$S_{RN}1$ Reactions of t-Butyl Chlorides

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t-Butyl chloride and 2-chloro-2-methyl-1-phenylpropane reacted with Ph_2P^- ions under irradiation to give reduction and substitution products and 6-chloro-6-methylhept-1-ene (used as a radical probe) reacted to give the cyclized substitution product. The bromides gave only elimination products.

The radical mechanism of nucleophilic substitution, or $S_{RN}1$, has been proposed in reactions of aliphatic substrates with electron-withdrawing groups,[1] with aryl[2] and vinyl halides,[3] and lastly with several alkyl halides such as perfluoroalkyl iodides,[4] bridgehead,[5] neopentyl,[6] and cyclopropyl halides.[7] It has been suggested that these haloaliphatic compounds without electron-withdrawing groups react with nucleophiles by the $S_{RN}1$ mechanism because they react slowly, or do not react at all by the polar mechanisms of nucleophilic substitution.[8]

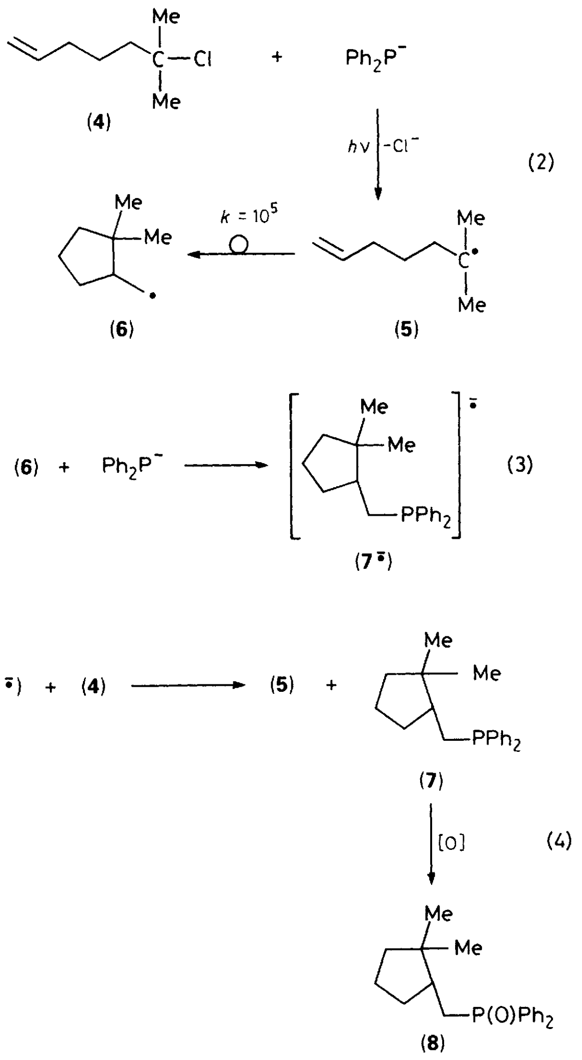
In general, 1-substituted bridgehead compounds are known to have low reactivity towards nucleophilic substitution reactions. However, the solvolytic rate of 1-substituted bridgehead halides increases as the strain decreases, and in some cases, they show a solvolytic rate similar to that of t-butyl chlorides.[9] We therefore thought it of interest to study the reactivity of t-butyl halides as tertiary halides without strain and compare their behaviour with that of bridgehead halides.

There was no reaction of t-butyl chloride (**1a**) with diphenylphosphide (Ph_2P^-) ions in liquid ammonia for 3 h (Cl^- ions 3% yield) in the dark; however, the reaction gave 50% yield of Cl^- ions under photostimulation (4 h).† In the reaction mixture we found the substitution product t-butyldiphenylphosphine, isolated as oxide (**3a**) (12%) (equation 1).‡ This photostimulated reaction was inhibited by 10 mol% of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and by 10 mol% of *p*-dinitrobenzene (21 and 13% yield of Cl^- ions, respectively). The difference in the yields between Cl^- ions and (**3a**) could be due to the formation of the reduced product Me_3CH (**2a**) which would be lost during the liquid ammonia evaporation.

$$\underset{(\mathbf{1})}{RCl} + Ph_2P^- \xrightarrow{h\nu} \underset{(\mathbf{2})}{RH} + RPPh_2 \xrightarrow{[O]} \underset{(\mathbf{3})}{RP(O)Ph_2} \quad (1)$$

a; R = Me_3C–; **b**; R = $PhCH_2CMe_2$–

2-Chloro-2-methyl-1-phenylpropane (**1b**) showed the same behaviour as (**1a**) in the dark, but in the photostimulated reaction we found 72% yield of Cl^- ions, with 22% yield of 2-methyl-1-phenylpropane (**2b**),§ and after oxidation, 36% yield of the substitution product (**3b**) (equation 1).† No products derived from elimination were found. As the total yield of the products recovered was lower than the Cl^- ion liberated, we performed a blank reaction by adding (**2b**) to liquid ammonia, and after distillation of the ammonia, we only recovered 43% of (**2b**). This difference in yields can then be attributed to the loss of (**2b**) when liquid ammonia is evaporated.



In order to know if t-radicals were intermediates in these photostimulated reactions, we synthesized the cyclizable radical probe[10] 6-chloro-6-methylhept-1-ene (**4**), which proved to be unreactive with Ph_2P^- ions in the dark. A 49% yield of Cl^- ions and a 43% yield of the substitution product (**7**), isolated as oxide (**8**),† were determined in the photostimulated reaction (4 h). This result can be explained by an $S_{RN}1$ reaction according to Scheme 1.

The photostimulated reaction between (**4**) and Ph_2P^- ions gave radical (**5**), which is trapped faster by the double bond to give the rearranged radical (**6**) (equation 2) than the reaction of radical (**5**) with the nucleophile. Radical (**6**) reacts with Ph_2P^- ions to give the cyclized radical anion of the substitution product (**7**$^{\bar{\bullet}}$) (equation 3), which by electron transfer to (**4**) gives (**5**) and the substitution product (**7**), the latter being isolated after oxidation as oxide (**8**) (equation 4). There is previous evidence showing that radicals with a suitable double bond formed in the propagation steps of the $S_{RN}1$ mechanism cyclize before the attack of the nucleophile.[11]

In the photostimulated reaction of (**1b**) [and (**1a**)], the reduction products were important; this being an indication that the coupling of the radical intermediate with the nucleophile is slow. In contrast, the reduction product was not as important with (**4**) as substrate, suggesting that the reaction of t-alkyl radicals with Ph_2P^- ions is slower than that of p-alkyl radicals such as (**6**).

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† Irradiation was conducted in a reactor equipped with four 250-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated).

‡ *Selected spectroscopic data* for (**3a**): ^1H NMR ($DCCl_3$) δ 1.60 (9 H, d, $^3J_{H-P}$ 14 Hz), 7.6—8.6 (10 H, m); *m/z* (relative intensity) 258 (M^+ = 4), 242 (4), 202 (100), 201 (28), 155 (31), 125 (22), 77 (45), 57 (12). (**3b**): ^1H NMR ($CDCl_3$) δ 1.13 (d, 6 H Me, $^3J_{H-P}$ 16 Hz), 2.92 (d, 2 benzylic H, $^3J_{H-P}$ 8 Hz), 6.95—7.2 (m, 15 aromatic H); ^{13}C NMR ($CDCl_3$) (C′ refers to phosphorus bonded phenyl rings and C″ to aromatic benzylic ring) δ 20.98 (C-3 and C-4, Me), 37.65 (d, C-2, $^1J_{C-P}$ 70 Hz), 40.56 (s, C-1, benzylic), 126.25 (s, C″-4), 127.92 (s, C″-2 and C″-6), 128.21 (d, C′-3 and C′-5, $^3J_{C-P}$ 10.87 Hz), 130.98 (s, C″-3 and C″-5), 131.43 (d, C′-4, $^4J_{C-P}$ 2.2 Hz), 132.23 (d, C′-2 and C′-6, $^2J_{C-P}$ 7.9 Hz), 133.23 (d, C′-1, $^1J_{C-P}$ 90.5 Hz); *m/z* (relative intensity) 335 (M^+ = 21), 334 (33), 333 (22), 318 (5), 259 (20), 243 (76), 242 (15), 243 (12), 203 (25), 202 (100), 201 (95), 133 (10), 91 (36), 77 (17), 43 (26). (**8**): ^1H NMR ($CDCl_3$) δ 0.76 (s, 3 H, *cis* or *trans*), 0.94 (s, 3 H, *cis* or *trans*), 1.1—2.6 (m, 9 H), 7.2—7.9 (m, 10 aromatic H); ^{13}C NMR ($CDCl_3$) δ 20.90 (C-5), 21.17 (C-7, Me), 26.89 (C-8, Me), 30.90 (C-6), 30.28 (d, C-1, $^1J_{C-P}$ 71.9 Hz), 40.26 (C-4), 41.53 (d, C-3, $^3J_{C-P}$ 12.60 Hz), 42.95 (d, C-2, $^2J_{C-P}$ 4.7 Hz), 128.30 (d, C′-3 and C′-5 aromatic, $^3J_{C-P}$ 10.41 Hz), 130.53 (d, C′-2 and C′-6 aromatic, $^2J_{C-P}$ 8.52 Hz), 131.2 (d, C′-4 aromatic, $^4J_{C-P}$ 1.89 Hz), 133.12 (d, C′-1, $^1J_{C-P}$ 113.2 Hz; *m/z* (relative intensity) 312 (M^+ = 8), 296 (5), 216 (42), 215 (58), 203 (17), 202 (100), 201 (42), 155 (18), 77 (7). Satisfactory analytical data were obtained.

§ Quantified by GLPC compared with an authentic sample of (**2b**).

We found a quite different behaviour with t-butyl bromide. There was a very fast dark reaction with Ph_2P^- ions in liquid ammonia (100% Br^- ions), but no substitution product was found. 2-Bromo-2-methyl-1-phenylpropane (**9**) also reacts very fast in the dark, and the only product found (100% yield) was the alkene 2-methyl-1-phenylpropene (**10**) (equation 5).¶ The substrate (**9**) does not react in liquid ammonia in the absence of the nucleophile Ph_2P^-.

$$\underset{(\mathbf{9})}{PhCH_2CMe_2Br} + Ph_2P^- \rightarrow \underset{(\mathbf{10})}{PhCH{=}CMe_2} \qquad (5)$$

All these results suggest that t-butyl chlorides and other t-alkyl chloride derivatives react under irradiation with Ph_2P^- ions by the $S_{RN}1$ mechanism, but in sharp contrast, the t-alkyl bromides react by an elimination reaction. We will study further the reaction of t-butyl chlorides and bromides with other nucleophiles, and in different solvents.

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¶ Quantified by GLPC compared with an authentic sample of (**10**).

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