$k_{-1}[H^+] > k_2$. Thus, the value of k_{-1} must also be large; from the pH at which the change in rate-determining step occurs this rate constant may be estimated to be on the order of $10^9\ M^{-1}\ sec^{-1}$. These rate constants are of the magnitude expected for diffusion-controlled reactions[8] and raise the possibility that the $k_{-1} - k_1$ step might represent a diffusion-controlled proton transfer. A rate-determining proton-transfer step of this kind should exhibit general acid-base catalysis with Bronsted β values of 0 or 1.0 when the acidities of the proton donors and acceptors are sufficiently different.[8,9] The value of β for the hydrolysis of ethyl trifluorothiolacetate[2] is approximately 0.3, which means either that this hypothesis does not hold for this ester or that the observed catalytic constants represent a curved portion of the Bronsted plot. In any case, the calculations serve to emphasize the high reactivity, low stability, and short lifetime of the addition intermediate even for the hydrolysis of thiol esters of trifluoroacetate; the line between the usual type of intermediate and a series of incompletely defined way stations along the reaction coordinate at which proton transfer may occur becomes increasingly hard to draw for these reactions.

Experimental Section

Ethyl S-trifluoroacetylmercaptoacetate [bp 106–107° (60–65 mm); ir 1709, 1739 cm^{-1} in acetonitrile, λ_{max} 242 $m\mu$ in water] was synthesized[2] from ethyl mercaptoacetate and trifluoroacetic anhydride at 0°. Phenyl thioformate[10] [bp 73–75° (1.5 mm); ir 1682, 782, 728 cm^{-1} in acetonitrile; λ_{max} 230 $m\mu$ in water, 236 $m\mu$ in hexane] was prepared from benzenethiol and the mixed anhydride formed from formic acid and ethyl chloroformate.[11] Pseudo-first-order rate constants for the hydrolysis of these esters were determined spectrophotometrically as described previously.[12] Good first-order kinetics were observed for at least two half times and the total change in absorbance was approximately the same at all pH values.

Registry No.—I, 20104-50-1; phenyl thioformate, 20104-51-2.

[8] M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

[9] R. Barnett and W. P. Jencks, *J. Amer. Chem. Soc.*, **90**, 4199 (1968); **91**, 2358 (1969).

[10] G. A. Olah and S. J. Kuhn, *ibid.*, **82**, 2380 (1960).

[11] T. Wieland and H. Köppe, *Ann. Chem.*, **581**, 1 (1953).

[12] W. P. Jencks and J. Carriuolo, *J. Amer. Chem. Soc.*, **82**, 675 (1960).

Ionic and Radical Reactions in the Bromination of Butadiene

VICTOR L. HEASLEY AND STEPHEN K. TAYLOR

Department of Chemistry, Pasadena College, Pasadena, California 91104

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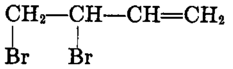
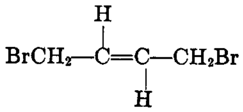
While continuing our studies on the bromination of dienes,[1] we became concerned that previous reports[1,2] which proposed ionic mechanisms in the bromination of dienes may have overlooked a possible radical component to these reactions. This concern was intensified by a report by Poutsma[3] confirming a radical route in the chlorination of butadiene at high diene concentrations. Therefore, we decided to reinvestigate the bromination of butadiene. The structures of the three possible dibromide products in this reaction are shown.



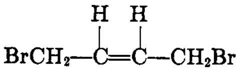
$CH_2Br-CHBr-CH=CH_2$

3,4-dibromo-1-butene (1)



$BrCH_2-CH=CH-CH_2Br$

trans-1,4-dibromo-2-butene (2)



$BrCH_2-CH=CH-CH_2Br$

cis-1,4-dibromo-2-butene (3)

Results and Discussion

Treatment of butadiene at various concentrations in carbon tetrachloride with bromine gave **1**, **2**, and **3** in the quantities indicated in Table I. The formation of **3** was not previously reported in the bromination of butadiene. The percentages of the dibromides were determined by vpc analysis. The material balances were obtained by the internal standard method using *p*-dichlorobenzene.

TABLE I

ADDITION OF BROMINE TO BUTADIENE UNDER VARIOUS CONDITIONS

Mole fraction of butadiene	% of 1	Yield, %
	Nitrogen, Safelight, − 15°	
0.020	60	
0.032	60	
0.045	56	100
0.067	51	100
0.11	45[a]	
0.39	21	100
1.0	21	
	Nitrogen, Illuminated, −15°	
0.020	58	
0.045	52	80
0.067	45[a]	
0.10	34	
0.14	21	85
1.0	23	
	Nitrogen, Safelight, 25°	
0.045	56	
0.10	45[a]	
0.18	37	
0.30	24	
	Nitrogen, Illuminated, 25°	
0.032	41[a]	
0.045	31	
0.10	21	85

[a] Dibromide **3** first appears here in trace amounts and increases with increasing concentration of butadiene until it becomes approximately 4% at complete radical conditions.

The results in Table I show that at −15° the percentages of **1** vary from approximately 60% at low concentrations of butadiene to approximately 20% at

[1] For previous paper, see. V. L. Heasley, C. L. Frye, R. T. Gore, Jr., and P. S. Wilday, *J. Org. Chem.*, **33**, 2342 (1968).

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

[3] M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966).

high concentrations of butadiene, both under safelight and illumination. The percentages of **1** and **2** (under safelight) are remarkably similar to the percentages of 3,4-dichloro-1-butene and *trans*-1,4-dichloro-2-butene reported by Poutsma[3] for the chlorination of butadiene. Poutsma[3] also observed that when the percentage of 3,4-dichloro-1-butene is high (*ca.* 60%), the reaction is following an ionic pathway. Conversely, when the percentage of 3,4-dichloro-1-butene is low (*ca.* 20%), a radical mechanism is operative.

These relationships also seem to apply to the bromination of butadiene under safelight at −15°, where we have determined that bromination of butadiene at low concentrations leads to **1** and **2** by an ionic pathway, whereas **1**, **2**, and small amounts of **3** are formed by a radical mechanism at high concentrations of butadiene. These conclusions are based on the following observations: (1) significant quantities of α-bromoethylbenzene are formed from ethylbenzene[4] and butadiene where the concentration of the latter is high, and the amount of α-bromoethylbenzene decreases with decreasing concentration of butadiene to become a mere trace (see Table II); and, (2) where the percentage of **1** is low, suggesting a radical reaction, it can be significantly increased by the addition of the radical inhibitor, 2,6-di-*t*-butyl-4-methylphenol (see Table III).

TABLE II

RELATIVE REACTIVITIES AT −15°

Mole fraction of butadiene and ethylbenzene[a]	Relative Reactivities	
	Safelight	Illumination
0.50	100	60
0.40	155	42
0.25	500	64
0.10	2000	5
0.032	[b]	161

[a] Where necessary, carbon tetrachloride was added to give a mole fraction of 1. [b] No α-bromoethylbenzene was detected at these conditions. When the mole fraction of ethylbenzene was increased to 0.968 (for butadiene, $n = 0.032$) a trace of α-bromoethylbenzene was detected.

TABLE III

EFFECT OF THE INHIBITOR AT −15°

Mole fraction of butadiene	Concentration, *M*, of the inhibitor	Percentage of 1	
		Safelight	Illumination
0.18	0.16		38
0.18	0.91		40
0.39	0.18	34	
0.39	0.46	39	

The results of bromination under illumination (−15°) are more difficult to understand. Assuming that a high percentage of **1** indicates an ionic reaction, then the results in Table I would suggest that an ionic reaction occurs at low concentrations of butadiene, even under illumination, and that the mechanism becomes completely radical at a mole fraction of approximately 0.13. However, the relative reactivities in Table II indicate that under illumination the reaction is following a radical course under all concentrations of butadiene. We are unable to explain this apparent anomaly, except to say that we have more confidence in the validity of the results indicating an ionic mechanism than in the relative reactivity results from ethylbenzene.[5]

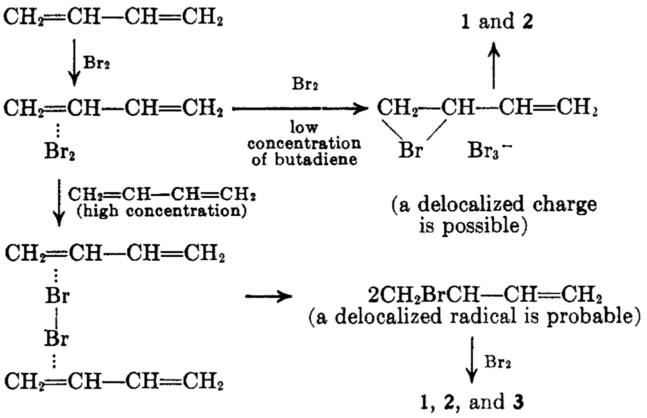
The results from the bromination of butadiene at room temperature under safelight and illumination are similar to those at −15° (Table I) with the exception that the reaction assumes a radical pathway at a lower concentration of butadiene.

The formation of *cis*-1,4-dibromo-2-butene (**3**) should be noted. As reported in Table I, **3** was observed only under radical conditions.

Table I shows that the earlier study of the bromination of butadiene by Hatch, *et al.*,[2] was carried out under essentially ionic conditions (*ca.* $n = 0.1$). Our investigation of isoprene[1] was undoubtedly in the ionic range since the concentration of isoprene was low (*ca.* $n = 0.1$).

A possible explanation for the change in mechanisms with a change in concentration of butadiene is suggested in Scheme I. These equations would seem to be general for the bromination of any linear[6] diene.

SCHEME I



Experimental Section

Materials.—Unless otherwise indicated, the solvents and reagents were obtained commercially in high purity. The butadiene was Matheson's instrument grade, 99.5%. α-Bromoethylbenzene was prepared by bromination of ethylbenzene in the presence of sunlamp illumination. The product had the following physical constants: bp 88° (15 mm), $n^{20}\mathrm{D}$ 1.5615. The reported values[7] are bp 86–88° (15–16 mm), $n^{20}\mathrm{D}$ 1.5612.

Bromination. General Procedure.—Butadiene was dissolved in carbon tetrachloride to give a solution of approximately 10 ml. To this solution, under the selected conditions, bromine was added until 10–20% of the butadiene had reacted. The resulting solution was then analyzed immediately by vpc.

The concentration of butadiene was determined by adding liquefied butadiene to the determined quantity of solvent, on a balance, until the appropriate weight was obtained. At 25°, and at high mole fractions of butadiene, some evaporation oc-

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[4] Ethylbenzene was used rather than cyclohexane because the selective bromine atom preferred addition to butadiene exclusively over abstraction of a hydrogen atom from cyclohexane. It was confirmed that under the reactions conditions of safelight (−15°), ethylbenzene did not react directly with bromine. Toluene was not employed in the study because its bromination product, benzyl bromide, had the same retention time as **2**.

[5] Ethylbenzene (illumination, −15°) seemed to have an erratic effect on the percentages of **1** and **2**. For example, in the presence of ethylbenzene the percentage of **1** remained at approximately 20% (beginning at $n = 0.5$ for butadiene until *ca.* $n = 0.02$ where it suddenly jumped to 58%. As indicated, in the absence of ethylbenzene the results are considerably different. Under safelight (−15°) the percentages of **1** and **2** were uneffected by the presence of ethylbenzene.

[6] For a discussion on the effect of branching on the addition of chlorine to olefins, see M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4285 (1965).

[7] "Dictionary of Organic Compounds," Vol. I, I. Heilbron and H. M. Bunbury, Editors, Oxford University Press, New York, N. Y., 1953, p 327.

curred. However, since the time required for bromination was very short, the effect of evaporation was negligible.

All brominations requiring the absence of light were carried out in a dark room with a photographic safelight.

Procedure for Analyses of Products.—The vpc analysis of the dibromides was accomplished with an Aerograph 90 P-3 chromatograph under the following conditions: flow rate (He) 300 cc/min; column length and diameter, 6 ft × 0.25 in.; column temperature, 50°; column composition, 2.5% SE-30 on 60-80 mesh DMCS Chromosorb W. Under these conditions the retention times of **1**, **2**, and **3** are, respectively, 108, 297, and 247 sec. The retention time of α-bromoethylbenzene was 372 sec.

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

The percentages of the dibromides were based on their adjusted areas in the chromatograms. The adjustments were based on the following determination: the ratio of A_1/A_2 divided by W_1/W_2 is equal to 0.85. The area/weight ratio for dibromides **2** and **3** was assumed to be unity on the basis of their similar molecular structures.

The relative reactivities of butadiene and ethylbenzene were determined from the following expression where C_8H_9Br refers

$$\left[\frac{2(1 + 2 + 3)}{(C_8H_9Br)}\right]\left[\frac{(C_8H_{10})_0}{(C_4H_6)_0}\right]$$

to the quantity of α-bromoethylbenzene formed in the reaction, and $(C_8H_{10})_0$ and $(C_4H_6)_0$ refer to the initial concentrations of ethylbenzene and butadiene, respectively.

The Authentic Dibromide Isomers.—Dibromides **1** and **2** were prepared according to the methods described by Hatch, *et al.*[2] Dibromide **3** was prepared as described by Valette.[8] The peaks assigned to dibromides **1** and **2** were confirmed by comparison of their retention times with those of authentic samples, and by collecting the compounds as they emerged from the vpc and comparing the absorption bands in their infrared spectra with the reported absorption bands.[2] The peak assigned to dibromide **3** was done so on the basis of a comparison of its retention with that of authentic **3**.

Registry No.—Butadiene, 106-99-0; **1**, 10463-48-6; **2**, 821-06-7; **3**, 18866-73-4.

Acknowledgment.—Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, and to Union Oil Co., Bea, Calif., for the support of this research.

(8) A. Valette, *Ann. Chim.*, **3**, 644 (1948).

Solvent Effects in the Oxymercuration of 2-Cyclohexenol and Related Allylic Derivatives

M. ROSS JOHNSON[1] AND BRUCE RICKBORN[2]

Department of Chemistry, University of California, Santa Barbara, California 93106

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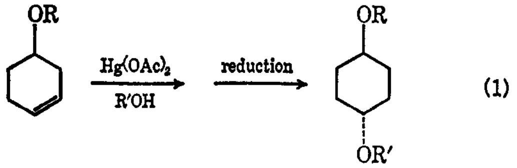
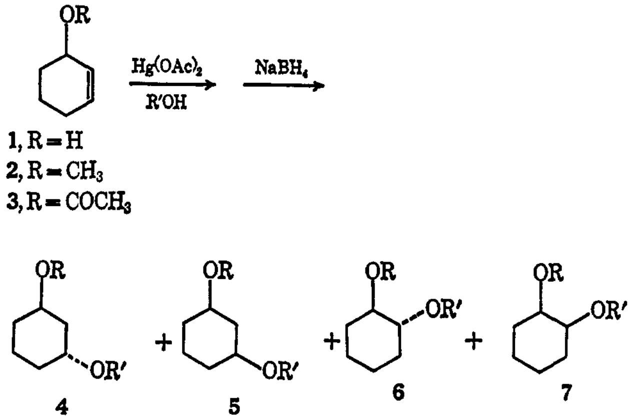
Stereoselective reactions are of great importance in the design of synthetic procedures. A number of simple olefin addition reactions exhibit this feature, which increases by a large factor the degree of synthetic utility. A related phenomenon, stereoselective addition controlled by a substituent in the vicinity of the double bond, has been explored in several reactions. Examples for which high selectivity has been reported include the epoxidation of 2-cyclohexeneol[3] (*cis*), the Simmons-Smith reaction of both allylic and homoallylic alcohols (*cis*),[4] and the hydroxymercuration of 3-cyclohexenol[5] (eq 1).



(1)

We have recently reported preliminary results on the hydroxymercuration of 2-cyclohexenol (**1**), its methyl ether (**2**), and acetate (**3**) derivatives.[6] The reaction proved to be only moderately stereoselective as normally carried out (THF-water), but appeared, in the limited range examined, to be somewhat solvent dependent. We report here the results of an expanded study of solvent effects with these systems. The products in each case were reduced by borohydride to the corresponding diols (or derivatives), which in turn were analyzed by vpc. The results are shown in Table I.



1, R = H
2, R = CH_3
3, R = $COCH_3$

4 **5** **6** **7**

R' = H, CH_3, or $COCH_3$ (2)

The most significant aspect to be noted is the high selectivity associated with the use of acetonitrile (5% water) as solvent. Thus all three substrates (**1**-**3**) give nearly pure (>94%) *trans*-3-hydroxy product in this medium. This feature should prove of synthetic utility.

All three starting materials show approximately the same responses to solvent changes, suggesting that nearly identical directive influences are exerted by the different substituents. The observed product distributions do not vary in any easily predictable manner with solvent change; the formation of 1,2 product appears to be associated with the less *trans*-3-selective reaction of **1**, but similar behavior is not found with the allylic acetate **3**.[7] In general, the preferred for-

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[1] NDEA Title IV Predoctoral Fellow.

[2] Alfred P. Sloan Fellow, 1967-1969.

(3) (a) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957). (b) For a recent example of solvent effect on epoxidation of a homoallylic alcohol, see R. Zurflüh, E. N. Wall, J. B. Siddall, and J. A. Edwards, *J. Amer. Chem. Soc.*, **90**, 6224 (1968).

(4) J. H. Chan and B. Rickborn, *ibid.*, **90**, 6406 (1968); references to earlier work are given here.

(5) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959).

(6) M. R. Johnson and B. Rickborn, *Chem. Commun.*, 1073 (1968).

(7) Two early runs with **3** in aqueous THF gave only product **4** in moderate yield;[6] numerous subsequent attempts to repeat this observation have all resulted in the distribution shown in Table I.