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STUDIES OF PEROXYCOMPOUNDS. COPPER SALT CATALYZED REACTIONS OF t-BUTYL PERBENZOATE WITH BENZYL ETHERS[1]

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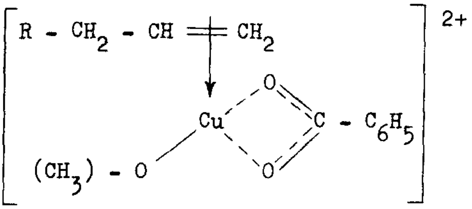
DURING recent years a series of publications has been produced from the late Dr. M. S. Kharasch's Institute of Organic Chemistry, dealing with the modifying influence of certain transition metal salts on homolytic reactions.[2-5] When t-butyl perbenzoate is decomposed in the presence of an olefin the benzoyloxygroup is introduced specifically into the allyl position[2] without any isomerization. A concerted mechanism has been postulated, and Denney <u>et al.</u>,[6] working with t-butyl perbenzoate (carbonyl O^{18}) suggest a reasonable intermediate, I, for these reactions.



I

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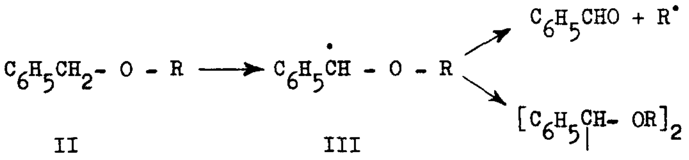
[1] Part III: S.-O. Lawesson and T. Busch, Acta Chem. Scand. **13**, 1716 (1959).

[2] M. S. Kharasch and G. Sosnovsky, J. Amer. Chem. Soc. **80**, 756 (1958).

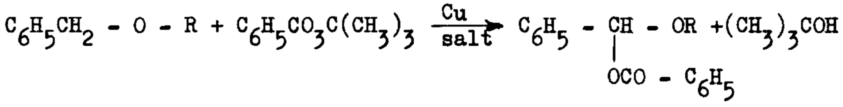
In our opinion this hypothesis, that free radicals are not completely free in the presence of copper salts, is probably correct and we are now able to present further support for this mechanism.

By decomposing t-butyl peroxide in the presence of different benzyl ethers, II, a hydrogen atom is abstracted from the ether and a radical, III, formed. Huang et al.[7,8] have shown that radical III may then either disproportionate or dimerize or both.



$$\underset{\text{II}}{C_6H_5CH_2-O-R} \longrightarrow \underset{\text{III}}{C_6H_5\dot{C}H-O-R} \begin{array}{l} \nearrow C_6H_5CHO + R^{\bullet} \\ \searrow [C_6H_5\underset{|}{C}H-OR]_2 \end{array}$$

We have now found that for different substituents R it is possible to introduce the bensoyloxygroup into ethers, and among them benzylic ethers, II, using the method of Kharasch, Sosnovsky and Fono.



$$C_6H_5CH_2-O-R + C_6H_5CO_3C(CH_3)_3 \xrightarrow[\text{salt}]{\text{Cu}} C_6H_5-\underset{\displaystyle \underset{\text{IV}}{OCO-C_6H_5}}{\underset{|}{CH}}-OR + (CH_3)_3COH$$

IV

Irrespective of the nature of R, only benzoates, IV, could be isolated, which is a strong indication that under these conditions the radicals are not completely free.

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[3] M. S. Kharasch and A. Fono, J. Org. Chem. **23**, 324 (1958).

[4] M. S. Kharasch and A. Fono, J. Org. Chem. **24**, 72 (1959).

[5] M. S. Kharasch and A. Fono, J. Org. Chem. **24**, 606 (1959).

[6] D. B. Denney, D. Z. Denney and G. Feig, Tetrahedron Letters **15**, 19 (1959).

[7] R. L. Huang and S. S. Si-Hoe, Proc. Chem. Soc. 354 (1957).

A full paper will be published in Arkiv for Kemi in early 1960. Additional work is in progress for a complete elucidation of these observations, with particular regard to reactions between perbenzoates and benzyl sulphides, cyclic ethers and thioethers, epoxy compounds and amines.

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[8] R.L. Huang and S.S. Si-Hoe, in Vistas in Free Radical Chemistry (Edited by W.A.Waters) p. 242. Pergamon Press, London (1959).