General Procedure for the Preparation of 2-Amino-α-arylcinnamic Acids.—*o*-Nitrobenzaldehyde, arylacetic acid, acetic anhydride, and triethylamine were refluxed and cooled, and water was added.[14] The nitro compounds were reduced with H_2S and ammonia. Melting points and mass spectra verified the crystallized compounds.

General Procedure for the Electrolytic Reduction.—The apparatus has been described previously.[7] Tetrabutylammonium perchlorate, the electrolytic support,[7] was dissolved in acetonitrile to make a 0.1 *M* solution. This solution was used for both cathode and anode compartments. The diazonium salt was dissolved in the degassed and cooled solution in the cathode compartment to make 0.01 *M*. The reaction was run at 0 V *vs.* sce under purified nitrogen. A run was considered complete when the current dropped to less than 1 mA and the test for diazonium salt was negative. After completion, each reaction mixture was taken to dryness under vacuum at room temperature. The solid was extracted with ether (four times). The ether solution was dried and evaporated, the residue was dissolved in ammonium hydroxide solution (10%), precipitated with dilute hydrochloric acid, and filtered, and the precipitate was washed with water several times and dried by suction. Dissolving, precipitating, washing, and drying were repeated three times to remove tetrabutylammonium perchlorate. The vacuum-dried products were identified by melting points and infrared. Mass spectral analysis, in each case, gave the proper parent peak and fragmentations for the cyclized products only. The phenanthrene-10-carboxylic acid and its derivatives (R's) were crystallized from glacial acetic acid with a loss of *ca.* 5%; the melting points reported are uncorrected: phenanthrene-10-carboxylic acid, mp 256–257° (lit.[15] 250–252°); R, 3-CH_3, mp 238–240° (lit.[16] 238–239°), R, 1-OCH_3, mp 218–220° (lit.[17] 215°); R, 2-OCH_3, mp 238° (lit.[18] 236.7°); R, 3-OCH_3, mp 240–241° (lit.[17] 239°); R, 3-Br, mp 285° (lit.[19] 290–291°); R, 1-Br, mp 296–297° (lit.[20] 295°).

Using Tetrapropylammonium Iodide for Reduction.—The diazonium salt was dissolved in dry, degassed acetonitrile at 0°. The solid iodide salt was added gradually with vigorous stirring under nitrogen. After 10 min sodium thiosulfate solution (2 g of $Na_2S_2O_3$/25 ml of water) was added and a precipitate formed. The precipitate was filtered, washed with water, and dried under vacuum to give pure phenanthrene-10-carboxylic acid (85%). The filtrate was concentrated, and ammonium hydroxide solution was added (10%) and filtered. The filtrate was acidified to give a precipitate which, after washing and drying, was identified as 2-iodo-α-phenylcinnamic acid (*ca.* 10%), mp 175–177° from ethyl acetate (lit.[21] 179–180°).

Using Tetrapropylammonium Bromide for Reduction.—Two sets of reactions were performed, one over a mercury pool and the other without mercury. The technique described for the iodide reaction was followed with no attempt to separate the 2-bromo-substituted products. At 0° the mercury reaction gave 82% phenanthrene-10-carboxylic acid in *ca.* 2.5 hr. The reaction without mercury was allowed to warm to room temperature overnight and gave 78% of cyclized product in *ca.* 22 hr. In both cases free bromine was produced.

Acid Reaction.—The diazonium salt was suspended in fluoroboric acid (10%) at room temperature with fast stirring. The temperature was raised gradually over 1 hr to 70° and kept at 70° for 10 min, at which time the test for the diazonium ion was negative. The reaction mixture was cooled and filtered. The solid was washed several times with water and then dried under vacuum. Fractional crystallization from glacial acetic acid gave the cyclized product (62%), 2-fluoro-α-phenylcinnamic acid (10%), mp 179° (lit.[22] 178°), 2-hydroxy-α-phenylcinnamic acid (3%), mp 198° (lit. 202–204°),[23] and 3-phenylcoumarin (~9%), mp 138.9°.

Acid and Copper Reaction.—The dry diazonium salt was added to a stirred suspension of copper in fluoroboric acid (10%). The reaction commenced at room temperature and the mixture was warmed to 70°. The cyclized products were isolated by the method described for the acid reaction.

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(14) D. F. DeTar and Yun. Wen Chu, *J. Amer. Chem. Soc.*, **76**, 1686 (1954).

(15) R. Pschorr, H. Tappan, R. Hofmann, F. Quade, M. Schütz, and J. Popovici, *Ber.*, **39**, 3106 (1906).

(16) R. Pschorr, *ibid.*, **39**, 3112 (1906).

(17) R. Pschorr, O. Wolfes, and W. Buckow, *ibid.*, **33**, 162 (1900).

(18) C. K. Bradsher, F. C. Brown, and P. H. Leake, *J. Amer. Chem. Soc.*, **79**, 1471 (1957).

(19) R. Pschorr, *Ber.*, **39**, 3118 (1906).

(20) R. Pschorr, *Justus Liebigs Ann. Chem.*, **391**, 48 (1912).

(21) S. M. Kupchan and H. W. Wormser, *J. Org. Chem.*, **30**, 3792 (1965).

(22) K. Bowden and D. C. Parkin, *Can. J. Chem.*, **46**, 3909 (1968).

(23) N. R. Krishnaswamy, T. R. Seshadri, and B. R. Sharma, *Indian J. Chem.*, **2**, 182 (1964).

Electroorganic Chemistry. VII. Anodic Oxidation of Cyclopropanes

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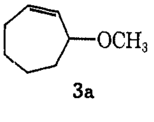
Received December 4, 1970

The electrochemical oxidation of bicyclo[4.1.0]heptane (1) and bicyclo[3.1.0]hexane (2) gave products in which the cyclopropane ring was opened. The structures or distributions of the products were completely different from those observed in the acidic solvolyses, metallic oxidations, and radical reactions of 1 and 2. It thus appeared that this electrochemical reaction was initiated by the direct oxidation of the carbon-carbon single bond of the cyclopropane ring. The bond cleavage was observed exclusively on the internal bond.

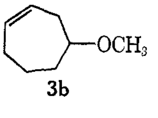
Synthetic reactions initiated by the anodic oxidation of the aromatic nucleus or aliphatic multiple bonds have been studied extensively,[1] while the electrochemical oxidations have never been studied on cyclopropanes in which the characters of the cyclopropane ring are considered to be similar, to a certain extent, to those of the olefinic bond. It was found in our laboratory that in the anodic oxidation of some arylcyclopropanes the aromatic nucleus rather than the cyclopropane ring was oxidized at the anode.[2] In the present study, we wish to report the first evidences that the carbon–carbon single bond in a cyclopropane ring could be anodically oxidized to yield ring-opened products which may be difficultly synthesized by the other methods.

Results

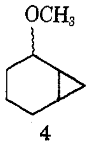
Bicyclo[4.1.0]heptane (1) and bicyclo[3.1.0]hexane (2) were selected as the starting cyclopropyl compounds. In the preparative experiment, the methanolic solution of **1** was oxidized at room temperature using tetraethylammonium *p*-toluenesulfonate as a supporting electrolyte. A carbon rod was used as the electrode and 2 *F*/mol of electricity was passed. The analysis of the reaction products indicated the formation of compounds **3a**, **3b**, **4**, **5a**, **5b**, **6** and a small amount



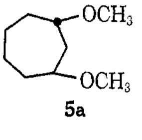
3a



3b



4



5a

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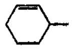
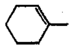
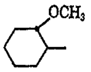
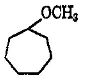
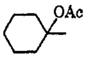
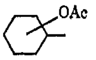
(1) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).

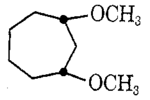
(2) T. Shono and Y. Matsumura, *J. Org. Chem.*, **35**, 4157 (1970).

TABLE I

DISTRIBUTION OF PRODUCTS YIELDED IN THE ACIDIC SOLVOLYSIS OF 1

	Products, %							
Condition								Selectivity in bond cleavage, external/internal
Methanolysis, TsOH, 24 hr, reflux	26.6	10	4.6	50.6	8.2			87.2/12.8
Acetolysis,[a] TsOH, 24 hr, 47°	39.9	12.0	5.1	32.6	6.0	3.4	1.0	88.9/11.1
Acetolysis,[a] H_2SO_4, 41 hr, 46.5°	1.0	0.5	1.6	64.0	19.2	1.7	12.0	79.2/20.8

[a] Products are the corresponding acetate; see ref 8.



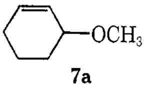
5b

$CH_2{=}CHCH_2CH_2CH_2CH_2CH(OCH_3)_2$

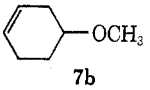
6

of unidentified product. Compounds **3a,b**, **4**, and **5a,b** were identified by the comparisons of their nmr spectra and gas chromatographic retention times with those of authentic samples synthesized independently.[3] Compound **6** was identified by its nmr spectrum and elemental analysis.

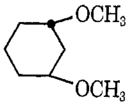
The oxidation of **2** in methanol gave compounds **7a**, **7b**, **8a**, **8b**, **9**, and a small amount of unidentified product.



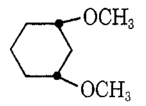
7a



7b



8a



8b

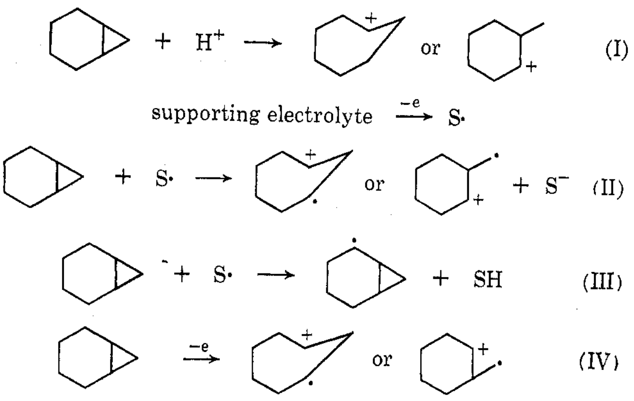
$CH_2{=}CHCH_2CH_2CH_2CH(OCH_3)_2$

9

The identification of the products were accomplished by the same methods as those used for compounds **3**, **4**, and **5**. The nmr data and elemental analysis of compound **9** supported the assigned structure. The compound corresponding to **4** was not detected in the oxidation products of **2**. All of the compounds **3**–**9** were the primary reaction products.

Possible Reaction Routes.—Although the products clearly indicated that the cyclopropane ring was opened under the anodic oxidation condition, it requires further evidences to establish that the reaction was initiated by the anodic oxidation of a carbon–carbon single bond in the cyclopropane ring.

The following four possible processes could be imagined for the initiation step. Process I, the attack of the proton which may be generated at the anode; process II, the oxidation of the cyclopropane ring by a certain oxidizing agent formed by the anodic oxidation of the supporting electrolyte or solvent; process III, the abstraction of a hydrogen from the substrate (**1** or **2**) by some radical species generated by the anodic oxidation; process IV, the electron transfer to the anode from a carbon–carbon single bond of the cyclopropane ring (direct anodic oxidation).



Methanolyses of 1 and 2.—Thus, the solvolytic reaction of **1** or **2** in methanol under acidic condition (catalyst, *p*-toluenesulfonic acid) was studied, and the results are indicated in Tables I and II along with some other reported data. The results indicated that the products obtained from the acidic solvolysis of **1** or **2** were completely different from those obtained in the anodic oxidation reaction.

Oxidations of 1 and 2 by Some Metal Acetates.—The reactions of **1** and **2** with some oxidizing agents such as lead tetraacetate or thallium triacetate have been studied by Ouellette and his collaborators.[4] The reported results are cited in Tables III and IV. Some of the products and their distributions were considerably different from the results observed in the anodic oxidation. Although a radical species generated from the supporting electrolyte or solvent by the anodic oxidation might behave as an oxidizing agent,[5] the oxidation of **1** or **2** by such an oxidizing agent would give considerably different products from those yielded in the present anodic oxidation. Furthermore, process II may be less probable since the oxidizing agent generated at a lower anode potential than that required for the direct oxidation of **1** or **2** must be incapable of oxidizing **1** or **2** and at the anode potential sufficiently anodic for the direct oxidation of **1** or **2**, process IV must become main reaction pathway.

Radical Reaction of 1.—It has been suggested in the anodic oxidation that a radical species yielded from the supporting electrolyte or solvent abstracts a hydrogen from substrates and the substrate radicals are anodically

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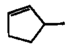
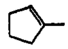
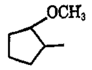
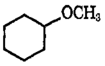
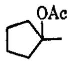
[3] Compound **3a**, A. C. Cope, T. A. Liss, and G. W. Wood, *J. Amer. Chem. Soc.*, **79**, 6287 (1957); **3b**, A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4843 (1962); **4**, W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967); **5a,b**, A. C. Cope, J. K. Heeren, and V. Seeman, *ibid.*, **28**, 516 (1963).

[4] R. J. Ouellette, A. South, Jr., and D. L. Shaw, *J. Amer. Chem. Soc.*, **87**, 2602 (1965).

[5] J. W. Britenbach and C. Srna, *Pure Appl. Chem.*, **4**, 245 (1962).

TABLE II

DISTRIBUTION OF PRODUCTS YIELDED IN THE ACIDIC SOLVOLYSIS OF 2

Condition	Products, %						Selectivity in bond cleavage, external/internal
							
Methanolysis, TsOH, 26 hr, reflux	26.7	22.1	3.1	39.1	9.0		87.9/12.1
Acetolysis,[a] TsOH, 41 hr, 48°	3.1	10.1	8.8	53.0[b] 5.1[c]	17.2	2.3	74.0/26.0

[a] Products are the corresponding acetate; see ref 8. [b] Trans isomer. [c] Cis isomer.

TABLE III

DISTRIBUTION[a] OF PRODUCTS YIELDED BY THE OXIDATION OF 1

	3a	3b	4	5a	5b	10	6	Selectivity in bond cleavage, external/internal
Anodic oxidation, Et$_4$NOTs[b]	48.3		8.1	10.4	13.0	0	20.2	0/100
Anodic oxidation, NaOMe[b]	23.4		35.2	10.2	11.0	0	20.2	0/100
Anodic oxidation at 1.3 V *vs.* sce, NaOMe[b]	0		100	0	0	0	0	
Kharasch reaction	Trace		*ca.* 100	0	0	0	0	
Pb(OAc)$_4$[c]	8.9	11.5	0	7.5	0	69.2	0	71/29
Tl(OAc)$_3$[c]	Trace	3.0	0	6.0	0	91.0	0	91/9

[a] The unidentified product was not included in the calculation of distribution. [b] Supporting electrolyte. [c] Products were the corresponding acetates; see ref 3.

TABLE IV

DISTRIBUTION[a] OF PRODUCTS YIELDED BY THE OXIDATION OF 2

	7a	7b	8a	8b	11	9	Selectivity in bond cleavage, external/internal
Anodic oxidation, Et$_4$NOTs[b]	23.1	24.0	15.2	19.5	0	18.2	0/100
Pb(OAc)$_4$[c]	24.0	27.0	Trace	24.5	24.5	0	24.5/75.5
Tl(OAc)$_3$[c]	19.6	24.9	3.4	5.6	46.5	0	46.5/53.5

[a] The unidentified product was not included in the calculation of distribution. [b] Supporting electrolyte. [c] Products were the corresponding acetates; see ref 3.

oxidized to cationic species.[6] This reaction process is mechanistically similar to the Kharasch reaction.[7] Thus, the behavior of **1** in the Kharasch reaction was studied and **4** was obtained as the exclusive product (Table III). Moreover, the controlled potential oxidation of **1** in methanol at 1.3 V *vs.* sce using sodium methoxide as a supporting electrolyte gave **4** exclusively (Table III). At the anode potential of 1.3 V *vs.* sce, the oxidation of the methoxide anion to the methoxy radical would be the only possible anodic process. It thus appeared that **4** was the product of the radical reaction initiated by process III, while **3a**,**b**, **5a**,**b**, and **6** were yielded by the other reaction pathway.

Reaction Route.—In the preparative anodic oxidation of **1**, the substitution of the supporting electrolyte of tetraethylammonium *p*-toluenesulfonate by sodium methoxide resulted in the increase in the formation of **4** (Table III). The oxidation potential of the former electrolyte is sufficiently higher than that of the latter. Thus, it would be concluded that the direct anodic oxidation of **1**, that is, the electron transfer to the anode from a carbon–carbon single bond of the cyclopropane ring of **1** (process IV), was the initiation process leading to the formation of **3a**,**b**, **5a**,**b**, and **6**. The reaction route of the anodic oxidation of **2** is similar to that of **1**. The reaction pathways are shown in Scheme I.

The remarkable characteristic of the anodic cyclopropane ring opening of **1** or **2** consisted of the high selectivity of the bond cleavage. The cyclopropane ring opening of **1** or **2** by the protonation, or **1** by the attack of an oxidizing agent, was observed almost at the external bond (Tables I–III). Furthermore, similar exclusive external bond cleavages were observed in the acidic solvolyses of *cis*- and *trans*-bicyclo[6.1.0]-nonane and *cis*-bicyclo[5.1.0]octane.[8] The internal

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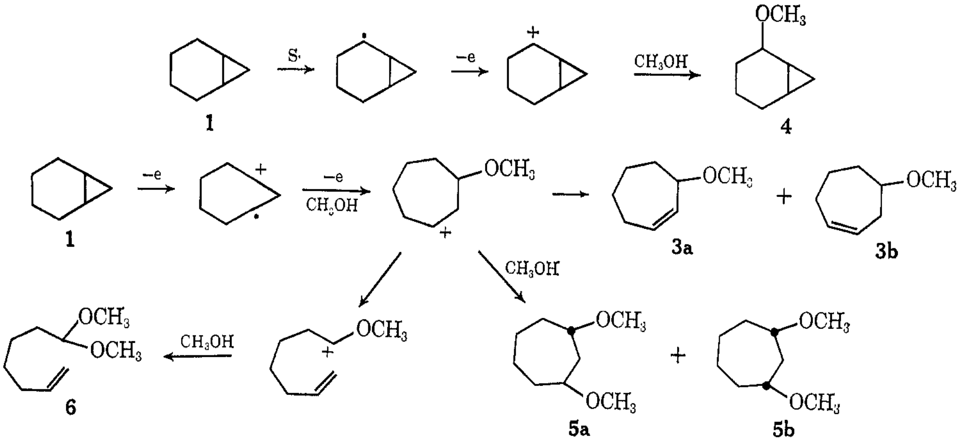
[6] T. Shono and T. Kosaka, *Tetrahedron Lett.*, 6207 (1968).

[7] C. Walling and A. A. Zavitsas, *J. Amer. Chem. Soc.*, **85**, 2084 (1963).

[8] K. B. Wiberg and A. deMeijere, *Tetrahedron Lett.*, 519 (1969).

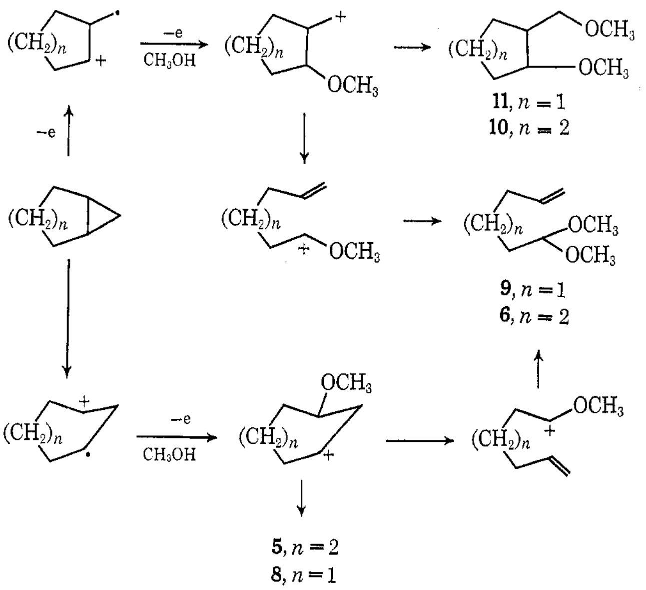
SCHEME I

supporting electrolyte or solvent $\xrightarrow{-e}$ S·



bond cleavages took place in the acidic solvolysis of highly strained compounds such as bicyclo[2.1.0]pentane[9] and *trans*-bicyclo[5.1.0]octane.[8] On the other hand, the anodic oxidation of **1** or **2** gave the products in which the bond cleaved was completely internal. Although the formation of **6** or **9** was explained by both external and internal routes, the lack of **10** or **11**[10] in the products make the external route less probable (Scheme II). The stereochemistry of the cleavage of the cyclopropane rings with electrophilic reagents is an attractive subject.[11,12] The nonstereoselective formation of compounds **5** and **8** in this anodic reaction suggests the carbonium ion character of the intermediate. The anodic oxidations of other polycyclic cyclopropyl systems and study on the reaction mechanism are in progress.

SCHEME II



Experimental Section

Anodic Oxidation of Bicyclo[4.1.0]heptane (1). Supporting Electrolyte, Tetraethylammonium *p*-Toluenesulfonate.—In a 100-ml cylindrical cell, equipped with a reflux condenser and two carbon-rod electrodes (diameter, 0.8 cm) was placed a solution of 2.40 g (0.025 mol) of **1** and 0.75 g (0.0025 mol) of tetraethylammonium *p*-toluenesulfonate in 20 ml of methanol. The solution was stirred magnetically and electrolyzed at room temperature under the condition of constant current of 0.25 A until 2 *F*/mol of electricity was passed. The reaction mixture was poured into an excess of water and extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate and distilled to remove ether. The residue was evaporated under reduced pressure and the distillate was trapped by a Dry Ice condenser. The gas chromatographic analysis (column, silicone DC 550) of the crude distillate [bp 70–96° (26 mm)] indicated that at least five compounds were contained in the products. Each compound was isolated by a preparative gas chromatograph (column, silicone DC 550), the total yield being 85.9%. Compounds **3a,b**, **4**, and **5a,b** were identified by the comparisons of their nmr spectra and gas chromatographic retention times (column, silicone DC 550, PEG 20M) with those of authentic samples synthesized independently.[3] Compound **6** was identified by its nmr spectrum and elemental analysis: nmr (CCl_4) τ 8.1 (m, 6, CH_2), 7.95 (m, 2, $CH_2CH=$), 6.8 (s, 6, OCH_3), 5.75 (t, 1, OCHO), 5.1 (m, 2, $CH_2=$), and 4.35 (m, 1, $=CH$).

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.66; H, 11.78.

Sodium Methoxide as the Supporting Electrolyte.—A solution of 2.40 g (0.025 mol) of **1** and 0.135 g (0.0025 mol) of sodium methoxide in 30 ml of methanol was electrolyzed by the same method described above. The total yield of the products was 86.9%.

Controlled Potential Electrolysis.—A solution of 0.96 g (0.01 mol) of **1** and 0.54 g (0.01 mol) of sodium methoxide in 10 ml of methanol was electrolyzed under the condition of controlled anode potential of 1.3 V *vs.* sce until about 3 *F*/mol of electricity was passed. The reaction vessel employed was the same as that used in the constant current experiment, and the anode potential was controlled by Yanagimoto controlled potential electrolyzer VE-3. The gas chromatographic analysis (column, silicone DC 550, PEG 20M) indicated that compound **4** was the sole product.

Reaction of 1 with *tert*-Butyl Perbenzoate in the Existence of Copper Catalyst (Kharasch Reaction).—To a mixture of 4.8 g (0.05 mol) of **1**, 0.005 g of Cu_2Cl_2, and 0.64 g (0.02 mol) of methanol was added dropwise a solution of 1.94 g (0.01 mol) of *tert*-butyl perbenzoate in 1 ml of dry benzene. The reaction mixture was refluxed for 6 hr and extracted with ether. The ethereal solution was washed with a 2 *N* solution of sodium carbonate and analyzed by a gas chromatograph (column, silicone DC 550, PEG 20M) indicating that compound **4** (yield 7.5%) was the only product detectable by gas chromatography.

Acidic Methanolysis of 1.—A solution of 4.8 g (0.05 mol) of **1** and 1.9 g (0.01 mol) of *p*-toluenesulfonic acid in 20 ml of methanol was refluxed for 24 hr. Ether was added to the reaction mixture and the ethereal solution was washed with a 2 *N* solution of sodium carbonate. The comparisons of the gas chromatographic retention times (column, silicone DC 550, PEG 20M) with those of authentic samples indicated the existence of 1- and 3-methylcyclohexenes, cycloheptene, 1-methoxy-2-methylcyclohexane,

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and cycloheptyl methyl ether in the ethereal solution. The total yield was 91.8%.

Anodic Oxidation of Bicyclo[3.1.0]hexane (2).—The electrolysis of a solution of 8.2 g (0.1 mol) of 2 and 3.0 g (0.01 mol) of tetraethylammonium *p*-toluenesulfonate in 40 ml of methanol was carried out by the same method used in the anodic oxidation of 1. The gas chromatographic analysis indicated the formation of compounds **7a,b**, **8a,b**, and **9**, the total yield being 50%. The identifications of **7a,b** and **8a,b** were accomplished by the comparisons of their nmr data and gas chromatographic retention times with those of authentic samples. The nmr spectrum and elemental analysis of **9** coincided with the assigned structure: nmr (CCl_4) τ 8.5 (m, 4, CH_2), 7.95 (m, 2, $CH_2CH{=}$), 6.88 (s, 6, OCH_3), 5.73 (t, 1, OCHO), 5.05 (m, 2, $={CH_2}$), and 4.35 (m, 1, CH=).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.68; H, 11.32.

Acidic Methanolysis of 2.—A solution of 2.1 g (0.025 mol) of bicyclo[3.1.0]hexane and 0.98 g (0.005 mol) of *p*-toluenesulfonic acid in 10 ml of methanol was refluxed for 26 hr. Work-up of the reaction mixture and product identification were carried out by the same method used in the methanolysis of 1. The total yield of products (Table II) was 90%.

Registry No.—**1**, 286-08-8; **2**, 285-58-5; **6**, 28995-68-8; **9**, 28995-69-9.

Acknowledgment.—The authors are grateful for the kind encouragement of Dr. Ryohei Oda.

Mechanism of the Diels–Alder Reaction of Halocyclopropenes[1a]

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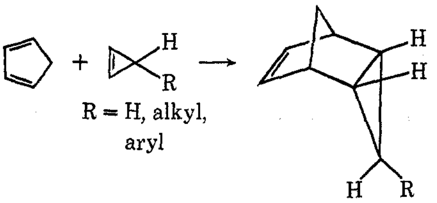
Received November 12, 1970

The possibility that perhalocyclopropenes undergo Diels–Alder reaction by first dissociating to a cyclopropenium halide ion pair which then reacts with diene is discussed. Several criteria for deciding between the one-step direct Diels–Alder mechanism and the two-step ionic process are described. Stereochemical studies and kinetic data (the order of the reaction, solvent polarity rate effects, activation parameters) appear to be consistent with the simple direct cycloaddition mechanism.

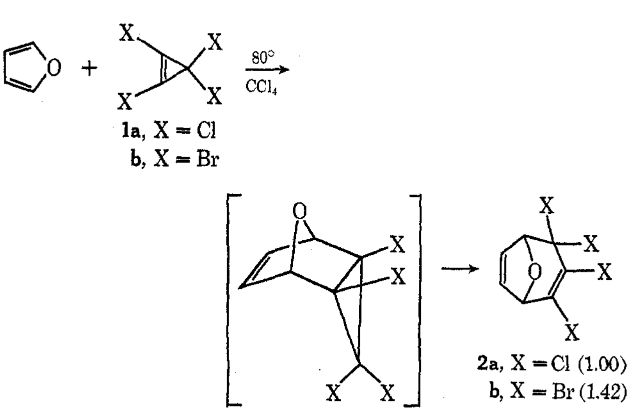
The great majority of cyclopropenes are excellent dienophiles in the Diels–Alder reaction, undergoing rapid cycloaddition with cyclopentadiene, for example, to produce the endo adduct;[2–4] monosubstitution at C_3 leads to formation of the endo–anti adduct[2a,b,d] and geminal disubstitution often inhibits reaction completely.[2a–d] This substituent effect has most reasonably been interpreted as being steric in origin.



R = H, alkyl, aryl

In contrast to these observations with alkyl- and aryl-substituted cyclopropenes, Law and Tobey[5] have argued that the Diels–Alder reactivity of perhalocyclopropenes, and the stereochemistry of their cycloadducts, has an electronic basis. Their study of the cycloadditions of six different perhalocyclopropenes with cyclopentadiene, furan, or butadiene revealed that all products have endo stereochemistry (or are derived from initial endo adducts by the cyclopropyl halide to allyl halide electrocyclic reaction[6]) and that the rate of cycloaddition to furan is greatest when the largest halogen (Br > Cl > F) is at C_3 of the starting material. Thus, relative to tetrachlorocyclopropene (**1a**), tetrabromocyclopropene (**1b**) reacts more rapidly, whereas all products from **3** and **6a–c** are formed more slowly (k_{rel} in parentheses).

Based upon these observations, Law and Tobey conclude (1) when the initially formed endo adduct has Br or Cl syn to the ethylene bridge, concerted ionization and disrotatory ring opening occurs[6] yielding the corresponding bicyclic diene (**2a,b**, **5**), and, when F is syn, the initial adduct is stable (**4**, **7a–c**); (2) since the rate of reaction increases as the C_3 substituent is changed from F to Cl to Br, neither the steric argument (above)



1a, X = Cl
b, X = Br

2a, X = Cl (1.00)
b, X = Br (1.42)

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[1] (a) Partial support of this work by the Robert A. Welch Foundation is gratefully acknowledged, as is the assistance of the National Science Foundation in the purchase of a Varian Associates A-56/60A nmr spectrometer. (b) To whom inquiries should be addressed at the Department of Chemistry, The University of Tennessee, Knoxville, Tenn. 37916. (c) National Defense Education Act Fellow, 1966–1969.

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