SHORT COMMUNICATIONS

Small Ring Compounds. I. Anodic Oxidation of 2,3-Dicarbethoxy-cyclopropanecarboxylic Acid

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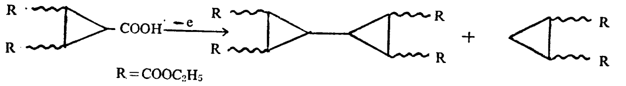
Highly strained small ring radicals have recently attracted special interest, and cyclopropyl radicals have been generated by several methods.[1] However, the yields are low and variable, and it would not be feasible to utilize the generated cyclopropyl radicals in various synthetic processes. In the anodic oxidation of cyclopropanecarboxylic acids, a common problem is the facile formation of a cationic intermediate, such as cyclopropyl cation or cyclopropanecarboxonium ion, by the additional one-electron oxidation of a generated cyclopropyl radical.[2] Cyclopropyl cations usually undergo concerted ring opening to afford many rearranged products.

We wish to report on attempts to generate an unrearranged cyclopropyl radical of high efficiency by anodic oxidation. For this purpose, 2,3-dicarbethoxy-cyclopropanecarboxylic acid (I), consisting of *trans,cis*- and *trans,trans*-isomers in the ratio 3: 2, was selected as the starting material. Compound I (0.02 mol) was electrolyzed in methanol (80 m*l*) containing sodium methoxide (0.02 mol) at 20—30°C for 6 hr: Anode, a platinum plate (1.5×20 cm); cathode, mercury-pool (surface area: *ca.* 13 cm^2); distance between the electrodes, *ca.* 1.0 cm; electrolytic cell, beaker-type vessel (150 m*l*) without diaphragm; initial current, 1.5 A (final value, 0.5 A); cell voltage, 60 V (final value 100 V).

2,2′,3,3′-Tetracarbethoxy-bicyclopropyl (II) and 1,2-dicarbethoxy-cyclopropane (III) were obtained in 13 and 62.5% yields, along with small quantities of 1,2-dicarbethoxy-3-hydroxymethyl-cyclopropane (IV) and 1,2-dicarbethoxy-3-carbomethoxy-cyclopropane (V). All the products except III were identified by spectroscopic methods and gas chromatographic technique. Compound II can exist in eleven forms, it being confirmed by VPC (DEGSP, 230°C) and their mass spectra that at least nine out of the eleven were formed. Only the major component, mp 155—157°C, was isolated by VPC in *ca.* 30% yield, and determined to be *trans, trans,trans,trans*-isomer. It is significant that no ring opening products were found. Anodic oxidation with platinum anode and cathode (1.5×2.0 cm on each), mounted parallel to each other and 0.3 cm apart, resulted in similar products and their distributions.



I II III

It should be emphasized that a cyclopropyl radical is consistently generated in *ca.* 70% yield on the electrode. No concerted ring opening occurred through a cationic intermediate. In order to obtain further information on the stability of the radical, the thermal decomposition and photolysis of *t*-butyl-perester of I in benzene have been studied. The radical was also generated almost quantitatively and II and III were obtained in somewhat different yields together with considerable amounts of 3-*t*-butoxyl- and 3-phenyl-1,2-dicarbethoxy-cyclopropanes. Both the present electrolytic conditions employed and the electronic effect of two carbethoxy groups on the increase of the ionization potential of a cyclopropyl radical might be of importance.

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