Disparate Reactivity of 4-Tricyclyl Iodide and Chloride in the $S_{RN}1$ Reaction; Bridgehead revisited†

Ana N. Santiago,[a] **David G. Morris,**[b]* **and Roberto A. Rossi**[a]*

[a] *Instituto de Investigaciones Fisicoquimicas de Córdoba (INFICQ), Departamento de Quimica Organica, Facultad de Ciencias Quimicas, Universidad Nacional de Córdoba, C.C. 61, Suc. 16, 5016 Córdoba, Argentina*
[b] *Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.*

The remarkably facile $S_{RN}1$ reaction of 4-tricyclyl iodide and the near inertia of 4-tricyclyl chloride under the same conditions are compared with the reactivity of other bridgehead compounds; the nature of the $S_{RN}1$ reaction for aliphatic substrates is discussed.

From the high temperature aqueous ethanolysis of 4-tricyclyl trifluoromethanesulphonate (**1**) it was estimated that the first order rate constant for the corresponding reaction of 4-tricyclyl toluene-*p*-sulphonate (**2**) in 60% aqueous ethanol at 25 °C is 4.8×10^{-18} s^{-1}; this corresponds to $t_{\frac{1}{2}} = 4 \times 10^9$ years. The 4-tricyclyl carbocation is the most reluctantly formed bridgehead carbocation so far observed.[1]

On account of a correlation[2] between the thermolysis rates of a series of bridgehead peresters at 80 °C and the solvolysis rates of the corresponding bromides in 80% aqueous ethanol at 25 °C, it is possible to estimate the rate of formation of 4-tricyclyl radicals from thermolysis of the perester (**3**). The rate constant for aqueous ethanolysis of 4-tricyclyl bromide (**4**) under the same conditions is estimated to be 2.7×10^{-20} s^{-1}. Extrapolation of this correlation to include the 4-substituted tricyclyl system indicates a rate constant of 1.3×10^{-8} s^{-1} ($t_{\frac{1}{2}}$ *ca.* 650 days) at 80 °C for the decomposition of perester (**3**). The less prohibitive situation for the formation of bridgehead radicals is due at least in part to the smaller force constant for out-of-plane bending than for the corresponding carbocations.[3]

Against this background we have carried out the $S_{RN}1$ reaction[4] of 4-iodotricyclene (**5**). Under conditions of photostimulation (**5**) reacts with Ph_2P^- ions (both substrates 3.3×10^{-3} M) in liq. NH_3 (−33 °C) to give, after oxidation with hydrogen peroxide in dichloromethane, a 58% isolated yield of phosphine oxide (**6**). Additionally, *ca.* 5% of the hydrocarbon tricyclene (**7**) was isolated and the assay for liberated iodide ion was 90%. The reaction was complete (*ca.* 10 $t_{\frac{1}{2}}$) within 20 min. The structure of (**6**) follows from the ^{13}C chemical shift[5] ($CDCl_3$, int. Me_4Si) with coupling to phosphorus, where observed, in parentheses: (C-1) δ 28.67 (11 Hz), (C-2, C-6) 19.35 (13 Hz), (C-3, C-5) 34.88 (5 Hz); (C-4) 46.81 (86 Hz), (C-7) 48.60, (C-8, C-9) 19.61, (C-10) 9.87. The ^{31}P chemical shift (ext. H_3PO_4) is 29.57 p.p.m. and a long range coupling between H-2 and P, $^4J = 2.34$ Hz, was confirmed by ^{31}P decoupling of the ^1H n.m.r. spectrum.

When the same reaction was carried out in the presence of 20 mol % of *p*-dinitrobenzene, a well known inhibitor of $S_{RN}1$ reactions,[4] the yield of iodide ion diminished to 28%.

Although a detailed kinetic analysis is not in order, it is apparent, after taking account of temperature differences,[6] that (i) the relative rate of the reaction of (**5**) with respect to aq. ethanolysis of (**2**) is *ca.* 10^{16}, (ii) the relative rate of reaction of (**5**) with respect to that of (**3**) is *ca.* 10^9. These comparisons demonstrate the great ease with which a highly strained radical is formed during the $S_{RN}1$ reaction of (**5**), and indicate that the donation of an electron to the bridgehead iodide (**5**) within the context of Scheme 1 produces a remarkably good leaving group.

The mechanism outlined in Scheme 1 was proposed for $S_{RN}1$ reactions of aromatic substrates, and radical anions of the type $(ArX)^-$ have been independently observed.[7] However, detection of their aliphatic counterparts is not possible in general[7] and it may be that the $S_{RN}1$ reaction of (**5**) is accompanied by a concerted displacement such as in the propagation cycle, the steps (2) and (4) of Scheme 1 are telescoped, and no discrete intermediate[8] is involved.

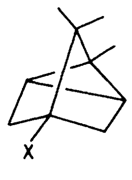
Attempts to perform the $S_{RN}1$ reaction with 4-chlorotricyclene (**8**) in liq. NH_3 with the powerful nucleophiles Ph_2P^- or Ph_2As^- were unsuccessful; after 240 min of irradiation <5% chloride ion had been released. Similarly unsuccessful were experiments with Me_2SO as solvent, and also the entrainment reaction.[9]

The near inertia of (**8**) compared with 1-chloroadamantane (liq. NH_3, Ph_2P^- ion, irradiation) which released 40% chloride ion after 105 min;[10] the corresponding results for reaction under the same conditions were: 1-chlorobicyclo[2.2.2]octane <6% chloride ion after 240 min;[11] 1-chlorocamphene, 7% chloride ion after 240 min; 1-chlorobicyclo[2.2.1]heptane after 240 min of irradiation <1% of chloride ion was released.

The sequence of reactivity of the bridgehead substituted chlorides is the same as that for carbocation formation, and that for perester decomposition. However, the relative ease with which the putative radical anions are formed is also relevant, and theoretical calculations carried out with the

$$\begin{array}{llcll}
\text{Initiation:} & R\text{–}I + Ph_2P^- & \xrightarrow{h\nu} & R\text{–}I^{\cdot -} + Ph_2P^{\cdot} & (1)\\
\text{Propagation:} & R\text{–}I^{\cdot -} & \longrightarrow & R^{\cdot} + I^- & (2)\\
 & R^{\cdot} + Ph_2P^- & \longrightarrow & (RPPh_2)^{\cdot -} & (3)\\
 & (RPPh_2)^{\cdot -} + R\text{–}I & \longrightarrow & RPPh_2 + R\text{–}I^{\cdot -} & (4)
\end{array}$$

Scheme 1



(**1**) X = OSO_2CF_3
(**2**) X = $OSO_2C_6H_4Mep$
(**3**) X = C(O)–O–O–CMe_3
(**4**) X = Br
(**5**) X = I
(**6**) X = $P(O)Ph_2$
(**7**) X = H
(**8**) X = Cl

---

† Presented at the EUCHEM Conference on Electron Transfer Reactions, Visby, Sweden, May 31st—June 5th, 1987.

semi-empirical MNDO method with complete geometry optimization show that the energy of the lowest unoccupied molecular orbital (LUMO), which is a measure of the reduction potential, increases as the bridgehead system becomes more constrained.‡

The original comment[13] that the overall reactivity in the $S_{RN}1$ reaction is a composite and that rate data for the individual steps are unavailable still holds. Nevertheless, we have shown that even in the most unpromising situation the $S_{RN}1$ reaction can be profitably employed for the replacement of iodide, and the synthetic utility of the reaction is hampered only by the range of nucleophiles[4b,c] that will participate in the reaction.

We thank CONICET, the Universidad Nacional de Córdoba, the Royal Society, and Professor J. M. Savéant.

Received, 30th October 1987; Com. 1579

References

1 S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Am. Chem. Soc.*, 1972, **94**, 4615.
2 C. Rüchardt, V. Golzke, and G. Range, *Chem. Ber.*, 1981, **114**, 2769.
3 L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, 1968, **46**, 3099; R. C. Bingham and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1971, **93**, 3189, and references cited in both papers.
4 For reviews see: (a) N. A. Kornblum, 'The Chemistry of Functional Groups,' eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1982, supplement F, ch. 10; (b) J. F. Bunnett, *Acc. Chem. Res.*, 1978, **11**, 413; (c) R. A. Rossi and R. H. de Rossi, *ACS Monogr.*, 1983, no. 178; (d) R. K. Norris, 'The Chemistry of Functional Groups, eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1983, supplement D, ch. 16.
5 D. G. Morris and A. M. Murray, *J. Chem. Soc., Perkin Trans. 2*, 1975, 734.
6 The estimates are based on the assumption that the reaction rate increases by a factor of 2.3, for a 10 °C rise in temperature. S. W. Benson, 'The Foundations of Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 92, cites an increase of 10^3 for a temperature rise of 100 °C. For comments on the generality of this approach, see J. E. House, *J. Chem. Educ.*, 1969, **46**, 674; R. Walker, *Educ. Chem.*, 1987, 5.
7 M. C. R. Symons, *Pure Appl. Chem.*, 1981, **53**, 223; C. P. Andrieux, J. M. Savéant, and K. B. Su, *J. Phys. Chem.*, 1986, **90**, 3815, and references cited therein; M. C. R. Symons and W. R. Bowman, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1133. Recently the lifetime of the radical anion of diphenylmethyl chloride was estimated to be <20 ps; J. D. Simon and K. S. Peters, *Organometallics*, 1983, **2**, 1867; see also M. Hotokka, B. O. Roos, and L. Eberson, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1979.
8 In another context, a reaction is described as concerted if no intermediate species has a lifetime greater than one vibration, S. L. Buchwald and J. R. Knowles, *J. Am. Chem. Soc.*, 1982, **104**, 1438.
9 N. Kornblum, R. T. Swiger, G. W. Earl, H. W. Pinnick, and F. W. Stuchal, *J. Am. Chem. Soc.*, 1970, **92**, 5513; see also ref. 4c, p. 225.
10 S. M. Palacios, A. N. Santiago, and R. A. Rossi, *J. Org. Chem.*, 1984, **49**, 4609.
11 A. N. Santiago, V. S. Iyer, W. Adcock, and R. A. Rossi, *J. Org. Chem.*, submitted for publication.
12 A. B. Pierini and R. A. Rossi, unpublished results.
13 Ref. 4b, p. 418.

---

‡ The LUMO values[12] for R_3C–Cl moieties in relevant bridgehead substituted compounds are: (**8**), 1.043; 1-chlorobicyclo [2.2.1] heptane, 0.971; 1-chlorobicyclo[2.2.2]octane, 0.835; 1-chloroadamantane, 0.809 eV.