Communications TO THE EDITOR

The Free Radical Chemistry of Cyclic Ethers: A Novel Free Radical Rearrangement

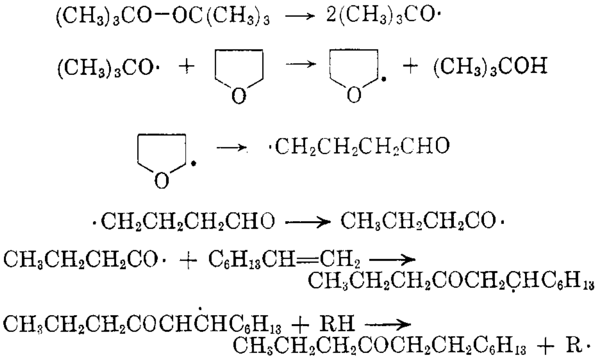
Sir:

The peroxide and light induced reactions of cyclic and acyclic aliphatic amines with olefins have been studied to some extent in the past.[1,2] The reaction mechanism involves alpha hydrogen atom abstraction from the amine in the chain-propagating step. The resulting alpha amino radical adds to the olefin in question to give a beta amino alkyl radical which then reacts with more amine in the chain transfer step to give the product. Thus, in the *tert*-butyl peroxide induced reaction of piperidine with 1-octene the 1:1 addition product is 2-octylpiperidine. However, no rearrangement products were reported.

As a logical extension of the above work we have investigated the *tert*-butyl peroxide induced reaction of 4-, 5-, and 6-membered cyclic ethers with 1-octene. The respective products were 3-undecanone, 4-dodecanone, and 5-tridecanone. This indicates that the alpha ethereal radical, initially formed by the abstraction of a hydrogen atom, undergoes a rearrangement before adding to the olefin. Apparently, an intramolecular hydrogen atom shift occurs simultaneously with the opening of each ring.

In a typical experiment, 1.32 moles of tetrahydrofuran (95 g.), 0.25 moles of 1-octene (28 g.), and 0.03 mole of *tert*-butyl peroxide (5 ml.) were heated in a Parr bomb under an inert atmosphere for 2 hr. at 150°. Atmospheric distillation removed the peroxide decomposition products and unreacted starting material. Further distillation under reduced pressure removed the unreacted 1-octene. The remainder was distilled to give 18.7 g. of 4-dodecanone (40.6% yield based on 1-octene). An infrared spectrum of the ketone displayed a strong carbonyl band at 5.85 μ. Product indentification was further established by gas chromatography and isolation of a solid derivative. A gas chromatogram of the product and an authentic sample of 4-dodecanone on a 10-ft. silicone column had the same retention time at 195°, and a mixture yielded a single peak. A hydantoin melted at 114–115° (reported[3] m.p. 114–115°). A mixture melting point with an authentic sample showed no depression.

The following mechanistic path seems most plausible for the formation of the ketone:



$$(CH_3)_3CO{-}OC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot$$

$$\cdot CH_2CH_2CH_2CHO \longrightarrow CH_3CH_2CH_2CO\cdot$$

$$CH_3CH_2CH_2CO\cdot + C_6H_{13}CH{=}CH_2 \longrightarrow CH_3CH_2CH_2COCH_2\underset{\cdot}{C}HC_6H_{13}$$

$$CH_3CH_2CH_2COCH\dot{C}HC_6H_{13} + RH \longrightarrow CH_3CH_2CH_2COCH_2CH_2C_6H_{13} + R\cdot$$

These results have prompted us to investigate morpholine which is both a cyclic amine and a cyclic ether in order to ascertain what mechanism predominates in this system.

Acknowledgment. The authors would like to acknowledge generous support by the National Science Foundation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CONNECTICUT
STORRS, CONN.

T. J. WALLACE[4]
R. J. GRITTER

Received September 21, 1961

---

[1] W. H. Urry, O. O. Juveland, and F. W. Stacey, *J. Am. Chem. Soc.*, **74**, 6155 (1952).

[2] W. H. Urry and O. O. Juveland, *J. Am. Chem. Soc.*, **80**, 3322 (1958).

[3] M. S. Kharasch, J. L. Rowe, and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

[4] Present address: Esso Research & Engineering Co., Process Research Division, Linden, N. J.

The Structure of Fervenulin, a New Antibiotic[1]

Sir:

Fervenulin, a new crystalline antibiotic isolated by Eble and co-workers[2] from culture filtrates of an actinomycete (from a California soil), *Streptomyces fervens* n. sp., has demonstrated broad-spectrum antibacterial, antifungal, antiparasitic, and antitumor cell activity *in vitro*.[3] No structure for fervenulin has been proposed. Its empirical formula has been reported as $C_7H_7N_5O_2$, and its infrared spectrum was interpreted[2] to indicate the presence of a six-membered enol lactone.

This antibiotic is of interest since the proposed empirical formula, $C_7H_7N_5O_2$, is identical with that of toxoflavin (I), an antibiotic recently synthesized in our laboratory.[4] The ultraviolet absorption spectrum of fervenulin is not identical, but strikingly similar, to that of toxoflavin; furthermore,

---

[1] This investigation was supported by research contract SA-43-ph-3025 from the Cancer Chemotherapy National Service Center, National Cancer Institute of the National Institutes of Health, Public Health Service.