

Organic Synthesis by Electrolysis. VI. Anodic Oxidation of Arylcyclopropanes

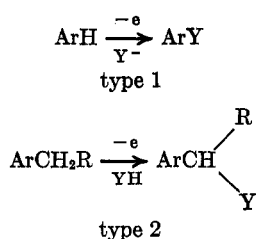
T. SHONO* AND Y. MATSUMURA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

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Cyclopropane ring-opened products were obtained in the anodic oxidation of some arylcyclopropanes in methanol. Controlled potential oxidation and product studies suggested that the reaction was initiated by the oxidation of the aromatic nucleus to a cation radical. Half-wave polarographic oxidation potentials of arylcyclopropanes were measured in acetonitrile and plotted against Hammett's σ^+ . The results indicated that the electron was transferred to the anode not from the cyclopropane ring but from the phenyl ring, and that the cyclopropane ring and the cation radical interacted conjugatedly in the intermediate.

Substitution reactions initiated by anodic oxidation of aromatic substrates may be classified into two categories.¹ The reaction of type 1 is an anodic nuclear substitution reaction and the type 2 reaction is a side chain substitution.



The type 1 reaction has been classified as an ECE mechanism involving anodic oxidation of the aromatic nucleus to a cationic species and subsequent reaction of the intermediate with a nucleophile.² On the other hand, two different mechanisms have been proposed to explain the reaction of type 2. One of them is an ECE process where the aromatic nucleus is oxidized to a cation radical and a proton is ejected from the α position of side chain of the intermediate.³ This reaction is a particular example of the general mechanism 2-1 where R_2 and R_3 are hydrogen. Hydrogen abstraction from the benzylic position of the aromatic substrate by an anodically generated radical and subsequent oxidation of the benzylic radical to a cation are another reaction route suggested for the type 2 reaction (mechanism 2-2).⁴

Some recent electroanalytical studies showed the preference for the mechanism 2-1,^{5,6} but some uncertainties still remain in the mechanism of the reaction of type 2. In the present study, the cyclopropane ring opening of some arylcyclopropanes by anodic oxidation was investigated, and the mechanism of this novel reaction was scrutinized and classified as a new substitution reaction belonging to the mechanism 2-1.

Results

Product Study.—The preparative oxidations of starting compounds **1a-d**, **2b**, **3a**, **4**, and **5** were carried out in methanol at room temperature using a carbon electrode. The supporting electrolyte was tetraethyl-

ammonium *p*-toluenesulfonate and the supplied voltage was 18–40 V. The disubstituted cyclopropanes used in the determination of the polarographic oxidation potential were trans isomers. The results are shown in

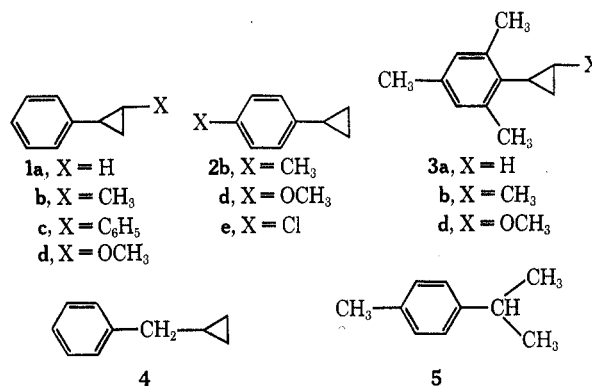


Table I. Since the product obtained from **1b** or **1c** was an equimolar mixture of two stereoisomers, the results indicate that the cyclopropane ring opening and subsequent solvent attack proceeded in nonstereospecific manner.

TABLE I
PRODUCTS AND YIELDS OF PREPARATIVE
OXIDATION OF **1a-d**, **2b**, **3a**, **4**, AND **5**

Starting compd	Product	Charge passed, equiv F ^a	Yield, %
1a	C ₆ H ₅ CH(OCH ₃)CH ₂ CH ₂ OCH ₃	1.2	74 ^b
1b	C ₆ H ₅ CH(OCH ₃)CH ₂ CH(OCH ₃)CH ₃	1.2	71
1c	C ₆ H ₅ CH(OCH ₃)CH ₂ CH(OCH ₃)C ₆ H ₅	1.2	66
1d ^c	C ₆ H ₅ CH(OCH ₃)CH ₂ CH(OCH ₃) ₂	1.9	64
2b	<i>p</i> -CH ₃ C ₆ H ₄ CH(OCH ₃)CH ₂ CH ₂ -OCH ₃	1.2	62
3a	2,4,6-(CH ₃) ₃ C ₆ H ₂ CH(OCH ₃)CH ₂ CH ₂ OCH ₃	1.2	60
4	C ₆ H ₅ CH(OCH ₃)—CH ₂ —Cyclopropane	2.6	25
5	<i>p</i> -CH ₃ OCH ₂ C ₆ H ₄ CH(CH ₃) ₂ <i>p</i> -CH ₃ C ₆ H ₄ C(CH ₃)=CH ₂ <i>p</i> -CH ₃ C ₆ H ₄ C(OCH ₃)(CH ₃) ₂	1.2	14 10 19

^a 1 equiv F = 2 F/mol; current density was 0.08 A/cm². ^b Constant potential oxidation at 1.70 V vs. SCE gave the product in a 96.8% yield. ^c The reaction was carried out at -30 to ~ -40°.

* To whom correspondence should be addressed.

- (1) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).
- (2) R. N. Adams, *Accounts Chem. Res.*, **2**, 175 (1969).
- (3) L. Ebersson, *J. Amer. Chem. Soc.*, **89**, 4669 (1967). Although an initial two-electron oxidation mechanism was also suggested by Ebersson, the ECE mechanism may be more favorable.
- (4) V. D. Parker and B. E. Burgert, *Tetrahedron Lett.*, 2415 (1968).
- (5) V. D. Parker and R. N. Adams, *ibid.*, 1721 (1969).
- (6) A. E. Coleman, H. H. Richtol, and D. A. Aikens, *J. Electroanal. Chem.*, **19**, 165 (1968).

Controlled Potential Oxidation.—The controlled potential oxidation of arylcyclopropanes might be an available method to learn whether the cyclopropyl compound is oxidized prior to the oxidation of solvent or supporting electrolyte. However, the polarographic determination of the oxidation potentials of arylcyclopropanes in methanol using carbon electrode was im-

possible. The oxidation half-wave potential of **1c** in acetonitrile (rotating platinum electrode; supporting electrolyte, LiClO_4) was 1.44 V *vs.* SCE and the initiation of the oxidation was observed at 1.15 V *vs.* SCE. As the analytical anodic limit of methanolic solution of LiClO_4 was reported to be 1.3 V *vs.* SCE,⁷ the compound **1c** was oxidized in methanol at the controlled potential of 1.2 V *vs.* SCE. The oxidation gave the same product shown in Table I in a quantitative current yield. Although the oxidation potential of **1c** in methanol is uncertain, the quantitative current yield may suggest that the reaction was initiated by the oxidation of the cyclopropyl compound.

Oxidation Potentials of Arylcyclopropanes.—The oxidation potentials of some arylcyclopropanes were determined in acetonitrile to establish whether the electron was transferred to the anode from the aromatic nucleus or from the cyclopropane ring, and to discuss the conjugative interaction of the aromatic nucleus and the cyclopropane ring in the intermediate cationic species. The results are shown in Table II.

TABLE II
HALF-WAVE OXIDATION POTENTIALS OF ARYLCYCLOPROPANES
Oxidation potential^a
(*vs.* SCE)

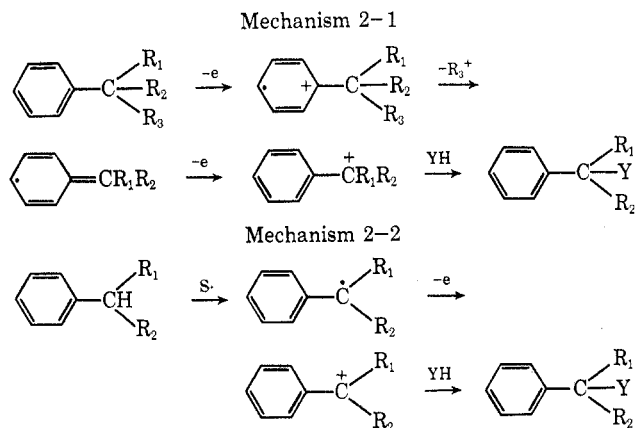
Compd	Oxidation potential ^a (<i>vs.</i> SCE)
1a	1.87
1b	1.71
1d	1.46
2b	1.59
2d	1.35
2e	1.97
3a	1.67
3b	1.61
3d	1.48

^a Supporting electrolyte, 0.5 N LiClO_4 ; anode, rotating platinum electrode.

A good linear relationship was observed in the plot of the half-wave oxidation potential against Hammett's σ^{+8} and the slopes were 0.73 for **2**, 0.53 for **1**, and 0.24 for **3** (Figure 1). These slopes are not the usual Hammett's ρ value since the slopes are given in volt units.⁹

Discussion

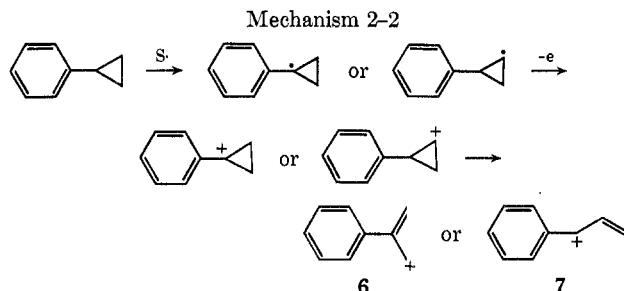
As mentioned before, the following two mechanisms have been proposed for the anodic aromatic side chain substitution reaction (type 2 reaction). The establishment of the mechanism of the type 2 reaction by the



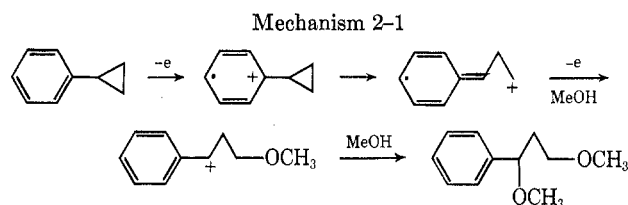
S· = radical generated by anodic oxidation of the supporting electrolyte.

electroanalytical methods or products studies may be difficult. In the anodic oxidation of arylcyclopropanes, however, the above two mechanisms would give different products.

Mechanism 2-2 is expected to give the products derived from the cationic intermediates **6** or **7**. In the

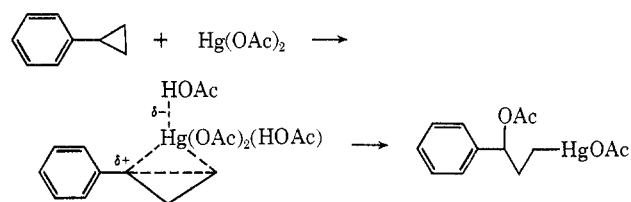


anodic oxidation of arylcyclopropanes, however, the compounds which suggest the formation of the intermediates **6** or **7** were not detected in the products. The results suggested a preference for mechanism 2-1.



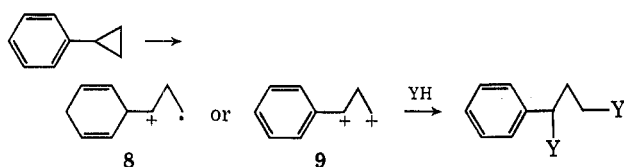
The products obtained by the anodic oxidations of arylcyclopropanes were fully in accordance with the mechanism 2-1. The moderately high yield and current efficiency shown in Table I may be explained by the preferential adsorption of aromatics on the electrode.¹ In the reactions corresponding to the mechanism 2-1, the ejections of R_1^+ , R_2^+ , and R_3^+ are competing reactions, and to a first approximation the most stable cation among them will leave most readily. Especially in the anodic oxidation of arylcyclopropanes, the extreme instability of the cyclopropyl cation resulted in the exclusion of a proton as the leaving cation. Reaction 2-1 is not limited to the oxidation of arylcyclopropanes but the reaction was observed in many compounds which will be reported in another paper. Recently, the oxidation of arylcyclopropanes by metallic acetate yielding the products in which the cyclopropane ring is opened has been reported and the mechanism of this oxidation reaction has been explained by the electrophilic attack of the molecule of metallic acetate on the cyclopropane ring.¹⁰

In the oxidation by mercuric acetate, the electron transfer from cyclopropane ring rather than from the phenyl ring has been considered.

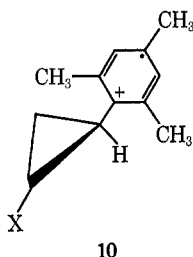


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 (8) (a) R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963);
 (b) E. N. Trachtenberg and G. Odian, *J. Amer. Chem. Soc.*, **80**, 4018 (1958).
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In the anodic oxidation of arylcyclopropanes, the formation of the cationic species **8** or **9** by the electron transfer from the cyclopropane ring might be another possible route.



This possibility could not be checked in methanol since the oxidation potentials of arylcyclopropanes in methanol were unmeasurable. Thus, the oxidation potentials of arylcyclopropanes in acetonitrile were measured to study whether the electron was transferred to the anode from the aromatic nucleus or from the cyclopropane ring, and were plotted against Hammett's σ^+ constant (Table II, Figure 1). Figure 1 clearly indicated that the slopes were $2 > 1 > 3$. In the case of electron transfer from aromatic nucleus, the intermediate cationic species is a kind of cyclopropylcarbinyl cation stabilized by the delocalization of positive charge into cyclopropane ring. In the oxidation of the compounds **3**, however, the stabilization of the intermediate cationic species by the delocalization of positive charge is expected to be substantially diminished, since the steric interaction of two *o*-methyl groups obstructs the bisect conformation, **10**,¹¹ in which the positive charge of the intermediate is most favorably delocalized into the cyclopropane ring.



Consequently, the order of slopes is expected to be $2 > 1 > 3$ and this order was completely in accordance with the experimental results. On the other hand, in the mechanism where the electron is transferred to the anode from the cyclopropane ring, the substituent effects in **1** and **3** would be of the same order and that in **2** would be smaller than those in **1** and **3**. This does not agree with the results indicated in Figure 1. Thus, it was concluded that in acetonitrile the electron was transferred to the anode not from the cyclopropane ring but from the aromatic nucleus, and this conclusion may be correct for the oxidation in methanol. The conjugate interaction of the cyclopropane ring and the adjacent carbonium ion has been observed in solvolytic studies, and the present study confirms the existence of the same conjugate interaction by the polarographic technique.

The fact that, in the anodic oxidation of **4**, the substitution reaction at the benzylic position was observed exclusively and the cyclopropane ring opened product was not detected may also disprove the electron transfer

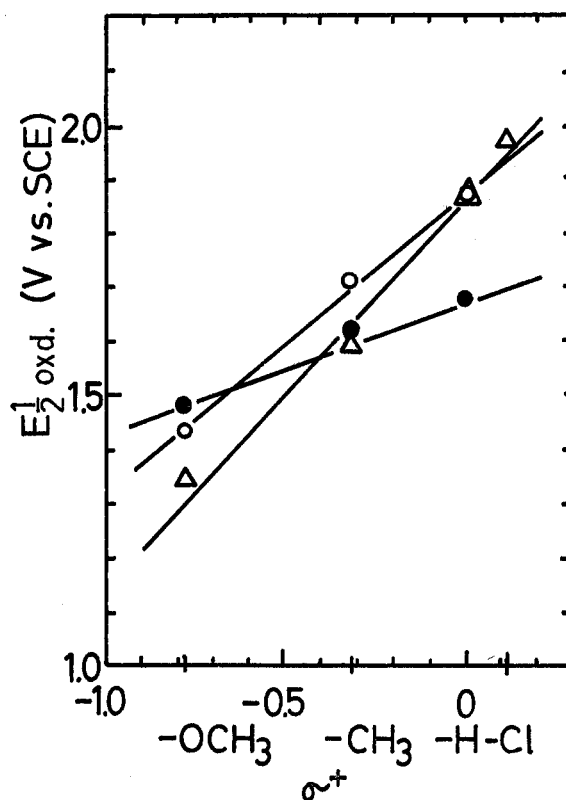
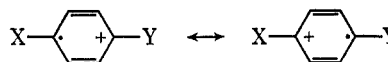


Figure 1.—Plot of Hammett's σ^+ vs. half-wave oxidation potentials of arylcyclopropanes: O, 1-substituted 2-phenylcyclopropane (**1**); Δ , para-substituted phenylcyclopropane (**2**); \bullet , 1-substituted 2-(2,4,6-trimethylphenyl)cyclopropane (**3**).

from the cyclopropane ring. The following two resonance structures could be supposed for the cation radical generated by the anodic oxidation of the para-disubstituted aromatic nucleus.



Relative contributions of these two resonance structures to the character of the cation radical may depend on the cation and radical stabilization abilities of the substituents X and Y. For example, in the oxidation of *p*-cymene the ratio between attack on the methyl group and that on the isopropyl group is 1:2. On the other hand, in the oxidations of **2b** and especially in **3a** the cyclopropane ring was attacked exclusively, suggesting the large cation stabilization ability of the cyclopropane ring.

Experimental Section

Phenylcyclopropane (**1a**),¹² *trans*-1-Methyl-2-phenylcyclopropane (**1b**),¹³ *trans*-1,2-Diphenylcyclopropane (**1c**),¹⁴ *p*-Methylphenylcyclopropane (**2b**),¹⁰ *p*-Methoxyphenylcyclopropane (**2d**),¹⁰ *p*-Chlorophenylcyclopropane (**2e**),¹⁰ and Benzylcyclopropane (**4**).¹⁵—The title compounds were prepared by the reported methods. Compounds **1b**–**c** were purified by preparative gas chromatography.

trans-1-Methoxy-2-phenylcyclopropane (**1d**).¹⁶—Under an atmosphere of nitrogen, a freshly prepared ethereal solution of

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(14) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

(15) W. J. Close, *J. Amer. Chem. Soc.*, **79**, 1455 (1957).

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methylolithium (methyl iodide, 30 g; lithium, 3.6 g; dry ether, 100 ml) was added with stirring to a solution of 11.5 g (0.1 mol) of dichloromethyl methyl ether in 200 ml of styrene at 10 to $\sim 25^\circ$. After the stirring was continued for an additional hour, the reaction mixture was poured into water and extracted with ether. The ethereal extract was washed twice with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_4$ and water and dried. The ether was removed under reduced pressure and the residue was distilled *in vacuo* to give 1d in a 23% yield, bp 97.5° (18 mm). This product was a mixture of trans (37%) and cis (63%) isomers. The trans isomer was isolated by preparative gas chromatography (column Apz L): nmr (CCl_4) τ 2.90 (s, 5, C_6H_5), 6.75 (s, 3, OCH_3), 6.60–7.00 (m, 1), 7.85–8.40 (m, 1), 8.70–9.20 (m, 2). *Anal.* Calcd for $\text{C}_{10}\text{H}_{12}\text{O}$: C, 81.04; H, 8.16. Found: C, 81.28; H, 8.34.

2,4,6-Trimethylphenylcyclopropane (3a).—2,4,6-Trimethylstyrene [bp 103° (18 mm)] was prepared by the dehydration of 2,4,6-trimethylphenyl methyl carbinol. To a mixture of 33 g (0.3 mol) of potassium *tert*-butoxide and 62 g (0.47 mol) of 2,4,6-trimethylstyrene in 100 ml of dry benzene was added dropwise 72 g (0.28 mol) of bromoform at 0 to $\sim -5^\circ$. After the reaction mixture was stirred for an additional 3 hr at 0 to $\sim -5^\circ$, it was allowed to stand at room temperature over night. Water was added to the reaction mixture, and it was neutralized with dilute HCl and extracted with ether. The ethereal extract was dried and distilled *in vacuo* to yield 16.6 g (18.6%) of 1,1-dibromo-2-(2,4,6-trimethylphenyl)cyclopropane, bp $121\text{--}123^\circ$ (2 mm). To a solution of 16.6 g (0.07 mol) of this dibromide in 70 ml of ether was added 23 g (1 g-atom) of metallic sodium in roughly 2-cm³ pieces during the course of the reaction. At the same time, wet methanol (4 ml of water and 100 ml of methanol) was added dropwise with rapid stirring. After the reaction was completed, 300 ml of water was added and the ethereal layer was separated, dried, and distilled to give 4.82 g (57.5%) of 3a: bp $110\text{--}115^\circ$ (15 mm); nmr (CCl_4) τ 3.37 (s, 2, C_6H_2), 7.68 (s, 6, ortho CH_3), 7.83 (s, 3, para CH_3), 8.22–8.70 (m, 1), 8.90–9.70 (m, 4). *Anal.* Calcd for $\text{C}_{12}\text{H}_{16}$: C, 89.94; H, 10.06. Found: C, 90.13; H, 10.23.

trans-1-Methyl-2-(2,4,6-trimethylphenyl)cyclopropane (3b) was prepared from *trans*-1-(2,4,6-trimethylphenyl)propene-1 by the method similar to that used in the synthesis of 3a. The starting olefin [bp 154° (93 mm)] was obtained by the dehydration of the corresponding alcohol. *trans*-1,1-Dibromo-2-methyl-3-(2,4,6-trimethylphenyl)cyclopropane was prepared from the olefin in a 12.5% yield, bp 139° (4 mm). The reduction of the dibromide gave 3b in a 61% yield: bp $132\text{--}134^\circ$ (23 mm); nmr (CCl_4) τ 3.36 (s, 2, C_6H_2), 7.70 (s, 6, ortho CH_3), 7.81 (s, 3, para CH_3), 8.75 (d, 3, CHCH_3), 8.5–9.5 (m, 4). *Anal.* Calcd for $\text{C}_{13}\text{H}_{18}$: C, 89.59; H, 10.41. Found: C, 89.32; H, 10.36.

trans-1-Methoxy-2-(2,4,6-trimethylphenyl)cyclopropane (3d) was obtained from 2,4,6-trimethylstyrene by a method similar to that used in the preparation of 1d, bp 145° (21 mm), yield 38.2%. The trans isomer was separated from the product (trans 20%, cis 80%) by gas chromatography (column Apz L): nmr (CCl_4) τ 3.38 (s, 2, C_6H_2), 6.75 (s, 3, OCH_3), 6.50–7.05 (m, 1, CHOCH_3), 7.72 (s, 6, ortho CH_3), 7.84 (s, 3, para CH_3), 8.20–8.60 (m, 1), 8.76–9.70 (m, 2). *Anal.* Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.54. Found: C, 82.05; H, 9.76.

Preparative Anodic Oxidation of Arylcyclopropanes. General.—Into a 100-ml three-necked flask equipped with a reflux condenser, magnetic stirrer, and two carbon electrodes was added a solution of 0.02 mol of arylcyclopropane and 0.01 mol of tetraethylammonium *p*-toluenesulfonate in 0.50 mol of methanol. The supplied terminal voltage was about 18 V. The electrolysis was carried out under constant current conditions until the quantity of electricity indicated in Table I were passed. The reaction mixture was poured into water, extracted with ether, dried on MgSO_4 , filtered, and concentrated successively. The residue was distilled *in vacuo* to give the oxidized products.

Phenylcyclopropane (1a) gave 1-phenyl-1,3-dimethoxypropane in 74% yield: bp $110\text{--}112^\circ$ (30 mm); nmr (CCl_4) τ 2.80 (s, 5, C_6H_5), 5.81 (q, 1, CHOCH_3), 6.35–7.10 (m, 2, CH_2O), 6.75 (s, 3, OCH_3), 6.85 (s, 3, OCH_3), 7.90–8.50 (m, 2, CH_2). *Anal.* Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.95. Found: C, 73.10; H, 9.11.

trans-1-Methyl-2-phenylcyclopropane (1b) yielded 1-phenyl-1,3-dimethoxy-*n*-butane (71%), bp $120\text{--}121^\circ$ (27 mm). The gas chromatographic analysis indicated that this product was an equimolar mixture of two isomers. The isomers were separated by gas chromatography. The elemental analysis and mass spectra of the two isomers gave the same results. *Anal.* Calcd

for $\text{C}_{12}\text{H}_{18}\text{O}_2$: C, 74.19; H, 9.34. Found: C, 74.38; H, 9.39; mol wt (mass spectrum), 194. The nmr spectra indicated that the isomers were geometrical isomers: nmr (CCl_4) one isomer, τ 2.84 (s, 5, C_6H_5), 5.79 (t, 1, CHOCH_3), 6.30–6.70 (m, 1, CHOCH_3), 6.72 (s, 3, OCH_3), 6.86 (s, 3, OCH_3), 8.40 (t, 2, CH_2), 8.93 (d, 3, CH_3); another isomer, τ 2.82 (s, 5, C_6H_5), 5.82 (t, 1, CHOCH_3), 6.60–7.15 (m, 1, CHOCH_3), 6.84 (s, 3, OCH_3), 6.90 (s, 3, OCH_3), 7.70–8.75 (m, 2, CH_2), 8.93 (d, 3, CH_3).

trans-1,2-Diphenylcyclopropane (1c) gave two isomers (50:50) of 1,3-diphenyl-1,3-dimethoxypropane in the total yield of 66%, bp $140\text{--}145^\circ$ (5 mm). The isomers were identified by the same method as those used in the oxidation of 1b: nmr (CCl_4) one isomer, τ 2.82 (s, 10, C_6H_5), 6.06 (t, 2, CHOCH_3), 6.95 (s, 6, OCH_3), 7.40–8.45 (m, 2, CH_2); another isomer, τ 2.82 (s, 10, C_6H_5), 5.10 (t, 2, CHOCH_3), 6.78 (s, 6, OCH_3), 8.18 (q, 2, CH_2). *Anal.* Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$: C, 79.65; H, 7.86. Found: C, 79.61; H, 7.73.

1-Methoxy-2-phenylcyclopropane (1d) yielded 1-phenyl-1,3,3-trimethoxypropane (64%): bp $126\text{--}128^\circ$ (25 mm); nmr (CCl_4) τ 2.75 (s, 5, C_6H_5), 5.60 (q, 1, $\text{CH}_2\text{OCHOCH}_3$), 5.85 (q, 1, CHOCH_3), 6.75 (s, 3, OCH_3), 6.80 (s, 3, OCH_3), 6.90 (s, 3, OCH_3), 7.95–8.30 (m, 2, CH_2). *Anal.* Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$: C, 68.54; H, 8.63. Found: C, 68.78; H, 8.55.

***p*-Methylphenylcyclopropane (2b)** gave 1-(*p*-methylphenyl)-1,3-dimethoxypropane in 62% yield: bp $120\text{--}124^\circ$ (25 mm); nmr τ 2.95 (s, 4, C_6H_4), 5.40–6.00 (m, 1, CHOCH_3), 6.30–6.80 (m, 2, CH_2OCH_3), 6.77 (s, 3, OCH_3), 6.90 (s, 3, OCH_3), 7.69 (s, 3, CH_3), 7.80–8.50 (m, 2, CH_2).

2,4,6-Trimethylcyclopropane (3a) yielded 1-(2,4,6-trimethylphenyl)-1,3-dimethoxypropane (60%): bp $135\text{--}142^\circ$ (20 mm); nmr (CCl_4) τ 3.35 (s, 2, C_6H_2), 5.30 (q, 1, CHOCH_3), 6.30–6.80 (m, 2, CH_2OCH_3), 6.76 (s, 3, OCH_3), 6.91 (s, 3, OCH_3), 7.70 (s, 6, ortho CH_3), 7.81 (s, 3, para CH_3), 7.90–8.40 (m, 2, CH_2). *Anal.* Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$: C, 75.63; H, 9.97. Found: C, 75.77; H, 10.14.

Benzylcyclopropane (4) gave α -methoxybenzylcyclopropane in a 24.8% yield: bp $106\text{--}115^\circ$ (33 mm); nmr (CCl_4) τ 2.75 (s, 5, C_6H_5), 6.40 (d, 1, CHOCH_3), 6.85 (s, 3, OCH_3), 8.75–9.20 (m, 1), 9.35–9.90 (m, 4). *Anal.* Calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.44; H, 8.70. Found: C, 81.41; H, 8.97.

***p*-Cymene (5)** yielded three products. Each product was isolated by gas chromatography and identified by the comparison of its gas chromatographic retention time and nmr spectrum with those of an authentic sample. The products were *p*-isopropenyltoluene (10%), 2-(*p*-tolyl)-2-methoxypropane (19%), and *p*-methoxymethylcumene (14%).

Constant Potential Oxidation of trans-1,2-Diphenylcyclopropane (1c).—A solution of 1.94 g (0.01 mol) of 1c and 2.98 g (0.028 mol) of LiClO_4 in 32 g (1.0 mol) of methanol was oxidized at the constant potential of 1.2 V vs. SCE using a ceramic diaphragm. 1,3-Diphenyl-1,3-dimethoxypropane was obtained in a quantitative current yield.

Polarographic Oxidation Potential.—The data were obtained at room temperature on a Yanagimoto PA-102 polarograph. The oxidations in anhydrous acetonitrile were carried out at a rotating platinum electrode with 0.5 N LiClO_4 as a supporting electrolyte.

Registry No.—1a, 873-49-4; 1b, 5070-01-9; 1c, 1138-47-2; 1d, 26269-57-8; 2b, 6921-43-3; 3a, 26269-59-0; 3b, 26269-60-3; 3d, 26269-61-4; 4, 1667-00-1; 5, 99-87-6; 1-phenyl-1,3-dimethoxypropane, 26278-67-1; 1-phenyl-1,3-dimethoxy-*n*-butane, 26278-68-2; 1,3-diphenyl-1,3-dimethoxypropane, 26278-69-3; 1-phenyl-1,3,3-trimethoxypropane, 26278-70-6; 1-(*p*-methylphenyl)-1,3-dimethoxypropane, 26278-71-7; 1-(2,4,6-trimethylphenyl)-1,3-dimethoxypropane, 26278-72-8; α -methoxybenzylcyclopropane, 5558-08-7.

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