Stability of the Adamant-1-yl Radical

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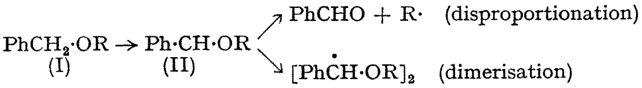
ATTEMPTS to assess the relative stabilities of adamant-1-yl and t-butyl radicals indicated either that the bridgehead radical is more stable than the t-butyl radical[1] or that the two radicals are of essentially identical stability.[2] In contrast, we have evidence to show that adamant-1-yl radical is much less stable than t-butyl radical.

In the reaction of a series of benzyl ethers (I; R = Me, Et, Pr^i, Bu^t, Ph, Bz, and Ph_2CH) with free t-butoxy-radicals, hydrogen abstraction by the latter takes place to give the benzyl radical (II),[3] which depending on the nature of R, then undergoes, either disproportionation or dimerisation, or both, as follows:



The dimer : aldehyde ratios

R	Me	Et	Pr^i	Bu^t	$PhCH_2$	Ph_2CH
Dimer : aldehyde ratio*	4·4†	1·2	0·44	0·33	0	0

* In computing the ratios, the total aldehyde is considered to include that in the aldehyde-derived products.

† R. L. Huang, Tong-Wai Lee, and S. H. Ong, *J. Chem. Soc.*, (*C*), 1969, 40.

The results show that there is a correlation between the dimer: aldehyde ratios and the relative stabilities of the radicals R. When R is either of the stable radicals $PhCH_2\cdot$ and $Ph_2CH\cdot$ disproportionation is the exclusive reaction. With benzyl methyl ether (R = Me) the dimer : aldehyde ratio is the highest, and decreases as R changes from Me to a more complex radical. Here we report the reaction of adamant-1-yl benzyl ether (R = adamant-1-yl; 15 mmole) with t-butyl peroxide (3·1 mmole) at 110° under nitrogen. The products obtained were the dimer, $(PhCH\cdot OR)_2$ (R = adamant-1-yl) in 66% yield (based on ether consumed), in both the *meso*-(III) and (±)-(IV) modifications and benzaldehyde (1·0 mmole). In addition, adamantane (0·008 mmole), adamantan-1-ol (1·0 mmole), unchanged ether (7·7 mmole), t-butyl alcohol (4·9 mmole), and acetone (0·68 mmole) were isolated. The structures of (III) and (IV) were determined by elemental analyses and by n.m.r. in $CDCl_3$; (III): signals centred at τ 9·0, 8·7, and 8·1 (30 adamantyl protons); 5·56s (2 benzylic protons), and 2·7 (10 aromatic protons); (IV): signals centred at τ 8·6, 8·45, and 8·0 (30 adamantyl protons), 5·4s (2 benzylic protons), and 2·92, 2·75 (10 aromatic protons). Both (III) and (IV) show strong ether absorption at 1110 and 1085 cm.$^{-1}$. The dimer : aldehyde ratio was 2·4 : 1 indicating that the stability of adamant-1-yl radical falls between that of the methyl and ethyl radicals and was less than that of the t-butyl radical.

Our results on the adamant-1-yl benzyl ether together with those already published[3] indicate that the adamant-1-yl radical [which cannot be planar because of its cage structure but exists in a pyramidal (sp^3) state] is less stable than the t-butyl radical [which is capable of existing in either a pyrimadal (sp^3) state or in a planr (sp^2) configuration]. This finding on the relative stability of the pyramidal adamant-1-yl radical and the probably planar t-butyl radical lends support to the spectroscopic evidence[4] that carbon radicals prefer planar configuration.

The isolation of adamantan-1-ol from the reaction mixture was unexpected. It is less likely that the alcohol arose through the mixed acetal, adamantyl α-t-butoxybenzyl ether as there was no change in the benzaldehyde concentration after treatment with acid. There is a possibility that it might have arisen by reaction with traces of oxygen present. An indication that this might have taken place is found in the isolation of adamantan-1-ol (0·023 mmole) from the reaction of 1-bromoadamantane (9·9 mmole) with tri-n-butyltin hydride (10 mmole) and azobisisobutyronitrile

(1·1 mmole) in benzene at 80° for 20 hr. under atmospheric oxygen; other products being adamantane (7·2 mmole) and unchanged 1-bromoadamantane (2·3 mmole).

We thank Professor R. L. Huang for his help and encouragement and Dr. D. G. Williamson, University of Aberdeen, for determination of the n.m.r. spectra.

(*Received, November 11th,* 1969; *Com.* 1538.)

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[1] D. E. Applequist and L. Kaplan, *J. Amer. Chem. Soc.*, 1965, **87**, 2194.

[2] (a) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Amer. Chem. Soc.*, 1968, **90**, 5266, and (b) R. C. Fort, jun., and R. E. Franklin, *J. Amer. Chem. Soc.*, 1968, **90**, 5267.

[3] R. L. Huang and S. S. Si-Hoe, "Vistas in Free Radical Chemistry", ed. W. A. Waters, Pergamon, London, 1959, p. 242; *Proc. Chem. Soc.*, 1967, 354.

[4] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147; J. R. Morton, *Chem. Rev.*, 1964, **64**, 453.