

Free-radical Displacement on a Hydroperoxide

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FREE-RADICAL displacements on carbon, oxygen, sulphur, and phosphorus generally take the form of an abstraction of a hydrogen or halogen atom.¹ Recently, intramolecular displacements of carbon radicals on carbon have been postulated in which halogen atoms^{2,3} and alkyl radicals⁴ constituted the leaving groups. Similar substitutions on disulphides have also been shown.⁵

We now report what is apparently the first example of a radical displacement on a hydroperoxide. Treatment of methyl isobutyrate with

t-butyl hydroperoxide under both thermal (150°) and photolytic (2537 Å) conditions afforded methyl 2-hydroxyisobutyrate, (I, 14—34% yield), in addition to the reported⁶ ester-derived products of coupling and disproportionation.

That the formation of (I) resulted from attack of the 1-carboxy-1-methylethyl radical on hydroperoxide was shown by decomposing dimethyl 2,2'-azobis(isobutyrate) in *t*-butyl hydroperoxide under deoxygenated conditions at 92°. Control experiments demonstrated that the hydroperoxide

TABLE

Yields of methyl 2-hydroxyisobutyrate from decomposition of the azo-compound.†

Solvent	Additive	Yield of (I)	
		Based on azo-compound	Based on reacted <i>t</i> -BuO ₂ H
<i>t</i> -Butyl alcohol	None	0.0%	0.0%
<i>t</i> -Butyl alcohol	<i>t</i> -Butyl hydroperoxide (1.3 M)	4.9	49.5
Methyl isobutyrate	<i>t</i> -Butyl hydroperoxide (1.3 M)	10.5	38.1
Methyl isobutyrate	<i>t</i> -Butyl hydroperoxide (1.3 M), and hydroquinone (0.06 M)	0.8	8.1

† Concentration of the azo-compound was 0.65 M in each instance; reaction temperature was 92°.

was thermally stable under these conditions. Reaction products were methyl isobutyrate (16.6%), methyl methacrylate (1.1%), dimethyl tetramethylsuccinate (43.5%), dimethyl 2,2,4-trimethylglutarate (3.1%), dehydro-trimers (21.6%), and compound (I) (4.9%).[‡]

Increased hydroperoxide concentration and the presence of a hydrogen-donor solvent enhanced the yield of (I), while added hydroquinone inhibited its formation. These results, summarised in the Table, are consistent with the notion of a short radical-chain sequence involving homolytic displacement of a t-butoxy-radical from the hydroperoxide.

[‡] Yields are based on initial concentration of the azo-compound.

¹ C. Walling, "Free Radicals in Solution", John Wiley, New York, 1957, p. 239.

² L. Kaplan, *J. Amer. Chem. Soc.*, 1967, **89**, 1753.

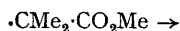
³ J. S. Shapiro and E. S. Swinbourne, *Chem. Comm.*, 1967, 465.

⁴ N. J. Friswell and B. G. Gowenlock, *Chem. Comm.*, 1965, 277.

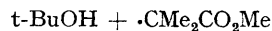
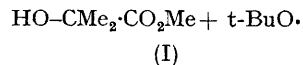
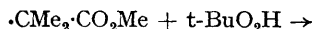
⁵ W. A. Pryor and H. Guard, *J. Amer. Chem. Soc.*, 1964, **86**, 1150.

⁶ A. F. Bickel and W. A. Waters, *Rec. Trav. chim.*, 1950, **69**, 312.

⁷ D. L. Heywood, B. Phillips, and H. A. Stansbury, jun., *J. Org. Chem.*, 1961, **26**, 281; D. Lefort, *et al.*, *Bull. Soc. chim. France*, 1959, 1385; 1961, 2373; 1962, 827.



Coupling and disproportionation



A similar process has been proposed⁷ to account for the hydroxylation of hydrocarbons by per-acids.

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