Tetrahedron Letters,Vol.25,No.34,pp 3769-3772,1984
Printed in Great Britain

0040-4039/84 $3.00 + .00

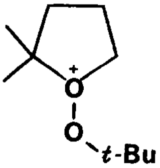
EVIDENCE FOR THE EXISTENCE OF PEROXONIUM INTERMEDIATES

John C. Mitchell* and Simon Heaton
Chemistry Department, Chelsea College, University of London, London SW3 6LX

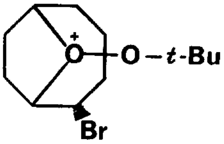
Ned A. Porter
P.M. Gross Chemical Laboratories, Duke University, Durham, North Carolina

Abstract: Low temperature ^{1}H and ^{2}H nmr are consistent with the presence of peroxonium intermediates in the intramolecular alkylation of two different bromoperoxides. In one case decomposition of this peroxonium intermediate results in unusual heterolytic oxygen-oxygen bond cleavage and methyl migration.

The intermediacy of peroxonium ions in the intramolecular alkylation of dialkylperoxides has been the subject of two recent reports.(1,2) To support the peroxonium mechanism, the authors have utilized trapping and product distribution studies implicating the proposed intermediates 1(1) and 2.(2)

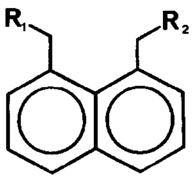


1



2

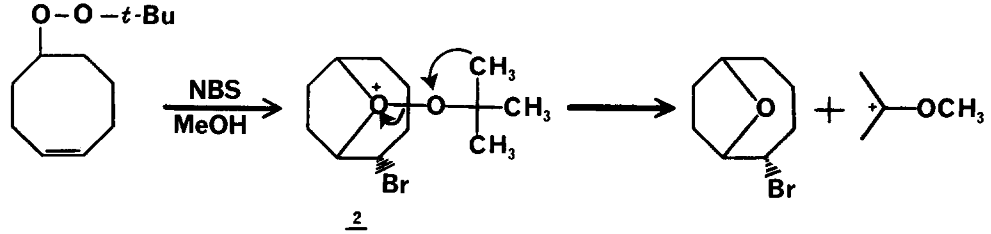
While such evidence for the existence of peroxonium ion is compelling, no direct observation of these intermediates has been cited. We report here on our attempts at formation and detection of these peroxonium ions, utilizing the known chemistry of 1 and the previously unreported silver induced reactions of 1-bromomethyl-8-t-butylperoxymethylnaphthalene 4.



3 $R_1 = R_2 = Br$
4 $R_1 = t\text{-BuOO}$
$R_2 = Br$
5 $R_1 = R_2 = t\text{-BuOO}$

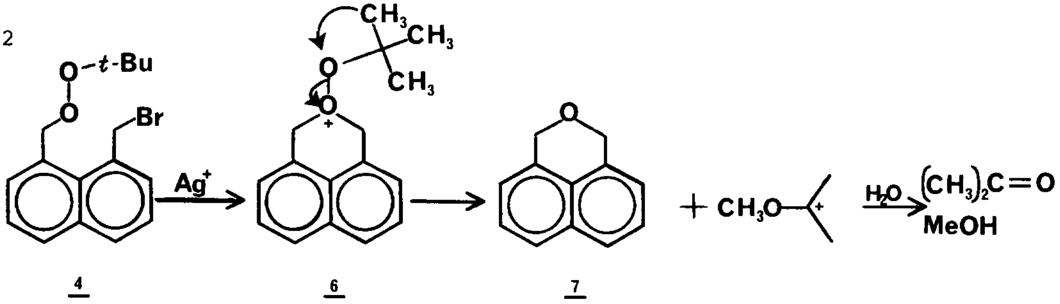
Dibromide 3 was synthesized from 1,8-naphthalic anhydride according to the method of Mitchell, et al.(3,4) Reaction of this dibromide with sodium hydride and t-butyl hydroperoxide results in the production of bromoperoxide 4(22%) and diperoxide 5(35%). Both peroxides were isolated and purified by normal phase liquid chromatography.(5) Bromoperoxide 4 was reasoned as a viable peroxonium precursor both because of known reactivity of bromoperoxides with silver salts and because of the particularly crowded condition of the 1,8-positions in these substituted naphthalene systems.(6) This so-called "peri-effect" led us to anticipate silver induced cyclization to the sterically preferred six-membered ring peroxonium ion 6. When bromoperoxide 4 was treated with silver tetrafluoroborate, the naphthopyran 7 was isolated in up to 55% yield.(7) Production of an ether and 2-methoxy-2-propyl cation in the intramolecular alkylation of t-butyl peroxides has been reported by Bloodworth, et al.(2) (Scheme 1)

Scheme 1



In similar fashion, silver induced peroxy-alkylation of 4 results in naphthopyran 7 and carbonium ion. Subsequent reaction of this 2-methoxy-2-propyl cation with aqueous media is likely to produce acetone and methanol. (Scheme 2) Indeed the presence of both these volatile species in the crude reaction mixture was confirmed by capillary column gas chromatography.

Scheme 2



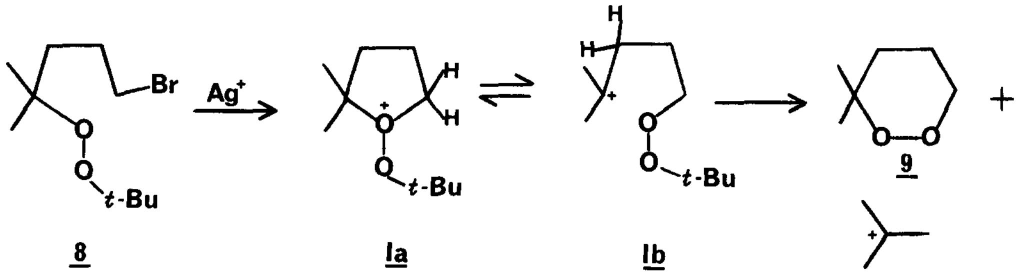
Formation of both 1 and 6 is strongly supported by low temperature ^{1}H nmr investigation. Reaction of the respective peroxonium precursor with silver tetrafluoroborate or antimony pentachloride resulted in the production of downfield signals not attributable to products or starting bromoperoxide.(8) (Table 1) Also noted, was the production from 8, of a singlet at 3.7ppm attributable to t-butyl cation and from 4, the appearance of singlets at 4.9ppm and 3.6ppm attributable to 2-methoxy-2-propyl cation.(9a,b)

Table 1. Transient signals observed in low temperature ^1H nmr spectra of 8 and 4 (ppm).

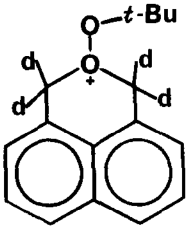
Precursor	$SbCl_5(SO_2ClF)$	$SbCl_5(CH_2Cl_2)$	$AgBF_4(CH_2Cl_2)$	Range °C	Assignment
8(ppm)	4.62(t,J=6.2Hz)		4.30(t,J=5.2Hz)	-90/-40	
	4.92(t,J=7.1Hz)		4.52(t,J=6.4Hz)	-90/-40	1a and 1b
4(ppm)		6.14(s)		-80/-40	6
			6.29(s)	-80/-60	6

The appearance of two transient triplets for 1 (Figure 1a) may be due to slowly interconverting peroxonium and carbocationic forms consistent with the proposed reaction mechanism for the silver induced cyclization of 5-bromo-2-methyl-2-(t-butylperoxy)pentane 8.(Scheme 3)

Scheme 3



To confirm whether the observed transient singlet at 6.14ppm, from low temperature reaction of 4 with antimony pentachloride results from hydrogens alpha to the charged oxygen in 6, deuterium was selectivly incorporated at these positions.



6-d4

Observation of low temperature ^2H nmr for this reation was supportive of peroxonium ion $6\text{-}d_4$. A transient downfield signal was observed from -80 to -40°C at 6.0ppm upon reaction of bromoperoxide $4\text{-}d_4$ with antimony pentachloride in methylene chloride.(Figure 1b) The observed singlet is downfield from starting deuterated bromoperoxide and is not attributable to any product.(10)

Figure 1a: Low temperature ^1H nmr of 1 with antimony pentachloride in sulfuryl chlorofluoride (-60°C).

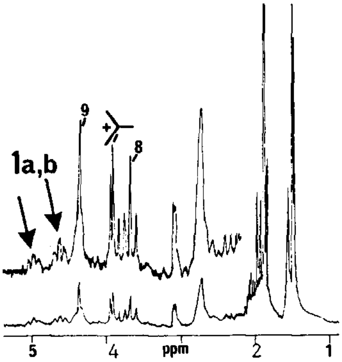
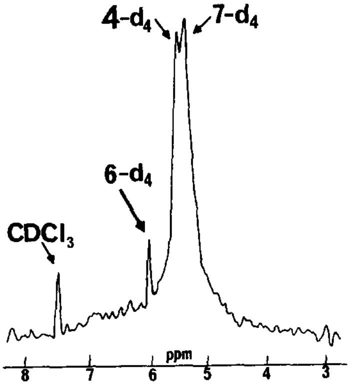


Figure 1b: Low temperature ^2H nmr of 6-d_4 with antimony pentachloride in methylene chloride (-55°C).



Peroxonium ions such as 1, 6, and 6-d_4 have been hitherto unobserved. We believe the appearence of otherwise unaccountable low temperature downfield nmr signals can best be explained by such intermediates. The search for other trialkyl peroxonium ions and, perhaps more intriguing, for the related dialkyl oxyoxonium ylids continues in our laboratories.

References and Notes

1. N.A. Porter, J.C. Mitchell, Tetrahedron Lett., 1983, 24, 543.
2. A.J. Bloodworth, J.L. Courtnidge, H.J. Eggelte, J. Chem. Soc., Chem. Commun., 1983,1267.
3. W.D. Mitchell. R.D. Topsom, J. Vaughan, J. Chem. Soc., 1962, 2526.
4. The previously unreported ^1H nmr of 1,8-bis(hydroxymethyl)naphthalene in DMSO-d_6 (ppm) is: 5.10(d,4H); 5.36(t,2H); 7.30-7.90(m,6H).
5. Structures of 3, 4, and 5 are supported by spectroscopy (^1H and ^{13}C nmr).
6. H.G. Guttengerger, H.J. Bestman, F.L. Dickert, F.S. Jorgenson, J.P. Synder, J. Amer. Chem. Soc., 1981, 103, 159 and references therein.
7. Structure supported by ^1H and ^{13}C nmr spectroscopy and elemental analysis.
8. ^1H nmr($CDCl_3$) ppm: For 8 1.18(s,6H); 1.20(s,9H); 1.50-2.12(m,4H); 3.42(t,J=7Hz,2H). For 9 1.25(s,6H); 1.50-1.85(m,4H); 4.12(t,J=5Hz,2H). For 4 1.20(s,9H); 5.22(s,2H); 5.63(s,2H); 7.30-7.95(m,6H). For 7 5.04(s,4H); 7.16- 7.65(m,6H).
9. a) E.M. Arnett, C. Petro, J. Amer. Chem. Soc., 1978, 100, 5402.
   b) G.A. Olah, J. Sommer, J. Amer. Chem. Soc., 1968, 90, 4323.
10. ^2H nmr(CH_2Cl_2) ppm: for 4-d_4 5.25(s,2D); 5.61(s,2D). For 7-d_4 5.08(s,4D).

(Received in UK 1 June 1984)