

Two grams of the hydrocarbon was brominated in the cold by Farmer's method.<sup>14</sup> Removal of the chloroform under reduced pressure left a black solid. This was washed with cold chloroform and the resulting white solid, m.p. 158–172°, was charcoaled and crystallized several times from chloroform. The product, m.p. 189.5–191.5°, was the high melt-

ing isomer of the tetrabromobicyclohexyl.<sup>22</sup> Elemental analyses were in excellent agreement with the required values.

(22) E. H. Farmer and G. G. Moore, *J. Chem. Soc.*, 131 (1951); H. Berlande, *Bull. soc. chim. France*, 9, 641 (1942).  
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

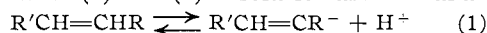
## The Vinyl Carbanion<sup>1</sup>

BY SIDNEY I. MILLER AND WARREN G. LEE

RECEIVED FEBRUARY 25, 1959

There is essentially no isotope rate effect in the dehydrobromination by methoxide of protonated and deuterated *cis*-dibromoethene in methanol; under the same conditions hydrogen exchange with the solvent appears to be *ca.* 25 times faster than elimination at 26°. While methyl acrylate, maleic anhydride, ethyl cinnamate, methyl chloromaleate, 1,1-diphenylethene, triphenylethene, *cis*- and *trans*-stilbene do not exchange, *cis*- and *trans*-dichloroethene, *cis*- and *trans*-dibromoethene, *trans*-diiodoethene, tribromoethene and  $\omega$ -bromostyrene exchange protons for deuterium in basic deuterium oxide. Upper limits to the *pK*'s of the 1,2-dihaloethenes are in the range 34–36. Lower limits to the activation energy for isomerization of vinyl carbanions formed from 1,2-dihaloethenes lie in the range 25–35 kcal./mole. In the light of these observations, a general mechanism of elimination reactions is proposed.

Accurate estimates for the free energies of the two processes (1) and (2) in solution are unavailable



The first involves the *pK* of an alkene; the second involves an inversion or a rotation barrier. In this paper preliminary results are reported which establish upper limits for the *pK* of some alkenes and lower limits for the energy barriers of related carbanions.

According to its bond properties, the acidity of a vinyl hydrogen should be greater than that of an alkane hydrogen but less than that of an alkyne hydrogen.<sup>2</sup> However, the compilations of *pK*'s of weak acids do not include a simple alkane or alkene.<sup>3–5</sup> Qualitatively, metal-hydrogen interchange experiments suggest that *pK*'s probably increase in the order acetylene, ammonia, ethylene, benzene and ethane.<sup>5,6</sup>

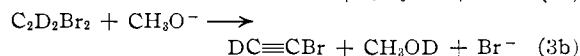
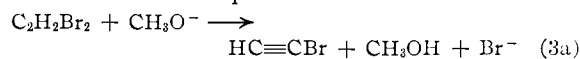
The vinyl carbanion has attracted increasing attention in recent years. It was considered briefly as a chain carrier in anionic polymerization.<sup>5</sup> As part of the three-step mechanism of dehydrohalogenation of haloalkenes by base, Cristol, *et al.*, have postulated that the anions of equation 2 equilibrate rapidly.<sup>7</sup> In contrast, analogy with isoelectronic nitrogen compounds, *e.g.*, oximes, suggests that vinyl carbanions may be sterically stable.<sup>8</sup> Indeed, a calculation for the *syn-anti*

inversion of the diimide, HN=NH, yields a value of 33 kcal./mole for the activation energy.<sup>9</sup> Stereospecific reactions (with retention) that involve the carbanion as an intermediate provide a necessary but not sufficient criterion of stability: inversion is usually competing with other processes that are either known to be fast or that may be fast. Such stereospecific reactions have involved uptake of protons<sup>10–12</sup> or deuterons<sup>13</sup> from a hydroxylic solvent, reaction with mercuric ions<sup>14</sup> or rearrangements.<sup>15</sup> Based on this evidence, the energy barrier of equation 2 remains ambiguous.

Stereospecific reactions of lithium or sodium alkenides have sometimes been considered to bear on this problem. Since the detailed mechanisms of their conversions are not known, their relevance is still obscure. The configurational stabilities of stereoisomeric vinylolithium compounds, for example, as considered by Curtin and Crump do bear directly on the problem.<sup>16</sup> The relevant data are qualitative, *e.g.*, *cis*- and *trans*-propenylolithium are stable for more than one hour in boiling ether or *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenylvinylolithium undergo appreciable interconversion after 0.5 hour at 0° in ether, etc. Such data are useful if the interconversion involves the vinyl anion: then they establish, however crudely, upper or lower values for the interconversion rates.

### Results

The kinetic isotope effect in the reactions



was measured in the solvent methanol (see Table

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(2) W. L. G. Gent, *Quart. Revs.*, **2**, 383 (1948); J. K. Wilmhurst, *J. Chem. Phys.*, **27**, 1129 (1957).

(3) W. K. McEwen, *THIS JOURNAL*, **58**, 1124 (1936).

(4) R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953).

(5) N. S. Wooding and W. C. E. Higginson, *J. Chem. Soc.*, 774 (1952).

(6) R. A. Benkeser, D. J. Foster, D. M. Sauve and J. F. Nobis, *Chem. Revs.*, **57**, 867 (1957); J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold Publishing Corp., New York, N. Y., 1945, p. 45.

(7) S. J. Cristol and A. Begoon, *THIS JOURNAL*, **74**, 5025 (1952); S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1954).

(8) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Chapt. IX.

(9) G. W. Wheland and P. S. K. Chen, *J. Chem. Phys.*, **24**, 67 (1956).

(10) S. I. Miller, *THIS JOURNAL*, **78**, 6091 (1956).

(11) E. Grovenstein and D. E. Lee, *ibid.*, **75**, 2639 (1953).

(12) W. H. Jura and R. J. Gaul, *ibid.*, **80**, 5403 (1958).

(13) E. F. Silversmith, Y. Kitahara, M. C. Caserio and J. D. Roberts, *ibid.*, **80**, 5840 (1958).

(14) M. Fitzgibbon, *J. Chem. Soc.*, 1218 (1938).

(15) A. A. Bothner-By, *THIS JOURNAL*, **77**, 3293 (1955).

(16) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958).

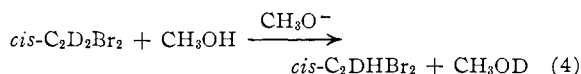
TABLE I  
RATES OF ELIMINATION REACTIONS OF DIBROMOETHENES WITH METHOXIDE ION

Compound	Temp., °C.	Dibromoethene, mole/liter	NaOCH <sub>3</sub> , mole/liter	k, liter/mole sec.
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub>	24.80 ± 0.02	0.02262	0.05339	(1.13 ± 0.05) <sup>a</sup> × 10 <sup>-4</sup>
	35.40 ± .05	.02231	.05265	(6.25 ± .12) <sup>a</sup> × 10 <sup>-4</sup>
		.03217	.05062	
		.02655	.08334	
	47.80 ± .05	.02272	.05323	(3.81 ± .03) <sup>a</sup> × 10 <sup>-3</sup>
	35.40 ± .05	.04260	.1109	
.02021		.06825		
<i>cis</i> -C <sub>2</sub> D <sub>2</sub> Br <sub>2</sub>	35.40 ± .05	.01580	.08338	(6.07 ± .01) × 10 <sup>-4</sup>
		.02169	.1017	

<sup>a</sup> Constants calculated from previous work are 1.22 × 10<sup>-4</sup>, 6.30 × 10<sup>-4</sup> and 3.80 × 10<sup>-3</sup> at 24.8°, 35.4° and 47.8°, respectively.

I). It was found that the rate constants for *cis*-dibromoethene checked those previously reported.<sup>17</sup> The *cis*-dibromoethene-*d*<sub>2</sub> had a rate constant essentially identical with that found for the protonated compound at 35.4°, that is,  $k_H/k_D = 1.03$ .

The rate of exchange



was followed by infrared analysis of the intensity of the C-D band at *ca.* 4.5 μ. The results are given in Table II and some of the pseudo first-order plots are given in Figs. 1. The falling off in the apparent

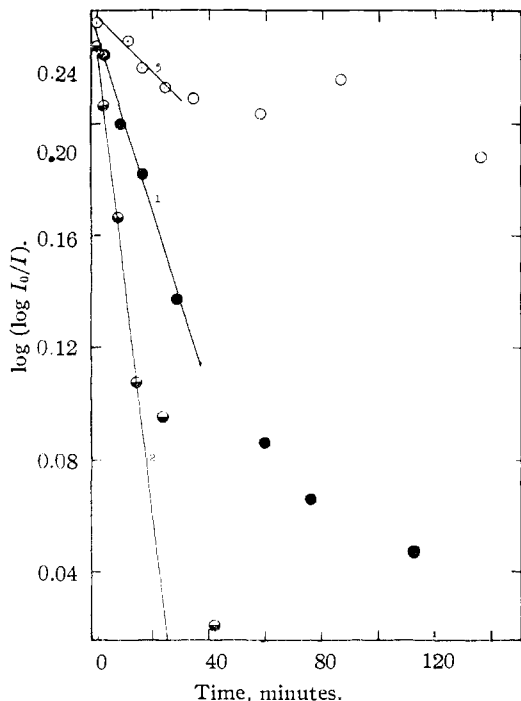


Fig. 1a.—Pseudo-first-order plots of hydrogen exchange of *cis*-C<sub>2</sub>D<sub>2</sub>Br<sub>2</sub> in methanol-methoxide (run numbers refer to Table II).

rate of exchange may be attributed to direct and indirect effects of the elimination. Clearly, the rate of exchange is ~25 times greater than the rate of elimination.

In order to investigate the generality of the exchange of a vinyl hydrogen, we treated several

(17) S. I. Miller and R. M. Noyes, *THIS JOURNAL*, **74**, 629 (1952).

alkenes with basic deuterium oxide, an approach first applied successfully to the synthesis of trichloroethene-*d*.<sup>18</sup> Table III contains some of the results under representative conditions. Apart

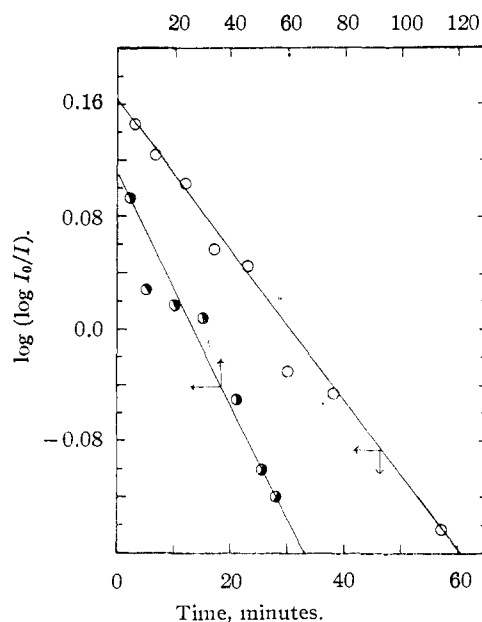


Fig. 1b.—Pseudo-first-order plots of hydrogen exchange of *cis*-D<sub>2</sub>C<sub>2</sub>Br<sub>2</sub> in methanol-methoxide (run numbers refer to Table II).

from *cis*-diiodoethene, which presumably dehydroiodinates, exchange was observed for five 1,2-dihaloethenes, tribromoethene and ω-bromostyrene. Even under forcing conditions no exchange could be detected with methyl acrylate, maleic anhydride, ethyl cinnamate, methyl chloromaleate, *cis*- and *trans*-stilbene, 1,1-diphenylethene and triphenylethene. A similar negative result recently was reported for the vinyl hydrogen in ClCH=C(C<sub>6</sub>H<sub>5</sub>)CHClCOOH and ClCH=C(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>COOH.<sup>13</sup>

The exchange reactions of the dihaloethenes were investigated in some detail. Their exchange rates decreased in the order *cis*-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> ~ *cis*-C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub> *trans*-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> > *trans*-C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub> > *trans*-C<sub>2</sub>H<sub>2</sub>I<sub>2</sub>. It was possible to observe base-catalyzed exchange without isomerization in each of the dichloroethenes. With the dibromoethenes isomerization

(18) L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **28B**, 35 (1950); T. J. Houser, R. B. Bernstein, R. G. Miekka and J. C. Augus, *THIS JOURNAL*, **77**, 6201 (1955).

TABLE II  
METHOXIDE-CATALYZED EXCHANGE OF *cis*-DIBROMOETHENE- $d_2$  WITH METHANOL

No.	<i>cis</i> -C <sub>2</sub> D <sub>2</sub> Br <sub>2</sub> , mole/liter	NaOCH <sub>3</sub> , mole/liter	Temp., °C.	( <i>k</i> × 10 <sup>3</sup> ), <sup>a</sup> liter/mole sec.
2	0.252	0.0758	25	4.1
1	.257	.0386	25	3.6
3	.250	.0211	31	10.0
4	.247	.0251	26	4.0
5	.262	.0138	25.5	2.6
6	.262	.00591	27	2.8
7	.262	.0138	27	2.8
		Mean at	26	3.3

<sup>a</sup> Initial slope of plots such as in Figs. 1.

TABLE III  
BASE-CATALYZED EXCHANGE OF VINYL HYDROGENS IN  
DEUTERIUM OXIDE

Compound	Temp., °C.	Time, hr.	Exchange, Cc-D/Cc-H <sup>a</sup>
<i>trans</i> -C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub>	25	65	0.24
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub>	25	45	.26
<i>trans</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	3	48	.03
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	70	20	1
<i>trans</i> -C <sub>2</sub> H <sub>2</sub> I <sub>2</sub>	55	20	1
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> I <sub>2</sub>	3, 25	45, 88	<0.05
HCB <sub>2</sub> =CBr <sub>2</sub>	25	2	.13
C <sub>6</sub> H <sub>5</sub> CH=CHBr	110	144	.06

<sup>a</sup> Extinction coefficients at C-H and C-D absorption assumed identical.

always occurred; in one case the *trans* was converted to a *cis-trans* equilibrium mixture before exchange had proceeded very far (~10%). It is probable that these isomerizations are unrelated to exchange by ionic mechanisms and arise by extraneous free radical processes.<sup>17</sup>

Every instance of a positive exchange with deuterium oxide given in the table also represents a synthesis of the D-labeled alkene. The dibromo- and dichloroalkenes already have been synthesized *via* acetylene- $d_2$ .<sup>19,20</sup> In the case of the 1,2-diiodoethenes, synthesis by exchange may be most convenient<sup>17</sup>; it was possible to obtain greater than 95% exchange for deuterium in our small scale experiments in a single equilibration.

### Experimental

*sym*-Tetrabromoethane- $d_2$ .—Commercial calcium carbide (160 g., 2.5 moles), 20–30 mesh, was heated at red heat in a Vycor "baker" connected to a vacuum system through a male ground glass joint. The baker was tilted slightly so that a decomposition product, a viscous greenish-black liquid (*ca.* 1 ml.), ran off into a side arm fitted with a stopcock. After 20 hours, the baker was allowed to cool and a strong stream of dried nitrogen was introduced through the sidearm.

After the baker was removed from the vacuum system, the portion of the tube above the carbide was wiped free of dark oil and the bulk of the solid was added to a dry 500-ml. round-bottom flask, the "generator." The remaining carbide was added to a straight connecting tube and loosely plugged with glass wool. The generator was fitted with a Claisen head surmounted by a dropping funnel and a vertical condenser.<sup>21</sup> This was followed by the connecting tube, stopcock S<sub>1</sub>, several cold traps and stopcock S<sub>2</sub>. The nitrogen stream over the carbide was stopped only after this generator system was assembled.

The system was pumped out through S<sub>2</sub> and the cold traps were cooled in Dry Ice-acetone or in liquid nitrogen as required; S<sub>2</sub> then was closed and purified dioxane (100 ml.) was added to the generator through the dropping funnel. A 1:1 solution of dioxane and 99.5% deuterium oxide (45 g., 2.25 moles) was added dropwise to the generator; the dropping funnel finally was rinsed with dioxane (50 ml.). After the reaction mixture was heated briefly, S<sub>1</sub> was closed.

The all-glass bromination system consisted essentially of three cold traps. Bromine (360 g., 2.25 moles) was placed in the center trap. This trap was surmounted by a bulb such that liquid could be driven from the trap to the bulb and *vice versa* with the application of pressure or vacuum. A tube joining the outer traps and fitted with a stopcock made it possible to by-pass the bulb and center trap when necessary.

The bromine was frozen at *ca.* -78°, the bromination system was pumped out, then opened to the line containing the acetylene- $d_2$ . After the acetylene- $d_2$  was transferred in, the bromination assembly was isolated. One of its outer cold traps was always kept at -78° or lower while the acetylene was distilled repeatedly through the liquid bromine. Bromine addition was slow, *ca.* 5 days. The bromine slowly diffused throughout the system and seemed to be most rapidly decolorized in the gas phase or in small droplets on the walls of the glass (the use of ultraviolet radiation has been reported to accelerate bromine addition).<sup>19</sup>

Fractionation of the liquid product yielded *ca.* 100 g. of a volatile mixture and three cuts (257 g.) of *sym*-tetrabromoethane- $d_2$ . The middle cut was decolorized with aqueous bisulfite and bicarbonate, washed with water, dried and redistilled. A heart cut had b.p. 56° at 0.04 mm., *n*<sub>D</sub><sup>25</sup> 1.6331 (for *sym*-tetrabromoethane, lit.<sup>22</sup> b.p. 65° at 1 mm., lit.<sup>23</sup> *n*<sub>D</sub><sup>25</sup> 1.6353). Infrared spectra of this sample as well as of the derived dibromoethenes showed no protonated material (<1%).

*Anal.* Calcd. for C<sub>2</sub>D<sub>2</sub>Br<sub>4</sub>: Br, 91.93. Found: Br, 91.60, 91.62.

1,2-Dibromoethene- $d_2$ .—The *cis-trans* mixture was prepared from *sym*-tetrabromoethane- $d_2$  by zinc debromination in ethanol, then separated by fractional distillation.<sup>17</sup> The absence of *trans* in the *cis* isomer was checked by gas phase chromatography. For *cis* *n*<sub>D</sub><sup>25</sup> was 1.5365 (for *cis*-C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub> lit.<sup>24</sup> *n*<sub>D</sub><sup>25</sup> 1.5370).

**Other Alkenes.**—The *cis*- and *trans*-dichloro-, dibromo- and diiodoethenes were prepared or purified as described previously.<sup>17</sup> Except for *cis*-diiodoethylene which contained *ca.* 20% *trans*, the compounds were of high purity. The  $\omega$ -bromostyrene was a distilled sample, *n*<sub>D</sub><sup>25</sup> 1.6056, containing *ca.* 20% *cis*.<sup>11</sup>

The tribromoethene was a distilled sample *n*<sub>D</sub><sup>25</sup> 1.5970 (lit.<sup>25</sup> *n*<sub>D</sub><sup>16</sup> 1.6045).

The other olefins were commercially available materials.

**Rate Studies.**—Methods for studying the elimination reaction have been described.<sup>17</sup> The data are given in Table I. The deuterium data are given in Fig. 2.

The hydrogen exchange of *cis*-dibromoethene- $d_2$  with methanol was followed in a Perkin-Elmer Infracord spectrophotometer. The 4.5  $\mu$  region of the C-D bond was scanned. Two calcium fluoride cells, *ca.* 0.1 mm., were used. A stock *cis* solution was first run against a solution of carbon tetrachloride in methanol. The concentration in the solvent cell was adjusted until the methanol absorption near 4  $\mu$  was negligible. This procedure ensured that the still weaker methanol band near 4.5  $\mu$  compensated that in the sample cell.

To begin a run, concentrated sodium methoxide was added by micropipet or hypodermic syringe to a known volume of stock *cis*-dibromoethene- $d_2$  in methanol. After mixing, a portion was added to the sample cell. At successive time intervals, *I* and *I*<sub>0</sub> were obtained. The cells were removed from the spectrophotometer between successive scannings so that ambient conditions fixed the temperature; in the light path of the Infracord, the temperature was 6–7° higher.

(19) M. de Hemptinne and S. I. Perlinghi, *Industrie Chem. Belge*, Spec. No. II, 271 (1955); *C. A.*, **50**, 16658a (1956).

(20) H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, **17**, 556 (1949).

(21) L. C. Leitch and A. T. Morse, *Can. J. Res.*, **30**, 924 (1952).

(22) D. R. Stull, *Ind. Eng. Chem.*, **37**, 517 (1947).

(23) A. I. Vogel, *J. Chem. Soc.*, 1850 (1948).

(24) R. M. Noyes, W. A. Noyes and H. Steinmetz, *THIS JOURNAL*, **72**, 33 (1950).

(25) E. Prilezhaeva and N. Prilezhaev, *J. Gen. Chem. (U.S.S.R.)*, **9**, 1766 (1939); *C.A.*, **34**, 3672 (1940).

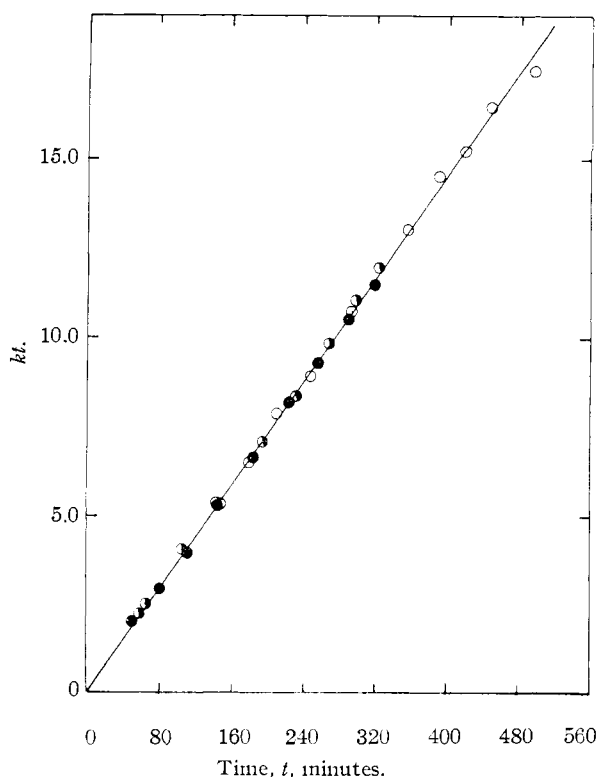


Fig. 2.—*cis*-C<sub>2</sub>D<sub>2</sub>Br<sub>2</sub>-NaOCH<sub>3</sub> reaction in methanol at 35.4°. Three runs of Table I are included.

To treat the data, the expression

$$k_1 = \frac{2.303}{bt} \log \frac{a}{a-x} \quad (5)$$

was used where  $b$  is the concentration of sodium methoxide,  $a$  is the initial concentration of *cis*-dibromoethene-*d*<sub>2</sub> and  $a-x$  is the concentration of deuterated *cis* at any time. Of necessity, it was assumed that *cis*-*d*<sub>2</sub> and *cis*-*d*<sub>1</sub> had identical extinction coefficients, obeyed Beer's law at  $\sim 4.5 \mu$  and had identical rates of exchange. Then  $\log I_0/I$  was proportional to  $a-x$ . From the slope of a plot of  $\log(I_0/I)$  versus time, the second-order rate constant could be calculated.

Sample plots are given in Figs. 1 and some of the data are given in Table II. It is probable that the precision of the rate data could be improved considerably by the use of a thermostated cell in a spectrometer of higher sensitivity. It is not obvious why there is a decrease in the apparent rate constant as *cis*-*d*<sub>1</sub> is formed. Possibly the extinction coefficients of *cis*-*d*<sub>2</sub> and *cis*-*d*<sub>1</sub> differ significantly. The consumption of methoxide was shown by calculation to be a minor factor; however, the product of elimination, monobromoacetylene, may have an overlapping  $\text{—C}\equiv\text{C—}$  band in the region analyzed.

**Qualitative Exchange Studies.**—Commercial sodium methoxide, 95% grade, was dissolved in deuterium oxide (99.5%) to give *ca.* 1 and 2 *M* solutions. Equal volumes (*ca.* 0.2 ml.) of these solutions and the ethylenes were mixed. In no case was there complete miscibility. The reactions were run in sealed tubes or in stoppered test-tubes. After given periods, the aqueous layer was removed, the organic product was dried with calcium chloride and its infrared spectrum taken. Solid olefins were taken up in carbon tetrachloride or in carbon disulfide and dried.

Since the spectra of the dihaloethenes were well known, it was simple to identify them and their deuterated analogs.<sup>20,26,27</sup> Otherwise, the C-D absorption region,  $4.5 \mu$ , was compared with that of the protonated compound. Although the C-D stretching band of alkenes is not the most

intense, it is usually the least likely to be confused or overlapped by other bands. In the case of  $\omega$ -bromostyrene, for example, bands at 4 and  $4.5 \mu$  appeared in the product indicating the presence of  $\text{—C}\equiv\text{C—D}$  and  $\text{>C=C—D}$ ; there was no indication of  $\text{—C}\equiv\text{C—H}$ .

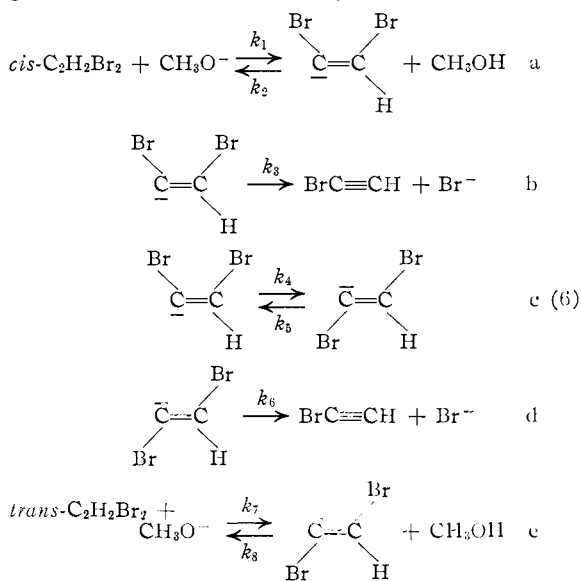
For *trans*-diiodoethene, hydrogen exchange was observed only after the melt was in contact with basic deuterium oxide at 55–70°. The new infrared bands which appeared will be reported elsewhere.

Positive hydrogen exchange data are given in Table III. The ratio of C-D to the C-H concentration,  $C_{\text{C-D}}/C_{\text{C-H}}$ , is an estimate based on the crude assumption that the extinction coefficients for C-D and C-H stretching frequencies are identical.

No exchange was found for methyl acrylate, maleic anhydride, ethyl cinnamate, methyl chloromaleate, *cis*- and *trans*-stilbene, 1,1-diphenylethene and triphenylethene. Typical reaction conditions were 2–6 days at 210°. Several of these "negative" alkenes, *e.g.*, the phenylalkenes and ethyl cinnamate, were mixed with a solution made from deuterium oxide and an excess of potassium *t*-butoxide, but to no avail. It was hoped that the stilbenes would be model compounds in this study. However, while the isomerization of *cis*- to *trans*-stilbene appeared to be more rapid in the presence than in the absence of bases, *e.g.*, methoxide, ethoxide, *t*-butoxide or deuteroxide, hydrogen exchange never was observed.

### Discussion

Information on the haloalkenes has advanced sufficiently so that the interrelated problems, their  $pK$ 's, the energy barrier separating their carbanions and their base-catalyzed elimination mechanisms should be considered together. Scheme 6 appears to cover the relevant steps of an over-all mechanism. By writing appropriate isomers of substituted ethanes or cyclic compounds for the geometric isomers pictured here, the scheme can be generalized to include these systems also.



Since the dehydrohalogenation data are relevant, they are summarized in Table IV; the present discussion of these data will modify our previous approach.<sup>17</sup>

**Alkene Acidity.**—Although a series of experiments under uniform conditions will be necessary to establish an order of acidity for various alkenes, it appears that these several observations will be useful.<sup>23</sup> Halogenated alkenes such as the di-

(26) J. M. Dowling, P. G. Puranik, A. G. Meister and S. I. Miller, *J. Chem. Phys.*, **26**, 233 (1957).

(27) S. I. Miller, A. Weber and F. F. Cleveland, *ibid.*, **23**, 44 (1955).

(28) At best, only a qualitative comparison with the results for related anions, *e.g.*, allylic (a), phenyl (b), heterocyclic (c) or cyclo-

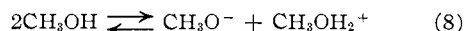
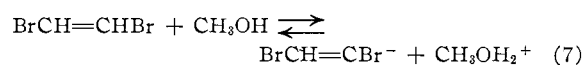
TABLE IV  
ACTIVATION ENERGIES FOR DEHYDROHALOGENATION, KCAL./MOLE<sup>a</sup>

Compound	$E_{\text{exp}}^{\text{C}}$	$E_{\text{exp}}^{\text{T}}$	$(k_{\text{elim}}^{\text{C}}/k_{\text{elim}}^{\text{T}})^{600}$
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	35.1	29.0	3 × 10 <sup>8</sup>
C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub>	28.1	33.4	5 × 10 <sup>6</sup>
C <sub>2</sub> H <sub>2</sub> I <sub>2</sub>	24.7	35.8	1 × 10 <sup>6</sup>

<sup>a</sup> The superscripts C and T refer to the *cis* and *trans* compounds, respectively.

and tribromoalkenes exchange their hydrogens with methanol in the presence of base. *cis*-Compounds such as the dichloro- or dibromoethenes exchange hydrogen more rapidly than their *trans* isomers. Di- and triphenylethenes or substituted acrylates appear not to exchange their ethylenic hydrogens. In  $\omega$ -bromostyrene a small amount of exchange is observed: apparently a compromise is reached between the accelerating effect of bromine and the retarding effect of phenyl. It is probable that carbonyl and phenyl next to a double bond offer 1,2- or 1,4-addition as energetically more favorable alternatives to carbanion formation. By contrast, in saturated systems halogen, carbonyl and phenyl substituents all increase the availability of an  $\alpha$ -H.<sup>4</sup>

To evaluate the acidity of an alkene, we consider reactions 6a, 7 and 8



For the  $pK$  of *cis*-dibromoethene in methanol

$$pK_7 = pK_8 + pK_{6a} = pK_8 + pk_{6a}^1 - pk_{6a}^2 \quad (9)$$

For  $k_{6a}^2$  very large,<sup>29</sup>  $\Delta F_2^*$  is small. Then the equilibrium constant for 6a can be approximated by  $hk_{6a}^1/2kT$  where  $1/2$  is a statistical factor correcting  $k_{6a}^1$  for the two available acidic hydrogens and  $kT/h$  is the frequency factor of absolute reaction rate theory. Combining this with the dissociation constant of methanol<sup>30</sup> which is  $8 \times 10^{-19}$ , a  $pK$  of 33.6 is calculated for *cis*-dibromoethene at 26°.

From the hydrogen exchange data it would appear that the  $pK$  of *cis*-dichloroethene is close to that of the *cis*-dibromoethene of  $\sim 34$ ; those of the three *trans*-dihaloethenes are perhaps one to two units higher. These estimates of the  $pK$ 's are upper limits: a free energy of activation in the back reaction of 6a would lower the  $pK$  by one unit for every 1.4 kcal./mole in  $\Delta F^*$ . In comparison with other weak acids whose  $pK$ 's have been variously listed in reference works as 22, 25, 30, 33 for ammonia, and 40, 43, 50 for methane, the estimates for the dihaloethenes are of high precision.<sup>31</sup>

In addition to the theoretical interest attached

propenyl (d) would be possible at this time: (a) H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958); (b) J. D. Roberts, D. A. Semenov, H. E. Simmons, Jr., and L. A. Carlsmith, *THIS JOURNAL*, **78**, 601 (1956); (c) R. Breslow, *ibid.*, **79**, 1762 (1957); (d) K. B. Wiberg, R. K. Barnes and J. Albin, *ibid.*, **79**, 4994 (1957).

(29) P. Delahay and W. Vielstich, *ibid.*, **77**, 4955 (1955).

(30) J. Koskikallio, *Suomen Kemistilehti*, **B30**, 111 (1957).

(31) Two recent estimates of the  $pK$  of ammonia are 36<sup>6</sup> and 25; R. A. Ogg, Jr., *Disc. Faraday Soc.*, **17**, 215 (1954).

to the acidity of any alkene, other applications are possible. The catalysis of some anionic polymerizations by a vinyl anion should at least be considered.<sup>5</sup> Since the product alkenes do not exchange hydrogen in liquid ammonia in the presence of amide ion,  $\alpha$ -elimination in the 1- or 2-deuterated alkyl halides with potassium amide appears to have been verified.<sup>32</sup> For synthetic work, the possibility of using vinyl anions, other than those pre-formed in organometallics, remain to be explored in depths.<sup>33</sup>

**Vinyl Anion Stability.**—It is now possible to provide an unequivocal lower limit to the energy barrier for the *cis* to *trans* isomerization of the anion C<sub>2</sub>HBr<sub>2</sub><sup>-</sup>. With reference to the data in Table IV, it is clear that the 1,2-dibromoethenes are dehydrobrominated at sufficiently different rates so that a common intermediate cannot precede the rate-determining steps. These data do not preclude *trans* to *cis* isomerization during elimination, but they do require that *cis* to *trans* isomerization is slower than dehydrobromination. The hydrogen exchange experiments show that reactions 6a and 6e of scheme 6 are fast compared to dehydrobromination. These facts establish the sequence  $k_1$  or  $k_2 > k_3 > k_4$  as well as  $k_{\text{elim}}^{\text{C}} > k_4$  (all  $k$ 's refer to scheme 6). Thus, an upper limit to the rate of *cis* to *trans* isomerization of C<sub>2</sub>HBr<sub>2</sub><sup>-</sup> has been set; alternatively, the activation parameters for dehydrohalogenation of the *cis*-dibromoethene (and *cis*-dichloroethene) set the minimum height for the energy barrier.<sup>34</sup>

The isomerization of anions derived from the 1,2-dihaloalkenes involves an energy barrier of at least 25–35 kcal./mole (see Table IV). This is in the range calculated for diimide.<sup>9</sup> The barrier height to inversion by in-plane bending can be calculated by a standard method<sup>35</sup> whose variable reliability has been discussed elsewhere.<sup>36</sup> The uncatalyzed isomerization of alkenes by out-of-plane rotation is slow involving either normal frequency factors and high activation energies ( $\sim 45$  kcal./mole) or low frequency factors and low activation ( $\sim 25$  kcal./mole).<sup>37</sup> There appears to be little reason to suppose that such isomerization of a vinyl anion by rotation should be any faster.<sup>38</sup>

(32) D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, *THIS JOURNAL*, **74**, 5599 (1952); S. M. Luck, D. G. Hill, A. T. Stewart, Jr., and C. R. Hauser, *ibid.*, **81**, 2784 (1959).

(33) C. R. Hauser and D. Lednicer, *J. Org. Chem.*, **22**, 1248 (1957).

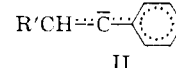
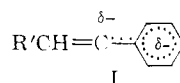
(34) In the stereospecific rearrangement of 2,2-diphenyl-1-haloethenes by base to 1,2-diphenylethyne, hydrogen exchange is faster than elimination. Here a lower limit is set on the barrier height; J. G. Pritchard and A. A. Bothner-By, Abstracts of Papers, 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 35-R.

(35) E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, New York, N. Y., 1957, p. 508.

(36) R. E. Weston, *THIS JOURNAL*, **76**, 2645 (1954).

(37) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 104.

(38) It has been suggested that an  $\alpha$ -phenyl-substituted anion is "mesomeric" and has no isomers.<sup>7</sup> Alternatively it has been suggested that the *cis* and *trans* anions may interconvert through an allenic form such as I.<sup>16</sup> To us, the planar ion II appears to be a more favorable transition state or intermediate; I and II, of course, differ spatially and cannot be mesomeric.



For the species  $R'CH=CR^-$ , the potential function

$$V = \frac{1}{2}(k_1(\Delta l)^2 + k_\theta(\Delta\theta)^2)$$

is assumed, where  $k_1$  and  $k_\theta$  are the stretching and in-plane bending potential constants of the C-R bond and  $\Delta l$  and  $\Delta\theta$  are the changes in bond length and in angle. Since  $\Delta l$  for changes in C-R from an  $sp^2$  bond ( $\theta = 120^\circ$ ) to an  $sp$  bond ( $\theta = 180^\circ$ ) are usually  $< 0.05 \text{ \AA.}$ , the contribution of the first term is unimportant. For  $R = H$ , alkyl or halogen  $k_\theta = 0.3 - 0.8 \times 10^{-11} \text{ dyne cm./radian}^2$ .<sup>26,39</sup> The range in the calculated barrier height at  $\Delta\theta = 60$  degrees or 1.05 radians is 24 kcal./mole,  $R = H$ , to 64 kcal./mole,  $R = Br$ . Not unexpectedly, our calculation of 64 kcal./mole for a bromovinyl anion is high. Judging from this overestimate, vinyl anions of the type  $R'CH=CR^-$  should have a low order of stability where  $R = H$  or  $R = \text{alkyl}$ .

**Elimination Mechanisms.**—Though portions of scheme 6 have been considered previously,<sup>40</sup> a unified kinetic analysis for base-catalyzed reactions is now necessary. The discussion will usually be cast in terms of *cis-trans* isomers, but relevant examples will also be taken from cyclic and acyclic systems. Mechanistic categories now lacking examples will be omitted. At the outset, the only restriction imposed is that the steady state condition may be applied to the anions. The rate of elimination is given by

$$d(Br^-)/dt = k_3(C^-) + k_6(T^-) \quad (10)$$

in which

$$(C^-) = \frac{k_1(C)(CH_3O^-)[k_3(CH_3OH) + k_5 + k_6] + k_3k_7(T)(CH_3O^-)}{[k_3(CH_3OH) + k_5 + k_6][k_2(CH_3OH) + k_3 + k_4] - k_4k_5} \quad (11a)$$

$$(T^-) = \frac{k_7(T)(CH_3O^-)[k_2(CH_3OH) + k_3 + k_4] + k_1k_4(C)(CH_3O^-)}{[k_3(CH_3OH) + k_5 + k_6][k_2(CH_3OH) + k_3 + k_4] - k_4k_5} \quad (11b)$$

The  $k$ 's refer to scheme 6, C is *cis*- $C_2H_2Br_2$ ,  $C^-$  is *cis*- $C_2HBr_2^-$ , T is *trans*- $C_2H_2Br_2$ ,  $T^-$  is *trans*- $C_2HBr_2^-$  and  $k_{elim}^C$  and  $k_{elim}^T$  are the elimination rate constants for the indicated isomers.

Case 1 takes hydrogen exchange, isomerization and elimination as competing processes. Cristol and Fix reported that  $\beta$ -benzene hexachloride becomes deuterated during base-catalyzed elimination.<sup>41</sup> Judging from their data, no isomeric hexachloride is formed. Labeling their starting material (T) the simplification in 11a and 11b that appears justified is  $k_2 = 0$  and  $(C) = 0$ . No information is yet available on the relative magnitudes of  $k_4$  and  $k_5$  as compared with  $k_3$  and  $k_6$ , though Cristol, *et al.*, usually have assumed  $k_6 = 0$  and that  $k_4$  and  $k_5$  are large.<sup>7,41</sup>

In case 2, hydrogen exchange is assumed to be negligible. This leads to

$$d(Br^-)/dt = k_1(C)(CH_3O^-) \text{ or } d(Br^-)/dt = k_7(T)(CH_3O^-) \quad (12)$$

(39) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., N. Y., 1945, p. 193.

(40) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Ch. 7.

(41) S. J. Cristol and D. D. Fix, *THIS JOURNAL*, **75**, 2617 (1953).

for stepwise mechanism 2a. Experimentally this situation is often indistinguishable from one-step elimination which will be called 2b. It is nevertheless meaningful to distinguish the stepwise from the concerted process, first, because the pattern of the activation parameters should be different and, second, because reverse additions are known.<sup>42</sup> Here proton availability is critical. The ratio  $k_{elim}^C/k_{elim}^T$  usually should be close to unity (factor of 100) and there appears to be no compelling reason for eliminations in the *trans* sense to be favored over corresponding eliminations in the *cis* sense.

Concerning the steps that are not rate determining, the relative magnitudes of  $k_3$ ,  $k_6$ ,  $k_4$  and  $k_5$  usually cannot be fixed. However, for the diastereoisomeric ions  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHCHBrI}$ , halide removal is faster than isomerization and  $k_3 > k_4$  and  $k_6 > k_5$ .<sup>43</sup> In fact, it is only for such a system that isomeric products are distinguishable.

Rate laws 12 may apply to our elimination data on *cis*-diiodoethene, the data on the dehydrobromination of bromobenzene by sodium amide<sup>28b</sup> and the data on dehydrohalogenation of the halomaleates and -fumarates.<sup>44</sup> By analogy with our substituted acrylates, it is assumed that the latter compounds do not undergo hydrogen exchange. But no decision can yet be made as to whether these examples do belong in category 2a or in the concerted category 2b. The rate data for the halomaleates and -fumarates are, however, consistent with the stepwise mechanism. Elimination in the *trans* sense is favored with  $k_{elim}^C/k_{elim}^T \sim 10$ .<sup>44</sup>

In case 2b, one-step elimination is assumed: proton and halide departure are simultaneous. Such a mechanism probably applies to the elimination reactions of 1-phenyl-2-haloethanes<sup>45</sup> and appears to have been demonstrated in the *cis* and *trans* eliminations from the 2-(*p*-tolylsulfonyl)-cyclohexyl and -cyclopentyl *p*-toluenesulfonates.<sup>46</sup> In these cyclic compounds there is a preference for elimination in the *trans* sense.

In case 3, the isomerization rates of the anions are taken to be small so that

$$k_{elim}^C = \frac{k_1k_3}{k_2(CH_3OH) + k_3} \text{ and } k_{elim}^T = \frac{k_7k_6}{k_3(CH_3OH) + k_6} \quad (13)$$

The further restriction of rapid exchange yields

$$k_{elim}^C = k_1k_3/k_2(CH_3OH) \text{ and} \quad (14a)$$

$$k_{elim}^T = k_6k_7/k_3(CH_3OH) \quad (14b)$$

The rate law, 14a, appears to be applicable to *cis*-dichloroethene, *cis*-dibromoethene, trichloroethene, tribromoethene and possibly the *cis*- $\omega$ -bromosty-

(42) Shilov's group has established the rate expressions for the additions of HX to acetylenedicarboxylic acid esters (A) in the presence of alkali halides: rate =  $k(A)(LiX)$  and rate =  $k'(HX)(LiX)$ . (A): (a) V. G. Ostroverkhov and E. A. Shilov, *Ukrain. Khim. Zhur.*, **22**, 590, 743 (1956); *C. A.*, **51**, 6515, 7813 (1957); (b) I. V. Smirnov-Zamkov and E. A. Shilov, *Doklady Akad. Nauk, S.S.S.R.*, **67**, 671 (1949); *C. A.*, **43**, 8824 (1949).

(43) S. I. Miller and P. K. Yonan, *THIS JOURNAL*, **79**, 5931 (1957).

(44) E. G. Grunwald and S. J. Cristol, *ibid.*, **79**, 2891 (1955).

(45) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957); W. H. Saunders, Jr., and D. H. Edison, Abstracts of the 135th Meeting of the American Chemical Society, Boston, April, 1959, p. 91-O.

(46) J. Weinstock, J. L. Bernardi and R. C. Pearson, *ibid.*, **80**, 4961 (1958).

renes.<sup>7</sup> It is not yet certain whether the stereospecific dehydroiodinations of the 2-benzenesulfonyl-3-iodobutanes fall in this category or in the concerted 2b category.<sup>47</sup> It seems certain, however, that the dehydrofluorination of fluorobenzene with sodamide falls in this category.<sup>28b</sup>

If *cis* eliminations are admitted, the dehydrohalogenation data of the *trans* compounds of Table IV are consistent with 14b. In contrast, Cristol takes  $k_6 = 0$  and uses isomerization step 5.<sup>7</sup> The following line of reasoning argues for *cis* elimination in the case of *trans*-dibromoethene. The ratio

$$k_{elim}^C/k_{elim}^T = k_1k_3k_3/k_7k_2k_{5,6} \quad (15)$$

is  $5 \times 10^6$ ;  $k_{5,6}$  corresponds either to elimination by path 5 (and 3) or by path 6. Taking  $k_2 \approx k_3$  and  $k_1/k_7 \approx 50$ ,  $k_3 \approx 10^{13}$  sec.<sup>-1</sup>. This corresponds to  $\sim 5.5$  kcal./mole in free energy of activation. Now if  $k_6 > k_5$ ,  $V > 5.5$  kcal./mole and if  $k_6 < k_5$ ,  $V = 5.5$  kcal./mole.<sup>48</sup> The barrier to *cis-trans*

(47) P. S. Skell and J. H. McNamara, *THIS JOURNAL*, **79**, 85 (1957).

(48) This approach to (15) was suggested by a referee who correctly argued by somewhat different assumptions that the isomerization barrier was given by  $V > 11$  kcal./mole.

conversion is not expected to differ drastically from the barrier to *trans-cis* conversion. Since the minimum in  $V$  has been set at 28 kcal./mole, we conclude  $k_6 > k_5$  and *cis*-dehydrobromination of the *trans*-dibromoethene occurs.

*cis-trans* pairs of compounds in this category exhibit large rate ratios as in expression 15. Although this may be attributed mainly to  $k_3/k_6$ , a more detailed analysis of the activation parameters must be deferred until more data on the individual steps are available. It would appear, however, that the theory of minimum orbital bending provides a quantum mechanical rationalization for the prediction that  $k_3/k_6 > 1$ .<sup>49</sup>

The preceding discussion of base-catalyzed eliminations emphasizes that apparently similar systems may eliminate by different paths. Alternative one-, two- or three-step mechanisms must be considered for any specific case. Perhaps the most interesting experimental problem to be solved here revolves around the fate of the vinyl carbanion: will it lose halide, isomerize or abstract a proton from the solvent?

(49) G. H. Stewart and H. Eyring, *J. Chem. Educ.*, **35**, 550 (1958). CHICAGO 16, ILL.

[CONTRIBUTION FROM THE EASTERN LABORATORY OF E. I. DU PONT DE NEMOURS AND CO.]

## Liquid Phase Nitration of Bicyclo [2.2.1]heptane and Decahydronaphthalene

BY GEORGE W. SMITH

RECEIVED MAY 17, 1958

The liquid phase nitration of bicyclo[2.2.1]heptane (norbornane) by nitrogen dioxide in carbon tetrachloride was investigated under various conditions to determine the positions attacked and the amounts of the mononitro derivatives formed. The major nitro compound formed was 2-nitrobicyclo[2.2.1]heptane which was isolated in conversions as high as 30%. Vapor phase chromatography and infrared analysis suggest that very small amounts (<1.0% conversion) of two other mononitro derivatives (alkali-insoluble) may have been formed in the reaction. The nitration of decahydronaphthalene was carried out under similar conditions to give a 9.0% yield of 9-nitrodecahydronaphthalene.

Substitution reactions involving bridgehead carbons have been of theoretical interest for some time. A review of the available literature to June, 1954, concerning this subject indicated the difficulty encountered in such displacement reactions.<sup>1</sup>

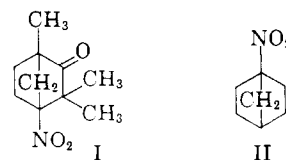
In 1915, Nametkin and co-workers reported that liquid phase nitration of camphane, isocamphane and camphenilane with dilute nitric acid at 140° yielded only secondary nitro derivatives and some ketones and dibasic acids.<sup>2</sup> No bridgehead nitro compounds were isolated in these experiments. However, *d*-fenchone was reported to yield both a secondary and a tertiary nitro compound when allowed to react with dilute nitric acid at 130°. The tertiary nitro derivative was believed by Nametkin to be the bridgehead compound I. More recently the vapor phase nitration of bicyclo[2.2.1]heptane at 400° by concentrated nitric acid was reported to give nitronorbornane of which approximately 50% was the bridgehead derivative II.<sup>4</sup> In view of the

(1) D. E. Applequist and J. D. Roberts, *Chem. Revs.*, **54**, 1085 (1954).

(2) S. Nametkin, *et al.*, *J. Russ. Phys. Chem. Soc.*, **47**, 409 (1915).

(3) S. Nametkin, *J. prakt. Chem.*, [2] **108**, 29 (1924).

(4) R. T. Blickenstaff and H. B. Hass, *THIS JOURNAL*, **68**, 1431 (1946).



results reported concerning the nitration of bicyclo[2.2.1]heptane derivatives, the liquid phase nitration of bicyclo[2.2.1]heptane was investigated with nitrogen dioxide as the nitrating agent and with conditions somewhat more vigorous than those used in previous liquid phase work to determine where substitution would occur.

Carbon tetrachloride was employed as a solvent for both bicyclo[2.2.1]heptane (a solid) and nitrogen dioxide in all runs except one in which gaseous nitrogen dioxide (preheated to 175°) was fed into the autoclave. After a relatively short reaction period (16-23 min.), 2-nitrobicyclo[2.2.1]heptane was obtained in conversions as high as 30%. The identity of this major product as the 2-nitro derivative was confirmed by infrared and elemental analyses. These results are in agreement with those obtained in the chlorination of bicyclo[2.2.1]heptane