of 3.46 g of crude 8 in 500 ml of dry CH_2Cl_2 was added 4.17 g of phosphorus pentachloride at room temperature. A clear solution resulted in about 10 min. After 1 hr, the volatile material was removed under reduced pressure and a slurry of the crude acid chloride in 500 ml of dry ether was added to a threefold excess of $(CH_3)_2CuLi$ reagent[10] at −78°.[11] After 30 min, aqueous ammonium chloride was added and the neutral fraction of the reaction products was crystallized from aqueous ethanol to yield 2.54 g (74%) of **9**, mp 147–149°. The analytical sample, mp 149–151°, was obtained by recrystallization from absolute ethanol.

6,13-Dimethyldibenz[*a,h*]anthracene* (4). A well-stirred mixture of 1.0 g of **9** and 30 g of 115% polyphosphoric acid[12] was held at 160° for 30 min and then poured on ice. The hydrocarbon was extracted with chloroform and crystallized from chloroform–ethanol to yield 0.82 g (92%) of **4**: mp 273–274°, nmr ($CHCl_3$, TMS) δ 2.81 (s, 6, Ar CH_3).[13] An attempt to oxidize **4** with sodium dichromate in acetic acid[14] yielded a mixture of products. The red 2,4,7-trinitrofluorenone derivative‡ of **4** melted at 282–284° after one recrystallization from benzene. The uv spectrum of **4** in $CHCl_3$ is recorded in Table I along with spectra[15] of dibenz[*a,h*]anthracene (**10**), 7,14-dimethyldibenz[*a,h*]anthracene (**11**), and picene (**12**).

Registry No.—**4**, 39179-15-2; 4 2,4,7-trinitrofluorenone derivative, 39179-14-1; **5**, 53092-64-1; **6**, 53092-65-2; **7**, 53092-66-3; **8**, 53092-67-4; **9**, 53092-68-5; **10**, 53-70-3; **11**, 35335-07-0; **12**, 213-46-7; *p*-dibromobenzene, 106-37-6; *N*-bromosuccinimide, 128-08-5.

References and Notes

(1) This work was supported by Grant 5-R01 CA-07394 from the National Cancer Institute, U. S. Public Health Service.
(2) Postdoctoral Research Associate.
(3) See M. S. Newman and R. F. Cunico, *J. Med. Chem.*, **15**, 323 (1972), for a discussion and references.
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(8) This procedure is based on work of R. J. P. Corrin and J. P. Masse, *J. Chem. Soc., Chem. Commun.*, 144 (1972).
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(13) The nmr equipment was purchased in part with funds from a departmental grant from the National Science Foundation.
(14) Compare J. W. Cook, *J. Chem. Soc.*, 1592 (1933).
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Attempted Synthesis of *cis*-Cyclobutene-3,4-dicarboxaldehyde

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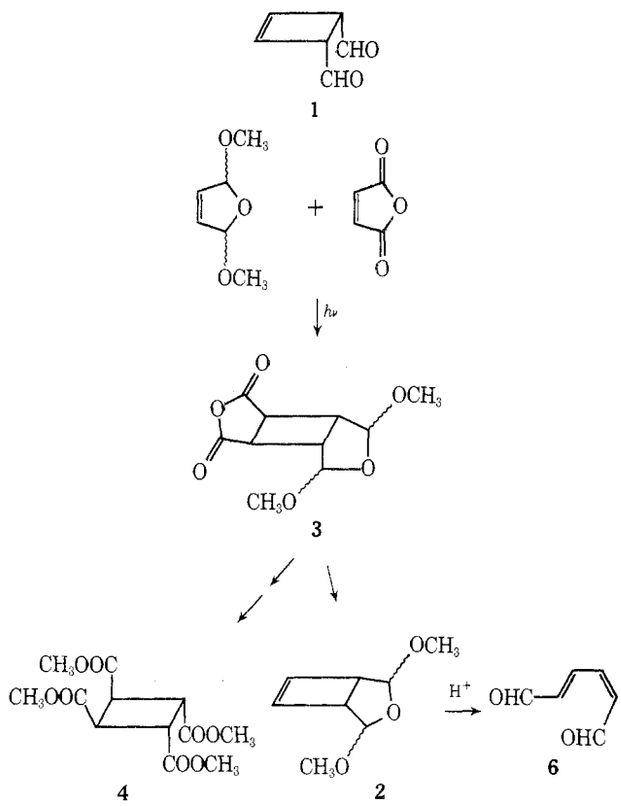
In connection with work aimed toward the synthesis of some polycyclic systems containing a fused cyclobutene ring, the preparation of the unknown *cis*-cyclobutene-3,4-dicarboxaldehyde (**1**) for use as a synethetic intermediate appeared attractive.

Consideration of potential routes for preparing substituted succindialdehydes led to the selection of the cyclic acetal **2** as a possible convenient precursor to **1**.[1] Accordingly, the preparation of **2** was carried out as outlined in Scheme I.

Scheme I



Benzophenone-sensitized photocycloaddition[3] of maleic anhydride to 2,5-dimethoxy-2,5-dihydrofuran (commercially available isomeric mixture) gave adduct **3** in 40% yield. The structure of **3** followed from its correct elemental analysis, mass spectrum, and the nmr spectrum, which clearly showed the correct number and kinds of hydrogens (see Experimental Section). Furthermore, dilute hydrochloric acid hydrolysis of **3** followed by potassium permanganate oxidation gave a tetracarboxylic acid characterized as its tetramethyl ester **4**, which was identical with an authentic sample[4] of *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane. These combined results clearly establish the gross structure of **3**.[5]

Dissolution of **3** in water containing triethylamine followed by electrolytic decarboxylation[6] in pyridine gave the desired cyclobutene **2** in 10% yield after evaporative distillation. Elemental analysis and mass spectral data were completely consistent with the assigned structure, and the nmr spectrum showed two olefinic protons as a triplet (J = 0.6 Hz), a characteristic feature of bicyclo[3.2.0]hept-6-enes.[7]

Unfortunately, **2** did not prove a ready precursor to **1**. Mild hydrolysis of **2** with aqueous mineral acid led to the formation of *cis,trans*-muconic dialdehyde (**6**)[8] in high yield. Hydrolysis of **2** was then examined using a broad spectrum of acidic reagents.

In all cases, only starting acetal **2** and/or dialdehyde **6** or total decomposition was observed. Some results are summarized in Table I.

In order to examine the possibility that **6** could be arising *via* acid-catalyzed cleavage of the central bond in **2**, monocyclic acetal **5** was prepared (Scheme II) and its hydrolysis examined.

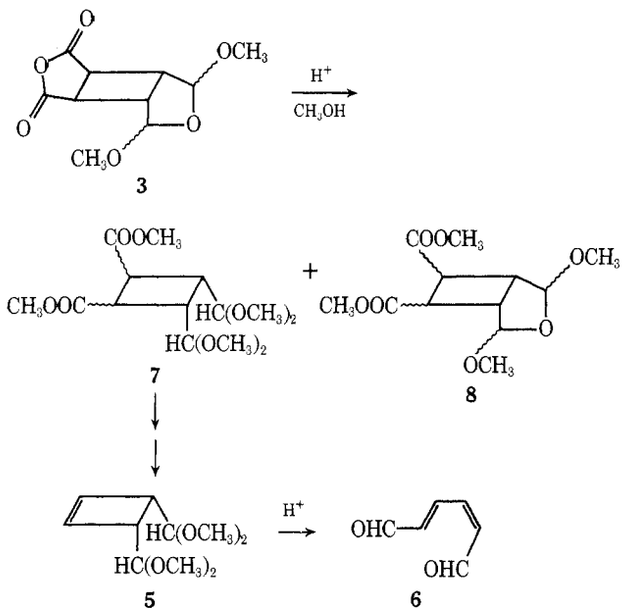
Boiling a solution of **3** in methanol containing a trace of sulfuric acid gave a mixture of **7** and **8** (90:10), from which an oil more enriched in **7** could be obtained. Basic hydrolysis of **7** (aqueous sodium hydroxide) followed, without isolation, by electrolytic decarboxylation[6] gave **5** as a colorless liquid. Analytical and spectral data were clearly in accord

Table I
Results of Treatment of Acetal 2 with Acidic Reagents

Expt	Acid reagent	Solvent	Temp, °C	Time	Product(s) (ratio)[a]
1	$MgSO_4$[b]	Wet $CHCl_3$	25	24 hr	**2**
2	1% acetic acid	H_2O	60–70	2 min	**2**
3	1% acetic acid	H_2O	90	5 min	**2** + **6**[c] (40:60)
4	Amberlite IR-120 (H^+) ion-exchange resin	H_2O	60–70	2 min	**2** + **6** (70:30)
5	0.1 *N* HCl	H_2O	70–80	3 min	**6**[c]
6	0.1 *N* $HClO_4$	H_2O	60–70	90 sec	**6**
7	0.1 *N* $HClO_4$	H_2O	25	18.5 hr	**2** + **6**(40:60)
8	BBr_3	CH_2Cl_2	−78	10 min	Decomposition
9	BBr_3	CH_2Cl_2	−60	5 min	Decomposition

[a] By nmr analysis. [b] J. J. Brown, R. H. Lenhard, and S. Bernstein, *J. Amer. Chem. Soc.*, **86**, 2183 (1964). [c] Some isomerization of *cis,trans*-muconic dialdehyde (**6**) to the trans,trans-isomer was observed.[8]

Scheme II



with the desired structure[9] (see Experimental Section). Unfortunately, mild acid hydrolysis of **5** gave again *cis,trans*-muconic dialdehyde (**6**) and not the desired dialdehyde **1**.

The factor(s) responsible for the remarkably facile and stereospecific ring opening observed on hydrolysis of acetals **2** and **5** is of interest. One explanation involves the intermediate formation of the desired *cis*-cyclobutenedicarboxaldehyde (**1**) followed by a rapid acid-catalyzed conrotatary[10] ring opening leading to the observed *cis,trans*-diene **6**. This is supported by the reported mild (acid-catalyzed?) thermal stereospecific ring opening of the structurally related tetramethyl *cis*-diacetoxycyclobutene.[11]

Of course, the ring opening of **2** and **5** need not proceed through the intermediacy of **1**. Indeed, as alternative explanation suggests that the observed stereospecific ring opening could be an example of a solvolytic electrocyclic reaction.[12] The developing positive charge on carbon formed during protonation of the acetal oxygen(s) in **2** and **5** stabilizes, and in turn is stabilized by, the developing π orbitals involved in the electrocyclic ring opening.[13] This phenomenon has recently been suggested as occurring in certain solvolytic Cope rearrangements.[12]

Experimental Section[14]

Photocycloaddition of Maleic Anhydride and 2,5-Dimethoxy-2,5-dihydrofuran. Preparation of 3. A solution of 26 g of distilled 2,5-dimethoxy-2,5-dihydrofuran (Eastman), 10 g of maleic anhydride, and 5 g of benzophenone in 270 ml of acetonitrile was irradiated (Hanovia 450-W lamp, Pyrex filter) under nitrogen for 48 hr. The solvent was removed under reduced pressure and the residue was treated with 250 ml of ethyl ether. The mixture was rapidly stirred for several hours, after which time the solid was collected and washed with ether giving 10 g (44%) of powdery crude product. A sample recrystallized two times from butyl acetate had mp 231–233°: ir (KBr) 5.40 and 5.58 μ (anhydride); mass spectrum *m/e* 227 (M − H),[15] 197 (M − OCH_3); nmr (DMSO-d_6, 90 MHz) δ 5.26 (s, 2 H), 3.25 (s overlapping m, 8 H), 3.04 (m, 2 H); upon standing in solution new absorptions appear, δ 5.04 (s) and 2.93 (m), at the expense of the original absorptions, indicating an isomerization phenomenon.

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.6; H, 5.30. Found: C, 52.8; H, 5.6.

2,4-Dimethoxy-3-oxabicyclo[3.2.0]hept-6-ene (2). A sample of 5.0 g of crude **3** was dissolved with warming in a mixture of 7 ml of triethylamine and 50 ml of water. This solution was added to 350 ml of pyridine in a water-jacketed electrolysis cell. The mixture was stirred and electrolyzed (platinum gauze electrodes) with an initial current of 0.8 A for 4–5 hr, after which time no additional current drop was noted. About 250 ml of pyridine was removed from the dark reaction solution by distillation at about 30 mm (pot temperature 50–55°). The concentrate was diluted with 400 ml of 5% aqueous nitric acid (mixture not acidic) and the solution was continuously extracted with ether overnight. The ether extracts were washed with 5% nitric acid until the washings were acidic, and then were washed with aqueous sodium bicarbonate solution. The dried organic layer was concentrated by distillation. The residue was evaporatively distilled (30 mm, pot temperature to 100°) to give 350 mg (10%) of **2** as a colorless to pale yellow liquid: mass spectrum *m/e* 155 (M − H)[15] 125 (M − OCH_3); nmr ($CDCl_3$, 90 MHz) δ 6.10 (t, 2 H, J = 0.6 Hz), 4.92 (s, 2 H), 3.45 (s overlapping multiplet, 8 H).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.5; H, 7.75. Found: C, 61.8; H, 7.9.

Acid Hydrolysis of 2. A mixture of 50 mg of **2** in 1 ml of 0.1 *N* $HClO_4$ was heated on a steam bath with shaking for 90 sec; the bright yellow solution was quickly cooled in ice and neutralized with sodium bicarbonate. The solution was extracted with 0.5 ml of $CDCl_3$. Nmr of the extracts showed no starting material and only absorptions attributable to *cis,trans*-muconic dialdehyde.[16] The $CDCl_3$ extract was dried and concentrated to an orange solid, mp 45–55°, which showed an ir spectrum identical with the published spectrum of *cis,trans*-muconic dialdehyde.[8] Recrystallized from ligroin, the material had mp 53–55° (lit.[8] mp 59°).

***cis*-Cyclobutene-3,4-dicarboxaldehyde bis(dimethyl acetal) (5).** A slurry of 2.28 g of **3** in 75 ml of methanol containing 1 drop of concentrated sulfuric acid was refluxed for 2 hr. The acid was neutralized with a small amount of solid sodium methoxide and the methanol removed under reduced pressure. The residue was dissolved in ether, filtered to remove a small amount of insoluble material, and the solvent was removed under reduced pressure. Upon standing, the oily residue partially recrystallized. A small amount of ether was added and the solid material was collected and washed with ether to give **8**, mp 140–144°: mass spectrum *m/e* 273 (M − H),[15] 243 (M − OCH_3); nmr ($CDCl_3$, 60 MHz) δ 4.98 (s, 2 H), 3.68 (s, 6 H), 3.41 (s, 6 H), 3.16 (m, 4 H). The ether filtrate was concentrated to an oil, which was evaporatively distilled (0.02 mm, pot temperature 150°) giving **7** as a viscous, colorless oil contaminated with a small amount of **8**. Mass spectrum *m/e* 305 (M − CH_3), 289 (M − OCH_3),[15] nmr ($CDCl_3$, 60 MHz) δ 4.55 (m, 2 H) 3.66 (s, 6 H), singlets at 3.34 and 3.30 obscuring multiplets (16 H).

A crude sample of **7** was refluxed 2 hr with aqueous sodium hydroxide. The resulting solution was stirred at room temperature with excess Amberlite IR-120 (H^+) ion-exchange resin and filtered. The resulting aqueous solution of bis(carboxylic acid) was neutralized with triethylamine and electrolyzed in pyridine exactly as described for the preparation of **2** above. Work-up as previously described and purification by preparative gas chromatography (5 ft × ¼ in., 5% SE-30 on Anakron ABS at 100°) gave **5** (5% overall from **3**) as a colorless liquid: mass spectrum *m/e* 171 (M − OCH_3),[15] 170 (M − CH_3OH); nmr ($CDCl_3$, 90 MHz) δ 6.12 (slightly broadened s, 2 H), 4.53 and 3.23 (4 H, AA'XX'), 3.39 (s, 6 H), 3.36 (s, 6 H).

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.4; H, 8.97. Found: C, 59.2; H, 9.1.

Acknowledgment. The author wishes to thank Mr. D. P. Maier and Dr. T. H. Regan of these laboratories for assistance in obtaining and interpreting mass spectral and nmr data, respectively.

Registry No.—**2,** 53042-82-3; **3,** 53042-83-4; **5,** 53042-84-5; **6,** 53042-85-6; **7,** 53042-86-7; **8,** 53042-87-8; maleic anhydride, 108-31-6; 2,5-dimethoxy-2,5-dihydrofuran, 332-77-4.

References and Notes

(1) This route is rendered even more attractive when one recalls that an analogous procedure represents a convenient method for the preparation of *cis*-cyclopropanedicarboxaldehyde.[2]
(2) G. Maier and T. Sayrac, *Chem. Ber.*, **101,** 1354 (1968).
(3) R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **98,** 3854 (1965).
(4) G. W. Griffin, A. F. Vellturo, and K. Furukawa, *J. Amer. Chem. Soc.*, **83,** 2725 (1961).
(5) Unfortunately, of course, this degradation study does not unequivocally establish the stereochemistry of **3** owing to the possible fortuitous isomerization of an all-cis structure during the acid hydrolysis. Although the gross stereochemistry of **3** was presumed trans, this question, in addition to the complicated question concerning the additional stereochemistry in **3** with respect to the dimethoxytetrahydrofuran ring, was not pursued further.
(6) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968); H. H. Westberg and H. J. Dauben, Jr., *Ibid.*, 5123 (1968).
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(8) M. Nakajima, I. Tomida, and S. Takei, *Chem. Ber.*, **92,** 163 (1959).
(9) Although the cis stereochemistry of **5** was not unequivocally established, the formation of *cis,trans*-muconic dialdehyde as the sole hydrolysis product substantiates this formulation.[10]
(10) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie, Academic Press, New York, N.Y., 1970.
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(12) R. Breslow and J. M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94,** 2111 (1972).
(13) A similar mechanism can be envisaged for the above-postulated acid-catalyzed ring opening of **1** and of the tetramethyl-*cis*-diacetoxycyclobutene.
(14) Melting points are uncorrected. Nmr spectra were determined on Varian T-60, Varian A-60, and Bruker HX-90 spectrometers. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Mass spectra were taken on a CEC 21-110B instrument. Gas chromatography was performed on a Varian Model 90-P instrument.
(15) Characteristic of tetrahydrofuran derivatives and acetals: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 6.
(16) J. A. Elvidge and P. D. Ralph, *J. Chem. Soc. C,* 387 (1966).

Reactions of Olefins with Bromine, *N*-Bromosuccinimide, and *N*-Bromoacetamide in Dimethyl Sulfoxide and Methanol

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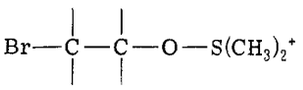
In the course of our studies on electrophilic addition of the elements of BrOH (NBS and H_2O) to olefins in dimethyl sulfoxide (DMSO), we became interested in the relative nucleophilicity of the DMSO molecule toward the intermediate bromonium ion. There are two studies in the literature which indicate that DMSO competes very favorably with other nucleophiles. In one of these studies, Dalton and coworkers[1] using isotope-labeling experiments showed that the bromonium ion is apparently opened exclusively by DMSO when an olefin is allowed to react with NBS in a mixture of DMSO and H_2O. In the other study, Torssell[2] examined the reactions of cyclohexene with $BrC(NO_2)_3$ in DMSO (with various ions present), and with Br_2 in DMSO, and observed in all cases that considerable solvent (DMSO) was incorporated. In neither case was a systematic study made of the nucleophilicity of DMSO. We proposed to do this.

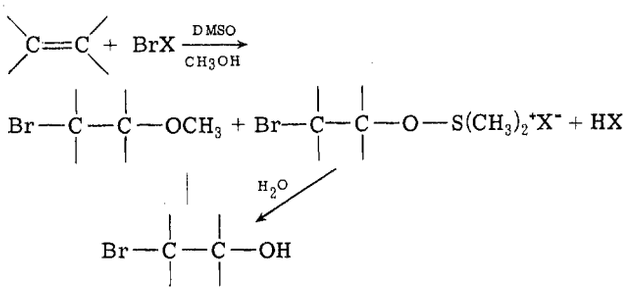
Both of these studies[1,2] provided evidence that solvent incorporation produced an intermediate sulfonium ion of the following structure



Results and Discussion

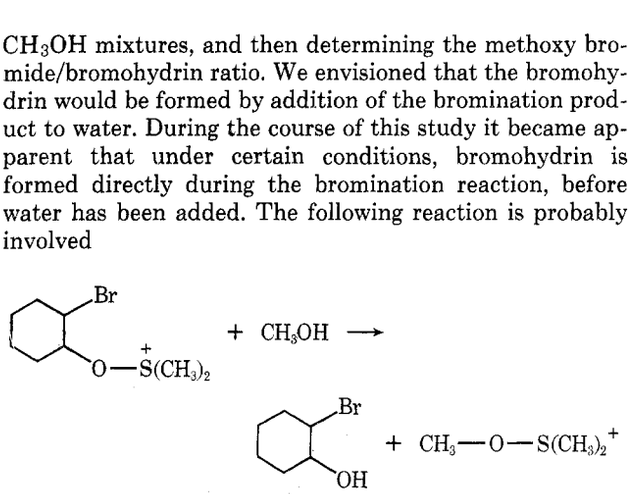
We proposed (Scheme I) to compare the nucleophilicities of DMSO and methanol by brominating olefins in DMSO–

Scheme I



X = bromide, succinimate, or acetamate

CH_3OH mixtures, and then determining the methoxy bromide/bromohydrin ratio. We envisioned that the bromohydrin would be formed by addition of the bromination product to water. During the course of this study it became apparent that under certain conditions, bromohydrin is formed directly during the bromination reaction, before water has been added. The following reaction is probably involved



Formation of bromohydrin by reaction of the sulfonium ion with methanol is important with NBS (and probably NBA), but not with Br_2 since a reasonably high temperature is required for this reaction,[3] and a sufficiently high temperature does occur with NBS and NBA. In order for Scheme I to be valid, it was necessary to establish that no methoxy bromide was formed by reaction of the intermediate sulfonium ion with methanol. To this end, sulfonium ion (**1**) was synthesized as previously reported,[2] and we