

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

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t-Butyl chloride and 2-chloro-2-methyl-1-phenylpropane reacted with  $\text{Ph}_2\text{P}^-$  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.

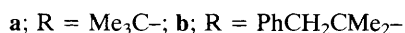
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The radical mechanism of nucleophilic substitution, or  $S_{RN}1$ , has been proposed in reactions of aliphatic substrates with electron-withdrawing groups,<sup>1</sup> with aryl<sup>2</sup> and vinyl halides,<sup>3</sup> and lastly with several alkyl halides such as perfluoroalkyl iodides,<sup>4</sup> bridgehead,<sup>5</sup> neopentyl,<sup>6</sup> and cyclopropyl halides.<sup>7</sup>

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.<sup>8</sup>

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.<sup>9</sup> 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 ( $\text{Ph}_2\text{P}^-$ ) ions in liquid ammonia for 3 h ( $\text{Cl}^-$  ions 3% yield) in the dark; however, the reaction gave 50% yield of  $\text{Cl}^-$  ions under photostimulation (4 h).<sup>†</sup> In the reaction mixture we found the substitution product *t*-butyldiphenylphosphine, isolated as oxide (**3a**) (12%) (equation 1).<sup>‡</sup> 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  $\text{Cl}^-$  ions, respectively). The difference in the yields between  $\text{Cl}^-$  ions and (**3a**) could be due to the formation of the reduced product  $\text{Me}_3\text{CH}$  (**2a**) which would be lost during the liquid ammonia evaporation.

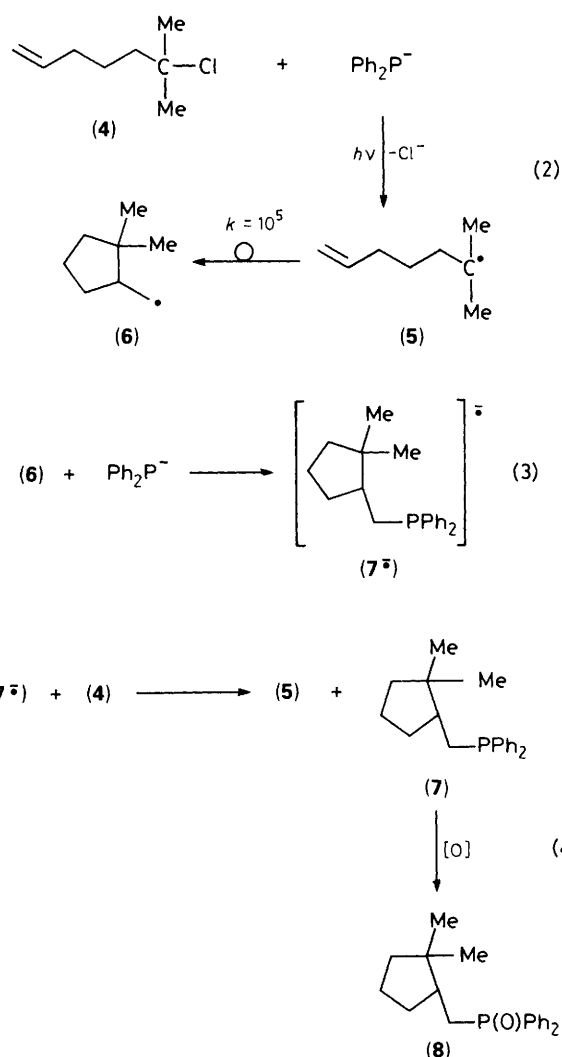


2-Chloro-2-methyl-1-phenylpropane (**1b**) showed the same behaviour as (**1a**) in the dark, but in the photostimulated reaction we found 72% yield of  $\text{Cl}^-$  ions, with 22% yield of 2-methyl-1-phenylpropane (**2b**),<sup>§</sup> and after oxidation, 36% yield of the substitution product (**3b**) (equation 1).<sup>†</sup> No products derived from elimination were found. As the total yield of the products recovered was lower than the  $\text{Cl}^-$  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.

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

<sup>‡</sup> Selected spectroscopic data for (**3a**): <sup>1</sup>H NMR ( $\text{DCCl}_3$ )  $\delta$  1.60 (9 H, d, <sup>3</sup>J<sub>H-P</sub> 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**): <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.13 (d, 6 H Me, <sup>3</sup>J<sub>H-P</sub> 16 Hz), 2.92 (d, 2 benzylic H, <sup>3</sup>J<sub>H-P</sub> 8 Hz), 6.95–7.2 (m, 15 aromatic H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ ) ( $C'$  refers to phosphorus bonded phenyl rings and  $C''$  to aromatic benzylic ring)  $\delta$  20.98 (C-3 and C-4, Me), 37.65 (d, C-2, <sup>1</sup>J<sub>C-P</sub> 70 Hz), 40.56 (s, C-1, benzylic), 126.25 (s, C<sup>''</sup>-4), 127.92 (s, C<sup>''</sup>-2 and C<sup>''</sup>-6), 128.21 (d, C'-3 and C'-5, <sup>3</sup>J<sub>C-P</sub> 10.87 Hz), 130.98 (s, C<sup>''</sup>-3 and C<sup>''</sup>-5), 131.43 (d, C'-4, <sup>4</sup>J<sub>C-P</sub> 2.2 Hz), 132.23 (d, C'-2 and C'-6, <sup>2</sup>J<sub>C-P</sub> 7.9 Hz), 133.23 (d, C'-1, <sup>1</sup>J<sub>C-P</sub> 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**): <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  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); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  20.90 (C-5), 21.17 (C-7, Me), 26.89 (C-8, Me), 30.90 (C-6), 30.28 (d, C-1, <sup>1</sup>J<sub>C-P</sub> 71.9 Hz), 40.26 (C-4), 41.53 (d, C-3, <sup>3</sup>J<sub>C-P</sub> 12.60 Hz), 42.95 (d, C-2, <sup>2</sup>J<sub>C-P</sub> 4.7 Hz), 128.30 (d, C'-3 and C'-5 aromatic, <sup>3</sup>J<sub>C-P</sub> 10.41 Hz), 130.53 (d, C'-2 and C'-6 aromatic, <sup>2</sup>J<sub>C-P</sub> 8.52 Hz), 131.2 (d, C'-4 aromatic, <sup>4</sup>J<sub>C-P</sub> 1.89 Hz), 133.12 (d, C'-1, <sup>1</sup>J<sub>C-P</sub> 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.

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

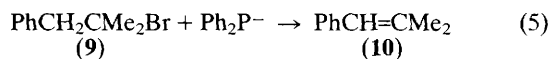


In order to know if *t*-radicals were intermediates in these photostimulated reactions, we synthesized the cyclizable radical probe<sup>10</sup> 6-chloro-6-methylhept-1-ene (**4**), which proved to be unreactive with  $\text{Ph}_2\text{P}^-$  ions in the dark. A 49% yield of  $\text{Cl}^-$  ions and a 43% yield of the substitution product (**7**), isolated as oxide (**8**),<sup>†</sup> were determined in the photostimulated reaction (4 h). This result can be explained by an  $\text{S}_{\text{RN}}1$  reaction according to Scheme 1.

The photostimulated reaction between (**4**) and  $\text{Ph}_2\text{P}^-$  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  $\text{Ph}_2\text{P}^-$  ions to give the cyclized radical anion of the substitution product (**7<sup>-</sup>**) (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  $\text{S}_{\text{RN}}1$  mechanism cyclize before the attack of the nucleophile.<sup>11</sup>

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  $\text{Ph}_2\text{P}^-$  ions is slower than that of *p*-alkyl radicals such as (**6**).

We found a quite different behaviour with t-butyl bromide. There was a very fast dark reaction with  $\text{Ph}_2\text{P}^-$  ions in liquid ammonia (100%  $\text{Br}^-$  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).<sup>¶</sup> The substrate (**9**) does not react in liquid ammonia in the absence of the nucleophile  $\text{Ph}_2\text{P}^-$ .



All these results suggest that t-butyl chlorides and other t-alkyl chloride derivatives react under irradiation with  $\text{Ph}_2\text{P}^-$  ions by the  $S_{\text{RN}}1$  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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<sup>¶</sup> Quantified by GLPC compared with an authentic sample of (**10**).

## References

- 1 N. Kornblum, 'The Chemistry of Functional Groups,' eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1982, Supplement F, ch. 10.
- 2 For reviews, see R. A. Rossi and R. H. de Rossi, 'Aromatic Substitution by the  $S_{\text{RN}}1$  Mechanism,' ACS Monograph 178, Washington, DC, 1983; W. R. Bowman, *Chem. Soc. Rev.*, 1988, 17, 283.
- 3 J. F. Bunnett, X. Creary, and J. E. Sundberg, *J. Org. Chem.*, 1976, 41, 1707.
- 4 A. E. Feiring, *J. Org. Chem.*, 1983, 48, 347; *J. Fluorine Chem.*, 1984, 24, 191; Q. Y. Chen and Z. M. Qiu, *ibid.*, 1986, 31, 301.
- 5 A. N. Santiago, D. G. Morris, and R. A. Rossi, *J. Chem. Soc., Chem. Commun.*, 1988, 220; A. N. Santiago, V. S. Iyer, W. Adcock, and R. A. Rossi, *J. Org. Chem.*, 1988, 53, 3016, and references cited therein.
- 6 E. R. N. Bornancini, A. B. Peñeñory, S. M. Palacios, and R. A. Rossi, *J. Phys. Org. Chem.*, 1989, 2, 255, and references cited therein.
- 7 R. A. Rossi and A. N. Santiago, *J. Chem. Res. (S)*, 1988, 172.
- 8 R. A. Rossi, A. B. Pierini, and S. M. Palacios, *J. Chem. Ed.*, 1989, 66, 720.
- 9 The solvolytic rate for 1-bromoadamantane is  $4.38 \times 10^{-7}$  whereas it is  $9.23 \times 10^{-6}$  for t-butyl chloride, see P. v. R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, 1961, 83, 2700.
- 10 For reviews, see W. F. Bailey and J. J. Patricia, *J. Organomet. Chem.*, 1988, 352, 1; E. C. Ashby, *Acc. Chem. Res.*, 1988, 21, 414.
- 11 E. C. Ashby, R. N. De Priest, and W.-Y. Su, *Organometallics*, 1985, 4, 1493; G. A. Russell and D. Guo, *Tetrahedron Lett.*, 1984, 25, 5239.