Electroorganic Chemistry XVIII[1)] Anodic Oxidation of Substituted Cyclopropanes

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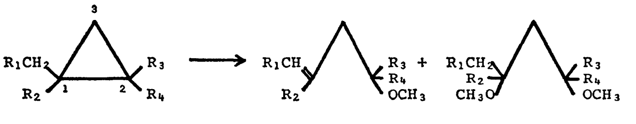
The anodic oxidations of polyalkyl-substituted cyclopropanes (**1**—**3**) and spiro[2.n]alkanes (**4**—**6**) were carried out in methanol. Monomethoxyolefin and dimethoxy compound resulted from the selective cleavage at the most substituted carbon-carbon bond. The decrease in the oxidation potential brought about by the substitution of the one methyl group was observed to be about 0.3 V *vs.* SCE. The analysis of the products and oxidation potentials of the cyclopropanes suggested that the σ-electron transfer from cyclopropane to the anode may be the initiation process and that the stereochemistry at the surface of the solid electrode plays an important role in this anodic oxidation.

The electrochemical oxidation of a cyclopropane ring seems quite interesting because of its olefin-like character. In a previous study,[2)] we have reported the first evidence that the carbon–carbon single bond in a cyclopropane ring could be anodically oxidized to yield ring-opened products which may be synthesized by other methods only with difficulty.

In the present study, we wish to report the effect of an alkyl substituent and some specific selectivity on the anodic ring cleavage of cyclopropanes.

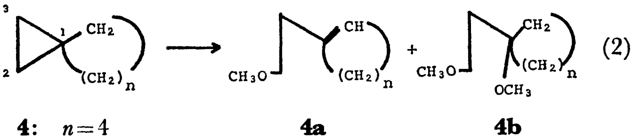
Results

Product Study. The anodic oxidations of polyalkyl-subsituted cyclopropanes (**1**—**3**) and spiro[2.n]alkanes (**4**—**6**) were carried out in methanol containing tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) as a supporting electrolyte (Eqs. (1) and (2)). Compounds **1**—**5** gave monomethoxy and dimethoxy products, which resulted from the cleavage of the most highly substituted carbon–carbon bond, although **3a** and **5a** were not isolated because of their further oxidation. Interestingly, spiropentane (**6**) was anodically stable.



1: $R_1=H$, $R_2=R_3=R_4=CH_3$ **1a** **1b**
2: $R_1=R_4=H$, $R_2=R_3=CH_3$ **2a** **2b**
3: $R_1=CH_3$, $R_2=CH_2CH_3$ $R_3=R_4=H$ **3a** **3b**

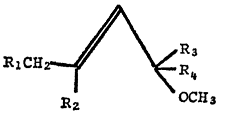
(1)



(2)

4: $n=4$ **4a** **4b**
5: $n=2$ **5a** **5b**
6: $n=1$

It is noticeable that in all of the unsaturated ethereal products (**1a**, **2a**), the unsaturated bond was formed in the direction of the side chain; further, products (**1a**′, **2a**′) which possess an unsaturated bond at the position corresponding to the cyclopropane 1,3-bond were completely lacking.



1a′: $R_1=H$, $R_2=R_3=R_4=CH_3$
2a′: $R_1=R_4=H$, $R_2=R_3=CH_3$

Table 1. Product yields[a)] and current efficiencies of anodic oxidations of **1**—**5**

Cyclopropane	Product yields (%) Monomethoxy	Dimethoxy	Current efficiencies (%)
1	**1a** (47)	**1b** (24)	71
2	**2a** (11)	**2b** (10)	21
3	**3a** (—)[b)]	**3b** (12)	12
4	**4a** (1)	**4b** (5)	6
5	**5a** (—)[b)]	**5b** (26)	26

a) Yields were calculated at the time when 2F/mol of electricity had been passed. b) The corresponding monomethoxy product could not be isolated.

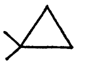
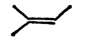
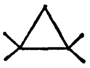
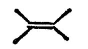
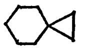
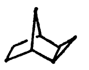
All products were identified by spectroscopic and elemental analysis. Yields and current efficiences are shown in Table 1.

Oxidation Potential and Current–Potential Relationship. In order to evalute the effect of alkyl substituents on the oxidation potentials of cyclopropanes, they were measured in acetonitrile containing tetraethylammonium tetrafluoroborate as a supporting electrolyte. All cyclopropanes gave one oxidation wave, showing the lowering of the oxidation potential in proportion to the increase in the number of alkyl substituent. Table 2 lists the oxidation potentials of cyclopropanes together with those of the corresponding olefins.

The current–potential relationship was measured under the condition of the preparative oxidation of cyclopropane. As the number of alkyl substituents increases, the current–potential curve becomes more cathodic, indicating a lowering of the oxidation potential of the cyclopropane.

Acid-catalyzed Methanolysis of Cyclopropanes. It has been well known[3)] that, owing to its olefin-like character, the cyclopropane ring may be able to be cleaved by the attack of an electrophile to yield ring-opened products. It seems interesting to compare

TABLE 2. OXIDATION POTENTIALS[a] OF CYCLOPROPANES AND OLEFINS

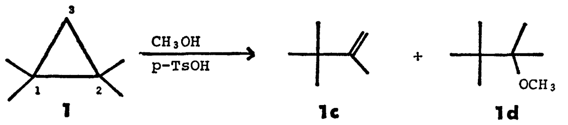
Cyclopropane		+E (V *vs.* SCE)	Olefin	+E (V *vs.* SCE)
	(**7**)	>2.5		
	(**2**)	2.30		1.96
	(**1**)	2.05		1.74
	(**4**)	2.38		
	(**8**)	2.40		2.26

a) Average of three measurements; solvent, CH_3CN; supporting electrolyte, Et_4NBF_4.

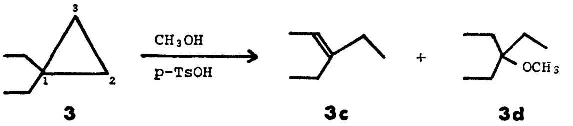
the mode of the anodic ring cleavage of cyclopropane with that observed in the acid-catalyzed methanolysis.

The reflux of a methanolic solution of **1** containing a catalytic amount of *p*-toluenesulfonic acid gave ring-opened products (**1c** and **1d**) as shown in Eq. (3). The similar treatment of compound **3** yielded **3c** and **3d** (Eq. (4)), and compound **4** gave **4c** and **4d** (Eq. (5)).

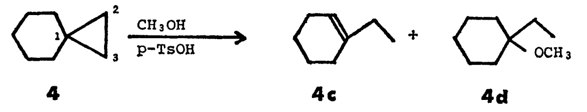
In contrast to the bond cleavage in the anodic oxidation, the 1,3-bond (compound **1**) or 1,2-bond (compounds **3** and **4**) was cleaved in the acidic methanolysis.



(3)



(4)

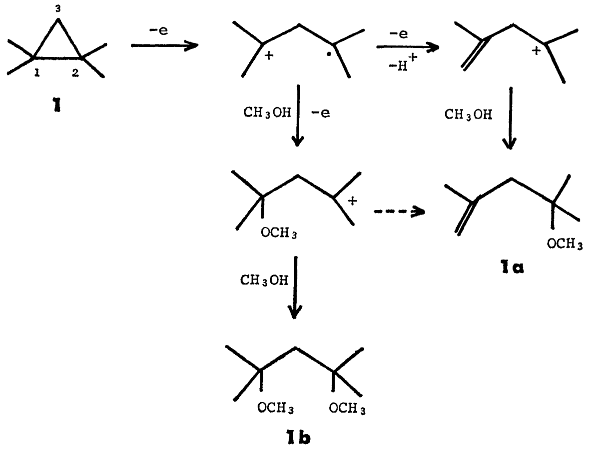


(5)

Discussion

Reaction Mechanism. As was pointed out in the previous study,[2] a direct σ-electron transfer from cyclopropane to the anode may be the initiation process of this anodic oxidation. The oxidation wave and the current–potential relationship support this proposal, which leads to the following reaction pathway (Scheme I):

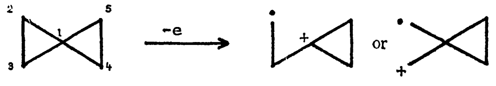
In the anodic electron transfer from the cyclopropane σ-bond, the electron must be ejected from the most strained σ-bond, where the ionization potential would be the lowest. In the cation radical generated from **1**, the free rotation of the bond between C-1 and C-3 may be hindered owing to the steric restriction brought about by the surface of the solid electrode. This stereochemical hindrance may be the reason why the unsaturated ether of type **1a**′ was not formed in the oxidation of **1**.



Scheme 1.

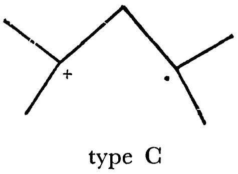
On the other hand, the attack of the proton in the acid catalyzed methanolysis occurs on the less hindered side, which is in disagreement with the selectivity of bond cleavage observed in the anodic reaction.

Oxidation Potential. The increase in the oxidation potential was observed in the order of **1**<**2**<**7**; this can be explained from the notion that the substitution of an alkyl group stabilizes the intermediate, whereas it increases the energy of the starting compound owing to the steric strain. The decrease in the oxidation potential brought about by the substitution of one methyl group was about 0.3 V *vs.* SCE (Table 2), and this amount is comparable to that which results from the substitution of an alkyl group into the olefinic system. In view of the strain energy, the oxidation of spiro[2.2]pentane (**6**) was expected to give a relatively high current efficiency. The disagreement of this prediction with the experimental observation may be explained by the instability of the intermediate.



6 type A type B

The intermediate of type A is analogous to a cyclopropyl cation, whose instability has been demonstrated by the solvolytic study.[4]



type C

Furthermore, the intermediate of type B may not be stabilized by the interaction with the neighboring cyclopropyl group since the direction of the vacant p-orbital of the cation may be orthogonal to the plane of the cyclopropane ring if the C_1–C_3 bond is not able to rotate freely at the time when the electron transfer from the C_2–C_3 σ-bond takes place on the surface of the anode. The absence of such free rotation is supported by the fact that **1a** was the only unsaturated ether from the intermediate of type C.

Experimental

Materials. Compounds **1**,(5) **2**,(6) **3**,(7) **4**,(7) and **6**(8) were prepared by the reported methods. Compound **5** was prepared by the Simmons-Smith method(9) from methylenecyclobutane(10) and identified spectroscopically by comparison with an authentic sample(11) (yield 28%).

Preparative Electrolysis of Cyclopropane. General: Into a 100 ml electrolysis cell equipped with a magnetic stirrer and two carbon electrodes were poured a solution of 0.05 mol of cyclopropane and 0.01 mol of Et_4NOTs in 0.50 mol of methanol. The electrolysis was carried out under the constant potential condition until 2F/mol of electricity had been passed. The reaction mixture was poured into water, extracted with three portions of ether, dried on magnesium sulfate, filtered, and concentrated successively. The residue was distilled to give the oxidized products.

1,1,2,2,-Tetramethylcyclopropane (**1**) was electrolyzed at the anode potential of 1.45 V *vs.* SCE and gave 2,4-dimethyl-4-methoxy-1-pentene (**1a**) and 2,4-dimethyl-2,4-dimethoxypentane (**1b**) in 47.2 and 24.2% yields respectively after 2F/mol of electricity was passed. **1a**: IR 3070 (olefin), 2820 (ether), 1640 (olefin), 1075 cm^{-1} (ether); NMR (CCl_4) τ 5.4 (d, 2, $C\underline{H}_2$=), 6.85 (s, 3, $OC\underline{H}_3$), 7.85 (s, 2, $C\underline{H}_2$), 8.20 (s, 3, $CC\underline{H}_3$), 8.87 (s, 6, $C\underline{H}_3$); (Found: C, 74.95; H, 12.57%. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58%). **1b**: IR 2820, 1075 cm^{-1} (ether); NMR (CCl_4) τ 6.90 (s, 6, $OC\underline{H}_3$), 8.37 (s, 2, $C\underline{H}_2$), 8.80 (s, 12, $C\underline{H}_3$); (Found:, C, 67.04; H, 12.70%. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.57%)

1,1,2-Trimethylcyclopropane (**2**) was electrolyzed at the anode potential of 1.6 V *vs.* SCE and yielded 2-methyl-4-methoxy-1-pentene (**2a**) (contaminated with a small amount of unknown products) and 2-methyl-2,4-dimethoxypentane (**2b**) in 10.7 and 9.9% yields respectively. **2b** was spectroscopically identified with the sample which was prepared by the methoxylation of hexylene glycol. **2a**: IR 3080, 1640 cm^{-1} (olefin); NMR (CCl_4) τ 5.30 (broad s, 2, $C\underline{H}_2$=), 6.85 (s, 3, $OC\underline{H}_3$), 6.6—7.0 (m, 1, $C\underline{H}$), 7.8 (d, 2, =C–$C\underline{H}_2$), 8.3 (s, 3, $C\underline{H}_3$), 8.9 (d, 3, $C\underline{H}_3$), mass spectrum parent peak, *m/e* 114. (Found: C, 73.79; H, 12.54. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36%). **2b**: IR 2840, 1090 cm^{-1} (ether); NMR (CCl_4) τ 6.6 (m, 1, $C\underline{H}$), 6.80 (s, 3, $OC\underline{H}_3$), 6.90 (s, 3, $OC\underline{H}_3$), 8.90 (s, 6, $C\underline{H}_3$), 8.95 (d, 3, $C\underline{H}_3$). (Found: C, 65.43; H, 12.68%. Calcd for $C_8H_{18}O_2$: C, 65.74; H, 12.41%).

1,1-Diethylcyclopropane (**3**) yielded 3-ethyl-1,3-dimethoxypentane (**3b**) in a 11.7% yield. **3b**: NMR (CCl_4) τ 6.65 (q, 2, $C\underline{H}_2$), 6.70 (s, 3, $OC\underline{H}_3$), 6.90 (s, 3, $OC\underline{H}_3$), 8.2—8.8 (m, 6, $C\underline{H}_2$), 9.20 (t, 6, $C\underline{H}_3$).

Spiro[*2.5*]*octane* (**4**) was electrolyzed at the anode potential of 2.30 V *vs.* SCE and yielded 1-(1-cyclohexenyl)-2-methoxyethane (**4a**) and 1-(1-methoxycyclohexyl)-2-methoxyethane (**4b**) in 1.1 and 4.8% yields respectively. 1,1-Dimethoxymethylcyclohexane was not detected; **4a**: IR 3050, 1630 (olefin), 2845, 1120 cm^{-1} (ether); NMR (CCl_4) τ 4.63 (broad s, 1, C=$C\underline{H}$), 6.70 (t, 2, $C\underline{H}_2O$), 6.75 (s, 3, $OC\underline{H}_3$), 7.7—8.7 (m, 10, $C\underline{H}_3$). mass spectrum parent peak, *m/e* 140. **4b**: IR 2840, 1115 cm^{-1} (ether); NMR (CCl_4) τ 6.7 (t, 2, $C\underline{H}_2$), 6.75 (s, 3, $OC\underline{H}_3$), 6.95 (s, 3, $OC\underline{H}_3$), 8.0—9.0 (m, 12, $C\underline{H}_2$). (Found: C, 71.58; H, 11.76%. Calcd for $C_{10}H_{20}O_0$: C, 77.09; H, 11.50%).

Spiro[*2.3*]*hexane* (**5**) was electrolyzed at the anode potential of 2.25 V *vs.* SCE and yielded 1-(1-methoxycyclobutyl)-2-methoxyethane (**5b**) in a 25% yield. **5b**: IR 2840, 1120 cm^{-1} (ether); NMR (CCl_4) τ 6.70 (t, 2, $C\underline{H}_2O$), 6.70 (s, 3, $OC\underline{H}_3$), 6.93 (s, 3, $OC\underline{H}_3$), 7.80—8.60 (m, 8, $C\underline{H}_2$), (Found: C, 66.33; H, 11.06%. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18%).

Spiro[*2.2*]*pentane* (**6**) yielded no detectable products.

Acid Catalyzed Methanolysis of Cyclopropane. General: A solution of 0.05 mol of cyclopropane in 0.50 mol of methanol containing 0.01 mol of *p*-toluenesulfonic acid was refluxed for one or two days.

After cooling, the solution was poured into water and extracted with ether. The ethereal layer was shaken with aqueous carbonate and water and dried on magnesium sulfate. After the magnesium sulfate was filtered and the ether was removed, the residue was distilled to give products.

1,1,2,2-Tetramethylcyclopropane (**1**) gave 2,3,3-trimethyl-1-butene (**1c**) and 2,3,3-trimethyl-2-methoxybutane (**1d**) in 6 and 60% yields respectively.

1c was identified spectroscopically by comparison with an authentic sample.(12) **1d**: IR 2840, 1080 cm^{-1} (ether); NMR (CCl_4) τ 6.85 (s, 3, $OC\underline{H}_3$), 8.90 (s, 6, $C\underline{H}_3$), 9.10 (s, 9, $C\underline{H}_3$). (Found: C, 73.98; H, 13.69%. Calcd for $C_8H_{18}O$: C, 73.78; H, 13.92%).

1,1-Diethylcyclopropane (**3**) yielded 3-ethyl-2-pentene (**3c**) and 3-ethyl-3-methoxypentane (**3d**) in 57 and 10% yields respectively. **3c**: IR 3020 cm^{-1} (shoulder, olefin); NMR (CCl_4) τ 4.85 (q, 1, C=$C\underline{H}$), 7.70—8.20 (m, 4, $C\underline{H}_2$), 8.4 (d, 3, $C\underline{H}_3$), 9.0 (double triplet, 6 $C\underline{H}_3$). Compound **3c** was also identified spectroscopically by comparison with an authentic sample.(13) **3d**: NMR (CCl_4) τ 6.97 (s, 3, $OC\underline{H}_3$), 8.40—8.80 (m, 6, $C\underline{H}_2$), 9.25 (t, 9, $C\underline{H}_3$).

Spiro[*2.5*]*octane* (**4**) yielded 1-ethylcyclohexane (**4c**) and 1-ethyl-1-methoxycyclohexane (**4d**) in 42 and 3% yields respectively. **4c**: IR 1630 cm^{-1} (olefin); NMR (CCl_4) τ 4.63 (broad s, 1, =$C\underline{H}$), 7.70—8.60 (m, 10, $C\underline{H}_2$), 9.00 (t, 3, $C\underline{H}_3$). **4c** was also identified spectroscopically by comparison with an authentic sample.(14) **4d**: IR 2840, 1080 cm^{-1} (ether); NMR (CCl_4) τ 6.97 (s, 3, $OC\underline{H}_3$), 8.10—8.80 (m, 12, $C\underline{H}_2$), 9.23 (t, 3, $C\underline{H}_3$); mass spectrum parent peak, *m/e* 142.

Oxidation Potential. The data were obtained at room temperature in dry acetonitril containing 0.1 M tetraethylammonium tetrafluoroborate(15) in a three-electrode polarography system (Yanako P8DP).

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