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]

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(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.

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(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]

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(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.

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

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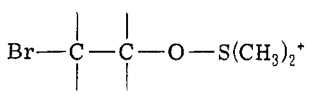
In the course of our studies on electrophilic addition of the elements of BrOH (NBS and H_2O) to olefins in dimethyl sulfoxide (DMSO), we became interested in the relative nucleophilicity of the DMSO molecule toward the intermediate bromonium ion. There are two studies in the literature which indicate 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

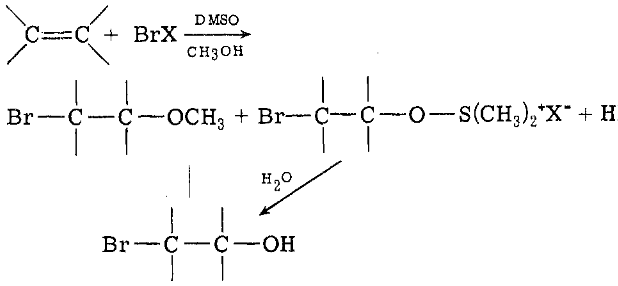


$$Br—C—C—O—S(CH_3)_2^+$$

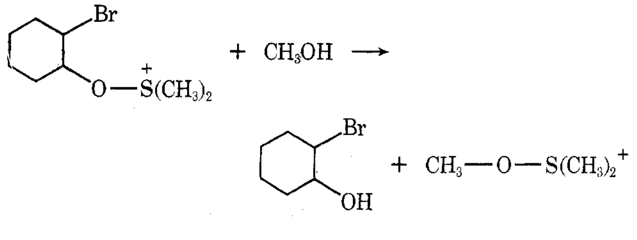
Results and Discussion

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

Scheme I



X = bromide, succinimate, or acetamate

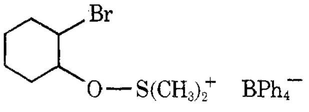


Formation of bromohydrin by reaction of the sulfonium ion with methanol is important with NBS (and probably NBA), but not with Br_2 since a reasonably high temperature is required for this reaction,[3] and a sufficiently high temperature does occur with NBS and NBA. In order for Scheme I to be valid, 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

Table I
Bromination of Olefins in Dimethyl Sulfoxide and Methanol

Entry	Reactants			Rel[g] reactivity	Products				Material[e] balance, %
	Hal,[a] concn[d]	Olefin, concn	CH_3OH/DMSO		Br,OH/Br,OCH_3	Br, OCH_3[b]	Br,OH[c]	DiBr	
1	NBS, 0.05	Styrene, 0.10	0.441	3.47	7.87	10.6	83.7	5.7	41.2
2	NBS, 0.10	Styrene, 0.05	0.441	3.80	8.62	8.6	74.1	17.3	66.8
3	NBA, 0.10	Styrene, 0.05	0.441	3.24	7.35	9.6	70.6	19.8	95.9
4	Br_2, 0.05	Styrene, 0.10	0.441	2.39	5.43	9.3	50.6	40.0	88.6
5	NBS, 0.09	Styrene, 0.045	1.77	2.15	1.22	37.0	45.3	17.7	101
6	NBS, 0.08	Styrene, 0.04	7.00	1.78	0.254	70.3	17.9	6.9	98.9
7	NBS, 0.05	Cyclohexene, 0.10	0.441	6.79	15.4	5.5	84.4	10.1	17.6
8	NBS, 0.10	Cyclohexene, 0.05	0.441	6.04	13.7	4.3	59.0	36.7	47.8
9	NBA, 0.10	Cyclohexene, 0.05	0.441	5.34	12.1	4.2	51.1	44.7	108
10	Br_2, 0.05	Cyclohexene, 0.10	0.441	2.69	6.10	3.9	23.7	77.3	103
11	NBS, 0.09	Cyclohexene, 0.045	1.00	3.36	3.36	14.7	49.4	35.9	56.0
12	Br_2, 0.45	Cyclohexene, 0.09	1.00	1.96	1.96	10.7	21.0	68.3	102
13[f]	Br_2, 0.45	Cyclohexene, 0.09	1.00	2.19	2.19	10.3	22.6	67.1	104
14	NBS, 0.09	Cyclohexene, 0.045	1.77	2.78	1.57	23.5	36.9	39.6	88.3
15	Br_2, 0.45	Cyclohexene, 0.09	1.77	1.82	1.03	17.9	18.4	63.7	113
16	NBS, 0.08	Cycloxene, 0.04	7.00	1.77	0.253	63.9	16.2	19.9	91.2

[a] Hal = halogenating agent. [b] Br,OCH_3 = methoxy bromide. [c] Br,OH = bromohydrin. [d] Concentrations are expressed as mole fractions. Ratios are computed on a molar basis. [e] Material balances are based on the olefin or halogenating agent (whichever is present in smallest amount). [f] Bromination was done from 45 to 50°. [g] The relative reactivity was obtained from the following expression: [(Br,OH/Br,OCH_3)(CH_3OH/DMSO)].



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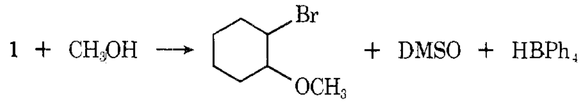
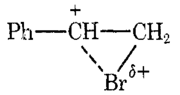
confirmed that the following reaction does not occur under our reaction conditions.



Furthermore, vpc analysis of a reaction mixture (resulting from olefin, solvents, and halogenating agent) indicated that the same amount of methoxy bromide was present before and after hydrolysis.

Table I contains data from the reactions of cyclohexene and styrene with NBS, NBA, and Br_2 in which the ratios of brominating agent to olefin and DMSO to CH_3OH are varied systematically. Under these conditions DMSO is observed to be *ca.* two to seven times more nucleophilic than CH_3OH. Although the relative reactivities do not vary greatly, some interesting observation can be made from these data. For example, the relative reactivities toward the intermediate bromonium ions (entries 4 and 10) when Br_2 is the electrophile are nearly identical, whereas with NBS and NBA (which react similarly, entries 2, 3 and 8, 9) the relative reactivity of DMSO increases (compared to Br_2) *ca.* 1.3 times with styrene and 2.2 times with cyclohexene.[4] This result suggests that NBS and NBA involve distinctly different brominating species than Br_2 and that the former do not brominate (at least primarily) *via* molecular Br_2.[5,6] An explanation for this difference in reactivity between these brominating agents may involve considerations of the intermediate ion pairs that result from the reactions of the brominating agents with the olefins. We anticipate that Br_2 would react *via* the bromonium ions (with bromide as the anion in the ion pair) shown below for styrene[7] (**2**) and cyclohexene (**3**), and that these reactive intermediates would show essentially the same relative reactivities toward DMSO and CH_3OH. However, since the ion pairs from NBS and NBA (succinimate and acetamate anions) would



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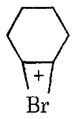

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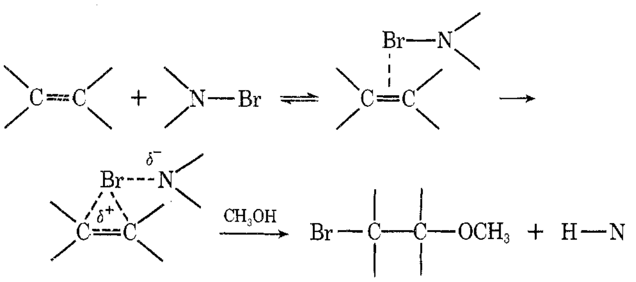
be of considerably higher energy than the ion pairs from Br_2, the former may not produce ion pairs at all, but may react with the nucleophile *via* a complex, as



The complexes would be less reactive than the bromonium ion and, therefore, the greater nucleophilicity of DMSO would be apparent.

The data also indicate that DMSO (with NBS and NBA) shows a lower relative reactivity with the complex from styrene than from cyclohexene. We interpret this to mean that greater carbonium ion character develops in the complex with styrene (because of the stability of the benzyl ration), and that the weaker nucleophile CH_3OH competes more favorably in this case than with the complex from cyclohexene.

Experimental Section

Reaction Conditions. To a well-stirred solution of the appropriate amount of DMSO, CH_3OH, and olefin (volume of the reaction *ca.* 60 ml) at 10° was added NBS (or NBA) as rapidly as possible with a spatula. After a brief induction period the temperature rose from 20 to 30°; stirring was continued for 15 min. The reaction was worked up by pouring the product into water and extracting it with ether.

Brominations with bromine were done in the same way with the exception that the bromine was added dropwise and the temperature was maintained at the indicated levels.

Vpc Analysis Conditions. The styrene reaction mixtures were analyzed on a 6 ft × 0.125 in. steel column packed with 2.5% SE-30 on 80–100 mesh DMCS Chromosorb with an oven temperature of 89° and a flow rate of 56 ml/min. The retention times (min) of the products were determined as follows: 1-methoxy-1-phenyl-2-bromoethane (8.5), 1-phenyl-2-bromoethanol (13.0), and 1,2-dibromo-1-phenylethane (15.7).

The cyclohexene reaction products were analyzed on a 6 ft × 0.125 in. steel column packed with 2.5% DNP at 75° and a flow rate of 60 ml/min. The retention times (min) of the products were determined as follows: *trans*-1-bromo-2-methoxycyclohexane (6.3), *trans*-2-bromocyclohexanol (8.6), and *trans*-1,2-dibromocyclohexane (13.9).

Percentages of products and material balances were determined by using *p*-dichlorobenzene as an internal standard.

Product Identification. Styrene dibromide was prepared by addition of bromine to styrene. The other products were synthesized as follows. **1-Methoxy-1-phenyl-2-bromoethane** (bp 57° (0.40 mm), lit.[8] 117–118° (15 mm), structure also confirmed by ir) and ***trans*-1-bromo-2-methoxycyclohexane** were prepared according to the procedure of Iovchev.[9] **1-Phenyl-2-bromoethanol** was synthesized (three different ways) by the procedures of Dalton, *et al.*[1] (bp 90° (0.3–0.5 mm)), Guss and Rosenthal[10] (82° (0.4 mm)), and by reduction of phenacylbromide with $NaBH_4$ (bp 84, 85° (0.4 mm)). Only the latter procedure afforded a product which was free of carbonyl absorption in its ir spectrum. ***trans*-2-Bromocyclohexanol** was synthesized as reported by Dalton, *et al.*[1] ***trans*-1-Dibromocyclohexane** was prepared by the bromination of cyclohexene in pentane (bp 47° (0.8 mm), $n^{25}\text{D}$ 1.5497; lit.[11] bp 145–146 (100 mm), $n^{25}\text{D}$ 1.5495).

A Summary of the Studies on the Intermediate Sulfonium Ion. The DMSO that was used in our study always contained a trace of water (as determined by vpc). We established, however, that this trace of water did not hydrolyze sulfonium ion (1) even after standing for hours. Addition of sufficient water to the mixture caused rapid conversion to the corresponding bromohydrin.

Early in this study we experienced considerable difficulty on direct vpc analysis of a DMSO–1 mixture since 1 decomposed in the injection port to produce the corresponding bromohydrin. We found that decomposition in the injection port could be avoided if the DMSO solution of 1 was mixed with THF before injection. Apparently THF caused instant volatilization in the injection port and did not permit the sulfonium salt to fall on the hot injection port and decompose.

We observed that methanol (in DMSO) does not react with 1 at 10°, however, when this mixture was heated at 50°, 1 was rapidly converted to the bromohydrin.

We confirmed that the sulfonium ion (with Br^- as the anion) is an intermediate in the bromination (Br_2) of cyclohexene in DMSO in the following manner. Vpc analysis of the reaction product resulting from the addition of Br_2 to cyclohexene in DMSO showed that no bromohydrin was present. Analysis after addition of water to this mixture indicated that bromohydrin was now present.

Stability of the Products to the Reaction Condition. We confirmed that all of the products of the bromination reactions (the bromohydrins, methoxy bromides, and dibromides) did not react further with the solvents or with each other.

Acknowledgment. Support for this work was provided by the Research Corporation and the Petroleum Research Fund, administered by the American Chemical Society.

Registry No.—NBS, 128-08-5; NBA, 79-15-2; Br_2, 7726-95-6; dimethyl sulfoxide, 67-68-5; methanol, 67-56-1; styrene, 100-42-5; cyclohexene, 110-83-8.

References and Notes

(1) D. R. Dalton, V. P. Dutta, and D. C. Jones, *J. Amer. Chem. Soc.*, **90**, 5498 (1968).

(2) K. Torssell, *Acta Chem. Scand.*, **21**, 1 (1967).

(3) Torssell[2] has shown that this reaction does take place at higher (~50°) solvent temperature. We have shown that it does not occur, or is very slow, at lower temperature (~10°).

(4) These values were obtained by averaging entries 1, 2, 3 and 7, 8, 9 and comparing the averages to the corresponding result with Br_2.

(5) Dalton, *et al.* (ref 1), question the nature of the brominating agent when NBS is used in DMSO; they conclude that Br_2 may be involved. Our results indicate that Br_2 is not the principal source of positive bromine under these conditions.

We do assume that some Br_2 is involved, however, since dibromides are formed. The Br_2 probably results from the reaction of HBr and NBS; bromination of the solvent (DMSO) by NBS may produce the HBr. We have established that the dibromides do not result from direct reaction between HBr and the intermediate sulfonium ion. Also, sodium bromide did not react with **1** in DMSO to give dibromide. We have no explanation for the fact that more dibromides are formed with cyclohexene than styrene.

(6) It occurred to us that conceivably the difference in relative reactivity ratio between Br_2 and NBS could result from decomposition of NBS to Br_2 at the higher reaction temperature (the temperature rises from *ca.* 10 to 40° during the NBS reactions), and addition of Br_2 to olefins at this higher temperature might give a higher Br,OH/Br,OCH_3 ratio. This does not seem to be the case, however, since brominations at 5–10° (entry 12) and 45–50° (entry 13) gave very similar results.

(7) We assume that bromonium ion **2** has unsymmetrical bridging between the bromine and the benzylic carbon. (See R. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1968).)

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