(2.24 g, 0.0126 mole) and a few milligrams of dibenzoyl peroxide were added to a solution of 7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide (**2**) (1.0 g, 0.0063 mole) in 50 ml of carbon tetrachloride. The reaction mixture was heated at 60–65° in a oil bath until all of the N-bromosuccinimide had been converted to succinimide (1–2 days). The succinimide (1.3 g) was removed by filtration and the carbon tetrachloride was washed successively with water, 5% aqueous sodium thiosulfate, and water and then dried over anhydrous sodium sulfate. Removal of the carbon tetrachloride under reduced pressure gave a clear oil which was treated for 12 hr at room temperature with 20 ml of triethylamine in benzene followed by a 3-hr period at the temperature of refluxing solvent. The triethylamine hydrobromide was removed by filtration and the benzene removed under reduced pressure to give 1.0 g of a brown oil. The oil was dissolved in chloroform, treated twice with decolorizing charcoal, and chromatographed on a column of Florisil. Elution with chloroform gave 0.6 g of a colorless oil which was sublimed (30°, 0.25 mm) to yield a white solid, mp 100–120°. Recrystallization from ether gave needles, mp 126–128°. The over-all yield to recrystallized product was about 3%.

Anal. Calcd for $C_7H_6O_2S$: C, 54.52; H, 3.92. Found: C, 54.58; H, 3.97.

The benzothiete sulfone had the following properties: infrared (KBr), 3025 (w), 2940 (w), 1465 (m), 1445 (m), 1300 (s), 1195 (s), 1175 (m), 1150 (m), 1125 (s), 720 (s), 710 cm^{-1} (s); nmr ($CDCl_3$), δ 5.1 (singlet, 2 H), 7.55 (singlet, 4 H); ultraviolet (CH_3CN), 260 (ϵ 8540), 267 (ϵ 13,600), 274 mμ (ϵ 13,600); mass spectrum, *m/e* 154 (parent ion, 14.8%), 137 (P − OH, 19.0%), 93 (15.8%), 91 (22.1%), 90 (P − SO_2; 56.8%), 89 (P − SO_2H, 100%), 77 (14.2%), 64 (19.5%), 63 (43.8%), 62 (17.9%), 51 (23.1%), 50 (15.3%), 39, (37.5%).

Reactions of *gem*-Dihalocyclopropanes with Electrophilic Reagents. Formation of Allyl Derivatives and/or Dienes

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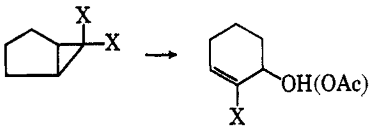
The reaction of *gem*-dihalocyclopropanes with silver acetate–acetic acid yields $R_1R_2C{=}CBrCR_3R_4OAc$ and/or $R_1R_2C{=}CBrCR_3{=}CR_4R_5$. The distribution of the two products depends on the number of methyl groups. Tetramethyldibromocyclopropane yields 3-bromo-2,4-dimethyl-2,4-pentadiene as the sole product. Reaction of both *cis*- and *trans*-1,1-dibromo-2,3-dimethylcyclopropane gave *trans*-3-bromo-2-acetoxy-3-pentene.

Ring-opening rearrangement reactions of *gem*-dihalocyclopropanes have been effected by the use of solvents with either electrophilic or nucleophilic reagents,[2] thermally[2,3] or by means of alkali or alkaline earth metals.[2,4] Solvolysis and thermal rearrangement give allyl derivatives, dienes, or alkynes; metals and organometallics give allenes (Scheme I). The use of boiling quinoline or pyridine leads largely to ring opening concurrent with dehydrohalogenation.[5]

The purpose of the present paper is to report some of the detailed data that were only briefly described in our earlier communication on *gem*-dihalocyclopropane ring expansions.[2f]

Results

Electrophilic Rearrangement of 6,6-Dichlorobicyclo[3.1.0]hexane and 6,6-Dibromobicyclo[3.1.0]hexane.—The experimental data in Table I indicate that the electrophilic rearrangement can be carried out under mild conditions with aqueous silver nitrate, silver perchlorate, silver acetate–acetic acid, mercuric acetate–acetic acid, and sodium acetate–acetic acid to give good yields of 2-chloro-3-hydroxycyclohexene (I), 2-bromo-3-hydroxycyclohexene (II), or their actate derivatives such as 2-bromo-3-acetoxycyclohexene (III). Under



X = Br or Cl

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Scheme I

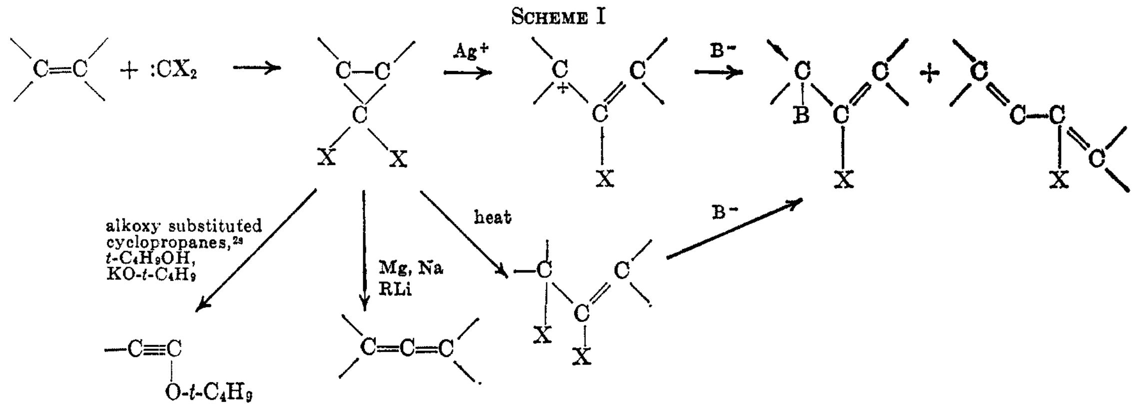


Table I

Rearrangement of *gem*-Dihalocyclopropanes

1,1-Dihalocyclopropane, mmoles	Electrophilic reagent, mmoles	Solvent, ml	Reaction temp, °C	Time, hr	Product	Yield, %	Bp, °C (mm)	n_D (t, °C)	Calcd, % C	Calcd, % H	Found, % C	Found, % H
6,6-Dichlorobicyclo[3.1.0]-hexane, 23.1	$AgClO_4$, 42.5	H_2O, 50	90–100	5.5	C_6H_9ClO (I)[a]	84	80 (11)	1.5093 (23)				
6,6-Dibromobicyclo[3.1.0]-hexane, 31.6	$AgNO_3$, 58.8	H_2O, 5	90–100	0.5	C_6H_9BrO (II)[b]	47	66–74 (2)	1.5382 (28)	40.70	5.08	41.38	5.22
6,6-Dibromobicyclo[3.1.0]-hexane, 79	$AgClO_4$, 87.7	H_2O, 100 (at pH 7 using NaOH)	28	1	C_6H_9BrO (II)[b]	66	62–63 (1.5–2.0)	1.5435 (21)				
6,6-Dibromobicyclo[3.1.0]-hexane, 37.5	$Hg(OAc)_2$, 40.8	HOAc, 50	118	6	$C_8H_{11}BrO_2$ (III)	45	75 (2)	1.5042 (20)				
6,6-Dibromobicyclo[3.1.0]-hexane, 33.7	NaOAc, 100	HOAc, 20	90–100	4.75	$C_8H_{11}BrO_2$ (III)	62	85 (3)	1.5031 (26)				
6,6-Dibromobicyclo[3.1.0]-hexane, 42.3	AgOAc, 56.5	HOAc, 7	90–100	24	$C_8H_{11}BrO_2$ (III)	46	73–75 (2)	1.5047 (20)				
7,7-Dichlorobicyclo[4.1.0]-heptane, 100	$AgNO_3$, 160 NaOAc, 200	HOAc, 100	118	480[c]	$C_9H_{13}ClO_2$ (IV)	43 (crude) 26 (distilled)	74 (0.5)	1.4890 (18)	57.30	6.90	57.20	7.17
7,7-Dibromobicyclo[4.1.0]-heptane, 93	AgOAc, 150	HOAc, 50	90–100	41	$C_9H_{13}BrO_2$ (V)	45	92 (2)	1.5060 (29)	46.30	5.57	46.40	5.69
7,7-Dibromobicyclo[4.1.0]-heptane, 93	AgOAc, 150	HOAc, 50	90–100	72	$C_9H_{13}BrO_2$ (V)	24	84 (0.45)	1.5038 (23)				
7,7-Dibromobicyclo[4.1.0]-heptane, 100	$AgNO_3$, 150 NaOAc, 200	HOAc, 100	118	24[d]	$C_9H_{13}BrO_2$ (V)	100 (crude) 36 (distilled)	71–75 (0.3)	1.5083 (19)	46.30	5.57	46.80	5.87
1,1-Dibromo-2,2-dimethyl-cyclopropane, 100	AgOAc, 150	HOAc, 50	90–120	24	$C_7H_{11}BrO_2$ (VI)	31	48–52 (2.2)	1.4700 (23)	40.60	5.32	40.79	5.54
					$C_7H_{11}BrO_2$ (VII)	50	65–66 (2.5)	1.4811 (23)	40.60	5.32	39.89	5.45
1,1-Dibromo-*cis*-2,3-di-methylcyclopropane, 50	AgOAc, 75	HOAc, 50	110–120	2.75	$C_7H_{11}BrO_2$ (VIII)	97 (crude) 69 (distilled)	60–61 (3.5–4.0)	1.4687 (25)	40.60	5.32	40.48	5.40
1,1-Dibromo-*trans*-2,3-di-methylcyclopropane, 100	AgOAc, 150	HOAc, 50	110–120	24	$C_7H_{11}BrO_2$ (VIII)	100 (crude) 93 (distilled)	62–63 (3.5–4.5)	1.4680 (25)	40.60	5.32	40.98	5.63
1,1-Dibromo-*cis*-2,3-di-methylcyclopropane, 63	$AgNO_3$, 253	H_2O, 100	90–100	1.5	C_5H_9BrO (IX)	36	75–76 (15)	1.4933 (25.7)				
1,1-Dibromo-*trans*-2,3-di-methylcyclopropane, 48	$AgNO_3$, 177	H_2O, 100	90–100	1.5	C_5H_9BrO (IX)	44	74–75 (15)	1.4918 (26)	36.30	5.42	36.01	5.32
1,1-Dibromo-2,2,3-tri-methylcyclopropane, 170	$AgNO_3$, 200	HOAc, 100	100–120	16	C_6H_9Br (X)	29	28–35 (8.5)	1.5147 (20)	44.70	5.59	45.07	5.78
	NaOAc, 300				$C_8H_{13}BrO_2$ (XI)[e]	13	82 (17)	1.4798 (20)	43.40	5.88	43.80	6.05
1,1-Dibromo-2,2,3,3-tetra-methylcyclopropane, 100	AgOAc, 150	HOAc, 50	100–120	0.75	$C_7H_{11}Br$ (XII)	73	44 (13)	1.4931 (21)	48.00	6.28	48.39	6.26
1,1-Dibromo-2-phenyl-cyclopropane, 50	AgOAc, 75	HOAc, 50	110–120	48	$C_{11}H_{11}BrO_2$ (XIII)	53	111–112 (0.3–0.35)	1.5612 (24)	51.70	4.31	52.56	4.25
1,1-Dibromo-2,2-diphenyl-cyclopropane, 50	AgOAc, 75	HOAc, 50	110–120	24	$C_{17}H_{15}BrO_2$ (XIV)[f]	91 (crude) 72 (distilled)	145 (0.15)	1.6020 (22)	61.60	4.53	62.11	4.88

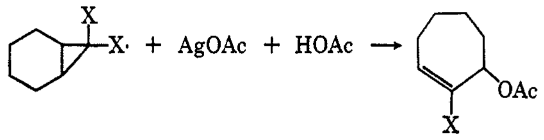
[a] Lit. bp 86–87° (15 mm); n^{25}_{D} 1.5088 (see ref 2m and M. Mousseron and R. Jacquier, *Bull. Soc. Chim. France*, 648 (1950). [b] Lit.[2l] bp 74–76° (4 mm); n^{25}_{D} 1.5387. [c] After refluxing for 24 hr some ester product began to appear in the glpc chromatograms. [d] The starting dibromide is 75% converted into the ester product after 1.5 hr and 100% after 5 hr as determined by glpc analysis. [e] Mol wt 227 (saponification) (calcd 221). [f] Permanganate oxidation yields benzophenone as determined by comparing the melting point with an authentic sample (undepressed mixture melting point).

the conditions used none of the 2,3-dihalocyclohexene isomer was isolated.

Electrophilic Rearrangement of 7,7-Dihalobicyclo[4.1.0]heptane.—Refluxing a mixture of silver acetate–acetic acid with 7,7-dichlorobicyclo[4.1.0]heptane for 480 hr yielded 43% crude and 26% distilled 2-chloro-3-acetoxycycloheptene (IV).

The dibromocarbene adduct of cyclohexene reacted more readily under similar conditions and after 5 hr was completely converted to 2-bromo-3-acetoxycycloheptene

(V) as determined with the aid of glpc. The product was isolated in 36% yield.

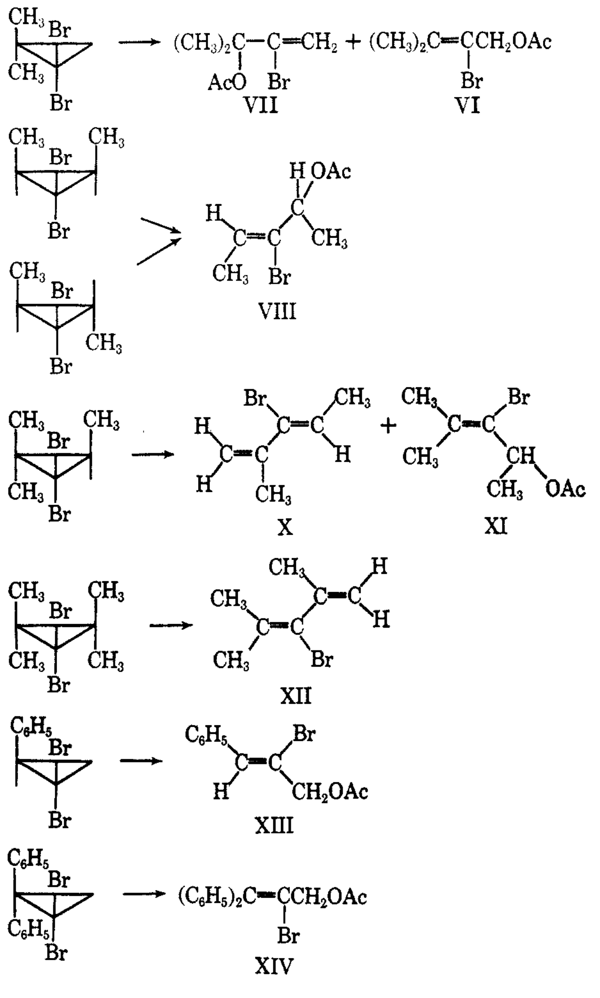


X = Br or Cl

Electrophilic Rearrangement of Substituted 1,1-Dibromocyclopropanes.—The dibromocyclopropanes having alkyl or aryl substituents rearranged in the presence of aqueous silver nitrate or silver acetate-acetic acid upon heating to yield either the corresponding allyl alcohol, allyl acetate, or diene derivative as shown in Table II.

TABLE II

PRODUCTS OF THE SILVER ACETATE-ACETIC ACID REARRANGEMENT OF 1,1-DIBROMOCYCLOPROPANES

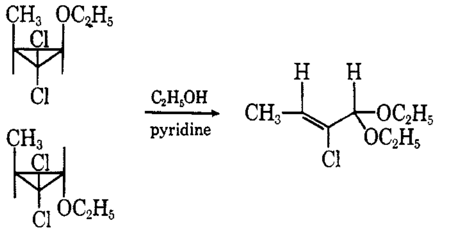


Discussion

The relative ease of the silver ion catalyzed rearrangement of the dibromocarbene adducts of cyclopentene and 2,3-dimethylbutene-2 is in sharp contrast to the more difficult to solvolyze dibromocarbene adducts of cyclohexene, styrene, isobutylene, and 4-methylpentene-1. The thermal rearrangement of these *gem*-dihalocyclopropanes also follows the same order of reactivity.[1b,21] Solvolysis in the absence of silver ion or bases in most cases is very slow and allows the isolation of the thermally rearranged dihalide.[2m,p] The relief of steric strain of the substituents enhances the ease of rearrangement. For example, the dibromocarbene adduct of *cis*-butene-2 reacts more rapidly than the dibromocarbene adduct of *trans*-butene-2 as determined by analyzing the reaction mixture periodically with the aid of a gas chromatograph or by titration of the liberated halide ion.

The dibromocarbene adducts of *cis*- and *trans*-butene-2 both yield the same isomeric rearranged product on reaction with silver acetate-acetic acid (VIII) or aqueous silver nitrate (IX) as determined by glpc, infrared, and nmr spectroscopy (Table IV).

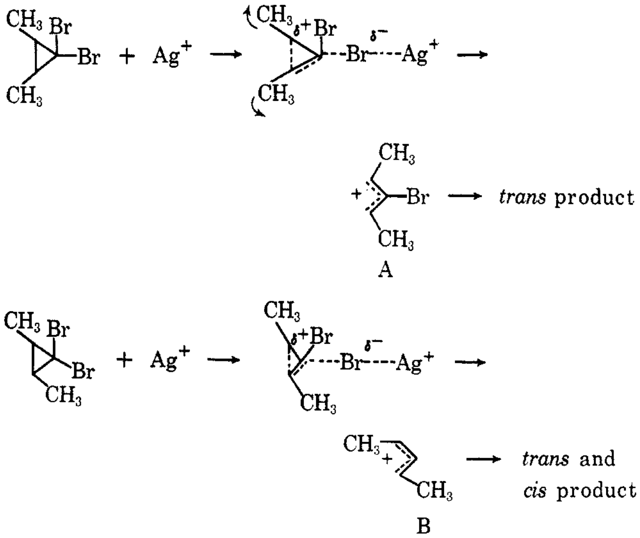
Skattebøl[2a] found a similar result for the thermal reaction in pyridine-alcohol solution for *cis*- and *trans*-1,1-dichloro-2-ethxoy-3-methylcyclopropane in which both gave *trans*-2-chloro-1,1-diethoxy-2-butene (eq 1).

 (1)

Woodward and Hoffmann[6] have suggested theoretical selection rules for electrocyclic reaction. In the case of the ring opening of a cyclopropyl cation, substituents would move disrotatory, either both inward or both outward. DePuy and co-workers[7] further suggested that in concerted ring openings the substituents *trans* to the leaving group rotate outward. Disrotatory opening of the *trans* isomer leads to a less favorable intermediate cation in which the H and alkyl groups are coplanar and thus interact sterically. However, disrotatory opening of the *cis* isomer leads to an intermediate allylic cation with less steric constraint in which only the hydrogen atoms interact.

In the case of *cis*- and *trans*-1,1-dibromo-2,3-dimethylcyclopropane the transition states obtained by the favored disrotatory process[3,6,7] can be formulated as in Scheme II.

SCHEME II



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(6) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

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TABLE III

PHYSICAL PROPERTIES OF THE SYNTHESIZED 1,1-DIHALOCYCLOPROPANES

Compd	Olefin, moles	Solvent, ml	Potassium *t*-butoxide, moles	Haloform,[a] moles	Yield, %	Bp (mm) or mp, °C (uncor)	n_D (*t*, °C)	Lit. bp (mm), n_D (*t*), or mp, °C
6,6-Dichlorbicyclo-[3.1.0]hexane	Cyclopentene, 1.0	None	0.75	C, 0.75	20	87–90 (61)	1.4907–1.4941[b] (27.2)	69 (20), 1.4985 (20)[f]
6,6-Dibromobicyclo-[3.1.0]hexane	Cyclopentene, 1.0	None	0.75	B, 0.82	42	63–69 (2)	1.5560–1.5594 (18)	63–63.5, 1.5570 (25)[g]
7,7-Dichlorobicyclo-[4.1.0]heptane	Cyclohexene, 1.0	*n*-Pentane, 400	1.0	C, 1.0	18	67–68 (6.0)	1.5038 (20)	78–79 (15), 1.5014 (23)[h]
7,7-Dibromobicyclo-[4.1.0]heptane	Cyclohexene, 1.0	Cyclohexane, 100	0.88	B, 1.18	35	98–100 (6–6.5)	1.5579[c] (23)	100 (8), 1.5578 (20)[h]
1,1-Dibromocyclopropane								
2,2-Dimethyl-	Isobutylene, 1.0	None	0.4	B, 0.3	28	47–48 (11)	1.5136 (23)	59–59.2 (20), 1.5121 (25.1)[i]
cis-2,3-Dimethyl-	*cis*-Butene-2, 1.0	None	0.4	B, 0.3	90	55–56 (11–12)	1.5188–1.5206 (23)	70–70.2 (23), 1.5170 (25.1)[i]
trans-2,3-Dimethyl-	*trans*-Butene-2, 1.0	None	0.4	B, 0.3	90	55–56 (11)	1.5110 (25)	64 (23), 1.5108 (25.1)[i]
2,2,3-Trimethyl-	2-Methylbutene-2, 1.0	None	0.6	B, 0.5	50	48–50 (3.8)	1.5167 (23)	83 (24), 1.5134 (25)[j]
2,2,3,3-Tetramethyl-	2,3-Dimethylbutene-2, 1.0	*n*-Pentane, 100	1.0	B, 0.9	60	75–76		77–78[j]
2-Phenyl-	Styrene, 1.0	None	0.25	B, 0.25	55	118–120 (5.7)	1.5996 (23)	94 (2), 1.5963 (25)[j]
2,2-Diphenyl-	1,1-Diphenylethylene, 0.14	*n*-Pentane, 100	0.25	B, 0.26	63	146–147[d]		151–152[j]
2-*sec*-Butyl-	4-Methylpentene-1, 1.0	None	0.25	B, 0.25	52	50 (1.0)	1.4992 (23)	*e*

[a] C = $CHCl_3$, B = $CHBr_3$, and I = CHI_3. [b] *Anal.* Calcd for $C_6H_8Cl_2$: C, 47.60; H, 5.30. Found: C, 47.98; H, 5.18. [c] *Anal.* Calcd for $C_7H_{10}Br_2$: C, 33.10; H, 4.00. Found: C, 33.06; H, 4.15. [d] Recrystallization from isopropyl alcohol. [e] *Anal.* Calcd for $C_7H_{12}Br_2$: C, 32.80; H, 4.68. Found: C, 33.22; H, 4.76. [f] See ref 2m. [g] See ref 21. [h] See ref 2a. [i] See ref 14. [j] See ref 15.

In agreement with the above predictions it is found that the *cis*-dimethyl isomer reacts faster than the *trans* isomer in both the dibromo-, monotosyl-,[8] and 1,1-dichloro-2-methyl-3-ethoxycyclopropane.[2s] In the case of *cis*- and *trans*-1,1-dibromo-2,3-dimethylcyclopropane and 1,1-dichloro-2-methyl-3-ethoxycyclopropane both isomers during solvolysis lead only to the *trans*-rearranged product. The fact that none of the *cis* isomer is produced may be due to either isomerization of the *cis* product during the reaction or to a preferred attack by a nucleophile on carbonium ion B to give only the *trans* product. Isomerization in another *cis*-α,γ-dimethylallyl system has been reported to give predominantly the *trans* product.[9]

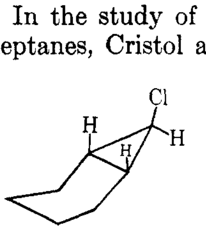
As indicated by the results described in Table II it is seen that groups capable of conjugating or hyperconjugating with the incipient double bond favor the formation of that double bond. These results are similar to that observed for olefin formation *via* HX elimination from a secondary or tertiary alkyl halide as described by the Saytzeff rule.[10] For example, arylated dibromocyclopropanes yield allyl derivatives with the double bond conjugated with the benzene ring as illustrated in the dibromocarbene adducts of styrene and 1,1-diphenylethylene.

Diene products are formed when starting with tri- or tetramethyldibromocyclopropanes because proton elimination is favored from the intermediate tertiary allylic carbonium ions to give a conjugated diene. When primary or secondary allylic carbonium ions are formed then reaction with a nucleophile accounts for the product.

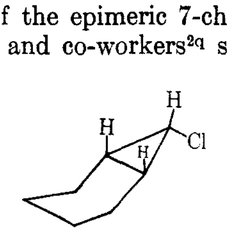
Earlier[2a,m] it was reported that the dibromo- and dichlorocarbene adducts of cyclohexene were all relatively stable to silver nitrate at room temperature. Doering[2a] reported that 7,7-dichlorobicyclo[4.1.0]heptane was stable after refluxing for several hours with alcoholic silver oxide. Cristol and co-workers[2q] studied the rate of solvolysis in glacial acetic acid–sodium acetate but the structure of the product was not described.

The results of our investigation indicate that both materials yield rearranged products after heating or refluxing for several hours with silver acetate–acetic acid. After 24 hr of refluxing, 7,7-dibromobicyclo[4.1.0]heptane yields 2-bromo-3-acetoxycycloheptene (V) and is isolated in 36% yield. In addition, 7,7-dichlorobicyclo[4.1.0]heptane under similar conditions gives 2-chloro-3-acetoxycycloheptene (IV) in 26% yield after 480 hr.

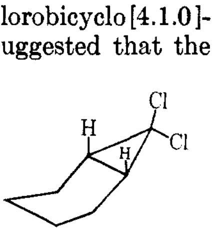
In the study of the epimeric 7-chlorobicyclo[4.1.0]heptanes, Cristol and co-workers[2q] suggested that the



$k = 8 \times 10^{-9}\ \text{sec}^{-1}$



$k = 1.4 \times 10^{-8}\ \text{sec}^{-1}$



$k^{11} = 4.5 \times 10^{-7}\ \text{sec}^{-1}$

loss of the halide ion *trans* to the hydrogen atoms at C-2 and C-4 is preferred by a large factor. Schleyer[8] has observed a similar order of reactivity in the solvoly-

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[8] P. von R. Schleyer, G. W. Van Dine, U. Schollkopf, and J. Paust, *J. Am. Chem. Soc.*, **88**, 2868 (1966).

[9] H. L. Goering, T. D. Nevitt, and E. Silversmith, *ibid.*, **77**, 5026 (1955).

[10] (a) A. Saytzeff, *Ann.*, **179**, 296 (1857); (b) D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 304.

TABLE IV

NMR[a] AND ULTRAVIOLET ABSORPTIONS OF THE NEW PRODUCTS

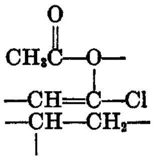
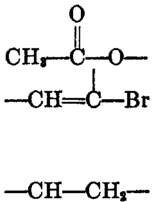
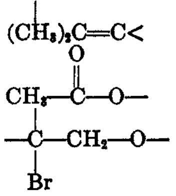
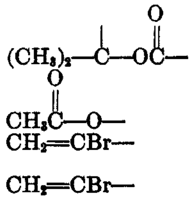
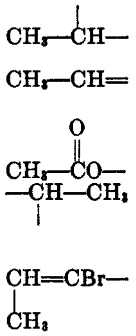
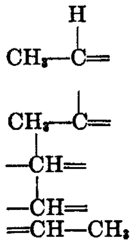
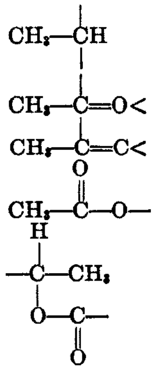
Product compd	δ, ppm	Chemical shift, cps	Multiplicity	Structural assignment	Ultraviolet spectra, mμ
IV	2.05	123	1	 $CH_3\overset{O}{\overset{\|}{C}}-O-$	
	5.36	324	2	$-CH=C-Cl$	
	5.45	328			
	6.0	361	3	$-CH-CH_2-$	
	6.12	367			
	6.24	373			
V	2.03	123	1	 $CH_3-\overset{O}{\overset{\|}{C}}-O-$	
	5.40	324	2	$-CH=C-Br$	
	5.50	330			
	6.26	375	3	$-CH-CH_2-$	
	6.37	381			
	6.47	387			
VI	1.90	114.5	1	 $(CH_3)_2C=C<$	
	2.02	121	1	$CH_3-\overset{O}{\overset{\|}{C}}-O-$	
	4.80	288	1	$-\underset{Br}{C}-CH_2-O-$	
VII	1.60	96.5	1	 $(CH_3)_2-C-O\overset{O}{\overset{\|}{C}}-$	
	1.96	118	1	$CH_3\overset{O}{\overset{\|}{C}}-O-$	
	5.50	330	2	$CH_2=CBr-$	
	5.55	332			
	5.79	347	2	$CH_2=CBr-$	
	5.82	350			
VIII	1.30	66.0	2	 CH_3-CH-	
	1.37	69.0			
	1.70	85.0	2	$CH_3-CH=$	
	1.76	88.0			
	1.96	99	1	$CH_3-\overset{O}{\overset{\|}{C}}O-$	
	5.18	259	4	$-CH-CH_3$	
	5.25	263			
	5.32	266			
	5.38	269			
	5.95	298	4	$\underset{CH_3}{CH}=CBr-$	
	6.04	302			
	6.10	305			
	6.16	308			
X	1.78	89	2	 $CH_3-\overset{H}{C}=$	$\lambda_{max}^{CH_3OH}$ 222 (ϵ_{max} 13,572)
	1.85	92			
	1.91	96	1	$CH_3-C=$	
	4.95	248	1	$-CH=$	
	5.36	268	1	$-CH=$	
	5.85	293	4	$=CH-CH_3$	
	5.92	296			
	5.99	299			
	6.05	302			
XI	1.25	63.0	2	 CH_3-CH	
	1.31	66.0			
	1.85	93.0	1	$CH_3-C=O<$	
	1.91	95.0	1	$CH_3-C=C<$	
	1.95	97.0	1	$CH_3-\overset{O}{\overset{\|}{C}}-O-$	
	5.55	277	4	$-\underset{O-\underset{O}{\underset{\|}{C}}-}{\overset{H}{C}}-CH_3$	
	5.60	280			
	5.66	283			
	5.71	286			

TABLE IV (*Continued*)

Product compd	δ, ppm	Chemical shift, cps	Multiplicity	Structural assignment	Ultraviolet spectra, mμ
XII	1.76	88	1	$CH_3-\overset{\vert}{C}=C<$	$\lambda_{max}^{CH_3OH}$ 248, 210 ϵ_{max} (248) 849 ϵ_{max} (210) very high
	1.84	92	1	$(CH_3)_2C=C<$	
	4.80	240	1	$\overset{\vert}{H}C=$	
	4.91	246	1	$\underset{\vert}{H}C=$	
XIII	2.02	101	1	$CH_3-\overset{O}{\overset{\Vert}{C}}-O-$	$\lambda_{max}^{CH_3OH}$ 251 (ϵ_{max} 11,985)
	4.75	238	1	$=\underset{Br}{\underset{\vert}{C}}-CH_2-O\overset{O}{\overset{\Vert}{C}}-$	
	6.93	346	1	$=CH-C_6H_5$	
	7.23	365	Complex	$C_6H_5-CH=$	
XIV	1.96	98	1	$CH_3-\overset{O}{\overset{\Vert}{C}}-O-$	$\lambda_{max}^{CH_3OH}$ 260 (ϵ_{max} 9010)
	4.76	238	1	$CH_2-O\overset{O}{\overset{\Vert}{C}}-$	
	7.16	358	Complex	$(C_6H_5)_2-C=$	

[a] The integrated nmr spectra are consistant with the number of protons indicated for the compounds.

sis in the epimeric monotosylbicyclo[4.1.0]heptanes. Cristol[2q] further reasoned that on the basis of the rates of solvolysis (carried out at 124.6° in glacial acetic acid–sodium acetate) that the same halogen leaves in 7,7-dichlorobicyclo[4.1.0]heptane.

The rate acceleration found for the solvolysis of 7,7-dibromobicyclo[4.1.0]heptane compared to the dichloro analog in the presence of silver ion is not surprising since it follows the order of reactivity observed for other substituted alkyl halides I > Br > Cl.[11] In fact similar rate differences are found for other 1,1-dihalocyclopropanes as will be described at another time.[12]

Experimental Section[13a,b]

The dihalocarbene adducts were generally prepared by adding 1.0 mole of haloform to 1.0 mole of dry potassium *t*-butoxide (M.S.A. Research Corp.) in 1.0 mole or more of the olefin in 200–300 ml of *n*-pentane at 0–10°. After the addition was complete the temperature was raised to room temperature and stirred for several hours. Water was added and the organic layer separated washed with water, dried, and concentrated at atmospheric pressure. The crude material was weighed, analyzed by glpc, and vacuum distilled to yield the pure product. This procedure is similar to those described earlier.[2a,m,14,15] The results are summarized in Table III.

General Procedure for the Rearrangement of 1,1-Dihalocyclopropanes.—To an erlenmeyer flask was added 0.1 mole of the 1,1-dihalocyclopropane, 0.15 mole each of silver acetate, silver nitrate, mercuric acetate, or sodium acetate, and 50–100 ml of the solvent (glacial acetic acid or water). A reflux condenser equipped with a drying tube was attached to the flask and then placed in an oil bath at 100–120° or on a steam bath for the hours indicated. The extent of the reaction was determined by periodically checking samples with the aid of a Burrell gas chromatograph. Tables I and IV summarize the data for the rearrangment experiments.

Silver Acetate Rearrangement of 1,1-Dibromo-2,2-Diphenylcyclopropane.—As a typical example of the rearrangement reaction described above, 17.6 g (0.05 mole) of the subject compound was added to an erlenmeyer flask followed by the addition of 12.5 g (0.075 mole) of silver acetate and 50 ml of glacial acetic acid. Silver bromide began to precipitate at room temperature and the flask was placed in an oil bath at 100–120° for 24 hr. The mixture was diluted with 200 ml of ether and filtered; the silver bromide precipitate obtained weighed 14.0 g (contains silver acetate). The ether filtrate was washed with water, sodium carbonate solution, water, and dried over anhydrous calcium chloride. Atmospheric distillation of the ether yielded 15.0 g (91%) of crude material which, as indicated by infrared analysis, was free of the starting dibromide. Vacuum distillation yielded two fractions: fraction 1, yield 5.0 g, bp 142–145° (0.15 mm), $n^{22}D$ 1.6023; and fraction 2, yield 7.0 g, bp 145° (0.15 mm), $n^{22}D$ 1.6020. The total yield was 72%. The ultraviolet spectrum of fraction 1 was $\lambda_{max}^{CH_3OH}$ 260 mμ (ϵ_{max} 8790) and of fraction 2 was $\lambda_{max}^{CH_3OH}$ 260 mμ (ϵ_{max} 9010), indicating conjugation. The nmr spectral data are described in Table IV and are consistent with the assigned structure as 1,1-diphenyl-2-bromo-3-acetoxy-1-propene ($(C_6H_5)_2C=C(Br)CH_2OAc$) (XIV). *Anal.* Calcd for $C_{17}H_{15}BrO_2$ (fraction 2): C, 61.60; H, 4.53. Found: C, 62.11; H, 4.88. Gas chromatographic analysis with the aid of an F & M Model 810 flame ionization chromatograph (2 ft 10% Carbowax 20M on firebrick, 250°, 90 ml/min of He) indicated that fractions 1 and 2 were identical and consisted of one peak.

Registry No.—III, 14310-04-4; IV, 14362-66-4; V, 14310-5-05; VI, 14310-06-6; VII, 14362-67-5; VIII, 14362-79-9; IX, 14310-10-2; X, 14310-11-3; XI, 14310-12-4; XII, 4773-87-9; XIII, 14310-14-6; XIV, 14310-15-7.

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(11) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 420.

(12) The rate of reaction of 7,7-dichlorobicyclo[4.1.0]heptane agrees with that found by the authors and a more detailed account will be the subject of another paper.

(13) (a) The elemental analyses were obtained by Dr. Stephen M. Nagy, Belmont, Mass. (b) Melting and boiling points are uncorrected. The nmr spectra were recorded on a Varian Associates A60A spectrometer and the δ values are in parts per million from tetramethylsilane. The ultraviolet spectra were obtained on a Beckman DKl recording spectrophotometer.

(14) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).

(15) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).