Anal. Calcd. for $C_{13}H_{14}N_4O_5$: C, 50.98; H, 4.58. Found: C, 51.32; H, 4.48.

Reaction of XI with Alkaline Hydrogen Peroxide.—A solution of 1 g. of potassium hydroxide (0.04 mole) and 8.5 ml. of 15% hydrogen peroxide (0.04 mole) in 50 ml. of methanol was added slowly to 2 g. (0.02 mole) of XI dissolved in 50 ml. of methanol cooled to −10°. The reaction mixture was kept at 0° for one hour and at 25° for 12 hr. It was then made acid to congo red paper (concd. HCl) and evaporated to a volume of 10 ml. at reduced pressure on a steam-bath. To the residue was added 10 ml. of water and the mixture was thrice extracted with 20 ml. of ether. The combined ether extracts were dried ($MgSO_4$) and the ether removed, whereupon the residue crystallized on cooling; crude yield of XII, 1 g. (40%). After one recrystallization from isopropyl ether it melted at 77–79° and showed no m.p. depression when mixed with the product (XII) prepared from the reaction of ketene with 3-acetoxytetrahydropyran-2-yl chloride, described below. Infrared spectra of the two samples were identical.

Tetrahydropyran-2,3-diol diacetate was prepared by the method of Hurd,[15] in which dihydropyran is oxidized with hydrogen peroxide in *t*-butyl alcohol in the presence of osmium tetroxide followed by treatment with acetic anhydride. In this method 30% aqueous hydrogen peroxide is mixed with *t*-butyl alcohol and the water is removed with anhydrous sodium sulfate. Here the volume of the sodium sulfate and water mixture indicated that less than half of the water had been removed, but the results obtained were about the same as those described. Using the same amounts that were given in the literature, a yield of 115 g. of tetrahydropyran-2,3-diol diacetate, b.p. 100–120° at 1–2 mm., was obtained, compared to the reported yield of 135 g. of b.p. 96–115° at 1 mm.

3-Acetoxytetrahydropyran-2-yl Chloride.—To 10 g. of tetrahydropyran-2,3-diol diacetate was added 15 g. of a 25% hydrogen chloride in anhydrous ether solution. The mixture was stored at 0° and it turned light brown in a few minutes. After three days the mixture was distilled at reduced pressure, first at 20 mm. and finally at 0.2 mm. The distillate from 51–54° at 0.2 mm. was collected; yield 7.0 g. (77%).

Anal. Calcd. for $C_7H_{11}ClO_3$: Cl, 19.9. Found: Cl, 17.7.

2-(3-Hydroxytetrahydropyran)-acetic γ-Lactone (XII).—Ketene was bubbled into 7 g. of 3-acetoxytetrahydropyran-2-yl chloride in 30 ml. of ethyl acetate containing 1 g. of zinc chloride at a rate of about 0.2 mole per hour for 4 hours at 0°. The entire mixture was distilled and the fraction boiling 70–90° at 0.2 mm. was collected. When 5 ml. of isopropyl ether was added to the distillate, it solidified and the solid was filtered off; yield 2.0 g. (43%). The material thus obtained melted at 77–79° and after recrystallization from isopropyl ether it melted at 79–80°.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.01; H, 7.10. Found: C, 58.81; H, 7.31.

EVANSTON, ILL.

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(15) C. D. Hurd and C. D. Kelso, THIS JOURNAL, **70**, 1484 (1948); C. D. Hurd, J. Moffat and L. Rosnati, *ibid.*, **77**, 2793 (1955).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Allylic Rearrangements. XLVII. The Silver Ion-assisted Hydrolysis of α- and γ-Methylallyl Chlorides. Preservation of Configuration in Allylic Cations[1]

BY W. G. YOUNG, S. H. SHARMAN[2] AND S. WINSTEIN

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The hydrolysis of *cis*- and *trans*-crotyl and α-methylallyl chlorides with aqueous silver nitrate is accompanied by structural isomerization, as well as formation of mixed butenyl nitrates. The compositions of the products from crotyl and α-methylallyl starting materials yield information on the degree of similarity of the respective cationic intermediates from which they arise. Evidence has been obtained in the present work that geometrical configuration of the allylic butenyl cation is preserved. Such preservation of configuration of allylic cations is expected on theoretical grounds, and recent related experiments and discussions are commented on.

In 1944, Young and Andrews[3] reported the results of a brief investigation of the silver ion-promoted hydrolysis of crotyl and α-methylallyl chlorides IP and IS, which gave some indication of *cis–trans* isomerization within the allylic cationic intermediate IV. However, sufficiently accurate analytical methods were not available to settle the question.

On theoretical grounds, *cis–trans* isomerization within a short-lived allylic cationic intermediate IV would be rather surprising, as was pointed out some time ago.[4,5] The bond order of the C_2–C_3 carbon–carbon bond and the expected barrier to rotation are still sufficiently high in a cation such as IV, that one would expect preservation of *cis* or *trans* configuration in the unrearranged product III even by way of a cationic intermediate.

With the recent introduction of vapor phase chromatography, it has become convenient to study isomerizations of the kind involved, and the hydrolysis of the butenyl chlorides has been studied further. The results of this study are reported and discussed in the present paper.

Results

Allylic Materials.—Methods of preparation were selected for the various allylic compounds necessary in the present study which would guarantee structural and geometric purity. α-Methylallyl and *trans*-crotyl alcohols IIIS and IIIPT were prepared by lithium aluminum hydride reduction of methyl vinyl ketone and *trans*-crotonaldehyde, respectively, in ether. As summarized in Table I, analysis by vapor phase chromatography (v.p.c.) indicated that the *secondary* alcohol IIIS contained none of its allylic isomer. Similar analysis indicated that the *trans-primary* compound IIIPT was not contaminated with the *secondary* isomer but contained 3.2 ± 0.7% *cis*-alcohol IIIPC. *cis*-Crotyl alcohol resulted from the semi-hydrogenation of 2-butyne-1-ol. It contained no *secondary* alcohol IIIS and 0.3 ± 0.2% of the corresponding *trans* isomer IIIPT. Due to the shape of the curves

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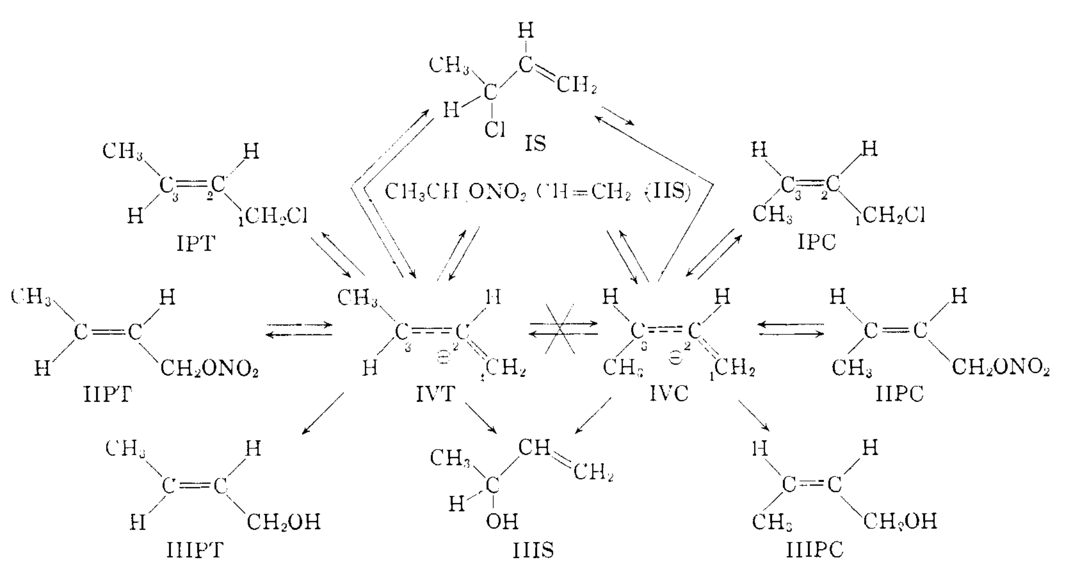
(1) This work was supported in part by a grant from the National Science Foundation.

(2) Standard Oil Co. of California Research Fellow, 1956–1957.

(3) W. G. Young and L. J. Andrews, THIS JOURNAL, **66**, 421 (1944).

(4) S. Winstein, *Bull. soc. chim. France*, **18**, C43 (1951).

(5) M. Daudel, *ibid.*, **18**, C8, 42 (1951).



obtained by v.p.c. analysis of the crotyl alcohols, values relating to configurational purity were considerably more accurate in the case of a mixture very rich in the *cis*-alcohol (±0.2%) than when the *cis* component was present to a very small extent (±0.7%).

TABLE I

SUMMARY OF PROPERTIES OF THE BUTENYL ALCOHOLS, CHLORIDES AND NITRATES

Compound[a]	B.p. °C.	B.p. Mm.	n^{25}D	Purity[b]
		Alcohols		
PT	121.6	748	1.4260	3.2 ± 0.7% PC; 0% S
PC	124.1	748	1.4321	
			1.4342[d]	0.3 ± 0.2% PT; 0% S
S	96.8	750	1.4125	0% P
		Chlorides		
PT	84.0	747	1.4322	<5% PC 0.6% S
			1.4341[d]	
PC	83.8	747	1.4360	<2% PT 0.1% S
	58.0	311	1.4390[d]	
S	63.2	749	1.4121	0.6% P
		Nitrates		
P	66.0	59	1.4282	1.6% S
	75.0–75.8	89.5		
S	53.0	59[c]	1.4135	0.4% P
	59.4	89.5		

[a] P = *primary* (crotyl); S = *secondary* (α-methylallyl); C = *cis*; T = *trans*. [b] Percentages of contamination by allylic structural isomer are accurate to ±0.2%. [c] Estimated with the aid of a vapor pressure nomograph; accurate to ±1.5°. [d] 20°.

For conversion of the crotyl alcohols IIIPT and IIIPC to the corresponding chlorides, treatment with thionyl chloride and tri-*n*-butylamine in ether was used since this was expected to preserve allylic structure and configuration.[6] In fact, the resulting *trans*-crotyl chloride IPT contained only 0.6% of its *secondary* allylic isomer and the *cis*-chloride IPC was contaminated with only 0.1% of the *secondary* isomer. While vapor phase chromatography was not suitable for analysis of the *primary* chlorides for configurational purity, the fact that allylic structure was preserved in the conversion reaction strongly suggests that geometric configuration of the crotyl system was also maintained. On this basis, on infrared evidence, and as a result of the behavior in solvolysis to be described later, the *cis*-crotyl chloride was assigned a configurational purity of at least 98% and the *trans*-chloride was assumed to contain no more than 5% of the corresponding *cis* isomer. α-Methylallyl chloride, prepared by the action of thionyl chloride on *trans*-crotyl alcohol in ether,[7] contained only 0.6% of *primary* chloride.

In the course of the investigation it became necessary to prepare and characterize crotyl and α-methylallyl nitrates IIP and IIS, and a mixture of these esters was made by treatment of *trans*-crotyl chloride IPT with solid silver nitrate in the absence of solvent. By fractional distillation there were obtained specimens of crotyl nitrate containing 1.6% of the *secondary* isomer and α-methylallyl nitrate contaminated with 0.4% of the crotyl ester. As in the case of the corresponding chlorides, configurational purity of the *primary* nitrate ester could not be determined by v.p.c.

Solvolyses.—In the early stages of the investigation, the three butenyl chlorides were subjected to complete hydrolysis with 0.8 *N* aqueous sodium hydroxide and also with 0.090 *N* aqueous silver nitrate solution. The compositions of the resulting alcohol mixtures were determined by v.p.c., and these are summarized in Table II. The results of some partial solvolyses of the two nitrate esters are also included in this table.

A more extensive study of the silver-ion-promoted hydrolysis of the three butenyl chlorides involved examination of the mixtures of compounds present at various stages of the reaction. A sample of allylic chloride was mixed quickly with a 5% excess of 0.099*N* aqueous silver nitrate and shaken vigorously for an allotted period of time. Then the reaction mixture was quenched and worked up by a standard procedure described in the Experimental section. The resulting mixtures, which contained both *primary* and *secondary* allylic chlorides, alcohols and nitrates, were analyzed by v.p.c. The data obtained are illustrated in Tables III, IV and V.

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(6) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

(7) F. F. Caserio, G. E. Dennis, R. H. DeWolfe and W. G. Young, THIS JOURNAL, **77**, 4182 (1955).

TABLE II

ISOMER DISTRIBUTION OF ALCOHOLS IN SOLVOLYSIS PRODUCTS

	Solvolysis reagent				
	0.8 N NaOH		0.090 N $AgNO_3$		
Compound^{a}	% P^{b}	% S^{b}	% P^{b}		% S^{b}
PT-RCl	61.0	39.0	48.6		51.4
PC-RCl	79.9	20.1	50.6	17.6% *trans*^{c} 82.4% *cis*	49.4
S-RCl	33.8	66.2	36.0		64.0
P-$RONO_2$	..	..	51.3^{d}		48.7
S-$RONO_2$	..	..	34.7^{e}		65.3

[a] P = *primary* (crotyl); S = *secondary* (α-methylallyl); C = *cis*; T = *trans*; R = C_4H_7: [b] Accurate to 1.6%. [c] Accurate to 0.2%. [d] At 6.4% reaction; recovered nitrate = 7.5% S-$RONO_2$, 92.5% P-$RONO_2$. [e] At 16% reaction; recovered nitrate = 15% P-$RONO_2$, 85% S-$RONO_2$.

TABLE III

REACTION OF *trans*-CROTYL CHLORIDE WITH 0.090 N AQUEOUS SILVER NITRATE

	Composition^{a,b}			S,^{a} % in^{b}		
Time, min.	% ROH	% RCl	% $RONO_2$	ROH	RCl	$RONO_2$
0.5	13.4	84.9	1.68^{c}	52.0	1.4^{c}	52.2
2.0	53.8	36.5	9.70	49.5	4.8^{c}	49.1
2.0	53.8	36.2	9.90	50.7	4.6^{c}	47.4
4.0	74.6	12.8	12.6	50.0	10.0	45.5
4.0	74.5	12.1	13.4	50.5	8.80	44.0
6.0	83.3	5.43	11.3	50.4	13.9	41.8
8.0	87.4	1.89^{c}	10.5	49.5	17.2	39.2
12.0	96.8	0.0	3.2	51.8	..	32.4

[a] S = *secondary* (α-methylallyl); R = C_4H_7. [b] Percentage values are mole per cent., accurate to ±1.6% (absolute) unless otherwise stated. [c] Accurate to ±0.6%.

TABLE IV

REACTION OF *cis*-CROTYL CHLORIDE WITH 0.090 N AQUEOUS SILVER NITRATE

	Composition^{a,b}			S,^{a} % in^{b}			
Time, min.	% ROH	% RCl	% $RONO_2$	ROH	RCl	$RONO_2$	*trans*, % in P-ROH^{c}
0.5	3.50	96.5	..	50^{e}	0.6^{d}	..	2.0
2.0	19.4	79.5	1.25^{d}	50.5	1.10^{d}	50.7	4.73
4.0	59.4	36.1	4.55	51.0	2.90	39.4	7.22
6.0	80.3	13.5	6.22	51.2	3.8	30.0	10.2
8.0	88.9	5.82	5.23	50.8	6.4	22.4	10.7
12.0	94.6	0.81	4.58	49.4	11^{e}	9.2	14.3

[a] P = *primary* (crotyl); S = *secondary* (α-methylallyl); R = C_4H_7. [b] Percentage values are mole per cent., accurate to ±1.6% (absolute) unless otherwise indicated. [c] Accurate to ±0.2%. [d] Accurate to ±0.6%. [e] Accurate to ±5%.

TABLE V

REACTION OF α-METHALLYL CHLORIDE WITH 0.090 N AQUEOUS SILVER NITRATE

	Composition^{a,b}			P,^{a} % in^{b}		
Time, min.	% ROH	% RCl	% $RONO_2$	ROH	RCl	$RONO_2$
0.5	28.2	69.5	2.20^{c}	33.4	4.9	45.6
2.0	67.9	22.3	9.77	35.7	17.4	50.8
4.0	77.6	8.78	13.6	35.6	29.6	54.0
6.0	84.9	2.06^{c}	13.0	34.8	45.1	59.0
8.0	87.3	0.85	11.8	38.0	51.9	49.7
14.0	99.1	0.0	0.9^{c}	37.0	..	76^{d}

[a] P = *primary* (crotyl); R = C_4H_7. [b] Percentage values are mole per cent., accurate to ±1.6% (absolute) unless otherwise stated. [c] Accurate to ±0.6%. [d] Accurate to ±5%.

As is clear from Tables III and IV, the alcohol from the silver-assisted hydrolysis of the *cis*- and *trans*-crotyl chlorides IPC and IPT was approximately a 50:50 mixture of *primary* and *secondary* isomers, the composition staying relatively unchanged during a run. In the case of the α-methylallyl chloride IS, as summarized in Table V, the *primary:secondary* ratio of alcohols in the hydrolysis product was again relatively constant throughout a run, although the ratio was now 35:65 instead of the 50:50 observed with the crotyl chlorides. As regards the composition of the *primary* portion of the alcohol product, the crotyl alcohol from *cis*-crotyl chloride IPC was nearly pure *cis* at the beginning of the run, but the proportion of *trans* increased steadily during the run up to *ca.* 15%. The proportion of *cis*-crotyl alcohol IIIPC in the *primary* alcohol component from *trans*-crotyl chloride IPT and α-methylallyl chloride IS was in the 5-10% range. However, because of the lower accuracy in the analysis for a small amount of *cis* in predominantly *trans*-alcohol, the trend of the values during the run was not as clear as in the case of the *cis*-crotyl chloride.

The silver ion-promoted hydrolysis of each of the chlorides was accompanied by an isomerization to the structurally isomeric chloride. Thus, during the run the *cis*- and *trans*-crotyl chlorides IPC and IPT developed α-methylallyl chloride IS until this latter material constituted *ca.* 15% of the residual chloride late in a run.[8] Similarly, α-methylallyl chloride developed crotyl chloride, so that at 87% hydrolysis the residual chloride was 52% *primary*.

The silver nitrate-promoted hydrolysis of all three chlorides was accompanied also by formation of butenyl nitrates. The yield of alkenyl nitrate rose to a maximum and then fell during a run, 13 or 14% of nitrate being observed at the maximum with *trans*-crotyl chloride IPT and α-methylallyl chloride IS, while *ca.* 6% was observed in the case of the *cis*-crotyl chloride IPC. The composition of the alkenyl nitrate varied during a run, this being initially somewhat over 50% α-methylallyl, and then decreasing in *secondary* content as the reaction progressed.

The inclusion of solid powdered calcium carbonate during the treatment of the chlorides with aqueous silver nitrate produced very little effect. There appeared to be a slight increase in the rate of disappearance of allylic chloride and a minor decrease in the percentage of nitrate formed at various stages of the reaction.

The reactions of the allylic chlorides with the aqueous silver nitrate simulated first-order behavior roughly within a run. However, when the silver nitrate concentration was reduced by a factor of 10 (with corresponding reduction in the quantity of allylic chloride), rates were reduced by a factor of at least 6 in the case of the *cis*-crotyl chloride and at least 3 in the case of the *trans*-crotyl and α-methylallyl chlorides. Because of the kinetic complications associated with such

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[8] Since *primary* and *secondary* chlorides lead to somewhat different P:S ratios in the alcohol product, this isomerization of starting chloride should cause a drift in the P:S ratio of alcohols as a run progresses. However, the calculated trend is small and within the accuracy of the analyses for *primary* and *secondary* components of the alcohol product.

heterogeneous reactions,[9] the kinetics of these reactions were not examined very closely. The order of reactivity of the three allylic chlorides in the initial stages of reaction is α-methylallyl > *trans*-crotyl > *cis*-crotyl. In the later stages of the reaction the difference between the *trans*-crotyl chloride and its *cis* isomer became very much smaller.

A variety of control experiments was carried out to assist in the interpretation of the significance of the results. First of all, it was clear that solvolysis of the butenyl chlorides and nitrates was negligible during the work-up procedure. Further, *cis*-crotyl alcohol was shown to survive the reaction conditions for the silver ion-assisted solvolysis of the chlorides as well as the work-up procedure with no rearrangement or geometric isomerization. As regards the dominance of the silver ion-assisted hydrolysis process over non-silver ion-assisted solvolysis, α-methylallyl chloride was shown to react only to the extent of 8.2% in the absence of silver ion during a period of time sufficient for 95% reaction in the presence of silver ion. Further, α-methylallyl chloride was approximately 50% hydrolyzed on treatment with solid silver chloride and an equivalent quantity of nitric acid in a period of time equivalent to 25 reaction half-lives in the silver ion-promoted reaction.

In control experiments on the alkenyl nitrates, it was found that in a period of time equivalent to approximately 12 half-lives of the silver ion-promoted reaction of the butenyl chloride, the *primary* and *secondary* nitrates were hydrolyzed to the extent of about 6 and 16%, respectively, in solutions containing silver nitrate and added calcium carbonate. The composition of the resulting alcohol mixture was in each case the same as that observed from the corresponding butenyl chloride. Analysis of the unreacted nitrate indicated that allylic rearrangement of the nitrate esters similar to that observed with the butenyl chlorides accompanied the hydrolysis reaction.

Discussion

Aqueous Sodium Hydroxide.—The compositions of the alcohol products resulting from solvolysis of *trans*-crotyl chloride IPT and α-methylallyl chloride IS with 0.8 N aqueous sodium hydroxide are in quite good agreement with those reported by Young and Andrews.[3] As is clear from Table II, the P:S ratio of alcohols from α-methylallyl chloride was essentially identical with that observed in the silver ion-assisted hydrolysis. It would appear that bimolecular attack by hydroxide ion is negligible in this case, and that the neutral hydrolysis yields the same product as does the silver-ion-assisted process. However, the product alcohol resulting from treatment of the *trans*- and *cis*-crotyl chlorides IPT and IPC with 0.8 N aqueous sodium hydroxide contained 11 and 30% more of the *primary* alcohol, respectively, than was observed in the silver-ion-assisted hydrolysis of these compounds. Very probably, bimolecular attack by hydroxide ion on C_α plays some role in the hydrolysis of the *trans*-crotyl chloride IPT and becomes even more important with the *cis*-crotyl chloride IPC. This is in line with the usually greater reactivity of *cis*-γ-substituted allyl chlorides compared to *trans* in bimolecular displacement reactions.[6]

Isomerization.—The solvolysis of any one of the butenyl chlorides and also the butenyl nitrates is accompanied by isomerization to the structurally isomeric chloride or nitrate, respectively. The amounts of structurally isomeric material developed depend on the relative rates of isomerization and the relative reactivities toward solvolysis of the various isomers. The mechanism of the isomerization is obviously akin to the ionization–internal return mechanism originally proposed by Young, Winstein and Goering[10] for the isomerization of α,α-dimethylallyl chloride accompanying acetolysis. This mechanism has since been employed in the interpretation of many other allylic rearrangements. In the present instance, a more complete explanation would require explicit consideration of the role of the surface of the freshly precipitated silver chloride and its electrophilic catalytic effect.[9]

***trans*- and *cis*-Butenyl Cations.**—In discussing carbonium ion reactions of butenyl derivatives, two allylic cations need to be considered, namely, the *trans*-IVT and the *cis*-IVC varieties. The first is related to the *trans*-crotyl derivatives, such as IPT and IIPT, while the second is related to the *cis* derivatives IPC and IIPC. α-Methylallyl derivatives, such as IS and IIS, could give rise to either allylic cation IVT or IVC, depending on the conformation from which they ionize. The high predominance of *trans* in the *primary* alcohol from hydrolysis of α-methylallyl chloride suggests that α-methylallyl chloride IS gives rise nearly exclusively to the *trans*-butenyl cation IVT. Therefore, as regards carbonium ion reactions, α-methylallyl chloride IS and *trans*-crotyl chloride IPT should be treated together and separately from *cis*-crotyl chloride IPC.

In considering the silver-ion-assisted reaction, it is interesting to examine the results for evidence relating to the question whether cationic intermediates from *primary* and *secondary* starting materials have achieved the same solvation shell prior to the determination of products. As regards formation of alkenyl nitrate, during silver nitrate-assisted hydrolysis of *trans*-crotyl chloride IPT and α-methylallyl chloride IS, the indications are that approximately the same P:S ratio of nitrates is produced from either *primary* or *secondary* chloride. This suggests that the intermediate has achieved the same solvation shell before nitrate is formed, whether the starting chloride was *primary* or *secondary*. On the other hand, the alcohol formed from *trans*-crotyl chloride IPT or crotyl nitrate IIPT differs appreciably from that which is formed from the *secondary* chloride or nitrate. Here, the familiar spread in product compositions from different starting allylic isomers is evident.[6] Obviously, products are determined in the case of the *primary* chloride and nitrate before cationic intermediates

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[9] *E.g.*, (a) G. Senter, *J. Chem. Soc.*, 346 (1910); (b) J. W. Baker, *ibid.*, 987 (1934); (c) E. D. Hughes, C. K. Ingold and S. Masterman, *ibid.*, 1236 (1937).

[10] W. G. Young, S. Winstein and H. L. Goering, This Journal, **73**, 1958 (1951).

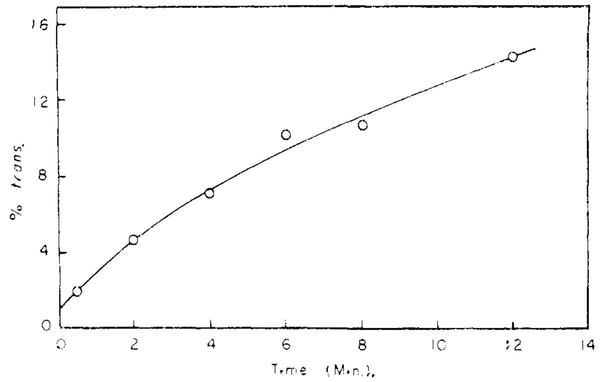


Fig. 1.—Plot of % *trans* in crotyl alcohol from silver-ion-assisted hydrolyses of *cis*-crotyl chloride *vs.* time.

have attained the same solvation shell as those from the *secondary* derivatives.

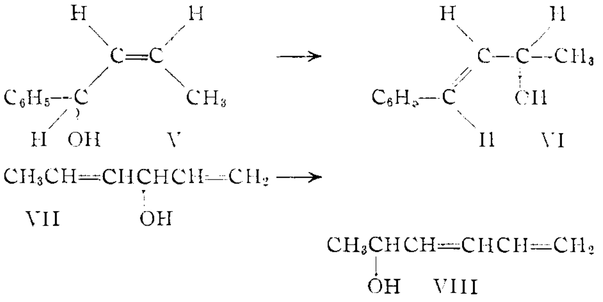
The present data do not enable us to compare the *cis*-butenyl cations IVC from *cis*-crotyl chloride IPC and α-methylallyl chloride IS, since so little of the *cis*-variety of cation IVC is involved in reactions of the *secondary* chloride IS. As regards products from the *cis* intermediate from *cis*-chloride IPC, it is interesting that the P:S ratio of products from *cis*-crotyl chloride IPC is quite similar to that in the products from the *trans*-crotyl chloride IPT. This is true both for the nitrates and alcohols formed from treatment of the chlorides with aqueous silver nitrate.

Retention of Configuration.—The most important aim of the present work was to determine whether or not the cationic species from a *cis*- or *trans*-butenyl reactant maintains the geometric configuration of the starting material. Because of the greater accuracy of analysis of a contaminant of *trans*-alcohol in *cis* than in the reverse situation, and because of the greater purity of the *cis*-crotyl alcohol than the *trans*, the most definitive answer to the above question may be obtained in silver ion-assisted hydrolysis of the *cis*-crotyl chloride IPC. The isomerization accompanying the hydrolysis complicates the matter because the *secondary* chloride from isomerization gives rise to some *trans*-crotyl alcohol, and therefore the percentage of this in the crotyl alcohol increases during a run. This difficulty is eliminated if we plot from Table IV the percentage *trans*-crotyl alcohol IIIPT in the crotyl alcohol from *cis*-crotyl chloride IPC *vs.* time as in Fig. 1. From this plot is clear that the percentage of *trans*-crotyl alcohol approaches 1% (±1%) at zero time. These data show not only that the starting *cis*-crotyl chloride was at least 98–99% pure *cis*, but that the *primary* alcohol part of the alcohol product from hydrolysis of the *cis*-crotyl chloride contains no more than *ca.* 1% *trans*. In other words, the retention of geometric configuration in the cationic intermediate is at least of the order of 99% in hydrolysis of *cis*-crotyl chloride.

Obviously, the observed retention of configuration of the allylic butenyl cation in silver ion-assisted hydrolysis of crotyl chloride is certainly in accord with theoretical expectations.[4,5] However, it would be interesting to investigate systems which give rise to more stable longer-lived allylic cations to see if any coördinate with a solvent molecule or another nucleophile more slowly than they lose configuration by rotation about the partial double bond.

The question of preservation of configuration of allylic cations has been considered previously by Prevost[11] and Valette[12] in connection with the reactions of such materials as the *cis*- and *trans*-2-butene-1,4-diols or dibromides. While there is considerable doubt as to which of the transformations they studied are pertinent for the present discussion of preservation of configuration in allylic cations, Prevost[11c] has summarized matters with the statement that the *primary* products are *cis* from *cis*-starting material and *trans* from *trans*-starting material. Prevost[11] and Valette[12] considered these matters while still employing the tripolar cationic intermediate of Prevost's earlier theory of synionism to explain allylic rearrangements. Since they expected free rotation in the tripolar ion, they anticipated the same mixture of *cis* and *trans* products from either starting material. From the fact that *cis–trans* mixtures were not observed, Valette[12] and Prevost[11c] were forced to consider ionization of *cis*- and *trans*-allylic isomers initially to different tripolar ions which reacted further before rotation rendered them the same.

In the more recent literature, *cis–trans* isomerization within allylic cations has been considered quite plausible by others.[13-15] Also, a certain amount of confusion has been introduced by the failure to distinguish carefully between the old double bond in an unrearranged product and the new double bond in a rearranged product. Our attention has so far been focused on the configuration of the old double bond in the unrearranged product, retention being expected. As regards the new double bond in a rearranged product, its configuration may be the same or different from that of the old double bond. For example, *cis*-V rearranges to *trans*-VI,[16] the configuration of the new double bond being different from that of the old double bond. On the other hand, *cis*-VII yields *cis*-VIII and *trans*-VII yields *trans*-VIII,[16] the configuration of the new double bond being



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(11) (a) C. Prevost, *Compt. rend.*, **187**, 946, 1052 (1928); (b) C. Prevost, *Ann. chim.*, [10] **10**, 113, 356 (1928); (c) C. Prevost, *Bull. soc. chim. France*, **18**, C-1 (1951).

(12) A. Valette, *Ann. chim.*, [12] **3**, 644 (1948).

(13) W. A. Waters and P. B. D. de la Mare, *Ann. Repts.*, **50**, 111 (1953).

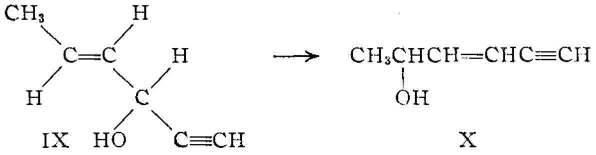
(14) D. Bethell and V. Gold, *Quart. Revs.*, **12**, 173 (1958).

(15) W. Oroshnik, G. Karmas and A. D. Mebane, THIS JOURNAL, **74**, 3807 (1952).

(16) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2085 (1951).

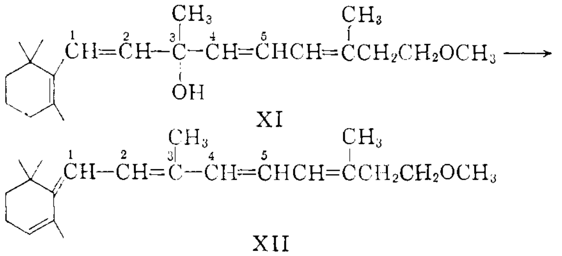
that of the old double bond. These latter transformations have been quoted by Waters and de la Mare[13] as evidence that no long-lived carbonium ion is involved as an intermediate. Similarly, the transformation of *trans*-IX to a mixture of *cis*- and *trans*-X[17] has been quoted by Bethell and Gold[14] as evidence for geometrical isomerization within allylic cations.

The acid-catalyzed conversion of either 4,5-*cis* or 4,5-*trans* varieties of XI to a mixture of 4,5-*cis* and 4,5-*trans* varieties of XII has been explained on the basis of a carbonium ion intermediate which loses configuration at the 4,5-bond.


IX

X

However, the loss of configuration at the 4,5-linkage could very well be due to formation of a neutral intermediate with a 4,5-single bond, *e.g.*, an isomeric alcohol, and more would need to be known about the transformation in question before one could conclude that loss of configuration occurred in the allylic cation.


XI

XII

Experimental

The Butenyl Alcohols.—α-Methylallyl and *trans*-crotyl alcohols were derived by lithium aluminum hydride reduction of the corresponding carbonyl compounds using standard techniques. *cis*-Crotyl alcohol was made by the standard method involving the semi-hydrogenation of 2-butyne-1-ol in methanol with the catalyst described by Lindlar.[18] The properties of the alcohol specimens are summarized in Table I.

Tri-*n*-butylamine.—Purification of Eastman Kodak Co. white label material by heating with excess acetic anhydride and fractionation through an efficient column gave rise to a product, b.p. 121.0–121.8° (44 mm.), n^{25}D 1.4270, n^{20}D 1.4290.

***cis*- and *trans*-Crotyl Chlorides.**—A 24.9-g. (0.210 mole) quantity of thionyl chloride, purified by the method of Cottle,[19] was added over a period of two hours to a stirred, ice–salt–water-cooled solution of 15.0 g. (0.209 mole) of the appropriate isomeric crotyl alcohol and 38.5 g. (0.209 mole) of purified tri-*n*-butylamine in 300 ml. of anhydrous ether. After addition was complete, the yellow reaction mixture was stirred at room temperature for 45 minutes. A low pressure flash distillation was subsequently performed, and that material was collected which came overhead at 1 mm. without heating above room temperature. After the bulk of the solvent had been removed from this distillate by fractional distillation, a few drops of water and 2 g. of anhydrous potassium carbonate were added to the liquid residue, and the mixture was stirred overnight with a magnetic stirring apparatus.

After low pressure flash distillation from the solid, the product was carefully fractionated through an efficient column. Analysis by v.p.c. of the fractions collected indicated that the total yield of crotyl chloride (which includes that material in the early fractions which was contaminated with small traces of the *secondary* isomer and solvent) was 90%, the yield of pure material being 81%. The physical properties of the chloride specimens are summarized in Table I.

α-Methallyl Chloride.—A 35-g. (0.48 mole) portion of *trans*-crotyl alcohol was added dropwise over a period of 1.5 hours to a stirred, ice–salt–water-cooled solution of 57.6 g. (0.48 mole) of purified thionyl chloride in 800 ml. of anhydrous ether. After addition was complete, the mixture was stirred at room temperature for one hour. The solvent was subsequently removed by distillation. Following the addition of a few drops of water and 2 g. of anhydrous potassium carbonate, the residue was successively flash distilled at reduced pressure, dried with magnesium sulfate, and carefully fractionated. The thirteen fractions collected were analyzed, and the resulting information indicated that the total yield of product (which includes the α-methallyl chloride in the early fractions contaminated with solvent) was 64%. The yield of high purity material (Table I) was 55%.

Butenyl Nitrates.—A 97-g. portion of pulverized silver nitrate was added slowly over a period of 1.2 hours to 22.4 g. of α-methallyl chloride contained in a 50-ml. round-bottom flask and stirred by a glass-covered magnet. The reaction was quite exothermic, and cooling with an ice-bath was required. The volatile portion of the reaction mixture was subsequently flash distilled from the solid at reduced pressure and fractionated through an efficient column at 89.5 mm. Both the *primary* and the *secondary* nitrate esters were isolated from this reaction, the total yield being 94%. The physical properties are summarized in Table I.

Anal. Calcd. for $C_4H_7O_3N$: C, 41.03; H, 6.02; N, 11.96. Found (crotyl nitrate): C, 41.05; H, 5.86; N, 11.87. Found (α-methallyl nitrate): C, 41.24; H, 6.00; N, 11.72.

The infrared spectra of both compounds showed absorption in the regions characteristic of nitrate esters. The assignment of *primary* and *secondary* structures was based on the infrared peaks characteristic of the crotyl and α-methylallyl systems, and relative boiling points and refractive indices, fairly reliable guides in the butenyl system. The behavior in solvolysis of the isomeric nitrates supported the assignment of structure.

Partial Solvolysis with 0.090 *N* Aqueous Silver Nitrate.—Three grams (0.0331 mole) of the butenyl halide was injected with a glass dropper into a separatory funnel containing 385 ml. of freshly prepared 0.090 *N* aqueous silver nitrate solution, and the mixture was shaken vigorously for a specified period of time. At the end of this period, enough sodium chloride to saturate the solution was quickly added. The mixture was then shaken for a few seconds and solid potassium carbonate was added to neutralize the acid formed in the reaction.

Eight extractions with ether were subsequently performed using 40-, 20- and 10-ml. portions successively. The ether layers were removed, combined, and dried by stirring with Drierite for approximately 3 hours. The drying agent was then removed by filtration, and the volume of the mixture was reduced to approximately 4.5 ml. by removal of the ether through a fractionating column over a period of 4 hours. The heating element was then removed from the distillation pot, and the system was allowed to cool. Two milliliters of dry ether was then injected into the top of the apparatus and allowed to drain through the column in order to ensure that all allylic compounds were returned to the pot. The colorless residue was then analyzed by v.p.c. Successful experiments were also performed in which 1.500 and 0.500 g. of the butenyl halide and correspondingly reduced volumes of the silver nitrate solution were employed, thus demonstrating that the entire technique was adaptable to very small-scale operations.

Partial Solvolysis in 0.009 N Aqueous Silver Nitrate.—Reactions at the lower concentration were performed in a manner similar to that employed for the experiments using 0.090 *N* solutions, except that the ether extraction process included six washings with 30-ml. and six with 15-ml. portions of ether to ensure the complete removal of the butenyl alcohols.

Partial Solvolysis with Added Calcium Carbonate.—Reactions with added calcium carbonate were performed in a manner identical with that described above, except that ap-

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(17) I. Bell, E. Jones and M. Whiting, *J. Chem. Soc.*, 2597 (1957).

(18) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(19) D. L. Cottle, THIS JOURNAL, **68**, 1380 (1946).

proximately 5 g. of calcium carbonate was added to the silver solution before the reaction was initiated. The addition of potassium carbonate after termination of the reaction was omitted.

Control Experiments.—A number of control experiments (ten) were performed in order to determine the efficiency of the techniques employed and the extent of solvolysis not attributable to reaction with silver ion. Since the experiments were relatively straightforward, detailed descriptions of all of them will not be presented. One example will be given.

In order to determine whether any appreciable amount of solvolysis of the butenyl nitrates occurred during the workup procedure, and, furthermore, to estimate the efficiency of the ether extraction technique employed, a mixture of the following composition (given in weight per cent.) was prepared: 19.29% *n*-decane, 31.32% *trans*-crotyl alcohol, 27.84% α-methallyl alcohol, 12.09% crotyl nitrate, 9.46% α-methallyl nitrate. The mixture was added to the heterogeneous system normally employed, containing sodium chloride, silver chloride and potassium carbonate. The mixture was shaken and subsequently worked up and analyzed by the standard technique. The results of the analysis were: 20.59% *n*-decane, 31.00% *trans*-crotyl alcohol, 27.56% α-methallyl alcohol, 11.93% crotyl nitrate, 8.91% α-methallyl nitrate. These data indicate that no measurable amount of solvolysis occurred during the workup procedure and that the ether extraction was essentially 100% efficient.

Vapor Phase Chromatography.—The instrument employed in this work was a Perkin–Elmer model 154B vapor fractometer. The two columns used were 2 meters in length and were filled with Perkin–Elmer packing "A" and "B," respectively. Helium was employed as the carrier gas.

Two separate analyses were performed on each of the ether solutions resulting from the partial solvolysis experiments. Analysis of a 20-microliter sample at 65° (gas pressure, 12 p.s.i.; flow meter reading 4.85) using column A provided data on the percentage composition of the mixture with respect to α-methallyl alcohol, α-methylallyl chloride and crotyl chloride. Under these conditions, *cis*- and *trans*-crotyl alcohols could not be resolved satisfactorily, nor could the area of the peak produced by crotyl nitrate be measured quantitatively. Accurate measurement of the relative percentages of the *primary* and *secondary* nitrate esters, *cis*- and *trans*-crotyl alcohols, and α-methallyl alcohol was possible when columns A and B were employed in series at 120° (gas pressure, 30 p.s.i.; flow meter reading, 4.72). At this temperature, however, a considerable amount of rearrangement of the butenyl chlorides was observed. Consequently, a combination of the data obtained from analyses at both temperatures was necessary for the calculation of the relative percentages of all compounds present. Under no conditions could *cis*- and *trans*-crotyl chlorides be resolved. No evidence of a separation of the two crotyl nitrates was observed.

Peak areas were calculated by evaluation of the product of the carefully measured values of the peak height and the width of each peak at half the altitude. Control experiments indicated that this method is very accurate. Since recorder response, and consequently peak area, cannot be correlated directly either with weight or mole per cent., a correction factor, *R*, was required. This factor was determined empirically by injecting samples of known composition into the instrument, measuring the peak areas, and calculating the factor by which the measured area of a peak need be multiplied in order to give a number representative of the weight per cent. of the corresponding compound present in the mixture. The following table gives the factor *R* for each of the eight compounds studied.

Compound	*R*
α-Methallyl alcohol	1.000
Crotyl alcohol (*cis*- and *trans*-)	1.009
α-Methallyl chloride	1.122
Crotyl chloride	1.045
α-Methallyl nitrate	1.242
Crotyl nitrate	1.239
n-Decane	0.961

Control experiments performed with mixtures of known composition and measurements of the reproducibility of analyses have shown that, unless otherwise stated, the percentage composition figures are accurate to ± 1.6% (absolute). In some cases, as noted in tables and the text, the accuracy is considerably greater.

Hydrolysis with Dilute Aqueous Sodium Hydroxide.—The method of Young and Andrews[3] was employed for reactions with 0.8 *N* aqueous sodium hydroxide. Analysis was by v.p.c. using columns A and B as described above.

LOS ANGELES 24, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Deuterium Isotope Effects During the Raney Nickel Catalyzed C1–C2 Cleavage of 2-Phenylethanol[1]

BY WILLIAM A. BONNER

RECEIVED JULY 27, 1959

In order to gain information as to the rate determining step in the Raney nickel catalyzed C1–C2 cleavage of 2-phenylethanol into toluene, this reaction has been studied from the viewpoint of its deuterium isotope effects, analyzing the mole ratios of cleavage product (toluene) to dehydroxylation product (ethylbenzene) by vapor liquid partition chromatography. When 1,1-dideuterio-2-phenylethanol reacted with ordinary Raney nickel in refluxing ethanol the toluene/ethylbenzene ratio was identical with that of a control using stock 2-phenylethanol. However when 2-phenylethanol reacted with deuterated Raney nickel in *O*-deuterioethanol solvent the toluene/ethylbenzene ratio decreased markedly, indicating a normal deuterium isotope effect of about 2.1 for the cleavage reaction. Mechanistically these observations are most reasonably interpreted as indicating that the attack on the substrate molecule by hydrogen adsorbed on the catalyst surface is the rate determining step in such heterogeneous C1–C2 hydrogenolyses.

In 1957 we reported the observation that the action of excess Raney nickel in refluxing ethanol on a variety of 2-substituted 2-aryl-ethanols resulted both in simple C1 dehydroxylation producing alkylaromatic hydrocarbons as well as C1–C2 carbon bond cleavage yielding alkylaromatics one homolog lower.[2] Since that time we have studied this hydrogenolytic cleavage reaction extensively with the aid of stereochemical as well as deuterium and radioactive carbon tracer techniques, with the additional findings (a) that the single carbon fragment produced in such C1–C2 cleavages consists of carbon monoxide strongly adsorbed on the nickel catalyst surface,[3] (b) that in neither dehydroxylation nor C1–C2 fission are intermediates produced which in their catalytic environment show an

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(1) This constitutes communication XIV in the series "The Stereochemistry of Raney Nickel Action"; for XIII see ref. 6.

(2) J. A. Zderic, W. A. Bonner and T. W. Greenlee, THIS JOURNAL, **79**, 1696 (1957).

(3) W. A. Bonner and T. W. Greenlee, *ibid.*, **81**, 2122 (1959).