4.311 g.) from this distillation gave a positive permanganate test for unsaturation. Vapor chromatographic analysis of this residue (didecyl phthalate column) indicated two major components (VIII and IX) formed in 32.5 and 6.7% yield, respectively. Two minor components were also observed, but these were formed in only about 3% total yield and were therefore not investigated further. By means of vapor chromatography, components VIII and IX were isolated for infrared and n.m.r. analyses in purities of 98.4 and 94.1%, respectively (determined by vapor chromatography of VIII in ether and IX in carbon tetrachloride solution). In both cases, the only contaminant observed was the other isomer. An analytical sample of VIII was obtained by refractionation of an ether solution of 98.4% pure material by vapor chromatography.

Anal. Calcd. for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.00; H, 10.04.

3-Methylenecylobutyl 3,5-Dinitrobenzoate.—A solution of approximately 70 mg. of 3-methylenecyclobutanol (VIII) in a mixture of carbon tetrachloride and ether, which contained 49 mg. of acetic acid as an impurity, was combined with 0.394 g. of 3,5-dinitrobenzoyl chloride and 1 ml. of pyridine and the resulting mixture heated under reflux for 55 min. The dark brown mixture was then cooled and poured into ice-water. The aqueous mixture was filtered and the precipitate and filtrate extracted separately with ether. The ether extracts were combined and washed first with saturated sodium bicarbonate solution and then with water. Evaporation of the ether solution to dryness yielded a red oil which deposited 76 mg. of pink crystals, m.p. 100–103.5° (softened 94°), upon addition of petroleum ether. An analytical sample (white crystals, m.p. 102–105°) was obtained by chromatography on Florisil, recrystallization from benzene–petroleum ether and sublimation under reduced pressure. The infrared spectrum of the material so obtained was identical in every respect with the spectrum of the crude product.

Anal. Calcd. for $C_{12}H_{10}N_2O_6$: C, 51.80; H, 3.62. Found: C, 51.99; H, 3.74.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra were measured with a Varian high resolution spectrometer (model V-4300B with super stabilizer). The spectra of III and IV were measured at 40 mc. with external methylene chloride as standard. Compound III was examined as a carbon tetrachloride solution containing 235 mg./ml. and IV as a deuterium oxide solution containing 200 mg./ml. The signal of the methylene chloride standard was taken to be at −0.65 p.p.m. from water. The spectra of the other substances were measured at 60 mc. with tetramethylsilane as an internal standard using the following solutions: V, 104 mg./ml. in carbon disulfide–phenol; VII, 164 mg./ml. in carbon disulfide–phenol; VIII, 216 mg./ml. in carbon tetrachloride; IX, approx. 60 mg./ml. in carbon tetrachloride. The signal of the tetramethylsilane standard was taken to be at 4.78 p.p.m. from water.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIF.]

The Addition of Hydrogen Chloride to Aliphatic Allenic Hydrocarbons[1]

BY THOMAS L. JACOBS AND ROBERT N. JOHNSON

RECEIVED AUGUST 17, 1960

The addition of hydrogen chloride to allene and 1,2-butadiene at −78° involves attack at a terminal methylene group of the allenic system. Allene requires a catalyst such as bismuth trichloride and yields a mixture of 2-chloropropene and 2,2-dichloropropane. Slight rearrangement to propyne occurs during the addition. 1,2-Butadiene yields a mixture of *trans*- and *cis*-2-chloro-2-butene in the ratio 87/13; 2-butyne is also formed but does not add hydrogen chloride under the conditions. The orientation of addition of hydrogen chloride to the allenic system is reversed when one end of the system is disubstituted; attack occurs at the middle carbon. At −78° 3-methyl-1,2-butadiene gives a mixture of 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene in the ratio 64/36; rearrangement to isoprene also occurs. It was shown that these allylic chlorides do not rearrange under the conditions employed. Hydrogen chloride adds to isoprene more rapidly under the same conditions to give the same products but the ratio is 83/17. This shows that not all of the addition to the allene occurs through isoprene and that the classical carbonium ion, which should be the same from both hydrocarbons, cannot be the intermediate in both instances. In these hydrogen chloride additions other possible addition products were absent; they could have been detected if present to the extent of 0.1%. The principal product of the addition of 2,4-dinitrobenzenesulfenyl chloride to allene is 2-(2,4-dinitrobenzenethio)-3-chloro-1-propene which represents the opposite orientation to that observed with hydrogen chloride. This reagent gives mixtures with 1,2-butadiene and 3-methyl-1,2-butadiene; pure addition products were not isolated.

The ionic addition of unsymmetrical reagents HA to allenic systems has not been studied extensively and some uncertainty remains about even the orientation in such reactions. Hydration of allene itself in the presence of sulfuric acid was shown to yield acetone in the first definitive paper on this compound[2] and aliphatic monosubstituted allenes $RCH{=}C{=}CH_2$ yield methyl ketones.[3-5] This orientation for the addition of reagents HA as H and A appears to be general for these classes of allenes. Other examples include the addition of hydrogen fluoride to allene to yield 2,2-difluoropropane[6] and of methyl alcohol to 1,2-hexadiene in the presence of boron trifluoride and mercuric oxide to yield the dimethyl ketal of 2-hexanone.[5] None of these reactions establishes which double bond is attacked first.

The reaction of 1,2-hexadiene with dry hydrogen chloride in the presence of bismuth trichloride gives a mixture of 2-chloro-2-hexene and 2,2-dichlorohexane.[5] This establishes that reaction can occur first at the terminal double bond, but attack at the secondary carbon is not excluded because the dichloride may have arisen mainly from 2-chloro-1-hexene which could react with hydrogen chloride more rapidly than its isomer.

A single example of the addition of hydrogen chloride to a tertiary allene has been reported[7];

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[1] Taken from a dissertation submitted by Robert N. Johnson in partial fulfillment of the requirements for the Ph.D. degree, University of California, Los Angeles, February, 1960. Most of this work was carried out under a contract with the Office of Ordnance Research, U. S. Army. Reproduction in whole or in part is permitted for purposes of the U. S. Government.

[2] G. Gustavson and N. Demjanoff, *J. prakt. Chem.*, [2] **38**, 201 (1888).

[3] M. Bouis, *Ann. chim. (Paris)*, [10] **9**, 402 (1928).

[4] W. H. Carothers and G. J. Berchet, THIS JOURNAL, **55**, 1628 (1933).

[5] G. F. Hennion and J. J. Sheehan, *ibid.*, **71**, 1964 (1949).

[6] P. R. Austin, U. S. Patent 2,585,529, Feb. 12, 1952; *C.A.*, **46**, 3799 (1952).

[7] I. W. Kondakov, *J. Russ. Phys.-Chem. Soc.*, **21**, 36 (1889); *Chem. Zentr.*, **61**, I, 311 (1890).

3-methyl-1,2-butadiene was said to give 3-chloro-3-methyl-1-butene. The assignment of the tertiary structure to the product seems doubtful because this chloride is completely isomerized to the more stable allylic isomer 1-chloro-3-methyl-2-butene under milder conditions than were employed for the addition.[8] However, it seems certain that this reaction did yield an allylic chloride and that the orientation in the ionic addition to an allene of the structure $R_2C{=}C{=}CH_2$ is different from that observed with monosubstituted allenes.

Several additions of hydrogen bromide to allenes have been reported, but these are less useful to establish orientations because in no instance has it been proved that ionic rather than radical addition was occurring.

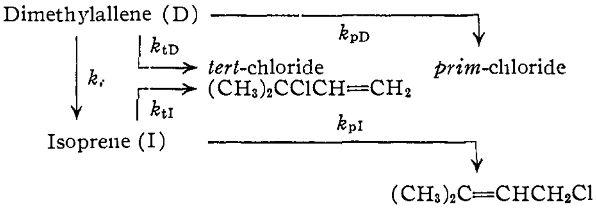
Early work in Favorskiĭ's laboratory[9] on the addition of hypochlorous acid to allene and to 3-methyl-1,2-butadiene established that mixtures were produced. From the former were obtained 3-chloro-1-hydroxy-2-propanone as the principal product (50%), and 2-chloro-2-propen-1-ol (10%) and 1,3-dichloro-2-propanone (15%) as minor products. 3-Methyl-1,2-butadiene gave 1-chloro-3-methyl-3-hydroxy-2-butanone (38%) and 2,2-dichloro-3-methylbutane-1,3-diol (7.5%); some evidence was presented that 2-chloro-3-methyl-1-buten-3-ol, 2-chloro-3-methyl-2-buten-1-ol and 1,3-dichloro-3-methyl-2-butanone were present in the mixture. Although further work is needed in this difficult system, these results indicate that the orientation of the major product with allene is the reverse of that observed with HA reagents, but is the same as for the tertiary allene.

The work described in the present paper was undertaken to establish the orientation of the addition of hydrogen chloride to a series of allenes varying in the extent of alkyl substitution on one of the carbons. Allene, 1,2-butadiene and 3-methyl-1,2-butadiene were studied at −78° without solvent, and a clean reversal of orientation between the di- and tri-substituted allenes was established. With allene and 1,2-butadiene the hydrogen of hydrogen chloride adds to the terminal methylene group, and if we assume the conventional picture of addition of the reagent to olefins, this means initial attack at the terminal position. With 3-methyl-1,2-butadiene, attack is on the central carbon of the allenic system. Alkyl substitution increases the rate of addition as with simple olefins. It was also found that rearrangement of the allenic system occurs during the addition reactions; allene gives propyne, 1,2-butadiene gives 2-butyne and 3-methyl-1,2-butadiene gives isoprene. Bismuth trichloride or other catalysts are required with allene, but with the others without catalyst at −78° the rates of rearrangement are comparable with the rates of addition. The results are summarized in Table I.

Formation of these rearrangement products made it necessary to examine the behavior of each in the addition reaction under the same conditions. Hydrogen chloride does not add to propyne at −78° in the absence of a catalyst nor does rearrangement to allene occur, but in the presence of bismuth trichloride slow addition occurs to give the same products that are formed from allene. Slight rearrangement of propyne to allene was also observed. It was reported many years ago[10] that these addition products were formed when propyne was allowed to stand in solution in excess cold hydrochloric acid for a long time. The addition of hydrogen chloride to 1- and 2-butyne has not been reported previously. When 1-butyne was treated at −78° with hydrogen chloride in the absence of solvents or catalysts no reaction could be detected by gas chromatography after six days and the starting material was recovered unchanged. 2-Butyne adds hydrogen chloride much more slowly than 1,2-butadiene; slight rearrangement to the allene also occurs (Table I). Thus the allene and 1,2-butadiene addition products reported in Table I do not arise by addition to the corresponding acetylenes.

Isoprene was found to add hydrogen chloride more rapidly than 3-methyl-1,2-butadiene to give the same products, but in different proportions (Table I). Isoprene recovered when the addition reaction was not carried to completion contained no 3-methyl-1,2-butadiene, but this is not surprising because the equilibrium between these two hydrocarbons would be expected to lie far on the isoprene side.

Although the experimental precision necessary for analysis of the complex addition of hydrogen chloride to dimethylallene was not attained, and a system containing no solvent is not ideal for the precise study that is needed, it is possible to learn a good deal qualitatively about the reaction from the data on hand. The reactions may be formulated as



If one assumes that the addition reactions for both D and I and the rearrangement are the same order in hydrogen chloride and first order in hydrocarbon, one may write

$$-\mathrm{d}D/\mathrm{d}t = k_{\mathrm{D}}(\mathrm{D})(\mathrm{HCl})^n \qquad k_{\mathrm{D}} = k_{\mathrm{r}} + k_{\mathrm{tD}} + k_{\mathrm{pD}}$$

$$-\mathrm{d}I/\mathrm{d}t = k_1(\mathrm{I})(\mathrm{HCl})^n - k_{\mathrm{R}}(\mathrm{D})(\mathrm{HCl})^n \qquad k_{\mathrm{I}} = k_{\mathrm{tI}} + k_{\mathrm{pI}}$$

$$\frac{\mathrm{d}D}{\mathrm{d}I} = \frac{k_{\mathrm{D}}(\mathrm{D})}{k_1(\mathrm{I}) - k_{\mathrm{r}}(\mathrm{D})}$$

This can be rearranged and integrated in terms of rate constant ratios: $k_{\mathrm{r}}/k_{\mathrm{D}} = a =$ fraction of dimethylallene that rearranges to isoprene; $k_{\mathrm{I}}/k_{\mathrm{D}} = b =$ specific rate for reaction of isoprene relative to dimethylallene. This gives

$$\frac{I - \left(\frac{a}{b-1}\right) D}{I_0 - \left(\frac{a}{b-1}\right) D_0} = \left(\frac{D}{D_0}\right)^b \text{ or}$$

$$I = \left(\frac{a}{b-1}\right) D\left[1 - \left(\frac{D}{D_0}\right)^{b-1}\right] + I_0\left(\frac{D}{D_0}\right)^b$$

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(8) A. J. Ultée, *J. Chem. Soc.*, 530 (1948).

(9) F. Smirnoff, *J. Russ. Phys.-Chem. Soc.*, **35**, 854 (1903); **36**, 1184 (1904); *Chem. Zentr.*, **75**, I, 576 (1904); **76**, I, 344 (1905).

(10) E. Reboul, *Compt. rend.*, **74**, 669 (1872).

TABLE I

ADDITION OF HYDROGEN CHLORIDE TO ALLENE, 1,2-BUTADIENE, 3-METHYL-1,2-BUTADIENE AND ISOPRENE AT −78°

Hydrocarbon taken	Equiv., HCl	Time, hr.	Reacn., %[a]	Product distribution, %				Ratio addn. prods.
Allene[b]				$CH_3C{\equiv}CH$	$CH_3CCl{=}CH_2$	$CH_3CCl_2CH_3$		Mono/di
	1.0	216	22	3	60	37		62/38
	1.5	336	31	3	33	64		34/66
Propyne				$CH_2{=}C{=}CH_2$	$CH_3CCl{=}CH_2$	$CH_3CCl_2CH_3$		
	1.22	216	2.7	[c]	2	Trace		
1,2-Butadiene				$CH_3C{\equiv}CCH_3$	$CH_3CCl{=}CHCH_3$			*trans/cis*
					trans	*cis*		
	1.8	43	20	40.0	53.5	6.5		89/11
	1.5	144	20	38.5	53.5	8.0		87/13
	1.8	144	24	38.9	52.3	8.8		86/14
	2.1	142	59	39.8	52.1	8.1		87/13
2-Butyne	1 to 2	144		Trace of *trans*-$CH_3CCl{=}CH_2$[d]				
3-Methyl-1,2-butadiene					Allylic chlorides			
				$CH_2{=}\overset{CH_3}{\overset{\mid}{C}}CH{=}CH_2$	*tert.*	*pri.*	D/I[e]	*tert./pri.*
	0.5	1.5	32.5	4.53	17.7	10.3	93.7/6.3	63/37
	.5	1.5	42.8	4.84	24.7	13.3	92.2/7.8	65/35
	.5	1.0	43.7	4.70	25.8	13.2	92.3/7.7	66/34
	.5	1.5	48.6	4.59	27.3	16.7	91.8/8.2	62/38
	.7	2.0	49.1	3.08	29.9	16.1	94.3/5.7	65/35
	.75	1.5	(65)	..	41.0	24.0	....	63/37
	1.12	1.63	87.5	2.5	54.4	30.6	83.1/16.9	64/36
	1.32	1.76	100		62.0	38.0	....	62/38
Isoprene				$(CH_3)_2CClCH{=}CH_2$	$(CH_3)_2C{=}CHCH_2Cl$			% of diadduct
	0.5	1.5	41	83	17			..
	.5	1.0	43	85	15			..
	.5	1.5	47	84	16			..
	1.3	2.33	100	76	24			41
	1.0	20	90	82	18			14
	1.12	2.75	98	80	20			1

[a] Values for % reaction represent yields of addition products plus yields of rearrangement products as determined by analysis of the recovered hydrocarbon mixt. [b] One gram of bismuth trichloride was added to 14.0 g. of allene as a catalyst. [c] The propyne used contained 0.03% allene initially, and the propyne recovered after reaction contained 0.7% allene. [d] The recovered 2-butyne contained 0.5% of 1,2-butadiene indicating slight rearrangement during the reaction. [e] D/I = % 3-methyl-1,2-butadiene/% isopropene in recovered hydrocarbons.

where D_0 and I_0 are initial concentrations of dimethylallene and isoprene, respectively. From the constant ratios of *tert*- to *pri*- allylic chlorides in the runs starting from pure D (64/36) and pure I (83/17), the limiting values of a in terms of the fraction, $k_{pD}/(k_{pD} + k_{tD})$, of the D undergoing addition which gives primary chloride are the following: direct addition to D gives only primary chloride, $k_{pD}/(k_{pD} + k_{tD}) = 1$, $a = 0.77$; D gives no rearrangement to isoprene, $k_{pD}/(k_{pD} + k_{tD}) = 0.36$, $a = 0$. However some rearrangement of D to I occurs because I can be isolated from runs starting from pure D. Observation of the maximum concentration of isoprene in such runs permits calculation of k_I/k_D in terms of the limits of a. At maximum I

$$dI/dt = k_r(D)(HCl)^n - k_I(I)(HCl)^n = 0$$
$$k_r(D) = k_I(I)$$

The determination is very inaccurate because the concentration of I remains almost constant near the maximum as D changes over a wide range. From Table I the percentage of I varies only from 4.53 to 4.84 between 32.5% and 48.6% reaction, where D changes from 67.5% to 51.4%. At I = 4.84%, D = 57.2% and $k_r = 0.0846k_I$ or $k_I = 11.8k_r$. Where $a = 0.77$ (addition to D gives only primary chloride), $k_I = 9.1k_D$; as a decreases, k_I/k_D becomes smaller. If the maximum I concentration has already been reached by 32.5% reaction and this concentration is taken as the average of the four readings between 32.5% and 48.6% reaction, I = 4.67 and D = 67.5. Then $k_I = 14.5k_r$ and at $a = 0.77$, $k_I = 11.1k_D$.

Competitive runs can be used to check these figures. Table II records the results of four such runs. Values for b between $a = 0.77$ and $a = 0$ were calculated using the integrated rate expression. The agreement between the runs is only fair, but it is possible to deduce a reasonable lower limit for a of around 0.62 because at $b = 9$, as low as the competitive runs will permit, the calculation from the maximum concentration of isoprene in the pure D runs makes $a = 0.62$ to 0.76. The range of $b = k_I/k_D$ based on $a = 0.62$ to 0.77 is 9.4 to 15.4. In runs 2 and 4 the calculated and observed ratios of 3-chloro-3-methyl-1-butene to 1-chloro-3-methyl-2-butene are in good agreement; run 1 is less satisfactory.

Tentative conclusions about the addition of hydrogen chloride to dimethylallene at −78° without solvent may be summarized as: (1) isoprene adds hydrogen chloride 9 to 15 times faster than di-

TABLE II

COMPETITIVE ADDITIONS OF HYDROGEN CHLORIDE TO ISOPRENE AND 3-METHYL-1,2-BUTADIENE AT −78°[a]

Run	D_0/I_0[b]	Reacn., %	D/I[c]	Range of b[d] a = 0.77	0.62	0	*tert*-chloride/*pri.* Obsd.	Calcd.
1	49.4/50.6	17.0	58.0/42.0	15.4	15.2	14.5	77/23	81.6/18.4
2	51.2/48.8	36.4	73.0/27.0	12.0	11.8	10.7	80/20	80.5/19.5
3	51.8/48.2	44.5	82.0/18.0	15.2	14.9	13.3		
4	50.0/50.0	46.3	78.0/22.0	9.7	9.4	8.1	80/20	79.7/20.3

[a] Contact time in runs 1 and 3 was 60 min., in 2 and 4 it was 90 min.; 0.5 equiv. of hydrogen chloride used. [b] Initial ratio of 3-methyl-1,2-butadiene to isoprene. [c] Ratio of D to I in hydrocarbon fraction recovered from run. [d] $a = k_r/k_D$; $b = k_I/k_D$.

methylallene; (2) rearrangement of the allene to isoprene is 1.5 to 3 times faster than direct addition; (3) direct addition of hydrogen chloride to the allene gives at least two-thirds and possibly exclusively 1-chloro-3-methyl-2-butene corresponding to initial attack at the central carbon of the allenyl system and addition to the terminal double bond.

The clean orientation observed in these addition reactions is one of their striking features. With each of the allenes it was shown by examining the behavior in the gas chromatographic apparatus of known samples of the other possible addition products that these could have been detected if present to the extent of 0.1% in the addition runs. In each instance no traces of these alternative products could be found.

The possibility of an allylic rearrangement of the chlorides produced in these addition reactions is of critical importance for these conclusions and is serious because hydrogen chloride is known to catalyze such a rearrangement.[8] Blank runs were carried through with known mixtures of these allylic isomers and hydrogen chloride using the procedure for workup and analysis as in the addition reactions. No rearrangement was observed nor was isoprene detected as a product.

When appreciable amounts of diadduct are formed, the ratios of the allylic isomers vary as might be expected. No attempt was made to determine whether the diadduct was 1,3-dichloro-3-methylbutane (the compound expected from primary chloride[11]), 2,3-dichloro-2-methylbutane (the expected but as yet undemonstrated product from tertiary chloride), or a mixture of these. The diadduct gave a single peak on a gas chromatogram, but examination of authentic dichlorides would be necessary to establish that this represented a single isomer. It is also possible that the higher concentrations of hydrogen chloride cause allylic rearrangement.

At first sight it may appear surprising that addition does not always start by attack of a proton on the central carbon atom of the allenic system to give an allylic carbonium ion

$$\rangle C{=}CH{-}\overset{+}{C}\langle$$

However, the geometry of allenes appears to exclude resonance of the allylic type in the transition state for the additions. The disposal of the groups at opposite ends of the system is in planes perpendicular to each other and the π orbitals are similarly arranged (Fig. 1).

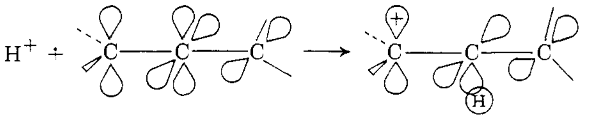

Fig. 1.

Attack at the center carbon allows development of positive charge on a terminal carbon only in a *p*-orbital which is in a plane perpendicular to the plane of the π-orbital not attacked unless twisting occurs about the line joining the carbons. To the extent that a carbonium ion is involved, the competition is thus between a route involving a vinyl type ion, Fig. 2, and a primary, secondary or tertiary ion. The vinyl ion is pictured as

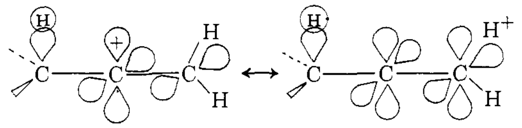

Fig. 2.

involving hyperconjugation with one of the terminal hydrogen atoms because the σ-bonds of these hydrogens are advantageously arranged in space for such hyperconjugation. However, the remaining hydrogen should be in line with the three carbons for maximum stability, and instead it is 60° away from this. Neither a primary nor a secondary carbonium ion is very stable, but one hardly expects the vinyl carbonium ion to be better because vinyl halides are so resistant to solvolysis. Perhaps the additions to allene and 1,2-butadiene involve some concerted or 4-center process different from the conventional ionic addition of hydrogen chloride to olefins.

Attack on 1,2-butadiene involves exclusively the terminal double bond. This would be expected if the transition state reflects the relative stability of products because a compound with a terminal double bond such as 1-chloro-2-butene should be unstable relative to its isomer with an internal double bond, 2-chloro-2-butene. No experimental study of stabilities of these olefins has been made, nor is it known whether *cis*- or *trans*-2-chloro-2-butene is the more stable. No explanation for the preponderance of the *trans* isomer in the product is apparent, nor, in the absence of more information about the mechanism of the addition, does it seem possible to draw conclusions from the observation. It was shown that a mixture of these geometric isomers containing greater than 99% *trans*-2-chloro-2-butene was stable to the reaction conditions for the addition, so it is unlikely that the product is the result of equilibration during reaction.

With 3-methyl-1,2-butadiene the addition mechanism may be very different from that with the less

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[11] W. J. Jones and H. W. T. Chorley, *J. Chem. Soc.*, 832 (1946).

substituted allenes, although this need not be true. A tertiary carbonium ion, Fig. 3, should be more stable than the secondary ion which could be derived from 1,2-butadiene by attack on the central carbon, and this might account for the changed orientation.

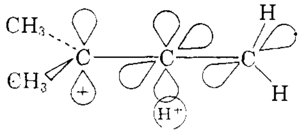

Fig. 3.

To the extent that hyperconjugation of the sort pictured in Fig. 2 is important, attack on the terminal methylene of 3-methyl-1,2-butadiene should be slower than on 1,2-butadiene because only hyperconjugation from a carbon–carbon σ-bond is available. Addition to the terminal double bond is especially puzzling in terms of the carbonium ion mechanism because attack on the central carbon might be expected on the π-orbital permitting development of charge on the adjacent tertiary carbon as shown in Fig. 3. One would have expected the chloride ion to attack this carbon to yield the tertiary allylic chloride unless the ion persisted long enough for twisting to occur, which would permit allylic resonance. Since isoprene and 3-methyl-1,2-butadiene give the same products in different proportions, the classical carbonium ion cannot be the intermediate in both instances, since both would yield the same ion. The addition of hydrogen bromide to 1,2-dimethylcyclohexene, 2,3-dimethylcyclohexene and 2-methylmethylenecyclohexane presents a similar example.[12]

Rearrangement of allenic hydrocarbons under acidic conditions has not been reported before although rearrangement under basic conditions or at higher temperatures over contact catalysts is well known. With each of our compounds the rearrangement product is that expected from the carbonium ion which would result if the addition reaction were proceeding through such an ion. It is attractive to consider such a common intermediate for both addition and rearrangement, but no proof has been obtained for this hypothesis. Solvolysis of either 3-chloro-3-methyl-1-butene or 1-chloro-3-methyl-2-butene yields some isoprene,[13] but vinyl chlorides such as 2-chloropropene and 2-chloro-2-butene would be expected to solvolyze very slowly and have not been studied.

A number of exploratory experiments were carried out in addition to the more detailed work recorded in Tables I and II. Addition of excess hydrogen chloride to 3-methyl-1,2-pentadiene at −78° without solvent gave a diadduct, probably 1,3-dichloro-3-methylpentane. In the presence of a little ether a 70% yield of a mixture of 3-chloro-3-methyl-1-pentene and 1-chloro-3-methyl-2-pentene (ratio 66/34) was obtained.

Addition of hydrogen chloride to 1,2-hexadiene in the presence of bismuth trichloride in dry benzene at 60° as described earlier[5] was carried out to determine the suitability of these conditions for more careful study. The reaction mixture was quite dark after two hours and addition was far from complete. Products included 13% of monoadduct, mainly 2-chloro-2-hexene as reported earlier[5] but probably containing a little 2-chloro-1-hexene, a low yield of diadduct and a small amount of a high boiling liquid.

Addition to 3-methyl-1,2-butadiene was carried out in ether at −40°; the reaction mixture stood at room temperature for twenty-four hours and gave more primary than tertiary allylic chloride probably as the result of allylic rearrangement. The reaction was also attempted at room temperature in glacial acetic acid, but a mixture of products was obtained which appeared to contain allylic acetates and alcohols as well as the primary chloride. An addition in refluxing benzene in the presence of bismuth trichloride gave a complex mixture of high boiling oils with a terpene-like odor. It has been reported[14] that isoprene undergoes reaction with 3-chloro-3-methyl-1-butene, 1-chloro-3-methyl-2-butene, etc., in the presence of Friedel and Crafts catalysts to yield a complex mixture of telomers of the terpene family. 3-Methyl-1,2-butadiene is not rearranged by bismuth trichloride in acetone or in the presence of acetic acid at −78°.

A quantitative study of addition of hydrogen chlorides to allenes and isoprene in solvents should be rewarding if allylic rearrangement of the products can be avoided. It is hoped that nitromethane, the solvent used recently for addition of hydrogen chloride to isobutylene,[15] will give interesting results.

Hydration of 1,2-butadiene and 3-methyl-1,2-butadiene was also investigated. The former gave 2-butanone in good yield, but no carbonyl compounds could be isolated from the latter. A low yield of material believed to be 1-methoxy-3-methyl-2-butene was obtained in one experiment which employed aqueous methanol, sulfuric acid and mercuric sulfate,[5] but tars and low polymers were the principal products. The experiments suggest that the same difference in orientation between these allenes exists in hydration as in the addition of hydrogen chloride. Formation of telomers from isoprene is known[14,16] and closer examination of the products from 3-methyl-1,2-butadiene would be expected to show similar compounds.

2,4-Dinitrobenzenesulfenyl chloride was examined because, like hypochlorous acid, it might give a different orientation. With 1,2-butadiene it gave only an oil, and with 3-methyl-1,2-butadiene a mixture of an oil and a solid which melted over a wide range; the isolation of pure addition products was not successful. With allene it was possible to isolate an 87% yield of 2-(2,4-dinitrobenzenethio)-3-chloropropene which is the product which would result if the orientation with this reagent was the reverse of that observed with hydrogen chloride. An oil was also obtained in 6% yield; this might have contained the other isomer, 3-(2,4-dinitrobenzenethio)-2-chloropropene. Attempts to prepare the latter by other methods gave only oils. If the addition of

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(12) G. S. Hammond and T. D. Nevitt, THIS JOURNAL, **76**, 4121 (1954).

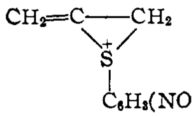
(13) S. Winstein, W. G. Young and A. R. Gagneux, private communication.

(14) A. A. Petrov, *et al.*, *Zhur. Obshchei Khim.*, **28**, 1435 (1958); K. V. Leets, *ibid.*, **28**, 1823, 3096 (1958).

(15) Y. Pocker, *J. Chem. Soc.*, 1292 (1960).

(16) T. Lennartz, *Ber.*, **76B**, 831 (1943).

this reagent to allene occurs through an intermediate ion of the type



as has been suggested[17] as the mechanism of addition of this reagent to simple olefins, one would expect the observed orientation because attack by chloride ion on the intermediate should be more rapid at the methylene carbon than at the vinyl carbon.

Experimental Part

All boiling points and melting points are uncorrected: the latter were determined with total immersion Anschütz thermometers. Infrared spectra were determined on a Perkin–Elmer model 21 spectrophotometer with sodium chloride optics. The fractionating columns used in this work were: Whitmore–Fenske type packed with glass helices 30 × 1 cm., 60 × 1.5 cm. and 100 × 2 cm.; high efficiency concentric tube type 85 × 1 cm.

Gas chromatograms were obtained on columns[18] constructed of 0.25 inch copper tubing containing 40/80 mesh acid washed firebrick impregnated with 20–30% of the appropriate liquid. Columns were enclosed in an insulated box[18] which maintained temperature constant to ± 0.2° near room temperature. Dry helium at constant flow was used as the carrier gas and detection accomplished with a 4-filament Gow-Mac hot wire cell. An all-transistorized power supply[18] was used and either a Varian model G-10 or a Leeds and Northrup Speedomax model G-1 recorder. Samples about 20 microliters in size were introduced into the gas stream through a Silicone rubber diaphragm with a Yale B-D 250 microliter capacity tuberculin syringe. Areas under the curves were determined by peak height × width at half-peak height or more precisely with sharp and narrow or unsymmetrical peaks by weighing the paper enclosed within the curve.

Chemicals.—Isoprene was obtained from the Phillips Petroleum Co. The material was designated as "polymerization grade" and was distilled prior to use to remove the stabilizer. Analysis through a 6-foot tetraisobutylene column indicated a purity of *ca.* 99.3%; 3-methyl-1,2-butadiene was absent. **1-Butyne** and **2-butyne** were obtained from the Farchan Chemical Co. Analysis through a 20-foot dimethyl sulfolane column indicated a purity of about 97.5% for the former; *ca.* 0.2% of 2-butyne and a trace of 1,2-butadiene were present among other impurities. 2-Butyne was of 99% purity; traces of 1-butyne and 1,2-butadiene were present among other impurities. **Propyne** was obtained from the Air Reduction Chemical Co. Analysis through a 20-foot dimethyl sulfolane column indicated about 0.03% allene was present among other trace impurities. **3-Butyn-2-ol** was kindly supplied by the Badische Anilin und Soda Fabrik and was redistilled through the 60-cm. helix column in the presence of about 1% succinic acid as described for propargyl alcohol[19]; b.p. 47.5° (51 mm.). **2-Methyl-3-butyn-2-ol** and **3-methyl-1-pentyn-3-ol** were kindly supplied by the Air Reduction Chemical Co.; the former was redistilled through the 60-cm. helix column before use; b.p. 103.8°, n^{25}D 1.4192. **2,3-Dichloropropene** was obtained from the Columbia Organic Chemical Co. and was redistilled through the 30-cm. helix column before use; b.p. 93.0°.

3-Chloro-1-butyne was prepared in 80% yield by the reaction of 3-butyn-2-ol with thionyl chloride in the presence of pyridine.[20] Analysis through the 4-foot didecyl phthalate column indicated that the crude product was a mixture of the acetylene and 1-chloro-1,2-butadiene in the ratio of 92/8; no other products were found. After distillation through the 60-cm. helix column, material containing about 5% of the allene was used in the subsequent reduction; b.p. 69–71°.

3-Chloro-3-methyl-1-butyne was prepared in 35% yield (pure) by the reaction of the corresponding carbinol with hydrochloric acid[21]; b.p. 75.5°, n^{25}D 1.4155; reported b.p. 75–76°, n^{25}D 1.4155.

3-Chloro-3-methyl-1-pentyne was prepared from 3-methyl-1-pentyn-3-ol and concd. hydrochloric acid[22] to give a 47.5% yield after two distillations through the 30-cm. column; b.p. 51.5–54.5° (135 mm.), n^{25}D 1.4312; reported[22] 51.9–52.2° (115 mm.), n^{25}D 1.4307.

Allene was prepared in 80% yield by the zinc dechlorination of 2,3-dichloropropene in dry boiling methyl Cellosolve with minor modifications of the described procedure.[23] Analysis through a 20-foot dimethyl sulfolane column indicated a trace of propylene as the only impurity.

1,2-Butadiene was prepared by the reduction of 3-chloro-1-butyne containing 5% of 1-chloro-1,2-butadiene by the zinc–copper couple method. The procedure was essentially that reported for 1,2-hexadiene.[5] The product which was obtained in 80% yield was analyzed by gas chromatography through a 20-foot dimethyl sulfolane column. In addition to the allene, 1-butyne (4.4%) and traces of *cis*- and *trans*-2-butene and 1-butene were found; retention times decreased in the order given. The butenes were identified by comparison of the retention times with authentic materials (Matheson Chemical Co.). The infrared spectrum exhibited bands expected for a mixture of the allene and the alkyne.[24] (1,3-Butadiene and 1-buten-3-yne also were absent.)

3-Methyl-1,2-butadiene was prepared by the reduction of 3-chloro-3-methyl-1-butyne in yields of 70 to 75% by the zinc–copper couple method.[25] The purified material, b.p. 40.6°, n^{25}D 1.4165, was 99.7% pure with isoprene and 3-methyl-1-butyne as impurities (analysis using the 6-foot tetraisobutylene column). The infrared spectrum was in accord with the pure allene; reported for 3-methyl-1,2-butadiene, b.p. 39.5–40.5°, n^{25}D 1.4159–1.4165[24]; b.p. 40.0–40.2°, n^{25}D 1.4148.[26]

3-Methyl-1,2-pentadiene was prepared as was 3-methyl-1,2-butadiene and distilled through the 30-cm. column, b.p. 70.5–73.0° (747 mm.), n^{25}D 1.4275, 73% yield. The product was yellow, and the color remained after distillation through the 100-cm. column, b.p. 71.2–72.0°, n^{25}D 1.4274; reported[24,26] b.p. 70° (760 mm.), n^{26}D 1.422 and b.p. 70.3° (754 mm.), n^{25}D 1.4257. The infrared spectrum showed the expected strong bands at 1960 and 845 cm.$^{-1}$ among others and also weak bands at 3280 and 1595 cm.$^{-1}$ indicating contamination by acetylenic, enynic and/or dienic compounds. The gas chromatogram obtained on a 4-ft. didecyl phthalate column at room temperature showed 4 impurities in very small amounts, 94% 3-methyl-1,2-pentadiene and 5% impurity in that order. Chromatography on didecyl phthalate or squalene columns at 61° indicated some decomposition or isomerization although the composition seemed to be about the same. Difficulty with further purification of the allene discouraged more than preliminary examination of its addition reactions.

General Procedure for Hydrogen Chloride Additions.—The apparatus consisted of a tank of hydrogen chloride (Matheson Chemical Co.), a 2-liter filter flask, a liquid-in-glass capillary-type flowmeter, a gas-washing tower containing 95% sulfuric acid, a 500-ml. filter flask filled with glass wool, a detachable Dry Ice trap (70-ml. capacity) which served as the reaction vessel and two additional −78° traps, all connected with rubber tubing in the order given. Purified *o*-nitrotoluene, b.p. 75° (3.5 mm.), was used in the flowmeter.

The flowmeter was calibrated by substituting anhyd. ether for the hydrocarbon in the reaction vessel and passing

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[17] N. Kharasch, *J. Chem. Educ.*, **33**, 585 (1956).

[18] Columns were constructed by Mr. Robert Wilcox and the rest of the apparatus by Mr. Byron Fisher and Mr. Richard Gillespie, all of this Department, who modified designs described in the literature.

[19] J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 106.

[20] Thomas L. Jacobs, Walter L. Petty and Eugene G. Teach, THIS JOURNAL, **82**, 4094 (1960).

[21] G. F. Hennion, J. J. Sheehan and D. E. Maloney, *ibid.*, **72**, 3542 (1950).

[22] G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

[23] P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg and F. L. Howard, *J. Research Natl. Bur. Standards*, **52**, 59 (1954).

[24] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," A.P.I. Researck Project Report 44, Carnegie Press, Pittsburgh, Pa., 1953.

[25] T. L. Jacobs, E. G. Teach and D. Weiss, THIS JOURNAL, **77**, 6254 (1955).

[26] W. J. Bailey and C. R. Pfeiffer, *J. Org. Chem.*, **20**, 95 (1955).

in hydrogen chloride at various rates for specific times. The contents of the reaction vessel were then transferred to an excess of standard sodium hydroxide solution and back titrated with standard acid. The amount of hydrogen chloride was determined in some cases by weighing the cold reaction vessel before and after introducing the reactants.

In a typical run the reaction vessel, filter flasks, traps and gas-washing tower were thoroughly cleaned, dried in a 160° oven for several hours and assembled while still hot. If the starting hydrocarbon boiled below room temperature its weight was determined by weighing the reaction vessel before and after its introduction. The sample size was 10 to 20 g. Hydrogen chloride was then admitted with the reaction vessel at −78° at a rate of 12 ± 2 mmoles./min. until the desired amount was present; it is quite soluble in the hydrocarbons at −78° so that 1 to 2 molar equivalents could be dissolved easily in any of the systems examined. When all manipulations were completed the inlet connection was broken, the inlet sealed with a small rubber bulb, and the solution left at −78° until the workup began. The solutions remained clear throughout all manipulations and it is believed that no more than traces of moisture were present. The times recorded in Table I represent the total time the hydrocarbon was in contact with hydrogen chloride and include a 20 minute period during which the reaction mixture was warmed to 0° and neutralized.

Addition to Allene.—Hydrogen chloride was passed into a suspension of 1 g. of bismuth trichloride in 14.0 g. (0.35 mole) of allene until 13.5 g. (0.77 mole) was present and the heterogeneous mixture was stirred intermittently with a magnetic stirrer for 9 days at −78°. The hydrogen chloride converted the catalyst to a voluminous precipitate which did not settle out rapidly, but made stirring difficult if more catalyst was used than specified above. If the reaction mixture was warmed to r.t. shortly after brief standing, hydrogen chloride was evolved, the precipitate lost its bulkiness and the allene was recovered unchanged.

The reaction vessel was connected in the following order to a 0° trap, 2 gas-washing towers containing dil. sodium hydroxide and water, respectively, a calcium chloride drying tower and a −78° trap protected by a calcium chloride tube. The reaction mixture was warmed to 20° and 9.7 g. of starting material collected in the −78° trap. The recovered allene was analyzed by gas chromatography on a 20-foot dimethyl sulfolane column at room temperature and found to contain 0.8% propyne. The reaction vessel contained 8.3 g. of product shown by gas chromatography on a 4-ft. didecyl phthalate column at room temperature to consist of 2-chloropropene and 2,2-dichloropropane in the proportions given in Table I. These chlorides were identified by comparison with authentic samples prepared from acetone with phosphorus pentachloride.[27] Allyl chloride and 1,2-dichloropropane were examined on the same column and could have been present in the reaction mixture to no more than 0.1%. Infrared spectra also showed that allyl chloride was absent.

A second run was carried out with 14 g. (0.35 mole) of allene, 1 g. of bismuth trichloride and 19.8 g. (0.54 mole) of hydrogen chloride for 14 days.

Allene in the absence of catalyst showed no reaction with hydrogen chloride at −78° after 112 hr.; no isomerization to propyne occurred. Aluminum chloride caused a more rapid reaction than bismuth trichloride, but the products were mainly polymeric; low yields of 2-chloropropene, 2,2-dichloropropane and propyne were also obtained.

Addition to 1,2-Butadiene.—Hydrogen chloride was added to about 10 g. of hydrocarbon to give the amounts and results recorded in Table I. The solutions were slightly reddish in color and most of the unreacted hydrogen chloride was evolved when they were warmed to 10°. The remaining solutions were then cooled to −78°, transferred to stoppered flasks and weighed. Losses during manipulation were around 5%, mainly hydrocarbon. The composition of the mixtures was determined by gas chromatography. No single column was found that would separate all components, but 4- or 8-ft. didecyl phthalate and 6-ft. tetraisobutylene columns separated all but 1,2-butadiene and 1-butyne. A 20-ft. dimethyl sulfolane column gave good separation of all of the hydrocarbons. Neither phthalate column gave good separation of known mixtures of *trans* 2-chloro-2-butene and 3-chloro-1-butene, but the tetraisobutylene column separated this pair easily and the latter was thus shown to be absent from the reaction mixtures. 1-Chloro-2-butene and 2-chloro-1-butene separate readily on any of the short columns and were shown to be absent. 2,2-Dichlorobutane separates smoothly on the 4-ft. didecyl phthalate column and was absent; it is unlikely than any of the dichlorobutane isomers were present. 1,3-Butadiene is detectable on any but the 6-ft. tetraisobutylene column and was absent. It is believed that the chlorides could be detected in amounts <0.1% and the hydrocarbons down to about 0.01%.

Authentic samples of *cis*- and *trans*-2-chloro-2-butene, 2-chloro-1-butene and 2,2-dichlorobutane were prepared from 2-butanone and phosphorus pentachloride.[28,29] Samples of 1-chloro-2-butene and 3-chloro-1-butene were kindly supplied by Dr. André Gagneux.

Known mixtures of the components present in these reaction mixtures were analyzed on the various columns to establish the reliability of the methods. Among the various chlorides or among the various hydrocarbons, peak areas were closely proportional to composition, but this was no longer true when a mixture of one of the chlorides and one of the hydrocarbons was analyzed. This situation has been discussed by Keulemans.[30] It was found that in a mixture of 2-butyne and *trans*-2-chloro-2-butene the ratio was high by a factor of 1.32–1.33. This factor was checked with several known mixtures and the areas for the chlorides were then multiplied by 1.3 in analyzing the reaction mixtures. The reproducibility of peak areas in these systems was about ±2.5%.

The hydrocarbon portion of one of the reaction mixtures was carefully removed through a short distilling column and the infrared spectrum of the residue was found to be identical with that of a known mixture of *cis*- and *trans*-2-chloro-2-butene. The following bands were absent: 940, 965 and 1250 cm.$^{-1}$ which are strong in the spectrum of 1-chloro-2-butene; 990 and 925 cm.$^{-1}$ which are strong for 3-chloro-1-butene; and 875, 1175 and 1630 cm.$^{-1}$ which are strong for 2-chloro-1-butene. The yield of chlorides determined by distillation agreed within 2% with the yield determined by gas chromatography.

It was shown that hydrogen chloride does not rearrange *trans*-2-chloro-2-butene to the *cis* isomer by allowing 1.5 g. of the former and 4.5 g. of hydrogen chloride to stand in 8.5 g. of pentane at −78° for 144 hr. Gas chromatography showed a very faint peak for the *cis* isomer and no peaks for 1-butyne, 2-butyne, 1,2-butadiene or 2,2-dichlorobutane.

Additions to 3-Methyl-1,2-butadiene and Isoprene.—Hydrogen chloride was added to 14 to 18 g. of these hydrocarbons to give the results recorded in Tables I and II. During the warm-up period unreacted hydrogen chloride was evolved from the solutions. When the solutions reached 0 to 10°, solid anhyd. potassium carbonate was added in small portions and the mixtures swirled until gas evolution ceased. The solutions were cooled to −78°, transferred to glass-stoppered erlenmeyer flasks and weighed; they were sometimes pale yellow in color. The mixtures were analyzed at once by gas chromatography on 1.5- or 3-ft. Silicone-on-Celite[31] columns at room temperature at a flow rate of about 300 ml./minute of helium. Above room temperature rearrangement begins to occur. Other columns mentioned earlier were not useful for separation of these allylic isomers nor were a 4-ft. 25% tricresyl phosphate-on-firebrick and a 3-ft. squalene-on-firebrick column useful. The Silicone columns did not separate the hydrocarbons which were determined on the 6-ft. tetraisobutylene column either directly or on the hydrocarbon fraction after distilling the reaction mixture through a short distilling column. These determinations were checked with known mixtures. It was shown by using known mixtures containing 2-chloro-3-methyl-1-butene, 2-chloro-3-methyl-2-butene and 2,2-dichloro-3-methylbutane that these were absent to within the error of the determination; it was estimated that 0.1% of any of these would have been detected. These results were confirmed by infrared measurements. Authentic samples

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[27] A. L. Henne and M. W. Renoll, THIS JOURNAL, **59**, 2434 (1937).

[28] A. L. Henne, M. W. Renoll and H. M. Leicester, *ibid.*, **61**, 938 (1939).

[29] P. Charpentier, *Bull. soc chim.* (*France*), [5] **1**, 1407 (1934).

[30] A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1957, pp. 31–34.

[31] This was a Perkin-Elmer packing designated as "Celite material C." We are indebted to Dr. André Gagneux who suggested the use of these columns for separation of the allylic isomers involved.

of 2-chloro-3-methyl-1- and 2-butene and of 2,2-dichloro-3-methylbutane were prepared by the reaction of 3-methyl-2-butanone with phosphorus pentachloride.[32] 2-Chloro-3-methyl-1-butene was the only one of these that did not give a separate new peak on the Silicone-on-Celite column and it was separated cleanly from the mixture of allylic chlorides on a 3-ft. 25% dimethyl sulfolane column (even though this column was useless to resolve the allylic chloride mixture).

Control experiments were carried out by analyzing mixtures of 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene containing 71.5, 47.4 and 27.5% of the latter, respectively, on the 1.5-ft. Silicone-on-Celite column; values of 72.0, 48.8 and 28.0% were obtained. A mixture containing 19.5% 1-chloro-3-methyl-2-butene, 30.0% 3-chloro-3-methyl-1-butene and 50.5% isoprene gave a *tert./pri.* ratio of 1.57 on the same column (calcd. 1.54), but isoprene was 20% high.[30] A similar mixture containing 23.9% 1-chloro-3-methyl-2-butene, 38.5% 3-chloro-3-methyl-2-butene and 37.6% dimethylallene gave 20.5, 33.4 and 46.0%; again the *tert./pri.* ratio of 1.63 is close to calcd. 1.61 but the allene is 22% high.[31] These corrections for hydrocarbon values were applied in the addition runs. Mixtures of dimethylallene and isoprene containing 86.4 and 97.3% of the former were analyzed on the 6-ft. tetraisobutylene column; found: 86.4 ± 0.5% and 97.2 ± 0.5%.

A blank run in which 9.0 g. (0.087 mole) of 3-chloro-3-methyl-1-butene containing 7.0% of its primary isomer was treated with about 0.02 mole of hydrogen chloride in the usual way was allowed to stand for 80 min. at −78° and worked up exactly as for the addition runs to yield 8.8 g. of the chloride mixture which contained 7.0% of the primary isomer on the basis of analysis on the Silicone-on-Celite column.

Addition to 3-Methyl-1,2-pentadiene.—A considerable excess of hydrogen chloride was added to 21.4 g. (0.261 mole) of this allene at −78° during 1 hr., the orange solution was left at −78° for 1.5 hr., and allowed to warm to room temperature; considerable hydrogen chloride was evolved. The solution at room temperature was purple and turned yellow when neutralized with anhyd. potassium carbonate. The crude product weighed 36 g. and was distilled at 3.5 mm. to give 5 g. of forerun and 25 g., b.p. 41–43°, 62% yield. Redistillation gave a middle fraction, b.p. 44–45° (5 mm.), n^{25}_{D} 1.4540. The gas chromatogram on a 6-ft. Silicone-on-Celite column at 144–146° indicated ~99% purity. An infrared spectrum showed no absorption in the 1500–2800 cm.$^{-1}$ region except a very weak band at 1645 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{12}Cl_2$: C, 46.46; H, 7.81; Cl, 45.73. Found: C, 46.70; H, 7.93; Cl, 45.93.

Acyclic compounds of this empirical formula seem never to have been reported. By analogy with other dihydrohalo addition products of tertiary allenes the compound is probably 1,3-dichloro-3-methylpentane.

A solution of 30 g. (0.365 mole) of 3-methyl-1,2-pentadiene in 13.5 ml. of dry ether at −78° was saturated with hydrogen chloride and allowed to stand for 20 hr. at that temperature. The solution was then allowed to warm to room temperature; hydrogen chloride was evolved. The solution was neutralized and dried with anhyd. potassium carbonate; removal of ether left 30 g. of product. Distillation of 25 g. of this material through the 85-cm. column at 62 mm. gave 12.0 g. of 3-chloro-3-methyl-1-pentene, b.p. 39.7°, n^{25}_{D} 1.4300; 3.0 g. of 1-chloro-3-methyl-2-pentene, b.p. 61.2–62.0°, n^{25}_{D} 1.4518; 5.0 g. of a mixture of these, b.p. 39.8–61.2°, n^{25}_{D} 1.4472; and 5 g. of residue. If one assumes a linear refractive index relationship for mixtures of the allylic isomers, the product consists of 6.9 g. of primary halide and 13.1 g. of tertiary; reported[33] for 3-chloro-3-methyl-1-pentene, b.p. 37.5–39.5° (60 mm.), n^{25}_{D} 1.4289; for 1-chloro-3-methyl-2-pentene, b.p. 62–63° (60 mm.), n^{25}_{D} 1.4518.

Hydration of 1,2-Butadiene.—A solution of 2.0 g. (0.037 mole) of 1,2-butadiene in 4.8 g. of methanol was added dropwise to a solution of 3.1 g. of concd. sulfuric acid, 3.2 g. of water, 4.8 g. of methanol and 0.5 g. of mercuric sulfate with stirring and the reaction mixture was allowed to reflux under a Dry Ice–acetone condenser with stirring for 2 hr. The reaction mixture was poured into a solution of 7.35 g. (0.038 mole) of 2,4-dinitrophenylhydrazine and 14.7 ml. of concd. sulfuric acid in 110 ml. of 96% ethanol. The orange precipitate was collected, washed and dried in vacuum to give 7.6 g. of 2-butanone 2,4-dinitrophenylhydrazone, m.p. 110–111°, no depression when mixed with authentic material.

Reaction of Allene with 2,4-Dinitrobenzenesulfenyl Chloride.—In a 50-ml. capacity glass tube were placed 1.4 g. (0.0060 mole) of 2,4-dinitro-benzenesulfenyl chloride, 30 ml. of chloroform, 7 ml. of dry ether, 0.5 g. aluminum chloride and finally 3.5 g. (0.087 mole) of allene. The tube was sealed at −78° at atmospheric pressure and allowed to stand at room temperature for 9 days. Testing the solution after this time with 15% potassium iodide indicated that the reaction was complete. The solution was poured into water, the chloroform layer separated and dried over anhydrous potassium carbonate, filtered, and aspirated to dryness. The pale yellow residue was recrystallized from absolute ethanol yielding 1.02 g. of pale yellow solid, m.p. 121–122°. Concentration of the mother liquor produced 400 mg. more crystals, m.p. 114–116°, which after another recrystallization had a m.p. of 121–122°. The remainder of the product was a light yellow oil. The total yield of the adduct, m.p. 121–122°, was 87%. The analytical sample had a melting point of 122.4–123.0°.

Anal. Calcd. for $C_9H_7N_2O_4SCl$: C, 39.34; H, 2.55. Found: C, 39.36; H, 2.67.

The reaction was repeated in the same way except the ether and aluminum chloride were omitted. After 8 days at room temperature a 75% yield of adduct and a small amount of starting reagent were obtained. The melting point of the adduct was 121–122° and did not depress the melting point of the adduct obtained in the presence of aluminum chloride.

Acknowledgment.—We are indebted to Professor R. L. Scott for assistance with the kinetic equations and to Professor S. Winstein and Dr. A. Gagneux for helpful discussions.

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[32] B. Gredy, *Bull. soc. chim.* (*France*), [5] **2**, 1951 (1935).

[33] I. D. Webb and W. G. Young, THIS JOURNAL, **73**, 777 (1951)