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SMALL RING COMPOUNDS. IV.[1] ANODIC OXIDATION OF CARBETHOXYCYCLOPROPANECARBOXYLIC ACIDS

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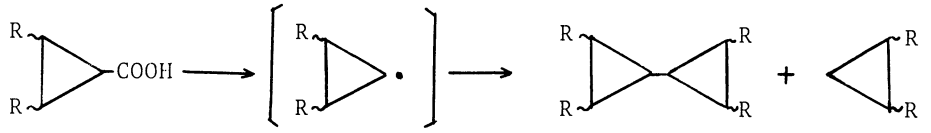
The substituent effect on the stability of a cyclopropyl radical generated by anodic oxidation of carbethoxycyclopropanecarboxylic acids is discussed, and then some synthetic applications of the cyclopropyl radical are demonstrated.

In a previous paper,[1] we have reported that the anodic oxidation of 2,3-dicarbethoxycyclopropanecarboxylic acid (I) in methanol containing sodium methoxide generated the cyclopropyl radical in high efficiency, which resulted in the formation of the hydrogen abstraction product chiefly, together with the coupling one.

In this paper, we describe the anodic oxidation of some cyclopropanecarboxylic acid derivatives in pyridine in order to suppress the unfavorable hydrogen abstraction by cyclopropyl radical for synthetic application, and demonstrate the effect of substituent on the stability of cyclopropyl radical generated in the present reaction.

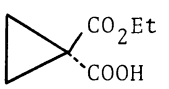
In addition, with a view to expanding the utility of this anodic oxidation for synthetic chemistry, we wish to report the addition of a cyclopropyl radical to acrylonitrile and the synthesis of 3-carbethoxycyclopropene whose existence has been postulated as unstable intermediate in some reactions.[2]

The anodic decarboxylations of cyclopropanemonocarboxylic acid derivatives (0.01 mole); 2,3-dicarbethoxy- (I), 1-carbethoxy- (II), and 2-carbethoxycyclopropane-1-carboxylic acid (III) were carried out for 5 hr using two stationary platinum wire gauze electrodes in 90% aqueous pyridine (90 ml) containing triethylamine (2.0 ml) and supplied currents were 2.0—0.6 A at 100 V. During the reaction, an internal temperature was maintained through lower than 20°. The anodic oxidation of (I) gave 2,2',3,3'-tetracarbethoxybicyclopropyl as the coupling product in 62.2% yield.



(I) R=CO_2Et 62.2% 2.8% in pyridine
13.0% 62.5% in methanol

On the other hand, in the cases of (II) and (III), the ring opening took place mainly, though the corresponding bicyclopropyl derivatives were obtained in 23.5% and less than 10%, respectively.



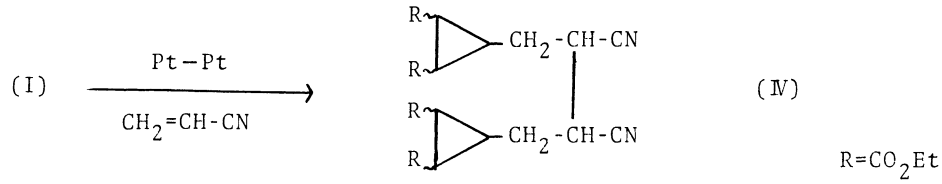
(II)

(III)

As proposed previously,[1] these results may be interpreted on the basis of the electronic effect of substituent on a cyclopropane ring, that is, two carbethoxy groups on a cyclopropane ring increase the ionization potential of generated cyclopropyl radical and, consequently, the one-electron oxidation of cyclopropyl radical to cyclopropyl cation is extremely depressed. However, the substituent effect of only one carbethoxy group, regardless of its substituted position, is insufficient to suppress the above oxidation of cyclopropyl radical, and so the ring opening through cyclopropyl cation occurs preferentially.[3]

Based on our fundamental study of the anodic oxidation, we have tried some reactions in order to apply the stable cyclopropyl radical to organic synthesis.

As a preliminary experiment on the addition of a cyclopropyl radical to olefins, the anodic oxidation of (I) in the presence of acrylonitrile, a good radical trapping reagent, was carried out. The addition with acrylonitrile occurred smoothly and resulted in the formation of dimerization product (IV)[4] in a moderate yield.

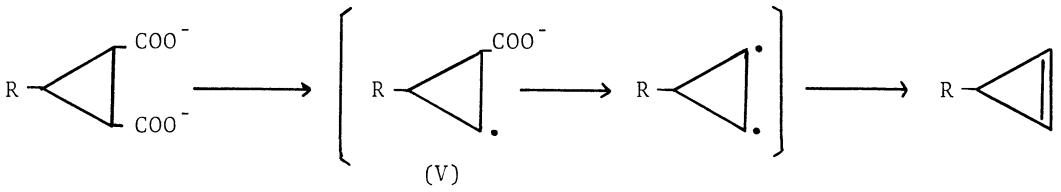


(IV)

R=CO_2Et

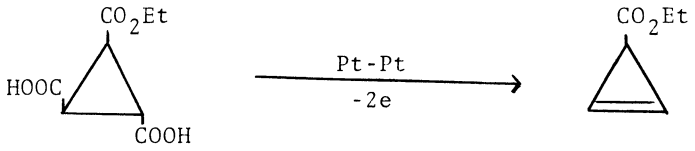
It is expected that this reaction using appropriate olefins will give various cyclopropane derivatives. Further work is being studied and details will be represented elsewhere.

In an anodic oxidation of 1,2-dicarboxycyclopropane derivatives, having an electronwithdrawing substituent at the 3-position, it may be expected that bisdecarboxylation proceeds stepwise via a stable monocarboxy-cyclopropyl radical intermediate (V) to form cyclopropene derivatives, represented by the following scheme;



(V)

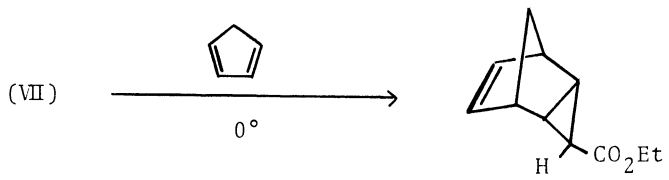
No attempts at the synthesis of cyclopropenes by the anodic oxidation have been made, though they have been synthesized by various methods.[5] Thus, the anodic bisdecarboxylation of *trans*-3-carbethoxy-1,2-cyclopropanedicarboxylic acid (0.01 mole) (VI) was carried out under the conditions similar to those used for anodic monodecarboxylation of (I).



(VI) (VII)

As expected, hitherto unknown 3-carbethoxycyclopropene (VII) was obtained in 28.2% yield, along with considerable amounts of oligomers mainly comprised of tetramers and pentamers. The spectral properties of (VII) are as follows, ν_{max} 3100 (=C-H), 1725 ($-CO_2C_2H_5$), 1660 (C=C) cm^{-1}; τ (in CCl_4) 3.16 (d, 2H, J=1.8 cps, C=C-H), 5.97 (q, 2H, $-CO_2-CH_2-$), 7.92 (t, 1H, $\rightarrow$CH), 8.78 (t, 3H, $-CO_2CH_2-CH_3$).

Like other simple cyclopropenes,[6] (VII)[7] readily polymerizes at room temperature to form oligomers mentioned above and its half-life time is estimated at 2.5 hr at 15° by measurement of the rate of disappearance of the infrared absorption at 1660 cm^{-1}. The (4+2) cycloaddition of (VII) with some cyclic 1,3-dienes, such as cyclopentadiene, and 1,3-diphenylisobenzofuran, occurred rapidly even at 0° to afford the corresponding endo-adducts[8] almost quantitatively.



Concerning the synthesis of cyclopropenes by the anodic bisdecarboxylation, the electrolytic conditions employed are of critical importance. When the anodic oxidation of (VI) was carried out with platinum anode and mercury cathode in methanol containing sodium methoxide,[9] the formation of (VII) was suppressed markedly.

Further studies on the utility of the present method for the synthesis of cyclopropenes are currently in progress and will be reported shortly.

REFERENCES AND FOOTNOTES

1) I. Minato, T. Takasuka, K. Kimura, T. Sakakibara, and Y. Odaira, *Bull. Chem. Soc. Japan*, 45, 965 (1972).

2) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Amer. Chem. Soc.*, 78, 5448 (1956); K. B. Wiberg, R. K. Barnes, and J. Albin, *ibid.*, 79, 4994 (1957); D. G. Farnum, G. Metha, and R. G. Silberman, *ibid.*, 89, 5048 (1967).

3) In the anodic oxidation of cyclopropanecarboxylic acids, having electrondonating substituent, ring opening takes place usually; T. Shono and R. Oda, *Tetrahedron Lett.*, 1965 (1969); R. Brettle and G. B. Cox, *J. Chem. Soc. C*, 1227 (1969).

4) The compound (Ⅳ) was also obtained under the typical conditions of Kolbe reactions using a diaphragm cell, though its stereochemistry was not confirmed perfectly, in both cases.

5) Z. Yoshida and H. Miyahara, "Chemistry of Cyclopropenes" in "Chemistry, Vol. 24", Kagakudojin, Kyoto, 1969, p. 996, 1094; G. Closs, "Cyclopropenes" in "Advances in Alicyclic Chemistry, Vol. I", Academic Press, New York and London, 1966, p. 91; H. Smith, "Rodd's Chemistry of Carbon Compounds, Vol. Ⅱ. Part A", Elsevier Publishing Co., Amsterdam, London, and New York, 1967, p. 19.

6) K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, 82, 6375 (1960).

7) Despite the considerable instability of (Ⅶ), the very nearly satisfactory result was obtained in its rapid elementary analysis.

8) Two endo-adducts gave satisfactory elementary analyses and spectral data.

9) In this case, 2,2'-dicarbethoxybicyclopropyl and oligomers were obtained as major products.

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