with $CHCl_3$ gave an additional 0.23 g (39%) of **6b**: mp 195–197° dec. The total yield obtained by this procedure was 0.37 g (63%).

Oxidation of 7-Chloro-3-cyano-2-methoxy-1H-indene (4c).—Upon being heated with CrO_3 (2 equiv) and worked up in a manner similar to the preceding experiment (procedure C), **4c** gave a 48% yield of 6-chlorohomophthalic acid (**6c**). Recrystallization from water gave colorless crystals: mp 174–176° with gas evolution; ir (KCl) 1680 cm^{-1} (aromatic COOH), 1705 cm^{-1} (aliphatic COOH). This product was identical with the authentic sample of **6c** prepared from *o*-chlorophenylacetic acid (see below) and the mixture melting point was not depressed.

Anal. Calcd for $C_9H_7ClO_4$: C, 50.36; H, 3.28. Found: C, 50.34; H, 3.01.

5-Chloro-1-thio-1,2,3,4-tetrahydro-1,3(2H,4H)-isoquinolinedione.—A mixture of *o*-chlorophenylacetyl chloride[21] (8.6 g, 0.046 mol), PbSCN (14.7 g, 0.046 mol), and 18 ml of benzene was refluxed with stirring for 5 hr, then filtered twice, and evaporated under reduced pressure. Short-path distillation of the residue gave 8.1 g (84%) of almost colorless liquid: bp 107–110° (0.25 mm); ir (KCl) 1730 cm^{-1} (C=O), 1980 cm^{-1} (broad, SC≡N). A solution of this *o*-chlorophenylacetyl isothiocyanate (8.0 g, 0.038 mol) in 10 ml of CS_2 was added dropwise to a stirred suspension of $AlCl_3$ (11.1 g, 2.2 molar equiv) in 30 ml of CS_2, while cooling in an ice bath. When addition was complete, the mixture was refluxed for 5 hr, then cooled in ice, and treated with 12 ml of 1 *N* HCl. The brown reaction product was broken up with a spatula to give a bright orange solid, which was filtered off and washed with water. Crystallization from glacial AcOH gave several crops of bright orange product (total 3.6 g, 45%): mp 247–250° dec. The analytical sample had mp 250–252° dec.

Anal. Calcd for C_9H_6ClNOS: C, 51.07; H, 2.86; N, 6.62. Found: C, 50.77; H, 2.90; N, 6.37.

6-Chlorohomophthalic Acid (6c).—5-Chloro-1-thio-1,2,3,4-tetrahydro-1,3(2H,4H)-isoquinolinedione (1.0 g, 0.0047 mol) was hydrolyzed with 40 ml of 40% KOH under reflux for 2.5 days in a flask of alkali-resistant glass. After being left at room temperature for 3 days, the mixture was refluxed an additional 6 hr, then cooled, acidified with HCl, diluted with water to dissolve the precipitated inorganic material, and extracted twice with ether. Evaporation of the dried ether extract gave 0.68 g (67%) of crude light yellow product: mp 157° with gas evolution. Crystallization from water afforded a small first crop of malodorous material probably containing sulfur. Extraction of the filtrate with ether gave light yellow material: mp 167–169° with gas evolution. Recrystallization from glacial AcOH gave pure **6c** as a white powder: mp 172–174° (gas evolution). The infrared spectra of this material and of the product obtained from the oxidation of **4c** were identical, and a mixture melting point was not depressed.

Registry No.—**1b**, 22479-38-5; **1c**, 22479-39-6; **2b**, 22479-41-0; **2c**, 22528-32-1; **3b**, 22479-42-1; **3c**, 22479-43-2; **4b**, 22479-44-3; **4c**, 22479-45-4; **5a**, 22479-46-5; **5b**, 22482-73-1; **6c**, 22482-74-2; 5-chloro-1-thio-1,2,3,4-tetrahydro-1,3(2H,4H)-isoquinolinedione, 22482-75-3; α,α'-dibromo-3-chloro-*o*-xylene, 22479-40-9.

Acknowledgments.—The laboratory assistance of Mrs. Josephine Battaglia and Mrs. Rebecca G. Stephenson is gratefully acknowledged. The authors are also indebted to Mr. Roger Cavallo and Mr. Chester Rosansky for the determination of infrared spectra.

(21) L. R. Cerecedo and C. P. Sherwin, *J. Biol. Chem.*, **58**, 215 (1923).

The Bromination of Butadiene in Methanol

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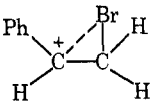
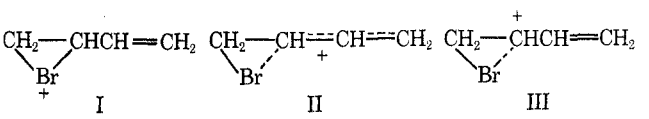
Recent studies[1,2] on the bromination of styrene and substituted styrenes suggest that the intermediates in these reactions are best described as unsymmetrically bridged bromonium ions with weak bonding between the bromine atom and the benzylic carbon atoms, as is illustrated below for styrene. Failure to achieve a



symmetrically bridged bromonium ion in these reactions is undoubtedly due to increased stabilization of the carbonium ion system by the phenyl ring. On the other hand, the bromonium ion involved in bromination of *cis*- and *trans*-2-butene was shown to involve symmetrical bridging.[2]

In the course of our studies on the bromination of dienes, we became interested in the nature of the bonding in the intermediates in these reactions. In the addition of bromine to butadiene, at least three charge distributions could be involved. Their structures are shown below. Intermediate I is a bromonium



ion with symmetrical bridging. Intermediate II represents the charge as highly delocalized across the bromine atom and the adjacent allylic system. Intermediate III shows the charge as essentially localized on the secondary carbonium ion. This intermediate should assume increasing importance as the polarity of the solvent becomes greater. In this regard, Rolston and Yates[2] and Buckles, Miller, and Thurmaier[3] have shown that, in the bromination of substituted styrenes and stilbenes, respectively, the charge becomes localized to form the most stable carbonium ion as the polarity of the solvent is increased.

It seemed to us that bromination in methanol might permit differentiation between these intermediates. Intermediate I should be attacked by the methanol molecule[4] at either carbon atom of the bromonium ion to give both 4-bromo-3-methoxy-1-butene (**1**) and 3-bromo-4-methoxy-1-butene (**2**). Intermediate II should lead to significant quantities of 1-bromo-4-methoxy-2-butene (**3**), presumably the *trans* isomer, by attack at the terminal carbon atom of the allylic system; **1** and perhaps some **2** would also be expected. Attack by methanol on III should give primarily **1**. All of the intermediates could give **3** by a S_N2' attack by methanol on the terminal carbon atom of the allylic system.

Formation of 3,4-dibromo-1-butene (**4**) and *trans*-1,4-dibromo-2-butene (**5**) would be expected.

Results and Discussion

The results in Table I show that, of the methoxybromides, 4-bromo-3-methoxy-1-butene (**1**) is the prin-

(1) R. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1968).

(2) J. H. Rolston and K. Yates, *ibid.*, **91**, 1469 (1969); J. H. Rolston and K. Yates, *ibid.*, **91**, 1477 (1969); J. H. Rolston and K. Yates, *ibid.*, **91**, 1483 (1969).

(3) R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, **32**, 888 (1967).

(4) It is possible that the weakly nucleophilic solvent might not open this bromonium ion (I). In that case, the product would be exclusively the dibromides.

TABLE I
BROMINATION OF BUTADIENE IN METHANOL AT −15°

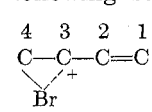
Butadiene, mole fraction	Methoxybromides, % 1	3	Ratio of 1/3	Dibromides, % 4	5	Ratio of 4/5	Yield, %
0.02	63	4.3	15	22	10	2.2	98
0.05	45	3.2	14	35	16	2.2	
0.07	34	3.9	8.7	42	20	2.1	
0.10	28	3.1	9.0	48	21	2.3	57
0.15	23	3.2	7.2	48	24	2.0	
0.20	21	2.3	9.1	51	25	2.0	
0.35	12	1.2	10	52	34	1.5	
0.50	13	1.3	10	53	33	1.6	67
0.02[a]	55	4.1	13	26	14	1.9	
0.50[a]	6.8	0.5	14	52	42	1.2	
0.02[b]	60	3.7	16	23	14	1.6	
0.50[b]	7.9	0.6	13	53	38	1.4	

[a] Oxygen was passed through the reaction solution. [b] The radical inhibitor, 2,6-di-*t*-butyl-4-methylphenol, was added to the reaction solution.

cipal product. A small amount of *trans*-1-bromo-4-methoxy-2-butene (**3**) was also formed;[5] no 3-bromo-4-methoxy-1-butene (**2**) was detected. Evidence for the absence of **2** is explained in the Experimental Section. As far as the dibromides are concerned, approximately twice as much **4** as **5** is formed under under all conditions.

Before the mechanism of these reactions can be discussed from an ionic standpoint, it is essential that the possibility of a radical pathway be eliminated. It has already been shown[6] that a 1,2 to 1,4 ratio of *ca.* 2 in the bromination and chlorination of butadiene is indicative of an ionic mechanism. From this standpoint, it seems that the addition of bromine to butadiene in methanol is following an ionic pathway at all mole fractions of butadiene. This viewpoint is supported by the fact that the radical inhibitors, oxygen and 2,6-di-*t*-butyl-4-methylphenol, did not substantially alter the ratio of **4**/**5**. However, it should be pointed out that addition of ethylbenzene, as a radical scavenger, to the reaction mixtures led to some α-bromoethylbenzene at all the mole fractions except 0.02. We have interpreted these data to mean that only at a mole fraction of 0.02 is an ionic pathway followed completely; at higher mole fractions ac ertain amount of radical reaction accompanies the principal ionic reaction. For this reason, and also because of the improved yield, all mechanistic considerations will be confined to the data which were obtained at a mole fraction of 0.02.

The almost exclusive formation of 4-bromo-3-methoxy-1-butene (**1**) over **2** or **3** seems to indicate that the intermediate involved in this reaction is best described by III, with, perhaps, slight delocalization of the charge across the allylic system. A comparison of the ratios **1**/**3** and **4**/**5** shows that the bromide ion (or tribromide ion) is much more effective at attacking position 1 (see the following structure) than is the



methanol molecule. One explanation for this observation might be that the larger bromide ion experiences severe steric hindrance when attacking at position 3 and therefore chooses position 1. Another more likely explanation involves considerations of intermediate III and the relative nucleophilic abilities of the methanol molecule and the bromide ion. In intermediate III, nucleophiles can either react with the carbonium ion at position 3 or attack position 1 by an SN2′ reaction. Since the bromide ion is a strong nucleophile, it readily reacts with position 1 by the SN2′ pathway. Methanol, on the other hand, is a weak nucleophile and reacts almost completely with the carbonium ion.

Experimental Section

Materials.—All solvents and reagents were obtained commercially in high purity unless otherwise indicated. The butadiene was Matheson Coleman and Bell instrument grade, 99.5% pure.

Bromination. General Procedure.—Liquefied butadiene was added to the determined quantity of methanol, on a balance, until the appropriate weight was obtained. The reaction solution has a magnitude of 80–100 ml. To this solution at −15°, under a nitrogen atmosphere, bromine was added dropwise until 10–20% of the butadiene had been allowed to react. The reaction product was poured into cold water (*ca.* 100 ml), sodium carbonate was added to destroy the HBr, and sufficient sodium chloride was added to saturate the solution and salt out the products. This solution was then extracted with 300–600 ml of low-boiling petroleum ether, in three portions. It was established that no rearrangement of the dibromides occurred during the reaction or isolation. It was also established that under the reaction and isolation conditions the dibromides did not solvolyze to give the methoxybromides.

All brominations were carried out in a dark room with a photographic safelight.

Procedure for Analysis of Products.—The vpc analyses of the products were accomplished with an Aerograph Model 90 P-3 chromatograph and an F & M Model 700 chromatograph. The conditions for analysis for the former instrument follow: flow rate (He), 334 ml/min; column dimensions, 6 ft × 0.25 in.; column temperature, 60°; column composition, 2.5% SE-30 on 60–80 mesh DMCS Chromosorb W. Under these conditions, the retention times of **1**, **3**, **4**, and **5** are, respectively, 45, 111, 72, and 189 sec. The conditions for analysis in the latter instrument follow: flow rate (He), 55 ml/min; column dimensions, 8 ft × 0.125 in.; column composition, identical with that given above. The retention times of **1**, **3**, **4**, and **5** are, respectively, 54, 132, 84, and 234 sec.

None of the products rearranged under the conditions of analysis. This was determined by collecting the product after it had passed through the chromatograph and observing that no change in composition had occurred on reinjection.

(5) *cis*-1-Bromo-4-methoxy-2-butene was synthesized unambiguously, and shown by vpc analysis to be absent in the bromination products.

(6) M. Poutsma [*J. Org. Chem.*, **31**, 4167 (1966)] has already discussed the variation in the ratio of 1,2 to 1,4 addition with a change in mechanism in the chlorination of butadiene. We have found that this ratio varies in nearly an identical manner in the bromination of butadiene. An article on our investigation has been accepted for publication in a forthcoming issue of this journal.

The percentages of the compounds were based on their adjusted areas in the chromatograms. The adjustments were based on the following determinations: the ratio of A_4/A_5 divided by W_4/W_5 is equal to 0.85; A_1/A_5 divided by W_1/W_5 is equal to 1.23; and A_3/A_5 divided by W_3/W_5 is equal to 1.18. The material balances were obtained by the internal-standard method using α-bromoethylbenzene. The area/weight ratio for α-bromoethylbenzene to **5** was found to be 1.30.

Identification of the Products Formed in the Bromination of Butadiene in Methanol.—The chromatogram of the product from the bromination of butadine in methanol showed four peaks. The second and fourth peaks were identified as **4** and **5**, respectively, on the basis of having retention times and ir spectra identical with those of the authentic isomers, which were synthesized according to the procedure of Hatch, *et al.*[7]

The first peak was assigned to 4-bromo-3-methoxy-1-butene (**1**) on the following basis. The bromination product was fractioned and the compound responsible for the first peak was isolated in pure form, bp 51–52° (30 mm), as indicated by vpc analysis. The compound gave the correct analysis for a bromomethoxybutene, C_5H_9BrO. *Anal.* Calcd for C_5H_9BrO: C, 36.39; H, 5.497; Br, 48.43. Found: C, 36.27; H, 5.57; Br, 48.69. The infrared spectrum[8] indicated either **1** or **2**, since it contained the hydrogen absorption band for the CH_3O group at 2810 cm^{-1} and the terminal vinyl absorption band at 928 and 985 cm^{-1}. The nmr spectrum was complex, but supported the structure of **1** or **2** by showing relative areas of three vinyl hydrogens to six methyl, methylene, and methine hydrogens. The compound was assigned the structure of 4-bromo-3-methoxy-1-butene (**1**) rather than 3-bromo-4-methoxy-1-butene (**2**) on the basis of stability. Heating the compound for 45 min at 115° gave no detectable rearrangement to *trans*-1-bromo-4-methoxy-2-butene (**3**), which would definitely be expected[9] if the compound were **2**.

trans-1-Bromo-4-methoxy-1-butene (**3**) was synthesized unambiguously, and when analyzed by vpc was found to have a retention time identical with that of the third peak. The synthesis of **3** is outlined in the following sequence.

trans-1,4-dibromo-2-butene $\xrightarrow[\text{HOAc}]{\text{KOAc}}$

trans-2-butene 1,4-diacetate $\xrightarrow{\text{Ba(OH)}_2}$ bp 73–75° (0.30 mm)

trans-2-butene 1,4-diol $\xrightarrow{(CH_3O)_2SO_2}$ bp 92–97° (0.25 mm)

trans-4-methoxy-2-buten-1-ol $\xrightarrow{PBr_3}$ bp 76–79° (3.3 mm)

trans-1-bromo-4-methoxy-2-butene bp 51° (4.1 mm)

The infrared spectrum of each of the intermediates in the above synthetic sequence supported the proposed structure. The infrared spectrum of the synthesized **3** showed the following absorption bands:[7] 2810 (hydrogens of the CH_3O group), 965 (*trans* vinyl hydrogens, strong), and 572 and 595 cm^{-1} (CBr group). The molecular analysis corresponded to C_5H_9BrO. *Anal.* Calcd for C_5H_9BrO: C, 36.39; H, 5.497; Br, 48.43. Found: C, 36.43; H, 5.63; Br, 48.19.

(7) L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1956).

(8) For a discussion of the position of absorption bands in the infrared, see D. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry," McGraw-Hill Publishing Co. Ltd., London, 1966.

(9) For a general discussion of the greater thermodynamic stability of 1,4- compared with 1,2-addition products from the chlorination and bromination of butadiene and isoprene, see B. T. Brooks, "The Chemistry of the Nonbenzenoid Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1950, p 362–366. In support of our assignment of structure **1** to this compound rather than **2** on the basis of stability, we would like to indicate that, under identical conditions, **4** rearranges to **5**. Also, under nearly identical conditions, 3,4-dibromo-2-methyl-1-butene rearranges extensively. [See V. L. Heasley, C. L. Frye, R. T. Gore, Jr., and P. S. Wilday, *J. Org. Chem.*, **33**, 2342 (1968).] We also observed that, upon standing, *cis*-1-bromo-4-methoxy-2-butene slowly rearranges to *trans*-1-bromo-4-methoxy-2-butene (**3**). Only a trace of what may be 3-bromo-4-methoxy-1-butene (**2**) was detected. This definitely confirms the greater thermodynamic stability of **3** compared with **2**.

Registry No.—Butadiene, 106-99-0; *trans*-2-butene 1,4-diacetate, 1576-98-3; *trans*-2-butene-1,4-diol, 821-11-4; *trans*-4-methoxy-2-buten-1-ol, 22427-04-9; **1**, 22427-00-5; **3**, 22427-01-6.

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Conformation of Bicyclo[3.3.1]nonane Systems. A Semiempirical Investigation

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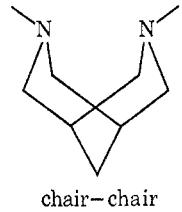
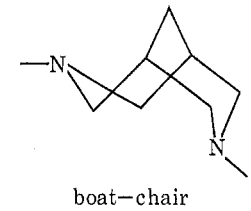
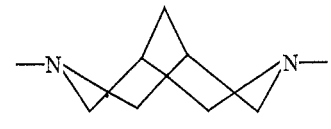
The structures of compounds belonging to the ring system bicyclo[3.3.1]nonane have been the subject of considerable interest in recent years.[1–6] Apart from various distorted structures, these species may exist in any of the following three conformations, all of which are free from bond-angle strain. In most of the cases studied thus far, the chair–chair structure with various degrees of distortion seem to be favored. Thus Brown,



chair–chair

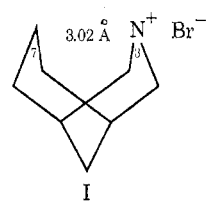


boat–chair

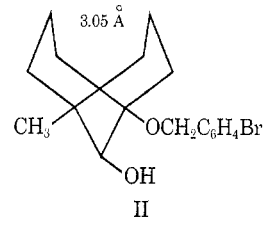


boat–boat

et al.,[2] and Dobler, *et al.*,[3] by their X-ray crystallographic studies, proved the chair–chair structures for compounds I and II with C_3–C_7 and N_3–C_7 distances of 3.05 and 3.02 Å, respectively. Douglass and Ratliff[1]



I



II

synthesized N,N′-dimethylbispidine and, based on dipole moment and nmr studies, tentatively assigned a flattened chair–chair structure for this compound.

(1) J. E. Douglass and T. B. Ratliff, *J. Org. Chem.*, **33**, 355 (1968).

(2) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

(3) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta.*, **47**, 695 (1964).

(4) C.-Y. Chen and R. J. W. LeFevre, *J. Chem. Soc., B*, 539 (1966).

(5) H. S. Aaron, C. P. Ferguson, and C. P. Rader, *J. Amer. Chem. Soc.*, **89**, 1431 (1967).

(6) N. W. J. Pumphrey and M. J. T. Robinson, *Chem. Ind.* (London), 1903 (1963).