CIDNP Studies on the β-Bromoethyl Radical

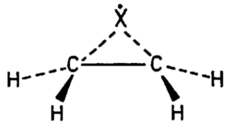
By J. H. Hargis and Philip B. Shevlin*

(*Department of Chemistry, Auburn University, Auburn, Alabama* 36830)

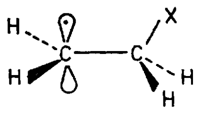
Summary CIDNP signals observed during the thermolysis of benzoyl-β-bromopropionyl peroxide show that the methylene protons in the β-bromoethyl radical are non-equivalent.

There is considerable interest in the structure of β-bromoalkyl radicals.[1] Explanations of the apparently increased stability of these radicals as compared to simple alkyl radicals have invoked either bridged structures[1a–c,e] (**1a**; X = Br) or radicals existing in a preferred conformation allowing hyperconjugative stabilization by halogen (**1b**; X = Br).[1f] A recent e.s.r. study[1f] of the β-bromoethyl radical (**1**) indicates a high spin density on bromine but does not distinguish between (**1a**) and (**1b**).

We report the results of a simple CIDNP[2] experiment which establishes that the methylene groups in (**1**) are non-equivalent. Homolysis of benzoyl-β-bromopropionyl peroxide (**2**) produces, after rapid decarboxylation of the β-bromopropionyloxy-radical† the radical pair (**3**). The polarizations of products emanating from (**3**) will depend upon the structure of (**1**). If (**1a**) is the ground-state configuration of (**1**), all protons are equivalent and should exhibit the same polarization. Thus, the cage recombination product, (**4**), should show the same polarization for both sets of methylene protons.‡ Products resulting from diffusion of (**1a**) from the solvent cage would show the same



(1a)



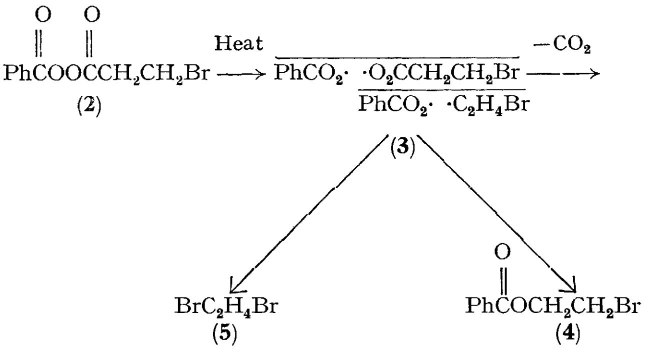
(1b)

---

† By analogy with other acyloxy-radicals,[3] the β-bromopropionyloxy-radical is expected to decarboxylate more rapidly than the benzoyloxy-radical.

‡ In the absence of information about the g factor and the proton hyperfine splitting expected for (**1a**), we can only predict that the α and β protons in products resulting from (**1a**) will exhibit the same polarization. This prediction is sufficient for the purpose of this study.

polarization in the two methylene groups, a polarization opposite to that observed in (**4**).



A different CIDNP result is predicted from (**1b**). If the benzoyloxy-radical in (**3**) has the higher *g* factor, emission should be observed for the α-methylene protons in (**4**) while the β protons should show enhanced absorption. Should (**1b**) have the higher *g* factor, the α protons in (**4**) will exhibit enhanced absorption while emission will result from the β protons. By analogy with studies on the decomposition of other peroxides,[3] the benzoyloxy-radical, with unpaired spin density on oxygen, is expected to have the higher *g* factor. Addition of bromotrichloromethane to the reaction mixture should serve to trap the majority of the β-bromoethyl radicals which escape the solvent cage and produce 1,2-dibromoethane (**5**). The reaction of (**1b**) with $BrCCl_3$ would produce (**5**) with little or no polarization as the oppositely polarized equivalent hydrogens in (**5**) would cancel any effect. Abstraction of bromine by (**1a**) is expected to yield (**5**) which will be polarized. A spectrum recorded during the 119° thermolysis of a chlorobenzene–bromotrichloromethane (3:1 v/v) solution of (**2**) gave emission at δ 4·5 due to the α protons of (**4**) while an enhanced absorption at δ 3·6 resulted from the β protons. An unpolarized singlet at δ 3·4 corresponded to the methylene protons of 1,2-dibromoethane. Decomposition of (**2**) in chlorobenzene containing no bromotrichloromethane yields the same polarization for the protons of (**4**) and an additional enhanced triplet at δ 2·7. The unidentified species responsible for this triplet must result from a radical which has escaped the solvent cage since it disappears when $BrCCl_3$ is added. Even in the absence of $BrCCl_3$, (**5**) showing no net polarization is produced by abstraction of bromine from (**2**).

These CIDNP results establish conclusively that the ground state of (**1**) has non-equivalent methylene groups. Further, interconversion of the methylene groups *via* bromine migration cannot occur at a rate greater than the rate of diffusion from the cage.

E.s.r. studies [1f,4] have shown that β substituted ethyl radicals (**1b**; X = Cl, SR, SiR_3, SnR_3) exhibit unusually small values for the β proton hyperfine splitting. These low values have been taken as evidence that these radicals have the conformation shown in (**1b**).

This study does not rule out a bridged radical in the transition state leading to (**1b**). Indeed, decarboxylation of the β-bromopropionyloxy-radical may be assisted by the bromine.

We thank the donors of the Petroleum Research Fund, Administered by the American Chemical Society, for partial support of this research.

(*Received*, 16*th October* 1972; *Com.* 1758.)

---

[1] (a) P. S. Skell, R. G. Allen, and N. D. Gilmour, *J. Amer. Chem. Soc.*, 1961, **83**, 504; (b) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, 1963, **85**, 2849; (c) P. S. Skell and P. D. Readio, *ibid.*, 1964, **86**, 3334; (d) D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *ibid.*, 1971, **93**, 5846, 4802; (e) J. G. Traynham and W. G. Hines, *ibid.*, 1968, **90**, 5108; (f) A. R. Lyons and M. C. R. Symons, *ibid.*, 1971, **93**, 7330; (g) D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *ibid.*, 1969, **91**, 7398; (h) D. J. Edge and J. K. Kochi, *Tetrahedron Letters*, 1972, 2427.

[2] H. R. Ward, *Accounts Chem. Res.*, 1972, **5**, 24; (b) R. G. Lawler, *ibid.*, p. 32.

[3] R. A. Cooper, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, 1972, **94**, 545.

[4] T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 1752; P. J. Krusic and J. K. Kochi, *ibid.*, 1971, **93**, 846