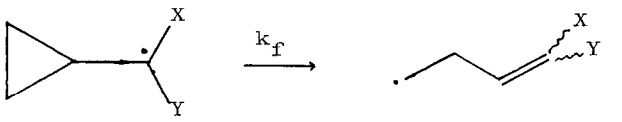
Tetrahedron Letters,Vol.23,No.43,pp 4477-4480,1982 0040-4039/82/434477-04$03.00/0
Printed in Great Britain ©1982 Pergamon Press Ltd.

THE INFLUENCE OF α-TRIALKYLSILYLOXY GROUPS ON THE RATE OF RING OPENING OF CYCLOPROPYLMETHYL RADICALS

By D.C. Nonhebel* and C.J. Suckling
(Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland)
and J.C. Walton
(Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland)

Summary The rate of ring opening of α-trialkylsilyloxycyclopropylmethyl radicals is about ten times slower than of the cyclopropylmethyl radical at 298K.

Despite the extensive use of the ring opening of cyclopropylmethyl radicals (1a) to but-3-enyl radicals (2a) as a mechanistic probe for the estimation of the rates of competing processes, virtually nothing is known about the influence on the rate of ring opening of substituents at the radical centre in substituted cyclopropylmethyl radicals.[1] The best estimate of the rate of ring opening of the parent cyclopropylmethyl is 2×10^8 s^{-1} at 25° (using an A-factor of $10^{13.0}$).[2] No rate studies of simple substituted cyclopropylmethyl radicals have been reported, although it might be expected that the rate of ring opening would be somewhat dependent on the spin density at the radical centre.



(1) (2)

a; X=Y=H
b; X=H, Y=OH
c; X=H, Y=$OSiMe_3$
d; X=H, Y=$OSiBu^tMe_2$
e; X=Me, Y=H
f; X=Me, Y=$OSiMe_3$

We are particularly interested in the rate of ring opening of α-hydroxycyclopropylmethyl radicals (1b) in view of the use of cyclopropanemethanols as a probe for the mechanism of hydrogen transfer by NAD(H) and alcohol dehydrogenase.[3] All previous attempts to observe these radicals by e.s.r. spectroscopy have failed : only the ring opened radicals (2b) could be observed at temperatures down to 150K.[4-6] At lower temperatures the limited solubility of the precursor alcohol in the solvent, cyclopropane, becomes a major problem. We thus decided to look at the rate of ring opening of α-trialkylsilyloxycyclopropylmethyl radicals (1c, 1d or 1f) by e.s.r. spectroscopy as it was expected[2] that the solubility of the precursor silyl ethers, c-$C_3H_5CHR^1OSiR_3$, in cyclopropane would be much greater than that of the corresponding alcohols; thus enabling the rearrangements to be studied in the temperature range 126-174K.

The α-trialkylsilyloxycyclopropylmethyl radicals were generated by photolysis of a 1/1/5 mixture of the silyl ether/di-t-butyl peroxide/cyclopropane in the cavity of the e.s.r. spectrometer. Table 1 records the spectral data for the unopened radicals. The trialkylsilyloxy groups lower the spin density at the radical centre as reflected by the lower values of a(α-H) in 1c and 1d compared to 1a, and by the lower value of a(Me) in 1f compared to that in 1e.[7] The small magnitude of a(β-H)[8] indicates that all the radicals exist in the bisected conformation. By analogy with previous work the higher of the two values of a(γ-H) is assigned to the anti-protons and the lower to the syn-protons of the cyclopropane ring.[8] In each case the e.s.r. spectrum of the ring-opened but-3-enyl radical increased in intensity at higher temperatures while the spectrum of the cyclopropylmethyl radical decreased in intensity.

Table 1 E.s.r. parameters of cyclopropylmethyl radicals

Radical	T/K	Hyperfine splitting/G a(α-H)	a(Me)	a(β-H)	a(γ-H)	Ref.
1a	123	20.74	--	2.55	2.98,2.01	8
1c	137	16.0	--	2.3	1.56,0.80	This work
1d	137	15.8	--	2.2	1.55,0.78	This work
1e	120	22.3	22.3	2.9	1.9,1.1	4
1f	137	--	19.2	2.6	1.4,0.6	This work

Table 2 records the rate constants for the ring opening of the α-trialakylsilyloxycyclopropylmethyl radicals : the rate constants were obtained using the standard e.s.r. procedure.[2,9] The value of $2k_t$ used in the calculations was that obtained recently for the pent-1-yl

radicals.[10] Following Ingold[1,2] the rates at 298K were calculated using an A-factor of $10^{13.0}$. These results show that the rate of ring opening of cyclopropylmethyl radicals is decreased measurably by the introduction of an α-trialkylsilyloxy group at the radical centre. The rates of ring opening of the secondary radicals (1c and 1d) are not significantly different from that of the tertiary radical (1f).

Table 2 Rates of ring opening of cyclopropylmethyl radicals

Radical	E(kJ mol^{-1})[a]	Rate constant[b], k_f, at 298K(s^{-1})	Ref.
1a	24.9	2.2×10^8	2
1c	31.3	1.7×10^7	This work
1d	29.4	3.5×10^7	This work
1f	30.3	2.4×10^7	This work

a Values are ± 5kJ mol^{-1}

b Calculated using a value of log A=13.0. A statistical factor of 2 was also introduced because either of the two bonds in the cyclopropane ring may cleave.[1,2]

We have also shown that there is little if any discrimination in the point of hydrogen abstraction by t-butoxyl radicals from $MeOCH_2CH_2OSiMe_3$ which gives approximately a 1:1 mixture of $MeOCH_2\dot{C}HOSiMe_3$ and $MeO\dot{C}HCH_2OSiMe_3$ (together with some $\dot{C}H_2OCH_2CH_2OSiMe_3$). Thus the rates of hydrogen abstraction from the two sites must be about equal which suggests the C-H bonds are weakened to approximately the same extent by adjacent MeO or R_3SiO groups. This result suggests that the lesser electronegativity of silicon with respect to carbon does not significantly diminish the ease of formation of radicals on the carbon bearing the ether. In the enzyme-catalysed reaction, an intermediate $ROZn\overset{\leftarrow}{\sim}$ species is formed at the active site prior to oxidation or reduction. The equal competition between silicon and carbon suggests that radical formation at the enzyme's active site will not be greatly influenced by complexation of the substrate with the electropositive zinc. It is therefore possible to employ the rates of ring opening of the cyclopropylsilyl ethers to provide an estimate of the maximum lifetime of a putative radical intermediate in redox reactions mediated by alcohol dehydrogenases for the radical to remain undetected by this probe technique: The maximum half life is approximately 3×10^{-8} s. This result reinforces our earlier conclusion that radical intermediates are improbable in this enzyme-catalysed reaction.

Acknowledgement The award of the Royal Society Smith and Nephew Senior Research Fellowship (C.J.S.) is acknowledged.

References

1. A. L. J. Beckwith and K. U. Ingold in 'Rearrangements in Ground and Excited States', Vol. I, Chap. 4, ed. P. de Mayo, Academic New York.
2. B. Maillard, D. Forrest and K. U. Ingold, J. Amer. Chem. Soc., 1976, 98, 7024; A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith and A. K. Serelis, J. Amer. Chem. Soc., 1980, 102, 1734.
3. I. MacInnes, D. C. Nonhebel, S. T. Orszulik and C. J. Suckling, J. Chem. Soc., Chem. Commun., 1982, 121.
4. J. K. Kochi, P. J. Krusic, and D. R. Eaton, J. Amer. Chem. Soc., 1969, 91, 1879.
5. A. G. Davies and B. Muggleton, J. Chem. Soc., Perkin Trans. 2, 1976, 502.
6. H. Itzel and H. Fischer, Tetrahedron Lett., 1975, 563.
7. A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, J. Chem. Soc. (A), 1971, 124.
8. J. K. Kochi, P. J. Krusic, and D. R. Eaton, J. Amer. Chem. Soc., 1969, 91, 1877.
9. D. Griller and K. U. Ingold, Acc. Chem. Res., 1980, 13, 317.
10. K. U. Ingold, B. Maillard and J. C. Walton, J. Chem. Soc., Perkin Trans. 2, 1981, 970.

(Received in UK 23 August 1982)