-Bu^t), δ (60 MHz; CDCl_3) 1.27 (9H, d, J_{PHa} 19.2 Hz, $3 \times \text{Me}^a$) and 1.35 p.p.m. (9H, s, $3 \times \text{Me}^b$). The chloride (1.9 g, 6.03 mmol) was hydrolysed with alkali to give (3-iso-propyl-5-t-butylphenyl)-t-butylphosphinic acid (IVb) (1.5 g, 5.07 mmol, 84%), m.p. 126–129° (from aqueous acetone after sublimation) (Found: C, 68.7; H, 10.1. $\text{C}_{17}\text{H}_{29}\text{O}_2\text{P}$ requires C, 68.9; H, 9.9%), ν_{max} (KBr) 2600, 2200, 1700, and 960 (P-O-H), 1170 (P=O), and 825 cm^{-1} (P-Bu^t), δ (100 MHz; CDCl_3) 1.00 (9H, d, J_{PHa} 15.3 Hz, $3 \times \text{Me}^a$), 1.22 (6H, d, J 7.5 Hz, $\text{Me}_2\text{C} \langle \rangle$), 1.28 (9H, s, $3 \times \text{Me}^b$), 2.89 (1H, sp, J 7.5 Hz, $\text{HC} \langle \rangle$), 7.2–7.7 (3H, m, ArH), and 9.99 p.p.m. (1H, s, OH), *m/e* 296 (M^+ ; 17%), 281 (M^+ - CH_3 ; 25), 240 (M^+ - C_4H_8 ; 100), 225 (M^+ - C_4H_8 - CH_3 ; 71), 175 ($\text{BuPrC}_6\text{H}_3^+$; 3), and 57 (C_4H_9^+ ; 57), m^* 211 (240 \rightarrow 225).

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⁸ J. Geuze, C. Ruinard, J. Soeterbroek, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1956, **75**, 301.

⁹ H.-D. Scharf and F. Döring, *Chem. Ber.*, 1967, **100**, 1761.