Hz), 8.88 (d, $J = 7$ Hz) (combined integration 3 H), 8.60 (broad s, 4 H), 8.12 (broad s, 2 H), 7.76 (q, $J = 7$ Hz, 1 H), 6.60 (broad s), 6.50 (broad s) (combined integration 2 H). Irradiation of the quartet at τ 7.76 with an external field collapsed the methyl doublets at τ 9.22 and 8.88 to singlets and also sharpened up the broad singlets at τ 6.60 and 6.50. The structure of this mixture was further verified by comparison with a sample independently synthesized as described below.

Catalytic Hydrogenation of the Crude Epoxidation Mixture Derived from 7-Methylnorbornadiene.—The crude epoxidation mixture (0.25 g) obtained from the treatment of 7-methylnorbornadiene with *m*-chloroperbenzoic acid was hydrogenated at 15 psig in a Paar shaker over 5% palladium on charcoal for 4 hr. After filtration to remove the catalyst, the solution was concentrated and submitted to preparative vpc. The residue was shown to contain two peaks. The minor peak (35%) in the chromatogram was a colorless oil whose spectral properties were identical with those of the mixture of isomers obtained from the photolysis of **10**. The major peak present in the vpc chromatogram (49%) was a colorless liquid whose structure is assigned as *exo*-8-methyl-2-oxabicyclo[3.2.1]oct-3-ene (**16**) on the basis of the physical data cited: ir (CCl_4) 3.45, 6.14, 6.85, 7.0, 7.25, 7.57, 7.7, 8.22, 8.45, 8.62, 9.12, 9.50 (s), 10.45, and 11.0 μ (s); mass spectrum *m/e* 124 (M^+), 109, 96, 95, 93, 91, 81 (base), and 68; nmr (CCl_4, 100 MHz) τ 9.14 (3 H, d, $J = 7$ Hz), 8.10 (broad s, 5 H), 7.70 (1 H, q, $J = 7$ Hz), 5.86 (1 H, broad s), 5.10 (1 H, t, $J = 6$ Hz), and 4.04 (1 H, d, $J = 6$ Hz).

Thermolysis of *exo*-4-Methylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde.—A 0.75-g sample of bicycylohexene **10** in 5 ml of benzene was heated in a sealed tube at 150° for 4 hr. The solvent was removed under reduced pressure and the residual oil was subjected to preparative thick layer chromatography. The plate was developed with a 25% ether–75% pentane solution. Extraction of the band (R_f 0.33) with methylene chloride followed by evaporation of the solvent gave 0.65 g (87%) of a colorless oil: ir (neat) 3.42, 3.52, 3.68, 6.02 (s), 6.24 (s), 6.45, 6.92, 7.45, 7.8, 7.97, 8.25, 8.70 (s), 9.7 (m), 10.8 (m), 11.55 (s), and 12.1 μ; uv (cyclohexane) λ_{max} 282 nm (ϵ 16,600); mass spectrum *m/e* 122 (M^+), 107, 93 (base), 91, 79, and 77; nmr (CCl_4, 100 MHz) τ 8.2 (s, 3 H), 7.4 (m, 2 H), 6.96 (m, 2 H), 4.28 (m, 1 H), 3.74 (1 H, broad s), 0.25 (1 H, d, $J = 6$ Hz). When the signal at τ 4.28 was saturated with an external field, the doublet at 0.25 collapsed to a singlet. On the basis of the data this compound is assigned the structure of unsaturated aldehyde **18**.

Another minor aldehyde (*ca.* 5%) was detected in the crude thermolysis residue but could not be separated from **18**. This compound has since been assigned the structure of **19** by Gilbert, Klumpp, and coworkers.[23]

Acknowledgment.—We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. The National Science Foundation provided financial assistance in the purchase of the nmr spectrometer used in this research.

Registry No.—**5,** 40156-12-5; **7,** 41828-73-3; **8,** 41828-74-4; **9,** 13437-93-9; **10,** 35391-55-0; **11,** 41828-77-7; **12,** 41828-78-8; **13,** 41828-79-9; **14,** 41828-80-2; **15,** 41828-81-3; **16,** 41828-83-5; **18,** 41828-82-4; *exo*-4-methylbicyclo[3.1.0]hex-2-ene-*endo*-6-carboxylic acid, 41828-84-6.

Electrochemical Preparation and Retrodiene Reaction of 1,4-Bis(methoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene

CRAIG B. WARREN* AND JORDAN J. BLOOMFIELD

Monsanto Company, Corporate Research Department, St. Louis, Missouri 63166

JAMES S. CHICKOS* AND ROBERT A. ROUSE

University of Missouri at St. Louis, St. Louis, Missouri 63121

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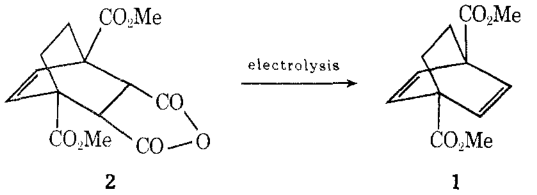
1,4-Bis(methoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene (**1**) was synthesized by electrolytic decarboxylation of the adduct of maleic anhydride and dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate. Addition of a small amount of 4-*tert*-butylcatechol to the electrolysis reaction was found to increase the yield of **1** from 30 to 65%. Replacement of the usual solvent system for this reaction (pyridine, water, triethylamine) with acetonitrile, water, pyridine, triethylamine decreased the reaction time from 12 to 2 hr. Compound **1** readily undergoes a retrodiene reaction to produce ethylene and dimethyl terephthalate. Energy parameters for this reaction are $\Delta H^{\ddagger}$, 26.8 ± 0.3 kcal/mol; $\Delta S^{\ddagger}$, −0.4 ± 0.9 eu. CNDO/2 calculations performed for this reaction indicate that the lowest energy reaction pathway involves loss of an ethylene-like two-carbon fragment from a nearly planar hexadiene ring.

The retro Diels–Alder reaction, particularly when aromatic products are produced, has been extensively used to generate unstable intermediates and relatively inaccessible olefins.[1,2] We would like to report[3] the synthesis of 1,4-bis(methoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene (**1**) and the activation parameters for the retrodiene decomposition of dihydrobarrelene **1** to dimethyl terephthalate and ethylene. The key step in the synthesis of compound **1** was achieved by electrochemical oxidation of 1,4-bis(methoxycarbonyl)bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (**2**)



2 **1**

at low temperature, a technique of considerable potential for the preparation of thermally unstable or chemically labile molecules.

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(1) For reviews of the retrodiene reaction see (a) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968); (b) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); (c) A. S. Onishchenko, "Diene Synthesis," Oldbourne Press, London, 1964.

(2) For use of the retrodiene reaction to generate unstable intermediates and inaccessible olefins see (a) E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, **84**, 685 (1962); (b) G. D. Peddle, D. N. Roark, A. M. Good, and S. G. McGeachin, *J. Amer. Chem. Soc.*, **91**, 2807 (1969); (c) N. D. Field, *ibid.*, **83**, 3504 (1961); (d) C. M. Wynn and P. S. Klein, *J. Org. Chem.*, **31**, 4251 (1966); (e) W. S. Wilson and R. N. Warrener, *Chem. Commun.*, 211 (1972); (f) U. E. Wiersum and W. J. Myo, *ibid.*, 347 (1972); (g) R. Kreher and J. Seubert, *Z. Naturforsch. B*, **20**, 75 (1965); (h) R. N. Warrener, *J. Amer. Chem. Soc.*, **93**, 2346 (1971).

(3) This work is a continuation of a program concerned with synthesis of bicyclic molecules that are functionally substituted at the bridgehead positions. For previous papers see D. C. Owsley and J. J. Bloomfield, *J. Amer. Chem. Soc.*, **93**, 782 (1971); *J. Org. Chem.*, **36**, 4160 (1971); *Org. Prep. Proced. Int.*, **3**, 61 (1971).

TABLE I

ELECTROLYTIC DECARBOXYLATION OF COMPOUND **2**[a]

Run no.	Initial current, A	Initial voltage, V	Temp, °C	Reaction time, hr	Solvent[b] system	Radical inhibitor (mg, mmol)	Yield of **2**, %
			Effect of *tert*-Butylcatechol				
1	0.5	150	20	12	1	None	30
2	0.5	150	20	12	1	TBC[c] (50, 0.3)	50
3	2.2	70	20	2	2	None	32
4	2.4	70	20	2	2	TBC (5, 0.03)	30
5	2.0	70	20	2	2	TBC (15, 0.09)	50
6	2.0	70	20	2	2	TBC (50, 0.3)	67
7	2.0	70	20	2	2	TBC (100, 0.6)	60
			Effect of Type of Radical Inhibitor (*cf.* also run 6)				
8	2.5	70	20	2	2	TBH[d] (50, 0.3)	38
9	2.5	70	20	2	2	PTA[e] (60, 0.3)	38
10	2.5	70	20	2	2	Binox[f] (128, 0.3)	47
11	2.5	70	20	2	2	Catechol (33, 0.3)	53
			Effect of Temperature (*cf.* also run 6)				
12	2.0	70	−10	2	2	TBC (50, 0.3)	27
13	2.5	70	30	2	2	TBC (50, 0.3)	65
			Effect of Solvent (*cf.* also runs 2 and 6)				
14	2.5	70	20	2	3	TBC (50, 0.3)	0

[a] Anhydride **1** (2.94 g, 10 mmol) was used for each reaction. [b] Solvent system 1: triethylamine, 3 ml; pyridine, 117 ml; water, 10 ml. Solvent system 2: triethylamine, 3 ml; pyridine, 10 ml; water, 10 ml; CH$_3$CN, 107 ml. Solvent system 3: triethylamine, 3 ml; CH$_3$CN, 117 ml; water, 10 ml. [c] TBC, 4-*tert*-butylcatechol. [d] TBH, *tert*-butylhydroquinone. [e] PTA, phenothiazine. [f] Binox is the Shell Chemical Co. trade name for 4,4′-methylenebis(2,6-di-*tert*-butylphenol).

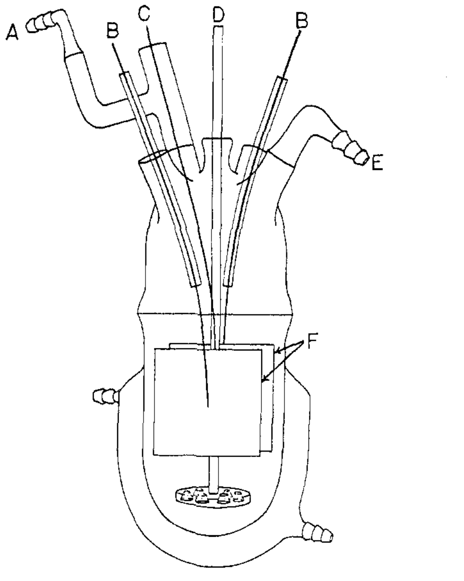

Figure 1.—Electrolysis cell: A, nitrogen gas inlet; B, copper wire lead to electrode; C, thermocouple; D, Vibromixer stirrer; E, gas outlet; F, platinum electrodes.

Bicyclooctadiene **1** was found to undergo a facile retro Diels–Alder reaction (even at room temperature) to give dimethyl terephthalate and ethylene. We have measured the kinetics and activation parameters for this reaction. To our knowledge this is the first time these parameters have been measured for this common type of retrodiene reaction. Finally, some of the bonding and structural changes that occur during the course of the reaction have been estimated by use of semiempirical quantum mechanical techniques.

Electrolysis Reaction.—Electrolytic oxidation of 1,2-dicarboxylic acids to olefins, first elucidated by Fichter,[4] has received renewed attention in recent years.[5-7] In particular, the electrolytic method smoothly decarboxylates bicyclic diacids containing proximal olefinic bonds.[5] Lead tetraacetate oxidation,[8] on the other hand, converts this class of compounds to lactones[5,6,9] and polymer.

Laboratory-scale Kolbe oxidations are generally carried out in an open beaker. We have constructed a more sophisticated cell (see Figure 1) from readily available glassware. The cell combines the vigorous agitation provided by a Vibromixer stirrer with a system that monitors and controls the reaction temperature in the area between the electrodes. These two features permit the maintenance of a high current density *and* a low reaction temperature for the oxidation of compound **2**.

Previous investigators[5-7] have always used pyridine–water–triethylamine as the solvent system for this reaction. Replacement of most of the pyridine with acetonitrile brought about a dramatic decrease in the internal resistance of the cell which, in turn, permitted the reaction to be run at higher current density and consequently a shorter period of time. Complete removal of pyridine, on the other hand, resulted in conversion of anhydride **2** to a brown oil. (For the effect of solvent on yields and reaction times see runs 2, 6, and 14, Table I.)

Electrolytic decarboxylation of the purified anhydride using typical reaction conditions[5-7] (run 1, Table I) produced the desired material in 30% yield. The remainder of the starting material was converted to an insoluble polymer which coated the reaction vessel and the platinum electrodes. In comparison, crude anhydride (washed with ether but not recrystallized) was cleanly electrolyzed—no insoluble polymer formation—to olefin **1** in about 60% yield. This increase in yield was reproducible and eventually it was discovered that traces of *tert*-butylcatechol (used as a radical inhibitor in the preparation of anhydride **2**) eliminated the for-

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[4] F. Fichter and H. Stenzel, *Helv. Chim. Acta*, **22**, 970 (1939).

[5] P. Radlich, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelin, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968), and references cited therein.

[6] H. H. Westberg, and H. J. Dauben, Jr., *Tetrahedron Lett.*, 5123 (1968).

[7] P. G. Gassman H. P. Benecke, and T. J. Murphy, *Tetrahedron Lett.*, 1649 (1969).

[8] C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

[9] C. M. Cimarusti and J. Wolinski, *J. Amer. Chem. Soc.*, **90**, 113 (1968).

mation of insoluble polymer. The effect of *tert*-butylcatechol on the yield of olefin **2** is presented in Table I (runs 1–7).

The effect of temperature (runs 6, 12, 13) and type of radical inhibitor (runs 8–11) on the yield of dihydrobarrelene **1** are also listed in Table I. The optimal conditions for this reaction are those of run 6.

Kinetics.—A search of the literature revealed that little qualitative and even less quantitative rate data have been reported for the commonly employed retrodiene reaction in which an aromatic molecule is one of the products. Alder and Rickert[10] were first to observe the reaction. They reported that 2,3-bis(ethoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene was converted to ethylene and diethyl phthalate at 200°. More recently Grob and coworkers[11] reported that bicyclo[2.2.2]octadiene (**3**) survived 150° for a brief period of time. Humber and coworkers[12] and Smith and coworkers,[13] on the other hand, were not able to prepare 1,4-bis(ethoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene at reaction temperatures below 150°. Instead, they obtained the retrodiene reaction products, *i.e.*, diethyl terephthalate and ethylene.

Bicyclooctadiene **1** readily cleaves to ethylene and dimethyl terephthalate at temperatures as low as 50°. No other products were detected by gas chromatography, while 99.5 ± 2.5% of the terephthalate was accounted for at the end of each kinetic run by ultraviolet spectroscopy.

The rate of the retrodiene reaction was followed by measuring the increase in uv absorbance of dimethyl terephthalate. Eight points were obtained for each run and conveniently fitted to eq 1 by a weighted non-

$$\frac{A - A_0}{A_\infty - A_0} = e^{-kt} \qquad (1)$$

linear least-squares regression program.[14] Activation parameters were similarly obtained *via* eq 2, where A_0,

$$\ln k_r = \ln kT/h - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R \qquad (2)$$

A, and A_∞ are the dimethyl terephthalate uv absorbances at zero time, at regular intervals during the reaction, and at infinite time, respectively.

The kinetic data are presented in Table II. For all runs, the deviation of the dependent variable from the calculated regression line was random; the total correlation coefficient squared was 0.9990 for the calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and ranged from 0.9855 to 0.9994 for the calculation of the first-order rate constants.

Calculations.—Of the many methods used to study the mechanism of the Diels–Alder reaction,[15] only secondary deuterium[16] and carbon-13[17] primary kinetic isotope effect measurements provide information about the structure of the transition state for this type of reaction.[18] The classical argument concerning the Diels–Alder reaction was whether the two σ bonds, created during the course of the reaction, were formed simultaneously or stepwise. Kinetic isotope effect measurements[15,16] suggest that the symmetry of bond formation or cleavage closely parallels the symmetry of the reactant(s). Orbital symmetry considerations,[19] predict that the reaction does not proceed through a biradical intermediate.

Table II

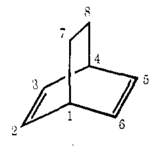
Summary of Kinetic Data[a]

Temp, °C	Run no.	Initial concn of **2** (10^4 *M*)	f[b]	10^6 k,[c] sec^{-1}
50 ± 0.01	1	1.55	0.71	4.32 ± 0.12
	2	2.42	0.70	4.12 ± 0.05
	3	1.42	0.86	3.96 ± 0.11
60 ± 0.01	4	2.19	0.92	15.0 ± 0.3
	5	2.45	0.86	14.8 ± 0.2
	6	2.16	0.83	14.6 ± 0.1
70 ± 0.01	7	3.20	0.96	45.1 ± 2.1
	8	3.59	0.84	45.7 ± 0.6
	9	3.32	0.86	50.5 ± 0.5
80 ± 0.1	10	2.85	0.84	161 ± 2
	11	2.80	0.98	168 ± 1
	12	2.20	0.77	150 ± 3

[a] $H^{\ddagger}$ = 26.8 ± 0.3 kcal/mol; $S^{\ddagger}$ = 0.4 ± 0.9 eu. [b] Maximum extent of reaction followed. [c] Errors are reported as standard deviations.

A search of the literature indicated that neither extended Hückel or CNDO/2 calculations have been carried out for the case of a retrodiene reaction that produces aromatic products. We thus thought it would be of interest to examine the retrodiene reactions of dihydrobarrelene (**3**) and its 1,4-bis(methoxycarbonyl) derivative (**1**) by means of the CNDO/2 method of calculation. In addition, both CNDO/2 and extended Hückel calculations were performed for the cycloaddition of ethylene to butadiene. In this way the two methods of calculation were compared and found to give similar results. These comparison calculations are presented in the Experimental Section.

During the course of the retrodiene reaction of adducts **1** and **3** several events must occur either simultaneously or successively. The cyclodiene portion of the ring must flatten with a subsequent lengthening and shortening of the bonds associated with the ring system; the C_7–C_8 bond distance must shorten with a flattening of the hydrogens attached to these carbons;



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[10] K. Adler and H. E. Rickert, *Justus Liebigs Ann. Chem.*, **524**, 180 (1936).

[11] C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

[12] L. G. Humber, G. Meyers, L. Hawkins, C. Schmidt, and M. Bonlerice, *Can. J. Chem.*, **42**, 2852 (1964).

[13] G. Smith, C. L. Warren, and W. R. Vaughan, *J. Org. Chem.*, **28**, 3323 (1963).

[14] Program NONLIN written by A. W. Dickinson of the Monsanto Computing Center was used on a CDC 6400 computer.

[15] For reviews on the mechanism of the Diels–Alder reaction see (a) S. Seltzer, *Advan. Alicyclic Chem.*, **2**, 1 (1968); (b) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967); (c) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[16] (a) P. Brown and R. C. Cookson, *Tetrahedron*, **21**, 1993 (1965); (b) S. Seltzer, *J. Amer. Chem. Soc.*, **87**, 1534 (1965); (c) D. E. Van Sickle and J. O. Rodin, *ibid.*, **86**, 3091 (1964).

[17] M. J. Goldstein and G. J. Thayer, Jr., *J. Amer. Chem. Soc.*, **87**, 1933 (1965).

[18] The term "no mechanism" has been used to describe this reaction because numerous kinetic studies have yielded little information about its detailed mechanism: W. von E. Doering and W. Roth, *Tetrahedron*, **18**, 67 (1962).

[19] (a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (c) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543 (1968).

and the C_1–C_7 and C_4–C_8 bonds must lengthen. The order in which these events occur can be investigated by varying them singly or simultaneously and observing the resulting effect on the total molecular energies. In order to reduce the dimension of such an energy surface to a few parameters, only those parameters suggested by experimental[16,17,20] and theoretical considerations[21] to be of importance were examined; reasonable estimates were chosen for the others. Absolute molecular energies cannot be obtained using the method employed here; however, the differences in energies obtained should offer insight into the nature of this reaction.

The following six reaction pathways involving symmetric lengthening of bonds C_1–C_7 and C_4–C_8 were investigated: 1a, loss of C_7–C_8 in an ethane conformation from nonplanar cyclohexadiene, and 2a, from planar cyclohexadiene; 1b, loss of C_7–C_8 in an ethylene conformation from nonplanar cyclohexadiene, and 2b, from planar cyclohexadiene; 1c, loss of C_7–C_8 in a conformation intermediate to ethane–ethylene from nonplanar cyclohexadiene, and 2c, planar cyclohexadiene. The two unsymmetrical pathways considered were stepwise breaking of bonds C_1 C_7 and C_4–C_8 in both the singlet and triplet states. Detailed geometries of the structures used for these series of calculations are presented in the Experimental Section.

The calculations indicated that the lowest energy process involved flattening of the cyclohexadiene ring and loss of the C_7–C_8 fragment in an ethylene-like conformation (process 1c). These calculations, however, were not pursued far enough to provide the transition state structure for this process.

Substitution of methoxycarbonyl groups at the bridgehead position did not alter the above mechanistic conclusions. Differences, particularly in the activation energy and atomic charges, were observed. The calculated difference in the total energy of the transition states for compounds **3** and **1** was found to be 17 kcal/mol, the latter compound being lower.

Results and Conclusions

Enthalpy of activation values for the retrodiene reaction vary from 73 (cyclohexane pyrolysis)[22] to 25 kcal/mol (anthracene–tetracyanoethylene adduct)[15a] and entropy of activation values vary from −2.7 to 17.3 eu.[1a] The low enthalpy of activation (26.8 kcal/mol) and entropy of activation (∼0 eu) for the retrogression of compound **1** suggest that the transition state occurs early along the reaction coordinate.

At present, there are not sufficient kinetic data on retrodiene cleavage of bicyclo[2.2.2]octadiene systems to allow for correlation of substituent effects with activation energies. Qualitatively, the effects of methoxycarbonyl groups are in accord with the CNDO/2 calculations. These calculations imply that electron-withdrawing groups should facilitate the retro Diels–Alder reaction.[23] The magnitude of these effects should vary, depending on the nature of the substituent and position of attachment. However, it is quite clear that these effects could be of considerable synthetic utility in designing new retro Diels–Alder reactions as routes to unstable intermediates.

Experimental Section

Melting points are uncorrected; nmr spectra were obtained with a Varian T60; uv spectra were obtained with a Perkin-Elmer 450 spectrometer; microanalyses were carried out at Monsanto's Physical Science Center. A Varian Aerograph 2100 dual column gas chromatograph equipped with flame ionization detectors was used in the single-column mode for gas chromatographic analyses. The signal from the chromatograph was fed to an Infotronics CRS-104 digital integrator and then to a Varian Aerograph Model 30 recorder.

Electrolysis Cell.—The electrolyses were carried out in the apparatus shown in Figure 1. Power was supplied by a Sorensen Model RC150-7.5 constant-voltage power supply. The reactions reported in this paper were run in a 100-ml jacketed reaction flask (Kontes K-296100). The reaction flask head was a Kontes K-296170 head to which two 10/30 outer joints had been added to accommodate the electrodes. The temperature of the reaction was monitored between the electrodes with an iron–constantan thermocouple (Aeropak, Model T-91M-12BJ8C) which was insulated with-$^1/_{16}$-in.-i.d. Teflon tubing (Fluorocarbon Co., Anaheim, Calif.). The thermocouple was connected to a West-Gardsman temperature controller which controlled a circulating pump. The coolant (1 l. of acetone, 4 l. of methanol) was pumped from a 4-l. dewar flask (mixing bath) through the reaction flask jacket, through a copper coil immersed in Dry Ice–acetone and back to the mixing bath. The square, smooth platinum electrodes (4.45 cm on an edge) were fashioned from 0.076 mm (3 mil) thick platinum foil and were spot welded to 18 gauge platinum wire which was imbedded into 6-mm-o.d. Pyrex glass tubing. Mercury was placed in the tube to provide an electrical contact between the electrode and the copper wire lead. The glass electrodes and the thermocouple were held in place by Teflon thermometer adapters.

1,4-Bis(methoxycarbonyl)bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Anhydride (2).—Dimethylcyclohexa-1,3-diene 1,4-dicarboxylate (55.7 g, 0.28 mol), which was prepared by the method of Kauer,[24] maleic anhydride (83.9 g, 0.85 mol), 4-*tert*-butylcatechol (1 g, recrystallized from heptane), and 400 ml of *o*-dichlorobenzene were placed into a three-neck, 1-l. flask equipped with a thermometer, overhead stirrer, and heating mantle. The reaction mixture was heated to 170° for 5 hr, solvent was removed *in vacuo*, and the crude adduct was washed with ether and recrystallized from hexane–chloroform to give 65 g (0.22 mol, 80%) of adduct, mp 183–185° (lit. mp 188.0–188.6).[24]

1,4-Bis(methoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene. A. Electrochemical Oxidation Reaction.—Anhydride 2 (2.49 g, 10 mmol) was heated with a mixture of triethylamine (3 ml), pyridine (10 ml), and water (10 ml) until a clear solution was obtained. This solution of hydrolyzed anhydride was washed into the reaction vessel with the remainder of the solvent (pyridine for runs 1 and 2, acetonitrile for runs 3–13). The radical inhibitor was added, the reaction mixture was flushed with nitrogen, and the power was turned on.

Work-up of the reaction mixture involved dilution with 100 ml of water [reactions run in C_5H_5N–H_2O–$(C_2H_5)_3N$] or reduction of the solvent *in vacuo* to a total volume of 30 ml followed by dilution with 50 ml of water [reactions run in CH_3CN, C_5H_5N, $(C_2H_5)_3N$, H_2O]. The diluted reaction mixture was then extracted with four 25-ml portions of pentane which were combined, washed with 50 ml of 1 *N* HCl, and dried over sodium sulfate. Removal of the pentane *in vacuo* left a white residue which was recrystallized

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(20) Primary carbon-13 isotope effects for the reaction of ^{13}C-labeled dicyanoacetylene with cyclopentadiene were correlated with a transition state in which the total constraints about the acetylenic carbons were approximately $^1/_3$ less (4.8 mdyn/Å) than for ground-state dicyanoacetylene. C. B. Warren, Ph.D. Thesis, Cornell University, 1970; M. J. Goldstein, C. B. Warren, and W. S. Morrison, to be published.

(21) J. W. McIver, Jr., *J. Amer. Chem. Soc.*, **94**, 4782 (1972).

(22) S. R. Smith and A. S. Gordon, *J. Phys. Chem.*, **65**, 1124 (1961).

(23) Recent work by Haberfield suggests that the transition state for the forward Diels–Alder reaction is electron rich relative to the reactants (electron-donor solvents stabilize the reactants; the more electronegative solvents stabilize the transition state). Whether a similar relationship holds for the reverse reaction is not known. P. Haberfield and A. K. Ray, *J. Org. Chem.*, **37**, 3093 (1972).

(24) J. C. Kauer, R. E. Benson, and G. W. Parshall, *J. Org. Chem.*, **30**, 1431 (1965).

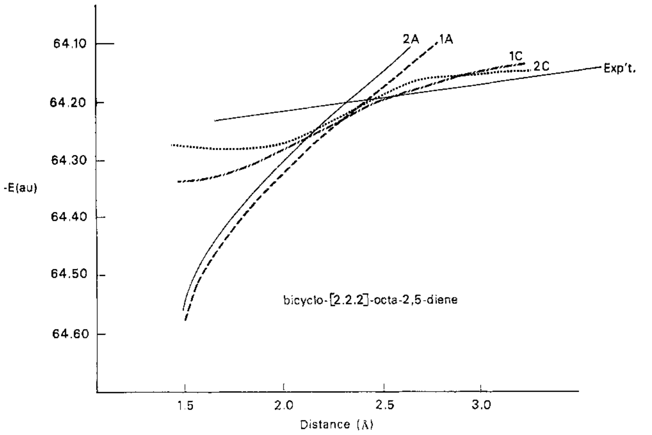


Figure 2.—Total molecular energies as a function of the perpendicular distance between lines connecting atoms C_1–C_4 and atoms C_7–C_8 in bicyclo[2.2.2]octadiene for various conformational changes. See the calculation part of the Experimental Section for a description of the conformations studied.

from pentane: mp 88–89°; nmr (DMSO-d_6) δ 6.55 (s, 4, vinyl hydrogen), 3.82 (s, 6, $COOCH_3$), 1.58 (s, 4, methylene hydrogen).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.90; H, 6.20.

B. Gas Chromatographic Analyses.—All gas chromatograms were run at an injection port temperature of 250°. At this temperature, dihydrobarrelene **1** was converted to dimethyl terephthalate and the bistriethylammonium salt of **2** was converted back to anhydride. The reactions listed in Table I were followed by gas chromatography. A 0.20-ml sample of the reaction mixture was withdrawn and spiked with 2 mg of 1-phenylnonane; 0.5 μl of this solution was injected on a 1.9 m × 2 mm glass U column packed with 3% OV-11 on 100/120 mesh Supelcoport. In two runs, the yields obtained by gas chromatography were compared to the weight of **1** isolated by pentane extraction and found to differ by about 5%. The reaction times listed in Table I were sufficient for the complete disappearance of starting material.

Kinetics.—Recrystallized bicyclooctadiene **1** which contained about 3% dimethyl terephthalate was used for the kinetic runs. Analysis of the material by gas chromatography showed no *tert*-butylcatechol in the sample; the nmr showed only dimethyl terephthalate and **1**. The kinetics of the reaction were followed by measuring the increase in uv absorbance of the product (dimethyl terephthalate) at all three of its uv max wavelengths, uv max (dodecane) 242 nm (ε 9000), 283 (810), 292 (705). Absorbance varied linearly with concentration to 0.9 absorbance units for λ_{max} 242, and to 0.5 absorbance units for λ_{max} 283 and 292. Uv measurements were carried out in a 1-cm or 0.1-cm cell depending on the concentration of the solution. All reactions were carried out in olefin-free dodecane.

Typically, a carefully weighed portion of a stock solution of **2** was diluted to 25.0 ml. After the initial absorbance had been measured, 4-ml portions of this solution were placed into six 5-ml vials which were then evacuated, sealed, and placed into a constant-temperature bath. The vials were withdrawn periodically and placed in a dewar flask filled with Dry Ice-acetone. After the run was finished the vials were warmed to room temperature and opened and the terephthalate absorbance was measured. One sample of the reaction mixture was then resealed into a vial and heated to 100° for 3 hr to provide an infinity sample. Comparison of the infinity time concentration of terephthalate to the initial concentration of bicyclic compound **1** showed that 99.5 ± 2.5% of starting material had been converted to product.

Calculations.—The structural parameters used in this study were obtained from the structural determinations of bicyclo[2.2.2]octadiene (**3**),[25] bicyclo[2.2.2]octene-2,3-*endo*-dicarboxylic anhydride,[26] and studies on bicyclo[2.2.2]octane-1,4-dicarboxylic acid.[27] Additional data for the methoxycarbonyl structure used to construct the molecular structure of **1** were obtained from interatomic distances.[28] These values are presented in Table III.

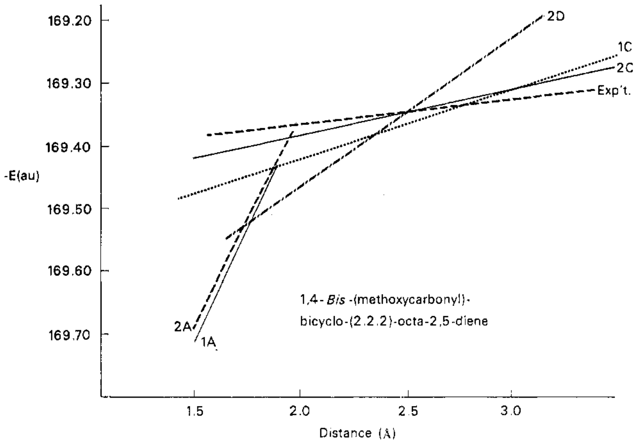
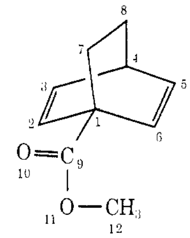


Figure 3.—Total molecular energies as a function of the perpendicular distance between lines connecting atoms C_1–C_4 and atoms C_7–C_8 in 1,4-bis(methoxycarbonyl)bicyclo[2.2.2]octa-2,5-diene.

TABLE III

BOND ANGLES AND DISTANCES FOR COMPOUND 1



1

Methoxycarbonyl	Bond length, Å	Bond angle, deg
C_9–O_{10}	1.22	
C_9–O_{11}	1.36	
O_{11}–C_{12}	1.46	
C_{12}–H	1.09	
C_1–C_9–O_{11}–C_{12} dihedral angle[a]		155
C_1–C_9–C_{10}		120
C_1–C_9–O_{11}		116
C_9–O_{11}–C_{12}		113

[a] Methyl points away from molecule.

The events and corresponding geometric changes investigated as a function of the separation distance between C_1–C_4 and C_7–C_8 follow.

(1) A bent, nearly planar hexadiene ring with a ring dihedral angle of 168° (also C_1–C_2–H, 121°) and with bond lengths intermediate between benzene and cyclohexadiene (C_1–C_2, 1.42 Å; C_2–C_3, 1.38 Å; C_2–H, 1.09 Å) and with either (A) near ethane C_7–C_8 bond distance (1.553 Å) and experimental methylene bond angles and bond lengths (C_7–H, 1.105 Å, H–C_7–H, 111.3°); (B) near ethane C_7–C_8 bond distance and planar ethane hydrogens (C_7–H, 1.09 Å; H–C_7–H, 122°); (C) near ethylene C_7–C_8 bond distances (1.39 Å) and planar ethylene hydrogens (C_7–H, 1.09 Å; H–C_7–H, 122°); (D) near ethylene bond distances (1.39 Å) with nonplanar hydrogens (H–C_7–H, 111.3°; C_7–H, 1.105 Å).

(2) A planar hexadiene ring with bond distances and angles for the ethyl fragment as reported in cases A–D above.

The results of the calculations for **3** are shown in Figure 2, where the total molecular energies are plotted as a function of the perpendicular distance between two lines joining atoms C_1–C_4 and C_7–C_8. Only four of the eight variations outlined above are in-

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[25] A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc., Jap.*, **44**, 1783 (1971).

[26] R. Destro, G. Fillippini, C. M. Gramaccioli, and M. Simonetta, *Tetrahedron Lett.*, **No. 29**, 2493 (1969).

[27] O. Ermer and J. D. Dunitz, *Chem. Commun.*, 567 (1968); *Helv. Chim. Acta*, **52**, 1861 (1969).

[28] "Tables of Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

cluded; the others either parallel those shown or were conformations of higher energy. At about 3 Å the "benzene-ethylene complex" (experimental ethylene-benzene bond angles and lengths, depicted as Exp't in Figures 2 and 3) has the lowest energy of all the conformations studied. In the stepwise bond-breaking process, the C_1–C_7 bond length was arbitrarily chosen to be twice as long as the C_2–C_8 value. Both singlet (^{1}S) and triplet (^{3}T) electronic states were studied.

Similar analyses were performed on compound **1**. The experimental geometry of dihydrobarrelene (**3**) was used to fix the ring geometries. The conformation of the methoxycarbonyl groups used was the one with the carbonyl groups colinear with C_1–C_4 and the C_7–C_1–C_9–O_{10} dihedral angle equal to 45°. The results of these calculations, shown in Figure 3, parallel those for compound **3**.

To test whether the retrodiene reaction was allowed under the conservation of orbital symmetry concept,[19b] we performed both extended Hückel[19a] and CNDO/2 calculations for ethylene-ethylene and ethylene-butadiene cycloaddition reactions. The two methods gave a slightly different ordering of energy levels but otherwise the same results were obtained. Similar CNDO/2 analyses were performed on both compounds **3** and **1**. The occupied reactant molecular orbitals (MO) were composed predominantly of linear combinations of benzene and ethylene MO's, of which the bonding product MO's were the major contributors, thus confirming the allowableness of the concerted retrodiene reaction of **3** and **1**.

Registry No.—**1**, 41894-67-1; **2**, 41894-68-2; dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate, 1659-95-6.

Electrochemical Reduction of (+)-(2*S*,4*S*)-2,4-Dibromopentane

ALBERT J. FRY* AND WAYNE E. BRITTON[1]

Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457

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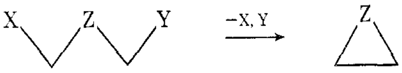
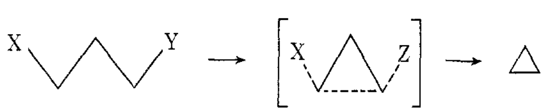
Electrochemical reduction of *meso*- and *dl*-2,4-dibromopentane (**2**) in dimethyl sulfoxide affords in each case roughly equal amounts of *cis*- and *trans*-1,2-dimethylcyclopropanes (**7** and **8**, respectively). The results are interpreted in terms of a stepwise reduction mechanism, *via* a γ-halo carbanion (**13**). (−)-(2*R*,4*R*)-2,4-Pentanediol was prepared by resolution of the racemic diol; the diol was then converted by means of phosphorus tribromide in pyridine into (+)-(2*S*,4*S*)-**2**. Electrochemical reduction of this material afforded (−)-(1*R*,2*R*)-**8** of high optical purity, demonstrating that cyclization of **13** occurs *via* a semi-W transition state. The reduction of *dl* and optically active **2** by a number of chemical reductants was also examined.

There exists a wide variety[2] of reactions which amount to overall 1,3 elimination of two substituents with formation of a carbon–carbon bond, *i.e.*

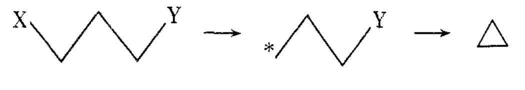


Z = carbon or a heteroatom

Generally, mechanisms proposed for such reactions have fallen into two classes, concerted (eq 1) or stepwise (eq 2). The carbon denoted by an asterisk in

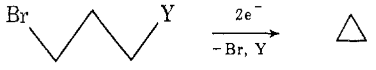


(1)



(2)

eq 2 may be a carbanion, carbonium ion, carbene, or radical; at any rate, a discrete intermediate intervenes on the way to product, while in the concerted mechanism the bonds to X and Y are both breaking as the new bond is forming. A great deal of recent evidence[3] has demonstrated that a number of such reactions formerly thought to be concerted actually proceed in stepwise fashion. Indeed, there does not now appear to exist any authentic example of a concerted 1,3 elimination.[3] In this light, we were attracted to a number of recent reports that electrochemical reduction of compounds of general structure **1** affords cyclopropanes in good

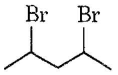


(3)

1, Y = Br, Cl, $^+N(CH_3)_3$

yields,[4] and especially to the suggestion that certain of of these reductions—primarily open-chain compounds—proceed by a concerted mechanism.[4]

We describe herein evidence that electrochemical reduction of the open-chain dibromides *meso*- and *dl*-2,4-dibromopentane (**2**) actually proceeds stepwise, *via* an intermediate γ-halo carbanion.[5] Further, we present the first unequivocal demonstration of the stereochemistry of cyclization of an acylic γ-halo carbanion. The study consisted of an analysis of the products, including stereochemistry, of the electrochemical reduction of *meso*- and *dl*-2,4-dibromopentane (**2**) and of (+)-(2*S*,4*S*)-**2**. Reduction of **2** by chemical reductants was also briefly investigated.



2

Results

Synthesis.—*meso*- and *dl*-2,4-dibromopentane (**2**) were prepared by an improved modification of the

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[1] (a) Excerpted in part from the Ph.D. thesis of W. E. B., Wesleyan University, 1972. (b) A portion of these results have been communicated in preliminary form: A. J. Fry and W. E. Britton, *Tetrahedron Lett.*, 4363 (1971).

[2] A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914 (1967), and many references therein.

[3] (a) F. C. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970); (b) L. A. Paquette, *ibid.*, **1**, 209 (1968).

[4] (a) M. R. Rifi, *Collect. Czech. Chem. Commun.*, **36**, 932 (1971); (b) M. R. Rifi, *Tetrahedron Lett.*, 1043, (1969); (c) M. R. Rifi, *J. Amer. Soc.*, **89**, 4442 (1967).

[5] It is well established that electrochemical reduction of alkyl halides involves carbanion intermediates: (a) A. J. Fry and R. G. Reed, *J. Amer. Chem. Soc.*, **94**, 8475 (1972); (b) J. L. Webb, C. K. Mann, and H. M. Walborsky, *ibid.*, **92**, 2042 (1970).