activated calcium silicate using chloroform as the eluent showed separation into several spots (*via* ultraviolet light). On spraying with a reagent consisting of an aqueous solution of *ca.* 10–15% sodium iodide acidified with acetic acid or hydrochloric acid and containing *ca.* 0.2–0.5% starch, one of the spots (R_f 0.6–0.7; 0.60 on the Eastman film) formed a reddish brown to purple color. Mesitoic acid did not migrate under these conditions; isopropyl mesityl ketone showed R_f 0.78 (Eastman film). Attempts were made to isolate the peroxide by collecting the scrapings from several plates and extracting with various solvents. No material containing peroxide could be eluted with the solvents tried, although the alumina still gave a peroxide test; thus, material was eluted with methylene chloride which showed an infrared carbonyl stretching band at *ca.* 5.83 μ and no hydroxyl stretching band, but this material gave a negative test for peroxide.

Identification and Isolation of Acetone.—Oxygen gas was passed through a fresh sample of liquid ketone using a sintered-disk arrangement and the exit gases were bubbled through a 2,4-dinitrophenylhydrazine solution. At room temperature the reaction proceeded very slowly, but it took place at a faster rate on heating the ketone (to *ca.* 110° in most of the experiments). The orange 2,4-dinitrophenylhydrazone precipitate was collected by filtration and recrystallized from 95% ethanol, mp 123.5–125.0°. A sample of the hydrazone prepared from authentic acetone was yellow and melted at 124.0–125.5°, mmp 123.5–125.0°. Both samples of hydrazone migrated at the same rate on a thin layer chromatogram on aluminum oxide G using a 1:2 nitrobenzene–cyclohexane solution for development. The R_f values ranged from 0.77 to 0.87 depending on various factors such as time of standing of the sample, size of sample, etc. The sample from the cold trap showed in addition a second smaller spot with R_f 0.43 (see below).

When the exit gases from the oxidation were passed through a Dry Ice–acetone trap, a colorless liquid condensed which formed a 2,4-dinitrophenylhydrazone precipitate. Since this precipitate gave only one spot in a thin layer chromatogram, it would appear that the second spot (R_f 0.43) observed above may be a product formed from oxidation of the 2,4-dinitrophenylhydrazone. However, this was not further investigated.[13]

Analysis of Autoxidation Cold-Trap Condensate.—The infrared absorption spectrum of the liquid from above, however, did not exactly match the spectrum of a sample of pure acetone, the main differences being a strong broad absorption band centered *ca.* 3.1 μ and a broader band than acetone in the carbonyl stretching region. It was suspected that water might also be present, causing the difference in the spectra. A similar spectrum was obtained from a *ca.* 2:1 acetone–water mixture (molar ratio). Further experiments were performed on the oxidation to establish conclusively that the water was actually formed in the oxidation and not introduced from the atmosphere or other sources. Thus, the oxygen was passed through a drying train at a flow rate of *ca.* 3 l./hr before being passed through the ketone and a phosphorous pentoxide drying tube protected the cold trap from moisture at the exit. A more accurate determination of the acetone–water ratio was made from the proton nmr curve using the integrated peaks[14] at δ 2.12 and 4.13 (acetone and water peaks, respectively) which showed a molar ratio of 1.85 in 15 hr[15] and 2.00 in 21 hr, the reaction still not being complete in the reaction times. The acid content in the 15-hr experiment was determined by titration of the reaction mixture in an aqueous dioxane solution.[16] In addition to the two main nmr peaks, several small peaks were present of which one was identified as coming from a trace of the starting ketone; some of these peaks evidently originated from a peroxide, since the material from the low-temperature trap was found to give a peroxide test. Thin layer chromatography showed that the peroxide was different than the one (IVb) observed above in the reaction mixture; this one did not move under the chromatographic conditions used. It was suspected that the peroxide might be formed from the oxidation of acetone in the low-temperature trap; however, in a control experiment, no peroxide was formed after passing oxygen through acetone in the low-temperature trap for 22.5 hr. Furthermore, no material was condensed in the cold trap when the oxygen was bubbled through isopropyl mesityl ketone at room temperature for the same period of time. No further study of this was made since the peroxidic material formed only a very small part of the total amount of material in the Dry Ice trap as evidenced by the nmr curve.

Infrared and Nmr Spectra.—Infrared spectra were taken with a KM-1 Baird-Atomic instrument. The acetone–water spectra were taken in IRTRAN-2 cells. Other spectra were taken in matched 0.1-mm sodium chloride cells in the concentration range of 3–5% (wt/vol) or in a sodium chloride sandwich cell for neat samples. All spectra were calibrated against polystyrene bands run on the same chart. The spectrum of mesitoic acid was obtained in carbon tetrachloride; the oxidation mixture and acetone–water were neat samples. The nmr spectra were obtained with a Varian Associates DP-60 spectrometer. Tetramethylsilane was used as an internal standard.

Registry No.—I, 2040-22-4; II, 480-63-7.

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[13] In a recent paper, autoxidation products of phenylhydrazones were prepared and characterized as hydroperoxides: H. C. Yao and P. Resnick, *J. Org. Chem.*, **30**, 3832 (1965). For earlier related work, see R. Criegee and G. Lohaus, *Ber.*, **84**, 219 (1951); M. Busch and W. Dietz, *ibid.*, **47**, 3277 (1914).

[14] The analysis was based on synthetic acetone–water mixtures which showed two sharp singlets at the same positions as the condensate.

[15] The total amount of condensate was 2.380 g starting with 9.391 g of ketone. The integration curve showed 50 units for the acetone protons and 9.0 units for the hydroxyl protons. Thus, the ratio acetone–water = (50/6)/(9/2) = 1.85 (acetone having six protons and water having two).

[16] The reaction mixture was dissolved in purified dioxane and the solution diluted to 100 ml in a volumetric flask. A 5-ml aliquot was diluted with 30 ml of dioxane and 15 ml of distilled water and titrated with standard sodium hydroxide (0.04906 *N*) using a Beckman pH meter with glass and calomel electrodes. The average amount of acid calculated for three runs was 23.57 mequiv. Since the amount of starting ketone was 49.35 mmoles (9.391 g), the relative amount of acid calculated is 0.478 equiv based on ketone = 1 000 equiv.

Allene Chemistry. VII.[1] Reaction of Chlorine with Allene under Ionic Conditions

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The noncatalyzed addition of chlorine to allene in the dark and in inert solvents was reported[2] to produce, in moderate over-all yields (approximately 50%), an almost equimolar mixture of 2,3-dichloropropene and propargyl chloride (Table I).

$$\mathrm{H_2C{=}C{=}CH_2 + Cl_2 \longrightarrow \underset{20\text{–}25\%}{H_2C{=}CClCH_2Cl} + \underset{30\text{–}35\%}{HC{\equiv}CCH_2Cl}}$$

The present work was undertaken in an attempt to optimize the selectivity of the reaction toward the monoadduct, 2,3-dichloropropene. At first glance it might seem that this goal should be easily attained simply by using more strongly ionic reaction conditions. For it was intimated[2] that formation of the yield-limiting by-product, propargyl chloride, was due to imperfect dissociation of chlorine in the initial π complex.

The application of ionic conditions could, however, *a priori* open the route for another side reaction, *viz.*,

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[1] Paper VI in this series: W. H. Mueller and K. Griesbaum, *J. Org. Chem.*, **32**, 856 (1967).

[2] H. G. Peer, *Rec. Trav. Chim.*, **81**, 13 (1962).

Table I

Chlorination of Allene in Various Reaction Media

Reaction medium	Molar ratio $C_3H_4:Cl_2$	Conversion, %	% selectivity of volatile addition products[a]							
			$CH_2{=}\underset{Cl}{\underset{\mid}{C}}{-}\underset{Cl}{\underset{\mid}{CH_2}}$[b]	$CH{\equiv}CCH_2Cl$[c]	$\underset{Cl}{\underset{\mid}{CH_2}}CCl_2\underset{Cl}{\underset{\mid}{CH_2}}$	$\underset{Cl}{\underset{\mid}{CH_2}}CCl_2CH_3$	$\underset{Cl}{\underset{\mid}{CH_2}}\underset{Cl}{\underset{\mid}{C}}{=}CHCl$	$\underset{Cl}{\underset{\mid}{CH_2}}CH{=}CHCl$	$CH_2{=}\underset{Cl}{\underset{\mid}{C}}CH_3$	$CH_3CCl_2CH_3$
CH_2Cl_2[c]	0.8	49.4	20 (40.5)	29.4 (59.9)						
$CHCl_2CHCl_2$[c]	0.9	53	25 (47)	35 (53)						
DMF[b]	1.1	53	25 (47)	35 (53)						
Boron trifluoride etherate	2.0	68	30.2 (40.2)	45.3 (59.8)	12.3	3.0	3.8	<1	. . .	. . .
$NaAlCl_4$–$KAlCl_4$	1.6	77[d]	60.0 (87)	8.9 (13)	16.2	0.9	6.1	0.7	4.5	<0.1
$NaAlCl_4$–$KAlCl_4$	9.6	77[d]	73.0 (88)	10.0 (12)	10.5	0.8	1.0	1.6	1.7	<0.1

[a] Very minor amounts of unidentified components were also detected by glpc analysis. [b] Relative ratios of 2,3-dichloropropene and propargyl chloride are reported in brackets. [c] Reactions reported in ref 2. [d] The remainder was a carbonaceous solid which was isolated from the melt.

cyclodimerization of allene. It was reported[3a] that the use of typical Lewis acids such as aluminum chloride and particularly boron trifluoride etherate caused a drastic change in the course of the chlorination of 2-butyne, yielding up to 45% dichlorotetramethylcyclobutene. Since allene is also susceptible to electrophilically induced cyclodimerizations,[3b] the high-yield synthesis of 2,3-dichloropropene from allene could, thus, have posed an insurmountable problem, caused by propargyl chloride formation in nonionic media and by cyclodimerization in more ionic media.

Chlorination of Allene in the Presence of Boron Trifluoride Etherate.—In order to examine the possibility of cyclodimerization reactions, we first studied reaction conditions which were reported to afford high yields in the cyclodimerization of 2-butyne.[3a] A rapid reaction occurred when allene and chlorine were condensed in a glass tube at −60 to −70°[4] in the presence of approximately 2.5 mole % of boron trifluoride–diethyl ether catalyst. This reaction produced a slightly colored mobile liquid which, after removal of the unreacted starting materials, was analyzed as such by glpc, glpc/time-of-flight mass spectroscopy (Table II), and nmr spectroscopy.

The above analyses showed (Table I) that the crude adduct mixture consisted mainly (75%) of a 40:60 mixture of 2,3-dichloropropene (I) and propargyl chloride (III) along with small amounts (12%) of the allene diadduct 1,2,2,3-tetrachloroethane (II) and minor amounts of 1,2,3-trichloropropene (V) and 1,3-dichloropropene (IV). No evidence for the presence of a cyclodimerization product was found. These results indicated on one hand that cyclodimerization is not a serious problem in the catalyzed chlorination of allene and on the other hand that it probably takes very strongly ionic conditions in order to substantially suppress formation of the undesired propargyl chloride.[5] We have, therefore, resorted to a $NaAlCl_4$–$KAlCl_4$ melt which is known to be a strongly ionic reaction medium.[6]

Chlorination of Allene in a $NaAlCl_4$–$KAlCl_4$ Melt.—A very rapid reaction occurred when allene and chlorine were introduced into a eutectic melt (maintained at 140°) of $NaAlCl_4$ and $KAlCl_4$. Analysis of the volatile products revealed that in this strongly ionic medium the formation of propargyl chloride was indeed substantially suppressed and that the selectivity toward the allene monoadduct 2,3-dichloropropene could be significantly increased. The ratio of 2,3-dichloropropene (I) to propargyl chloride (III) changed from approximately 45:55 in the cases of the uncatalyzed[3a] and BF_3-catalyzed reactions to approximately 88:12 in the reactions carried out in the melt (Table I). This ratio was largely independent of the allene to chlorine ratio in the feed. The over-all yield of 2,3-dichloropropene (I), on the other hand, did change

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[3] (a) R. Criegee and A. Moschel, *Chem. Ber.*, **92**, 2181 (1959); (b) K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Am. Chem. Soc.*, **87**, 3151 (1965).

[4] The cyclodimerization of 2-butyne[3a] was carried out at −20°. Since it is known that the cyclodimerization of allene by HBr and HCl is favored at lower temperatures,[3b] it appeared advisable to perform this particular reaction, which was aimed at examining the possibility of cyclodimerization in the allene chlorination, at temperatures comparable with those of the HBr-induced cyclodimerizations.

[5] For all intents and purposes the ratio of I:III in the catalyzed chlorine addition was the same as in the uncatalyzed addition described in ref 2.

[6] W. Sundermeyer, *Angew. Chem.*, **77**, 241 (1965).

Table II

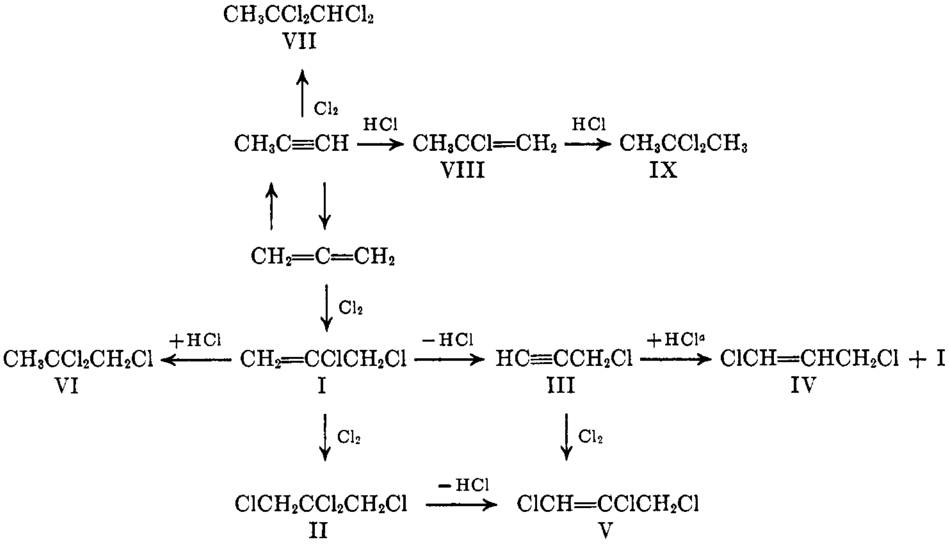
Mass Spectral Data from Allene Chlorination Products

Structure	m/e	Formula	Significant fragment ions
$H_2C{=}C(Cl)CH_2Cl$	110	$C_3H_4Cl_2$	*m/e* 75 (M − Cl); *m/e* 61 (M − CH_2Cl); *m/e* 49 (CH_2Cl); *m/e* 39 (C_3H_3)
$ClCH_2C(Cl)_2CH_2Cl$	180	$C_3H_4Cl_4$	*m/e* 145 (M − Cl); *m/e* 144 (M − HCl); *m/e* 131 (M − CH_2Cl); *m/e* 109 (145 − HCl)
$ClCH_2C{\equiv}CH$	74	C_3H_3Cl	*m/e* 73 (M − H); *m/e* 48 (CHCl); *m/e* 39 (C_3H_3)
$CH_3C(Cl)_2CH_2Cl$	146	$C_3H_5Cl_3$	*m/e* 111 (M − Cl); *m/e* 97 (M − CH_2Cl); *m/e* 75 (111 − HCl); *m/e* 49 (CH_2Cl)
$ClCH{=}C(Cl)CH_2Cl$[a] *cis* and *trans*	144	$C_3H_3Cl_3$	*m/e* 109 (M − Cl); *m/e* 83 ($CHCl_2$); *m/e* 73 (109 − HCl)
$ClCH_2CH{=}CHCl$[a] *cis* and *trans*	110	$C_3H_4Cl_2$	*m/e* 75 (M − Cl); *m/e* 49 (CH_2Cl); *m/e* 39 (C_3H_3)
$CH_3C(Cl)_2CHCl_2$	180	$C_3H_4Cl_4$	*m/e* 165 (M − CH_3); *m/e* 145 (M − Cl); *m/e* 97 (CH_3CCl_2); *m/e* 83 ($CHCl_2$)
$CH_3C(Cl){=}CH_2$	76	C_3H_5Cl	*m/e* 61 (M − CH_3); *m/e* 41 (M − Cl); *m/e* 39 (C_2H_3)
$CH_3C(Cl)_2CH_3$	112	$C_3H_6Cl_2$	*m/e* 97 (M − CH_3); *m/e* 77 (M − Cl); *m/e* 76 (M − HCl)

[a] Identical fragmentation was observed for the *cis* and *trans* isomer.

Scheme I

Reaction of Chlorine with Allene and Subsequent Side Reactions



[a] The catalyzed addition of HCl to propargyl chloride produces a mixture of 2,3-dichloropropene (I) and 1,3-dichloropropene (IV): W. Kirmse and M. Kapps, *Chem. Ber.*, 99, 2869 (1966).

with the feed ratio, a large excess of allene leading to a higher yield of I. As Table I shows, this increased yield of 2,3-dichloropropene is at the expense of the diadduct (II) and its HCl elimination product (V).

The allene chlorination in the melt also produced up to 30% carbonaceous solid and, in analogy to the BF_3-catalyzed reaction, led again to a number of minor volatile by-products (IV–IX), as well as trace amounts of yet unidentified components. The identification of by-products IV–IX was established by glpc/time-of-flight mass spectroscopy (Table II) and in some cases (VIII, IX) further supported by comparison of their glpc retention times with those of authentic samples. The major products were actually isolated by fractional distillation and identified by nmr spectroscopy.

The most probable reaction paths leading to the several products obtained are depicted in Scheme I. In this arrangement all the true chlorination reactions are arranged vertically while the side reactions involving dehydro- or hydrochlorinations are arranged horizontally. Most of these reactions are straightforward and have been reported previously in the literature. Although allene was shown not to isomerize if it was subjected to the $NaAlCl_4$–$KAlCl_4$ melt all by itself, it is believed that the compounds VII–IX are the result of a HCl-catalyzed allene isomerization[7] and subsequent addition to methylacetylene. In summary, it has been demonstrated in the present work that high yields of 2,3-dichloropropene can be obtained by the chlorination of allene if the reaction is carried out under strongly ionic conditions.

Experimental Section

Materials.—The allene used was +99% pure. It contained traces of propane and propene. Chlorine was a Matheson product of 99.5% minimum purity. The sodium and potassium chloride were reagent grade from the Baker Chemical Co. Aluminum trichloride was "anhydrous, purified" from the Matheson Coleman and Bell Co.

Methods of Analysis.—The product mixtures were analyzed by gas–liquid chromatography using an F & M Model 500 linear programmed temperature gas chromatograph with a 6-ft, 0.25-in.-o.d. column. The packing consisted of 10% SE 30 (silicon gum rubber) on Chromosorb W. Operating conditions were as follows: detector temperature, 230°; injector temperature, 190°;

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[7] Isomerization of allene into methylacetylene has been reported for the $BiCl_3$-catalyzed addition of HCl to allene at much lower temperatures than those applied in the present work: T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960).

flow rate, 65 cc/min; column heating rate, 5.6°/min; starting temperature, 50°; final temperature, 240°. For better resolution of the low-boiling components, glpc analyses were also performed on a 10-ft, 0.25-in.-o.d. Carbowax 1500 column. Operating conditions, with the exception of the final temperature of 140°, were as above. An Aerograph Model 471 digital integrator was used to record the peak areas of the chromatograms.

Gas-liquid chromatograph time-of-flight mass spectroscopy analyses were obtained with an F & M Model 500 temperature programmed gas chromatograph (SE 30 column and conditions used were the same as above) gauged to a time-of-flight mass spectrometer. The effluent from the gas chromatograph was metered into the spectrometer through a connecting line and a high-temperature metering valve manufactured by Varian Associates heated to 200+°. The spectrometer was a Bendix Instrument, Type 12-101, which has been modified so as to include a 1.66-m flight tube, multigate recording, and improved electron beam focusing. A multichannel Minneapolis-Honeywell Visi-corder was used to record the mass spectral data obtained (Table II). Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer as *ca.* 50% solution in CCl_4 with tetramethylsilane as an internal standard.

$NaAlCl_4$–$KAlCl_4$ Eutectic.—NaCl (35 mole %), KCl (15 mole %), and $AlCl_3$ (50 mole %) were mixed and molten under a nitrogen atmosphere. This eutectic melts at *ca.* 135°. Small amounts of free $AlCl_3$ in this melt were removed by sublimation at 200° for 15 hr. This precaution was taken to avoid hydride transfer reactions of $AlCl_3$ with allene.

Chlorination of Allene in the Presence of Boron Trifluoride Etherate.—In a 100-ml thick-wall glass tube, equipped with a Teflon-tipped needle valve on the top, allene and chlorine were condensed successively at −78°. Then the boron trifluoride etherate catalyst was added with a syringe and the tube was closed and kept in a dewar flask, cooled to −60 to −70° by a Dry Ice–2-propanol mixture. The unreacted gases were largely removed by allowing the mixture to gradually warm to room temperature. The crude adduct mixture was analyzed by glpc, glpc/time-of-flight analysis, and nmr spectroscopy.

Chlorination of Allene in a $NaCl_4$–$KAlCl_4$ Melt.—*Ca.* 150 g of the above melt was placed in a cylindrical Pyrex vessel of 37 mm i.d. and 200 mm height and kept at 140°. Two inlet tubes with perforated ends, reaching to the bottom of the vessel, served to introduce separately allene and chlorine into the melt. The reactant ratio was monitored through calibrated precision bore flowrator tubes. The chlorine flow was kept constant at 0.05 mole/hr and the desired reactant ratios (Table I) were adjusted by variations of the amount of allene introduced. To maintain a constant flow rate and residence time, changes in the allene flow were balanced with nitrogen. *Caution* is in order with a large excess of allene if little or no nitrogen is admixed. In this case, small flashes caused by the ignition of allene were observed in the reaction chamber. The excess allene and nitrogen served as a carrier gas for the products, which were removed through a gas outlet on the top of the reactor and collected in three consecutive cold traps at −20°. In addition to the volatile products, *ca.* 20–30 wt % of the total product was isolated as carbonaceous solid upon hydrolysis of the melt.

The structural assignments of I–VIII are supported by mass spectral data which are summarized in Table II. Compounds II, III, VII, and VIII were also identified by comparison of their glpc retention times with those of authentic samples. The 2,3-dichloropropene (I) and 1,2,2,3-tetrachloropropane (II) were obtained in *ca.* 90% purity each, on fractional distillation. The nmr spectrum of compound II shows a singlet for the methylene protons at 4.13 ppm. In one of the distillation fractions, compound V was also enriched. Its nmr spectrum showed broad singlets at 6.37 and 6.64 ppm attributable to the vinyl proton of the *cis* and *trans* isomer, respectively. Similar singlets for the allylic protons were found at 4.65 ppm for the *cis* isomer and at 5.09 ppm for the *trans* isomer.

Registry No.—I, 78-88-6; II, 13116-53-5; III, 624-65-7; *cis* IV, 10061-01-5; *trans* IV, 10061-02-6; *cis* V, 13116-57-9; *trans* V, 13116-58-0; VI, 3175-23-3; VII, 13116-60-4; VIII, 557-98-2; IX, 594-20-7; allene, 463-49-0.