

Chlorination Studies of Unsaturated Materials in Nonpolar Media.

VIII. Ionic Chlorination of Some Simple Allenes¹

MARVIN L. POUTSMA

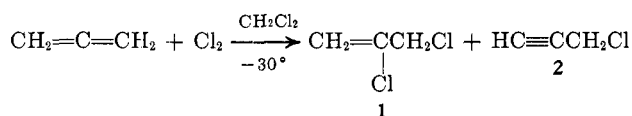
Union Carbide Research Institute, Union Carbide Corporation, Tarrytown, New York 10591

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Chlorinations of tetramethylallene (**3**), 1,1-dimethylallene (**8**), and allene have been carried out in nonpolar media in the presence of oxygen as a radical inhibitor. The only chlorination product of **3** at 25° in C₂F₃Cl₃ solution is 3-chloro-2,4-dimethyl-1,3-pentadiene (**4**). However, the hydrogen chloride coproduct leads to extensive isomerization of **3** to form 2,4-dimethyl-1,3-pentadiene (**5**) and subsequent telomerization of **5** in large part to 1,3,3,5,5-pentamethyl-4-isopropenylcyclohexene (**6**). Dimer **6** can also be prepared from **5** by boron trifluoride catalysis. Similar chlorination of **8** gave 2-chloro-3-methyl-1,3-butadiene (**9**), 2,3-dichloro-3-methyl-1-butene (**10**), and 1,2-dichloro-3-methyl-2-butene (**11**) in a ratio of ca. 85:2:13, the exact ratio being slightly dependent on the nonpolar solvent used. Chlorination of neat allene at -30° gave, in addition to the expected 2,3-dichloropropene (**1**) and propargyl chloride (**2**), a large number of other products. Two of these have been identified as compounds containing two allene units, namely, 2-chloro-1-hexen-5-yne (**15**) and 2,5-dichloro-1,5-hexadiene (**16**). Possible ionic mechanisms are discussed for formation of these products. Relative rate measurements show that **3** and **8** are as reactive as or even more so than the correspondingly substituted olefins, tetramethylethylene and isobutylene. Chlorination of **8** under nitrogen leads to significant initiation of radical reactions.

In spite of recent interest in the chemistry of allenes² few reports have appeared concerning chlorination of simple alkylated allenes in nonreactive solvents. We herein report studies of chlorination of allene, 1,1-dimethylallene, and tetramethylallene in nonpolar solvents in the presence of oxygen to inhibit potential radical reactions.^{3a} While not so extensive as our previous studies of olefin chlorination,³ they reveal some significant synthetic aspects of allene chlorination; namely, the high tendency for allenes with chain branching at a double bond to give substitution products (chloro-1,3-dienes) and the tendency for allene itself to undergo condensation reactions. Thus, in apparent contrast to bromination,^{2a} uncatalyzed chlorination of simple allenes does not seem to be a particularly efficient route to 2,3-dichloropropenes.

Peer⁴ reported that treatment of allene itself in methylene chloride or tetrachloroethane solution at -30° with chlorine in the dark under nitrogen gave 2,3-dichloropropene (**1**) and propargyl chloride (**2**) in yields of 20–25% and 30–35%, respectively; it was noted that reaction did not occur in carbon tetrachloride solution in the absence of light. An electrophilic attack of chlorine was proposed to give an intermediate "propadiene-Cl⁺ complex" which stabilized itself by chloride ion addition to give **1** or proton loss to give **2**.



More recently, allene chlorination at ca. -60° in the presence of boron trifluoride catalyst was reported⁵ also to give similar amounts of **1** (30%) and **2** (45%)

along with minor amounts of 1,2,2,3-tetrachloropropane, 1,2,2-trichloropropane, 1,2,3-trichloropropene, and 1,3-dichloropropene. These by-products which all retained the C₃ skeleton were postulated to result from chlorination-hydrochlorination-dehydrochlorination sequences subsequent to the primary reaction. In particular, no evidence was obtained for cyclodimerization products (cyclobutanes) such as have been observed from hydrobromination and hydrochlorination of allene.⁶ Formation of dichloride **1** did occur in much better yield (60–73%) when chlorination was conducted at 140° in a NaAlCl₄-KAlCl₄ eutectic melt.⁵ Dichloride **1** has been produced in good yield by vapor phase chlorination at 420° with a N₂-allene-Cl₂ ratio of 15:2:1.⁷

Treatment of tetramethylallene (**3**) in 1,1,2-trichlorotrifluoroethane solution with a limited amount of chlorine under an oxygen atmosphere at 25° gives a single chlorine-containing product in essentially quantitative yield based on chlorine as determined by glpc analysis with an internal standard. Spectral characteristics and Diels-Alder condensation with tetracyanoethylene indicate its structure to be 3-chloro-2,4-dimethyl-1,3-pentadiene (**4**); the same compound has been prepared from thermal rearrangement of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane.⁸ However, more than 1 mol of allene **3** is consumed/mol of chlorine introduced. Considerable isomerization to 2,4-dimethyl-1,3-pentadiene (**5**) occurs, and a fraction of this diene is telomerized. A single predominant dimer was detected in all chlorination runs although higher telomers were probably present. These isomerization and dimerization side reactions can be significantly suppressed by the presence of solid sodium carbonate during chlorination; on the other hand, they can be effected by treatment of allene **3** with hydrogen chloride alone in the absence of chlorine. Therefore it seems likely that the hydrogen chloride coproduct from formation of chlorodiene **4** is responsible for the complications observed. (See Scheme I.) Some typical runs are summarized in Table I.

(1) For previous paper, see M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966).

(2) For recent reviews, see (a) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967); (b) M. V. Mavrov and V. F. Kucherov, *Russ. Chem. Rev.* (English Transl.), **36**, 233 (1967); (c) K. Griesbaum, *Angew. Chem. Intern. Ed. Engl.*, **5**, 933 (1966).

(3) (a) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2161, 2172 (1965); (b) M. L. Poutsma, *ibid.*, **87**, 4285 (1965); (c) M. L. Poutsma, *Science*, **157**, 3792 (1967).

(4) H. G. Peer, *Rec. Trav. Chim.*, **81**, 113 (1962). See also H. G. Peer, German Patent 1,132,121; *Chem. Abstr.*, **58**, 3313 (1963).

(5) W. H. Mueller, P. E. Butler, and K. Griesbaum, *J. Org. Chem.*, **32**, 2651 (1967).

(6) K. Griesbaum, W. Naegle, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965).

(7) J. Van Leeuwen, British Patent 908,219; *Chem. Abstr.*, **58**, 6693 (1963).

(8) (a) L. Skattebøl, private communication; (b) G. C. Robinson, *J. Org. Chem.*, **33**, 607 (1968).

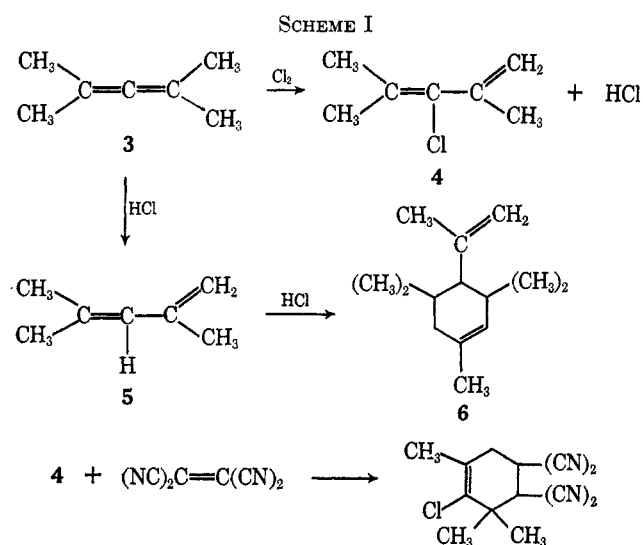


TABLE I
CHLORINATION OF TETRAMETHYLALLENE
UNDER OXYGEN AT 25.0°

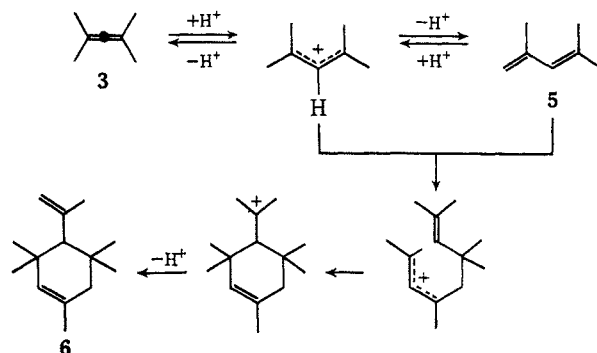
Allene	Reactants, mmol		Conditions	Products, mmol	
	C ₂ F ₃ Cl ₂	Cl ₂		4	6
36.4	41.7	1.4	a, b	1.35	0.75
36.4	41.7	1.4	c, d	1.39	0.06
7.3	75.1	1.2	a, e	1.24	0.46
7.3	75.1	1.4	f, g	1.45	2.13

^a Chlorine introduced in an oxygen stream; product yields determined by glpc analysis with an internal standard added after reaction. ^b Final C-7 fraction is 16% diene 5. ^c Solid sodium carbonate added. ^d Final C-7 fraction is 7% diene 5. ^e Final C-7 fraction is 30% diene 5. ^f Oxygen sweep rate slower than other runs. ^g No allene remaining after reaction; only ~5% of original C-7 fraction present as diene 5.

A number of reports of dimers of diene 5 have appeared⁹ without definitive structural assignment. Several of these prepared by treatment of the diene or diene precursors with acidic catalysts^{9a,b,d,f,h,i,j} may well be the same compound. We have prepared a product in >40% yield, identical with the by-product formed during chlorination of allene 3, by treatment of diene 5 with boron trifluoride etherate. Hydrogenation indicates two dissimilar double bonds (and hence one ring based on C₁₄H₂₄) while ir analysis indicates that at least one of them is of the R₂C=CH₂ type. The nmr spectrum shows three distinct olefinic protons in rather narrow multiplets, nine protons in the allylic hydrogen region six of which seem to be in only slightly split -CH₃ groups, and twelve protons ascribable to saturated unsplit -CH₃ groups. These data coupled with a reasonable mode of acid-catalyzed formation of a cyclic dimer support the assignment 1,3,3,5,5-penta-

(9) (a) V. Grignard, *Ann. Chim. Phys.*, **24**, 477 (1901); (b) T. von Fellenberg, *Ber.*, **37**, 3579 (1904); (c) B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1940; *Chem. Abstr.*, **8**, 1420 (1914); (d) G. S. Whitby and W. Gallay, *Can. J. Res.*, **6**, 280 (1932); (e) Ya. M. Slobodin, *J. Gen. Chem. USSR*, **6**, 1806 (1936); *Chem. Abstr.*, **31**, 4264 (1937); (f) R. Ya. Levina, A. M. Panushkina, N. A. Sheheglava, N. A. Smirnova, K. D. Shcherbakova, and N. I. Shor, *J. Gen. Chem. USSR*, **11**, 411 (1941); *Chem. Abstr.*, **35**, 5862 (1941); (g) R. Jacquemain, *Compt. Rend.*, **215**, 200 (1942); (h) R. Ya. Levina, N. P. Shusherina, N. I. Volchinskaya, and M. Yu. Lure, *Zh. Obshch. Khim.*, **23**, 400 (1953); *Chem. Abstr.*, **48**, 3885 (1954); (i) M. A. Chel'tsova, E. A. Chernyshev, and A. D. Petrov, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (English Transl.)*, 459 (1955); *Chem. Abstr.*, **50**, 6288 (1956); (j) R. Ia. Levina, Iu. S. Shabarov, and V. K. Daukshas, *J. Gen. Chem. USSR (English Transl.)*, **28**, 2089 (1958).

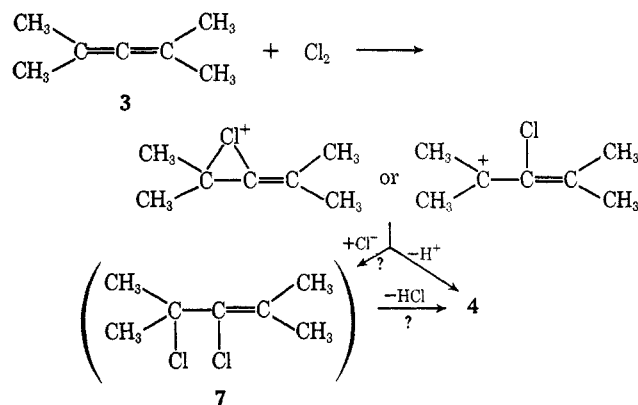
methyl-4-isopropenylcyclohexene (6).¹⁰ This assignment is also consistent with earlier reports that the compound absorbed 1.86 mol of iodine^{9d} and gave on ozonization formic acid and a nonvolatile acid whose silver salt contained 31.16% silver⁹ⁱ (calculated 30.9% if 6 gives the expected diketo acid by ozonization of both double bonds). This structure was suggested



earlier by Merezhkovskii^{9c} for a dimer from thermal polymerization of diene 5. In our hands simple thermal treatment (Diels-Alder conditions) in the presence of a radical inhibitor (hydroquinone) and an acid acceptor (sodium carbonate) gave at least three significant dimers, of which the major seemed to be 6.

In competition experiments with added trimethylethylene under oxygen,^{3b} allene 3 reacted at a rate comparable with that of its similarly substituted olefin, tetramethylethylene ($k_3/k_{\text{trimethylethylene}} \approx 60$).

The production of chlorodiene 4 proceeded smoothly under an oxygen atmosphere under conditions where added cyclohexane was not attacked^{3a} and hence is ascribed to an ionic rather than radical pathway.^{3b} The most probable mechanism involves direct loss of a proton from an intermediate chlorocarbonium ion in analogy to the behavior of branched olefins.^{3b} Although the possible intermediacy of 3,4-dichloro-2,4-dimethyl-2-pentene (7) with rapid thermal dehydrochlorination cannot be completely ruled out, no evidence for 7 was ever obtained from a chlorination run. The intermediacy of 7 seems unlikely in light of the considerable thermal stability of the corresponding



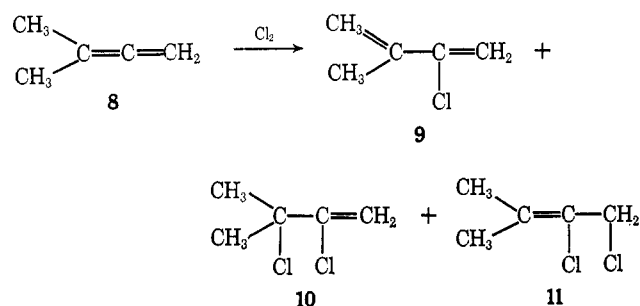
analog with a terminal methylene rather than isopropylidene group (see 10 below); analog 10 was

(10) A referee has pointed out that our data do not totally eliminate 1,3,3,4,4-pentamethyl-5-isopropenylcyclohexene as a possible structure. However, its formation would require an unlikely addition of tetramethylallyl cation at the more crowded terminus of 5 to give the less stable product ion rather than that proposed.

distilled at 120°, whereas the chlorination of **3** occurred at 25°.

Under a nitrogen atmosphere, compound **4** remained the only detectable chlorination product, and added cyclohexane was not attacked to a significant extent; hence the reaction remains ionic, and potential spontaneous initiation of radical chains^{3a} cannot compete effectively for this tetraalkylallene.

Chlorination of 1,1-dimethylallene (**8**) under oxygen gives three products which account for all the chlorine introduced. These were shown by comparison with authentic materials (see Experimental Section) to be 2-chloro-3-methyl-1,3-butadiene (**9**), 2,3-dichloro-3-methyl-1-butene (**10**), and 1,2-dichloro-3-methyl-2-butene (**11**) in a ratio of ~85:2:13; exact values depended slightly on the solvent as shown in Table II.



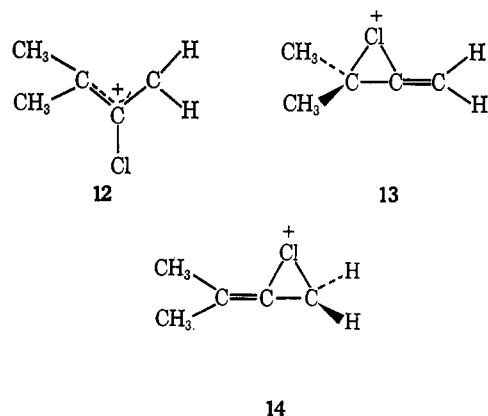
In this case the dichloride **10** showed no tendency to dehydrochlorinate, and hence diene **9** is definitely a primary chlorination product. In contrast to tetramethylallene, allene **8** did not isomerize to isoprene under the reaction conditions. In competitive experiments with trimethylethylene,^{3b} allene **8** reacted at a rate some 20 times faster than that of its similarly substituted olefinic analog, isobutylene ($k_{\text{trimethylethylene}}/k_{\mathbf{8}} \approx 10$).

TABLE II
CHLORINATION OF 1,1-DIMETHYLALLENE
UNDER OXYGEN AT 25.0°

Allene	Reactants, mmol		Cl ₂	Products, mmol ^a	Product composition, % ^a		
	Solvent				9	10	11
80.1	None		2.0	1.55	82.0	2.8	15.2
20.0	C ₂ F ₃ Cl ₃	66.8	1.2	1.25	83.1	1.8	15.2
10.0	C ₂ F ₃ Cl ₃	75.1	1.3	1.25	83.6	1.3	15.1
50.1	<i>c</i> -C ₆ H ₁₂	46.3	1.65	1.65 ^b	82.0	2.2	15.6
10.0	<i>c</i> -C ₆ H ₁₂	83.3	1.4	1.45 ^b	88.6	1.9	9.5
7.5	<i>c</i> -C ₆ H ₁₂	85.6	1.5	1.45 ^b	87.6	2.3	10.0
3.0	<i>c</i> -C ₆ H ₁₂	89.8	0.5		90.6	1.5	7.9

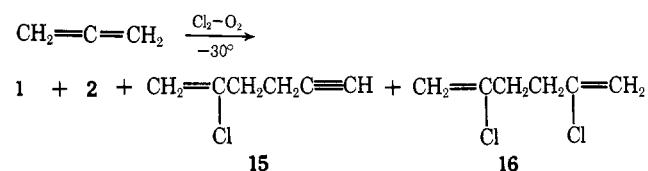
^a Determined by glpc analysis with an internal standard added after reaction. ^b <0.005 mmol of cyclohexyl chloride.

Again the failure of added cyclohexane to be chlorinated demonstrates an ionic pathway. However, the details of the mechanism cannot be specified because, whereas products **9**–**11** could all arise from a single 1,1-dimethyl-2-chloroallyl cation (**12**) formed by electrophilic attack at the central carbon and rotation of the carbon skeleton to attain a planar resonance-stabilized structure, one can equally well imagine two separate bridged chloronium ions (**13** and **14**), which maintain the unique perpendicular allenic geometry, with **13** being the precursor of products **9** and **10** and **14** being the precursor of **11**.

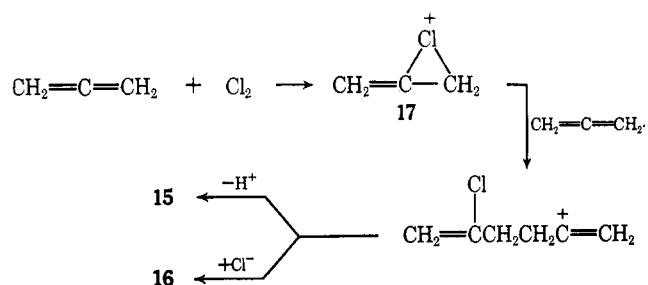


Replacement of oxygen with nitrogen does lead to radical-initiation reactions^{3a} for allene **8**. Added cyclohexane is chlorinated to a significant extent, and the addition products of **8** (**10** and **11**) become more important. However, the radical pathway has not been explored in detail and will not be considered further here.

Neat refluxing allene (~-30°) was treated with 0.5 equiv of chlorine under oxygen. Glpc analysis revealed a multitude of products, four of which have been isolated. Dichloride **1** (23%) and propargyl chloride (**2**, 20%) were produced as expected. A third product, isolated in 4.3% yield, was found to have the empirical formula C₆H₇Cl. Since exhaustive catalytic hydrogenation gave *n*-hexane, a linear chain is indicated. Spectral properties accord with the structure of 2-chloro-1-hexen-5-yne (**15**). The final isolated product (1.5%) was shown in similar fashion to be 2,5-dichloro-1-



5-hexadiene (**16**). A reasonable pathway for formation of these dimeric products would involve addition of an (allene-Cl)⁺ species (**17**) (whether bridged or open is again a question) to another allene molecule. Such



a process is reminiscent of the initial steps postulated for the cyclodimerization of allene and hydrogen bromide,⁶ although in this latter case the initial proton addition must be terminal rather than central. Such a dichotomy is not unreasonable if the species **17** is a bridged ion and the (allene-H)⁺ complex is not. The chlorination in our hands gave even higher molecular weight products not explored further; however they suggest that products **15** and **16** are representative of a family of products containing more than one allene unit and that condensation reactions play a significant

role in polar chlorination of neat allene. Although our conditions were not identical with either of those previously reported,^{4,5} these condensation reactions may explain the only moderate amounts of **1** and **2** obtained, particularly by Peer.⁴

The occurrence of what seemed to be slight inhibition periods even under oxygen caused us to consider the possibility of radical reactions.³ Thus, product **15** could be formulated as the result of terminal addition of propargyl radical to allene followed by chain transfer with chlorine molecule. However, it seems highly likely that the propargyl radical would be much more effectively trapped by either chlorine or oxygen. An alternative possibility is that the hydrogen chloride produced along with products such as **2** and **15** serves as a catalyst for the polar chlorination.

Experimental Section

Infrared spectra were determined as 10% carbon disulfide and carbon tetrachloride solutions on a Beckman IR-10 instrument. Nmr spectra were determined as 20% carbon tetrachloride solutions on a Varian A-60A instrument, and the results are expressed in parts per million downfield from internal tetramethylsilane. Boiling points are uncorrected.

Materials.—Tetramethylallene (Columbia Organic Chemicals) was distilled through an all-glass helix-packed column and showed single glpc and nmr (δ 1.63 ppm) bands; distillation through a platinum spinning-band column led to extensive isomerization apparently to diene **5**. 1,1-Dimethylallene was prepared by reduction of 3-chloro-3-methyl-1-butyne with a zinc-copper couple in ethanol by the general procedure of Hennion and Sheehan¹¹ and purified by repeated distillation, bp 41°. Allene was purchased from the Matheson Co., minimum purity 99%.

Chlorination of Tetramethylallene (3). Product Isolation.—To 50 ml (36.3 g) of tetramethylallene at 0° was added 0.14 mol of gaseous chlorine (measured as a liquid at -78°) in a flowing nitrogen stream over a 30-min period. Glpc analysis revealed two major products. Distillation through an 18-in. spinning-band column gave, after removal of some unreacted starting material, the following fractions: (1) 1.9 g, bp 32–54° (60 mm); (2) 11.0 g, bp 53–55° (50 mm), n_D^{20} 1.4608; (3) 2.0 g, bp 32° (13 mm)–52° (5 mm); and (4) 10.0 g, bp 55–61° (3 mm), n_D^{20} 1.4766; 5.0 g of pot residue remained.

Glpc analysis of fraction 2 showed it to be the more volatile product in good purity. The ir spectrum agreed with that of a sample of 3-chloro-2,4-dimethyl-1,3-pentadiene (**4**) prepared by Skattebøl^{6a} [lit.^{6b} bp 58° (65 mm)]. The nmr and uv spectra were consistent with those reported.^{6b} A mixture of 0.50 g of fraction 2 and 0.45 g of sublimed tetracyanoethylene in 10 ml of benzene was heated at reflux for 1 hr. The benzene was evaporated and the semisolid residue was suspended in pentane and recovered by filtration to give 0.90 g of crude product, mp 103–109°. Recrystallization from benzene-hexane gave 0.65 g, mp 113–114°. The nmr spectrum showed the expected singlets for 2-chloro-4,4,5,5-tetracyano-1,3,3-trimethylcyclohexene at 3.20, 2.00, and 1.75 ppm in a ratio of 2:3:6.

Anal. Calcd for C₁₃H₁₁ClN₄: C, 60.35; H, 4.29; N, 21.66; Cl, 13.71. Found: C, 60.45; H, 4.21; N, 21.70; Cl, 13.54.

Glpc analysis of fraction (4) showed ~10% each of two impurities of similar volatility to the major component. Preparative glpc gave a "best" sample still containing 5–10% of the more volatile impurity. Spectra of this sample showed it to correspond to diene dimer **6** described below.

Chlorination of Tetramethylallene (3). Quantitative Runs.—The general apparatus has been described previously.^{3a} In all cases the reaction mixture was purged with the carrier gas used for 15 min after chlorine introduction ceased to remove hydrogen chloride. Glpc analyses were then carried out on a Microtek 2500R instrument equipped with a flame ionization detector and 2-m Perkin-Elmer "O" columns (silicone grease) operated at a helium flow rate of ca. 200 ml/min with the following temperature program: isothermal operation for 7 min at 52°,

linear temperature increase to 120° in 8 min, and isothermal operation at 120° for another 25 min. In a typical run a major band appeared at 14 min, four minor bands appeared at 16–18 min (<10% of the 14-min band), and a second major band appeared at 32 min flanked by at least two minor bands. The major products were assigned structures **4** and **6** as shown above. Yields were determined by addition of toluene as an internal standard after chlorination was complete. Areas were converted into molar quantities by use of calibration factors determined from mixtures of authentic materials. The amount of **3** remaining could be semiquantitatively estimated by comparison of glpc spectra of aliquots of constant size before and after chlorination. In a typical case considerably more than 1 mol of **3** disappeared for each mole of chlorine introduced, and a new peak appeared which had the same retention time as re-arranged diene **5**. The minor peaks at 16–18 min were simulated by chlorination of diene **5** alone. If solid sodium carbonate was added to the reaction flask, the loss of **3** was much closer to stoichiometric, the formation of diene was reduced, the formation of dimer was practically eliminated, and the peaks at 16–18 min disappeared. Treatment of **3** with gaseous hydrogen chloride instead of chlorine gave extensive conversion into diene **5** and dimer **6**. Inclusion of cyclohexane in the medium under either oxygen or nitrogen did not lead to production of significant quantities of chlorocyclohexane. Some individual runs are summarized in Table I.

To compare the relative rates of ionic chlorination, competitive chlorinations of **3** and trimethylethylene were carried out under oxygen as described previously;^{3b} sodium carbonate was added to suppress isomerization of **3**. The amount of chlorodiene **4** produced was compared to the amount of 3-chloro-2-methyl-1-butene formed with the assumption that trimethylethylene produces 85% of the latter.^{3b} From three runs which covered a sixfold variation in ratio of hydrocarbons the allene was found to be 58 ± 7 times more reactive than the olefin; to the extent that allene **3** is isomerized to diene **5** during the run, this is a minimum value.

Condensations of 2,4-Dimethyl-1,3-pentadiene (5).—To 25 g of 2,4-dimethyl-1,3-pentadiene (Aldrich) was added three small drops of boron trifluoride etherate. The mixture became very warm and required external cooling to prevent boiling. A second similar addition of catalyst gave no further heating. After 15 min, the mixture was partitioned between carbon tetrachloride and water, and the organic layer was dried and evaporated to give 25 g of residue. Glpc analysis showed a major band in the region expected for dimers along with a significant minor band and several very small bands. Distillation through an 18-in. spinning-band column gave the following fractions: (1) 2.7 g, bp 96–99° (16 mm), 93.5% the major product by glpc; (2) 5.7 g, bp 99° (16 mm), 96.5% the major product; (3) 2.3 g, bp 99° (16 mm), n_D^{20} 1.4785, >98% pure; (4) 4.0 g, bp 57–120° (1 mm); and (5) 6.0 g of residue which did not distill at 200° (1 mm). The ir spectrum of fraction 3 showed bands at 1645 and 1635 cm⁻¹ (m) (C=C), 1405 and 1392 cm⁻¹ (s) [(CH₃)₂C<], and 895 cm⁻¹ (s) (>C=CH₂). The nmr spectrum showed three multiplets at 5.03, 4.92, and 4.70 ppm of equal size, complex absorption from 1.90–1.60 ppm consisting of two rather narrow multiplets superimposed on a broader background, and three singlets at 1.03, 0.98, and 0.93 ppm in the ratio ~1:1:2; the relative areas of the three regions were 2.9:9.4:11.7. Hydrogenation of fraction 3 in acetic acid over 5% Pd-C catalyst at atmospheric pressure consumed 1.88 mol of hydrogen/mol of starting material, the first mole being consumed more rapidly than the second. The most reasonable structure based on spectral data and mode of formation is 1,3,3,5-pentamethyl-4-isopropenylcyclohexene (**6**).¹⁰

The same peak was observed in the glpc spectrum when a solution of diene (20 g) in 1,1,2-trichlorotrifluoroethane (50 ml) was treated with anhydrous hydrogen chloride. Work-up in the usual fashion after washing with sodium bicarbonate solution gave on distillation 1.0 g of product, bp 68° (3 mm), with an nmr spectrum the same as that observed above.

Diene **5** (25 g) was heated in an autoclave at 195° for 30 hr in the presence of solid sodium carbonate and hydroquinone; the maximum autogeneous pressure was 70 psi. Distillation gave 14.5 g of recovered diene and 1.8 g of liquid, bp 78–85° (5 mm), the last portions of which tended to crystallize in the distillation head. The nmr spectrum was more complex than that observed above and suggested additional types of olefinic protons and saturated methyl groups. The glpc spectrum showed

(11) G. F. Hennion and J. J. Sheehan, *J. Amer. Chem. Soc.*, **71**, 1964 (1949).

three major components in the ratio of ~60:10:30, the first of which had the same retention time as that of 6, plus several minor components.

Chlorination of 1,1-Dimethylallene (8). Product Isolation.—1,1-Dimethylallene (6.54 g, 96 mmol) was treated at 0° with gaseous chlorine (40 mmol) introduced in a flowing oxygen stream over a 15-min period. Glpc analysis showed three products in a ratio of ~68:4:28 in order of increasing retention time. Distillation gave two major fractions: (1) 0.8 g, bp 46° (140 mm), n_D^{20} 1.4630; and (2) 0.5 g, bp 50–60° (40 mm). Fraction 1 was mainly the most volatile product contaminated by a small amount of starting allene determined by glpc analysis, and its ir spectrum agreed with that of authentic 2-chloro-3-methyl-1,3-butadiene (9). Fraction 2 contained both of the less volatile materials by glpc analysis and was separated into its components by preparative glpc. These were identified by spectral comparison to authentic materials as 2,3-dichloro-3-methyl-1-butene (10) and 1,2-dichloro-3-methyl-2-butene (11). The poor recovery of the chlorodiene apparently results from its polymerization during distillation as evidenced by a considerable pot residue which also contained residual higher boiling dichloroolefin 11 by glpc analysis.

Chlorination of 1,1-Dimethylallene (8). Quantitative Runs.—The chlorination procedure and analysis was identical with that used for tetramethylallene above. No evidence was obtained for greater than stoichiometric losses of allene, and no isoprene was ever detected by glpc analysis. Deliberate chlorination of isoprene gave a set of glpc peaks which were never observed during chlorination of 8. Typical runs are summarized in Table II, p 4082.

The relative reaction rate was compared with that of trimethylallene as described above. In four runs which covered a twofold variation in ratio of starting hydrocarbons, trimethylallene was found to be 10 ± 1 times more reactive than allene 8.

Authentic Products from 1,1-Dimethylallene Chlorination.—Dehydration of 2-methyl-3-butyn-2-ol (Farchan Research Laboratories) with *p*-toluenesulfonic acid by the method of Carothers and Coffman¹² gave 2-methyl-1-buten-3-yne. Hydrochlorination of the latter in the presence of concentrated hydrochloric acid, ammonium chloride, and cuprous chloride¹³ gave 2-chloro-3-methyl-1,3-butadiene (9), bp 42° (120 mm), n_D^{20} 1.4672 [lit.¹² bp 41° (113 mm), n_D^{20} 1.4689]. The nmr spectrum showed three multiplets at 5.57, 5.38, and 5.13 ppm (~1:2:1) and a slightly split band at 1.97 ppm in the ratio 4.0:3.0. This material polymerized slowly on standing, and the samples required for glpc calibration were distilled bulb to bulb at room temperature (20 mm) immediately before use. Chlorination of 1-chloro-3-methyl-2-butene (Eastman Organic Chemicals) in refluxing carbon tetrachloride with sulfuric chloride by the method of Ultée¹³ gave 1,2,3-trichloro-3-methylbutane, bp 76–78° (22 mm), n_D^{20} 1.4746 [lit.¹³ bp 76.5–77° (20 mm), n_D^{20} 1.4748]. This trichloride was dehydrochlorinated over solid potassium hydroxide,¹³ and fractional distillation gave samples (>95% pure) of the two dichloro olefins in ~15% yield each. The nmr spectrum of 2,3-dichloro-3-methyl-1-butene (10), bp 120–123°, n_D^{20} 1.4560 [lit.¹³ bp 50° (60 mm), n_D^{20} 1.4618] showed an AB pattern with the doublets centered at 5.60 and 5.28 ppm ($J = 1.9$ cps) and a singlet at 1.78 ppm in the ratio 2.0:6.0. The nmr spectrum of 1,2-dichloro-3-methyl-2-butene (11), bp 154–156°, n_D^{20} 1.4808 [lit.¹³ bp 58.5–60° (15 mm),

n_D^{20} 1.4812], showed a singlet at 4.23 ppm and a singlet at 1.88 ppm in the ratio 2.0:6.0.

Chlorination of Allene.—Into 120 ml (~2 mol) of liquid allene held under a Dry Ice filled condenser was passed 1 mol (43 ml liquid) of chlorine diluted in an oxygen stream at the boiling point of the mixture (allene bp -32°) in a 1-hr period. A yellow color built up early in the reaction but seemed to dissipate in the later stages. After reaction was completed, excess allene was allowed to escape through a water-cooled condenser set for reflux. Glpc analysis at 125° (Perkin-Elmer column "O") showed four rather volatile components, A–D, in a ratio of ca. 6:8.5:3:1. Analysis at 150° showed these same peaks plus several others of longer retention time. Distillation on an 18-in. spinning-band column gave the following fractions: (1) 12.5 g, bp 55–60°, n_D^{20} 1.4309; (2) 4.0 g, bp 60–90°; (3) 18.8 g, bp 90–93°, n_D^{20} 1.4565; (4) 3.0 g, bp 93° (760 mm)–40° (90 mm); (5) 4.9 g, bp 40–60° (90 mm); (6) 1.3 g, bp 45–47° (55 mm), n_D^{20} 1.4576; (7) 3.2 g, bp 50–68° (45 mm); (8) 4.9 g, bp 44–70° (18 mm); (9) 8.3 g, bp 55–90° (2 mm); and (10) 7.5 g, bp 70–110° (0.2 mm). Considerable tarry residue remained. While this distillation is not claimed to have been particularly efficient, it does show the complexity of the reaction mixture. Fraction 1, almost completely A by glpc analysis, was shown to be propargyl chloride (2) by comparison with an authentic sample. Fraction 3, almost completely B, was similarly shown to be 2,3-dichloropropene (1). Component C was most cleanly found in fraction 6 and component D in fraction 7. Fractions 8–10 contained mainly higher boiling materials than D by glpc analysis. By combination of the weights of fractions 1–7 corrected for their composition as determined by glpc analysis, the isolated yields were 14.5 g of A (20% propargyl chloride), 25.2 g of B (23% 2,3-dichloropropene), 4.9 g of C (4.3% based on C_6H_7Cl , see below), and 2.3 g of D (1.5% based on $C_6H_8Cl_2$, see below). Pure samples of C and D were obtained by preparative glpc.

Compound C showed infrared absorption at 3320 (s) ($C\equiv CH$), 2120 (w) ($C\equiv C$), 1635 (s) (unsymmetrical $C=C$), and 890 cm^{-1} (s) ($R_2C=CH_2$). The nmr spectrum showed a singlet at 5.20, a multiplet at 2.47, and a triplet ($J = 2.5$ cps) at 1.88 ppm in the ratio 2.2:3.9:0.9. Hydrogenation in acetic acid over Adams catalyst followed by dilution with water and extraction with carbon tetrachloride gave an organic solution containing *n*-hexane as determined by glpc retention time and nmr analysis (spectrum identical with that of a known sample; in particular the correct $-CH_2-/-CH_3$ area ratio was observed). These data allow assignment of the structure of 2-chloro-1-hexen-5-yne (15) to C.

Anal. Calcd for C_6H_7Cl : C, 62.89; H, 6.16; Cl, 30.95. Found: C, 62.07; H, 6.24; Cl, 31.21.

Compound D, n_D^{20} 1.4700, had ir bands at 1635 (s) (unsymmetrical $C=C$) and 885 cm^{-1} (s) ($R_2C=CH_2$) and nmr singlets at 5.20 and 2.58 ppm of equal area. Hydrogenation as above again gave *n*-hexane. The structure of 2,5-dichloro-1,5-hexadiene (16) is assigned to D.

Anal. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34; Cl, 46.95. Found: C, 47.35; H, 5.38; Cl, 46.72.

Registry No.—3, 1000-87-9; 5, 1000-86-8; 8, 598-25-4; 15, 17396-43-9; 16, 14225-24-2; allene, 463-49-0; 2-chloro-4,4,5,5-tetracyano-1,3,3-trimethylcyclohexene, 17414-31-2.

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