tilled at about 248°. The best fraction (11.8 g.) was collected from 242–249°, n_D^{20} 1.5164 (Lit. b.p. 244–246°[21]).

2. *Phenol and propylene.* Distillation of the reaction product gave two cuts which were largely *o*-isopropylphenol: (a) 19.9 g., b.p. 210–215°, n_D^{20} 1.5208, (b) 43.7 g., b.p. 215–217°, n_D^{20} 1.5267 (Lit. b.p. 214.5°, n_D^{20} 1.5263, *m*-isopropylphenol b.p. 228°, *p*-isomer b.p. 228.2°).[23] The aryloxyacetic acid derivative crystallized as white fluffy needles from mixed hexanes, m.p. 131.4–132.4° (Lit. 130° uncorr.).[24]

Anal. Calcd. for $C_{11}H_{13}O_3$: C, 66.65; H, 6.72. Found: C, 66.65, 66.54; H, 6.90, 6.79.

The transition and higher boiling cuts were partitioned between Claisen's alkali and mixed hexanes to separate neutral products. Distillation of the phenolic fraction gave additional *o*-isomer and two di-alkylphenol cuts: (a) 6 g., b.p. 226–242°, n_D^{20} 1.5182, (b) 13 g., b.p. 242–248°, n_D^{20} 1.5146. These are probably mixtures of 2,4- and 2,6-diisopropylphenols. There was no inflection in the distillation curve to indicate the presence of *p*-isopropylphenol.

Distillation of the neutral fraction gave 19 g. of isopropylphenyl ether, less than 1 g. of transition cuts, 5 g. of product distilling from 223–240°, which was mainly the isopropyl ether of *o*-isopropylphenol, and 7 g. of higher boiling products.

3. *Phenol and 1-butene.* The product was mainly *o*-*s*-butylphenol. This was collected in two cuts: (a) 24.9 g., b.p. 227.0–227.5°, n_D^{20} 1.5231, (b) 17.9 g., b.p. 227.5–228°, n_D^{20} 1.5227 (Lit. b.p. 228°).[19] Infrared analysis based on a strong band at 13.3 μ showed the product to be largely *o*-alkylphenol. The structure was confirmed by preparation of the aryloxyacetic acid derivative, m.p. 111.0–111.6° (Lit. 111°).[19]

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.21, 69.30; H, 7.68, 7.73.

4. *Phenol and cyclohexene.* After removal of phenol and some unidentified low boiling material by distillation, the product was partitioned with Claisen's alkali. Distillation of the phenolic fraction gave solid *o*-cyclohexylphenol, b.p. 151° at 17 mm., m.p. 55° (Lit. 55°).[8]

5. *Phenol and diisobutylene.* The product was treated as described for the ethylene experiment. Distillation of the phenolic fraction gave 10.7 g. of *o-tert*-butylphenol and 4.0 g. of the *p*-isomer. It was assumed that the bottoms (5.1 g.) were octylphenols.

6. *Phenol and tert-butyl alcohol.* This product was worked up as described for the isobutene experiments.

7. *Phenol and isopropyl ether.* Very little alkylation occurred. Distillation of the product gave 4.2 g. of material, b.p. 181–214°, 0.4 g. b.p. 214–220° and 0.5 g., b.p. 220–230°. However, 6% of the ether decomposed during reaction and was recovered as a mixture of propylene and propane.

8. *o-Cresol and isobutene.* The composition of the product was estimated from the distillation curve and by infrared analyses of the distillation cuts. The principal phenolic component boiling in the range of 234–242° was a 1,2,3-trisubstituted benzene, probably 2-methyl-6-*tert*-butylphenol. Approximately 14% of the material was a 1,2,4-trisubstituted benzene; this was probably 2-methyl-4-*tert*-butylphenol.

9. *Aniline and isobutene.* No reaction occurred when 47 g. of aniline and 60 g. of isobutene were heated at 315–327° for 3 hr.

Thermal rearrangement of phenyl n-butyl ether. This ether was recovered unchanged after heating for 3 hr. at 315–327°.

Acknowledgment. This work was supported by The Oronite Chemical Co.

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[23] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

[24] J. B. Niederl and E. A. Storch, *J. Am. Chem. Soc.*, **55**, 284 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Addition of Halogens and Halogen Compounds to Allylic Chlorides. I. Addition of Hydrogen Halides[1]

J. REID SHELTON AND LIENG-HUANG LEE[2]

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The addition of hydrogen chloride to allylic chlorides was found to be extremely difficult under the conditions employed, except in the case of allyl chloride. 3,3-Dichloropropene isomerized instead to give 1,3-dichloropropene. 3,3,3-Trichloropropene isomerized to 1,1,3-trichloropropene in the presence of hydrogen chloride, with no addition observed.

The addition of hydrogen iodide to allylic chlorides was found to be accompanied by halogen exchange, reduction, and allylic isomerization. The addition products observed were: 2-iodo-1-chloropropane for allyl chloride, 2-iodo-1,1-dichloropropane for 3,3-dichloropropene, 3-iodo-1,1,1-trichloropropane for 3,3,3-trichloropropene, 1-iodo-1,3-dichloropropane for 1,3-dichloropropene, and 1-iodo-1,1,3-trichloropropane for 1,1,3-trichloropropene.

The addition of hydrogen halides to allylic chlorides has been studied by Kharasch and coworkers,[3–5] including both allyl chloride and a trichloropropene. In order to gain a better understanding of the mechanism of electrophilic attack on unsaturated compounds, Swindale, Swedlund, and Robertson[6] compared halogen addition to allylic halides with halogen substitution in benzyl halides.

Early work on the nitration of benzylic chlo-

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[1] This is an abstract of a part of the doctoral thesis submitted by Lieng-huang Lee.

[2] Present address: Research Division, Dow Chemical Company, Midland, Mich.

[3] M. S. Kharasch, S. C. Kleiger, and F. R. Mayo, *J. Org. Chem.*, **4**, 428 (1939).

[4] M. S. Kharasch, J. A. Norton, and F. R. Mayo, *J. Am. Chem. Soc.*, **62**, 81 (1940).

[5] M. S. Kharasch, E. H. Rossin, and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2558 (1941).

[6] L. E. Swindale, B. E. Swedlund, and P. W. Robertson, *J. Chem. Soc.*, 812 (1950).

rides[7,8] indicated that the amount of *meta*-isomer (toluene, 3%; benzyl chloride, 14%; benzal chloride, 34%; benzotrichloride, 64%) was related to the number of negative substituents on the alpha-carbon. It has been suggested that two mechanisms are superimposed, one governed by the inductive electron-attracting effect of the halogen, and the other by the hyperconjugative effect associated with the alpha C—H group.

A series of allylic chlorides were employed for this study to see if similar effects could explain the variable nature of addition products reported with allylic halides. The following compounds were selected for study:

$CH_2{=}CH{-}CH_2Cl$ $CH_2{=}CH{-}CHCl_2$ $CH_2{=}CH{-}CCl_3$
(Allyl chloride) (3,3-Dichloropropene)
(3,3,3-Trichloropropene)

The progressive replacement of hydrogen by chlorine on the alpha carbon thus gives a series of compounds analogous to the benzylic chlorides referred to above. Certain isomers of the allylic chlorides were also included in the study in order to detect any allylic isomerization. The compounds used were *cis*-and *trans*-1,3-dichloropropene and 1,1,3-trichloropropene.

The method used by Kharasch, Rossin, and Fields[5] to prepare 3,3,3-trichloropropene was found by Kirrmann[9] to yield 1,1,2-trichloropene instead. This would explain why 1,1,1,2-tetrachloropropane was obtained when hydrogen chloride was allowed to react with the compound they prepared, while the present study gave no evidence of addition of hydrogen chloride to 3,3,3-trichloropropene under the conditions employed. Nesmeyanov's method[10] of preparation for 3,3,3-trichloropropene was modified for use in this study.

Reaction with hydrogen chloride. The products of the reaction of hydrogen chloride with allylic chlorides were chiefly determined by infrared analysis of the reaction mixtures in a 0.02 mm. sodium chloride cell, using a Perkin-Elmer Model 21 Recording Spectrophotometer. The infrared spectra of the series of allylic chlorides used in this study are shown in Fig. 1.

The addition of hydrogen chloride to allyl chloride (Fig. 2A) gave 1,2-dichloropropane. The changes in the spectrum of allyl chloride after addition involved the disappearance of the vinyl double bond absorption bands and the appearance of the methyl group bands (*e.g.* 1374 cm.$^{-1}$). If the same type of addition occurred with 3,3-dichloropropene and 3,3,3-trichloropropene, the spectra would have shown the same kind of changes.

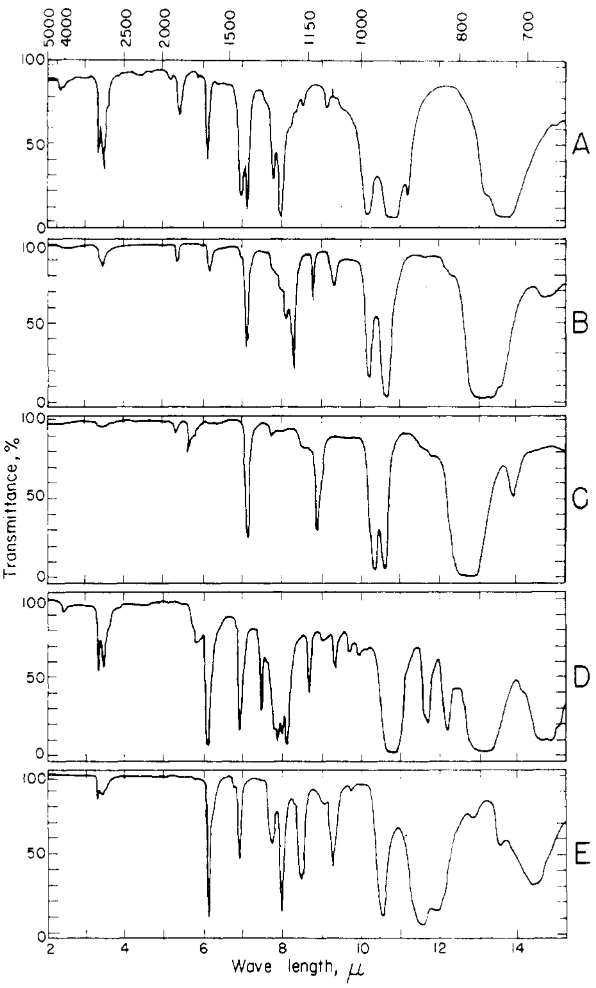

Fig. 1. Infrared spectra of allylic chlorides: A, allyl chloride; B, 3,3-dichloropropene; C, 3,3,3-trichloropropene; D, *cis*- and *trans*-1,3-dichloropropene; E, 1,1,3-trichloropropene (cell thickness: 0.02 mm.)

The products resulting from the reaction between hydrogen chloride and 3,3-dichloropropene were shown by the spectrum (Fig. 2B) to be 1,3-dichloropropene and the unreacted 3,3-dichloropropene. This was obvious when the spectrum of the known 3,3-dichloropropene and the known 1,3-dichloropropene from Fig. 1 were superimposed to give a composite spectrum which corresponded to the observed spectrum shown in Fig. 2B. A weak band at 1374 cm.$^{-1}$ in the observed spectrum could indicate a trace of addition product of HCl to 3,3-dichloropropene, so that some 1,1,3-trichloropropane might have been present. However, the main course of reaction was isomerization instead of addition.

The same result was found for 3,3,3-trichloropropene (Fig. 2C). Only 1,1,3-trichloropropene was found as the result of allylic isomerization.

Reaction with hydrogen iodide. The addition of hydrogen iodide to allyl chloride was found to yield 1,2-dihalide by Kharasch, Norton, and Mayo.[4] The same allylic chlorides were used as in the reactions with hydrogen chloride described above.

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(7) A. F. Holleman, J. Vermeulen, and W. J. de Mooy, *Rec. trav. chim.*, **18**, 267 (1899).

(8) B. Flürscheim and E. L. Holmes, *J. Chem. Soc.*, 1607 (1928).

(9) A. Kirrmann, *Chem. Abstr.*, **42**, 5840 (1948); *Bull. soc. chim. France*, 166 (1948).

(10) A. N. Nesmeyanov, *Otdel. Khim. Nauk.* 1951, 505-11; *Chem. Abstr.*, **46**, 7034 (1952).

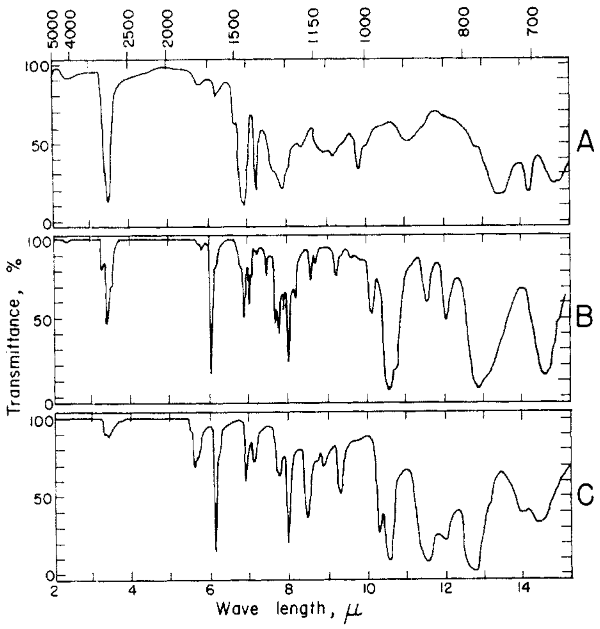

Fig. 2. Infrared spectra of the reaction products of hydrogen chloride with allylic chlorides: A, 1,2-dichloropropane from allyl chloride; B, 1,3-dichloropropene in 3,3-dichloropropene; C, 1,1,3-trichloropropene in 3,3,3-trichloropropene (cell thickness: 0.02 mm.)

The disadvantage of using hydrogen iodide was found to be the side-reactions which accompanied additions, such as halogen exchange, reduction, and allylic isomerization:

1. Reduction, $RI + HI \longrightarrow RH + I_2$
2. Halogen exchange, $RCH_2Cl + HI \longrightarrow RCH_2I + HCl$
3. Reduction after exchange, $ClCH_2CH_2CH_2Cl \xrightarrow{HI} ClCH_2—CH_2—CH_2I \xrightarrow{HI} ClCH_2—CH_2—CH_3$
4. Isomerization with exchange, $Cl_3C—CH{=}CH_2 \xrightarrow{HI} Cl_2C{=}CHCH_2I$

Additions to 3,3-dichloropropene and 3,3,3-trichloropropene could be accomplished without isomerization only by using a large excess of hydrogen iodide. In the presence of a smaller amount of hydrogen iodide, the prolonged contact of the allylic chlorides and hydrogen iodide caused allylic isomerization.

The methods used to identify the products generally involved fractionation of the mixtures under reduced pressure, followed by infrared analysis. The infrared spectra of the fractions were compared with those of known compounds or with those of similar halogen compounds. For instance, 3-iodo-1,1,1-trichloropropane was prepared for the identification of the addition product of HI to 3,3,3-trichloropropene. It was found by Kitson[11] that the halogenated compounds of the same structure and composition, except for the identity of one halogen atom, had similar spectra. For instance, we found that 3-iodo-1,1,1-trichloropropane, 3-bromo-1,1,1-trichloropropane, and 1,1,1,3-tetrachloropropane had very similar spectra. Another important method was to detect the formation or disappearance of a specific structural group. For example, in the case that halogen added to the second carbon atom and hydrogen to the first, a methyl group was formed and it gave several sharp bands.

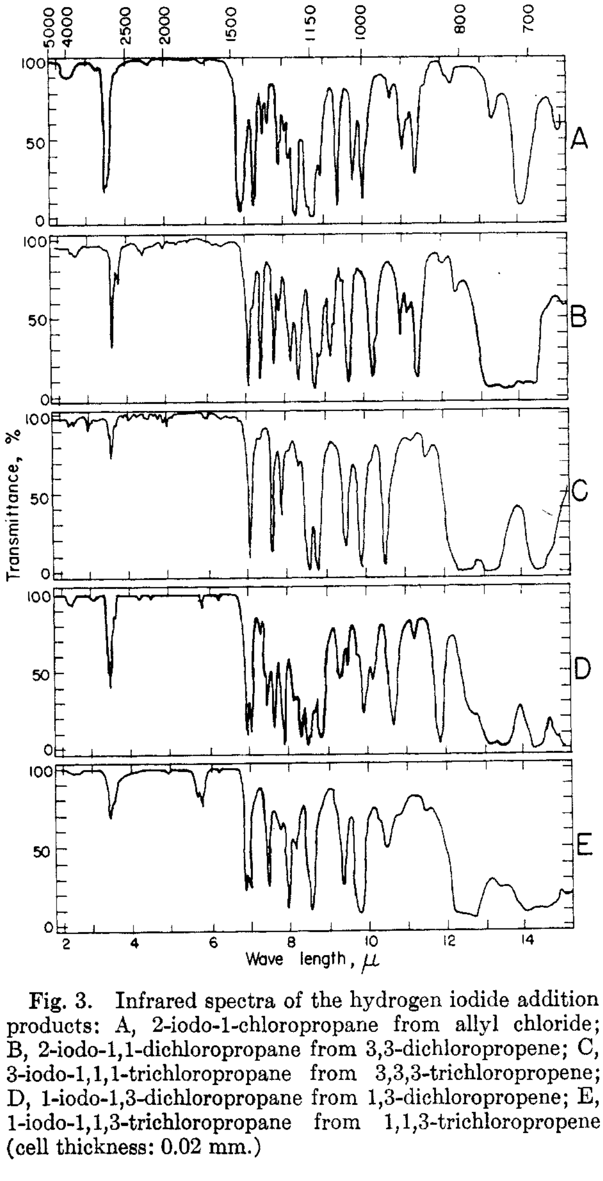

Fig. 3. Infrared spectra of the hydrogen iodide addition products: A, 2-iodo-1-chloropropane from allyl chloride; B, 2-iodo-1,1-dichloropropane from 3,3-dichloropropene; C, 3-iodo-1,1,1-trichloropropane from 3,3,3-trichloropropene; D, 1-iodo-1,3-dichloropropane from 1,3-dichloropropene; E, 1-iodo-1,1,3-trichloropropane from 1,1,3-trichloropropene (cell thickness: 0.02 mm.)

In Fig. 3A and B the spectra of the addition products of allyl chloride and 3,3-dichloropropene are very similar. A band at 1374 cm.$^{-1}$ was used to show the presence of a methyl group. A band around 1150 cm.$^{-1}$ is common to most of the iodo compounds.[11] The spectrum of 3-iodo-1,1,1-trichloropropane (Fig. 3C) does not have the methyl band at 1374 cm^{-1}. The whole spectrum was compared with 3-bromo-1,1,1-trichloropropane and 1,1,1,3-tetrachloropropane.

The spectrum of the addition product of hydrogen iodide to 1,3-dichloropropene (Fig. 3D) con-

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[11] R. E. Kitson, *Anal. Chem.*, 25, 1470 (1953).

TABLE I

ADDITION PRODUCTS[a] OF HYDROGEN IODIDE TO ALLYLIC CHLORIDES

	Molar Ratio of HI to Allylic Chloride		
Allylic Chlorides	1:1	3:2	3:1
Allyl chloride $CH_2=CH-CH_2Cl$	$CH_3-CHI-CH_2Cl$	$CH_3-CHI-CH_2Cl$ $(CH_3-CH_2-CH_2Cl)$	—
3,3-Dichloropropene $CH_2=CH-CHCl_2$	$CH_3-CHI-CHCl_2$ $(ClCH=CH-CH_2I)$	$CH_3-CHI-CHCl_2$ $(ICH_2-CH_2-CHCl_2)$	$CH_3-CHI-CHCl_2$ $(ICH_2-CH_2-CHCl_2)$
3,3,3-Trichloropropene $CH_2=CH-CCl_3$	$Cl_2C=CH-CH_2I$	$Cl_2C=CH-CH_2I$	$ICH_2-CH_2-CCl_3$ $(CH_3-CH_2-CCl_3)$
1,3-Dichloropropene $ClCH=CH-CH_2Cl$	—	$Cl-CHI-CH_2-CH_2Cl$ $(ClCH_2-CH_2-CH_2Cl)$	$ClCH_2-CH_2-CH_2Cl$ $(ClCHI-CH_2-CH_2Cl)$
1,1,3-Trichloropropene $Cl_2C=CH-CH_2Cl$	—	$Cl_2CI-CH_2-CH_2Cl$ $(Cl_2CH-CH_2-CH_2Cl)$	$Cl_2CH-CH_2-CH_2Cl$ $(Cl_2CI-CH_2-CH_2Cl)$

[a] Minor products found in small amounts are indicated by parentheses.

tains a band at 1140 cm.$^{-1}$ The spectrum was compared with that of 1,1,3-trichloropropane. It was confirmed that the iodine atom added to the terminal carbon to form 1-iodo-1,3-dichloropropane. A weak band at 1370 cm.$^{-1}$ could indicate a trace of exchange and reduction product with a methyl group.

The addition product of 1,1,3-trichloropropene (Fig. 3E) was identified by the same method. The spectrum was compared with that of 1,1,1,3-tetrachloropropane and, on the basis of the great similarity, the product was confirmed to be 1-iodo-1,1,3-trichloropropane.

The observed addition products are summarized in Table I. Minor products are indicated by parentheses. The major products formed by addition were: 2-iodo-1-chloropropane for allyl chloride, 2-iodo-1,1-dichloropropane for 3,3-dichloropropene, 3-iodo-1,1,1-trichloropropane for 3,3,3-trichloropropene, 1-iodo-1,3-dichloropropane for 1,3-dichloropropene, and 1-iodo-1,1,3-trichloropropane for 1,1,3-trichloropropene. The modes of addition are thus different between allyl chloride and 3,3-dichloropropene on the one hand, and 3,3,3-trichloropropene on the other. The modes of addition are also different between 3,3-dichloropropene and 1,3-dichloropropene.

Discussion A detailed discussion of the significance of these results in terms of the possible mechanisms which could account for the observed behavior will be reserved for the final paper of this series when other pertinent information will be available. A few comments can be made, however, on the basis of the results obtained in the present study:

1. The failure to obtain addition products with two and three chlorine atoms in the allylic position in the reaction with hydrogen chloride could be attributed to the inductive effect, which would lower the electron density to give a double bond with less tendency for an electrophilic addition. The competing reaction of isomerization would also diminish the chance to observe any addition reactions which might otherwise occur to some extent.

2. In the case of allyl chloride with both HCl and HI, the mode of addition appears to be determined by the hyperconjugative effect. With two allylic halogens the hyperconjugative effect still predominates, but with three halogens present in the allylic position, the inductive effect appears to be predominant in controlling the orientation of the addition of hydrogen iodide. In the case of the vinyl halides, the entering halogen goes to the carbon atom to which the vinyl halogen is attached, as is commonly observed; the mode of addition appears to be determined by an electromeric displacement involving available electrons on the vinyl halogen.

EXPERIMENTAL

A. Synthesis of allylic chlorides. 1. Preparation of 3,3-dichloropropene. The method of Stitz[12] was modified by using chloroform as solvent. 3,3-Dichloropropene obtained had the following properties: (b.p. 84–85° (760 mm.), n_D^{20} 1.360) (reported[12,13] 84.4°).

2. *Preparation of 3-bromo-1,1,1-trichloropropane.* An adaptation of the method of Kharasch, Reinmuth, and Urry[14] was used. Bromotrichloromethane (400 g.) and benzoyl peroxide (9.4 g.) were placed in a 400 ml. stainless steel autoclave, equipped with a shaking device. Ethylene was injected into the autoclave up to 100 p.s.i. before heating was started. The rise of temperature was controlled by a regulator with an automatic control device. It usually took an hour to heat the contents up to 75°. The peroxide-catalyzed reaction started around 65 to 70°; the initial reaction was indicated by the fast rise of temperature to 85° and the rapid drop of pressure. Nine to 10 additions of ethylene were required during the remaining 3 hr. of reaction at a tem-

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(12) F. Stitz, *Östern, Chem-Ztg.*, 48, 186–8 (1947).

(13) Beilstein's *Handbuch der Organischem Chemie*, Band I, p. 199 (1918).

(14) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, 69, 1105 (1947).

perature between 75 and 80°. Caution was taken to keep the injection pressure from going over 150 p.s.i., and the temperature from going over 90°. After the autoclave was cooled, the mixture was distilled to separate the unreacted solvent. 3-Bromo-1,1,1-trichloropropane (180 g.) boiled at 113–114° at 103 mm. (Lit.:[14] 113.5–114° at 104 mm.).

3. *Dehydrohalogenation of 3-bromo-1,1,1-trichloropropane to 3,3,3-trichloropropene.* 3-Bromo-1,1,1-trichloropropane (200 g.) was dissolved in ethanol (69 ml.) and cooled to −10°. Ice cold alcoholic potassium hydroxide (52 g. in 600 ml. absolute alcohol) was gradually added to the mixture with vigorous stirring. After an additional hour of stirring following the addition, water was added rapidly to wash off inorganic salts and alcohol, and the organic layer was separated, rewashed, and dried over anhydrous sodium sulfate. 3,3,3-Trichloropropene was distilled out at 45–45.5° (103 mm.), n_D^{20} 1.4673. (Lit.:[10] b.p. 101–102°, n_D^{20} 1.4680).

4. *Preparation of 1,3-dichloropropene and 1,1,3-trichloropropane.* The method used in preparing 3,3-dichloropropene also gave 1,3-dichloropropene (b.p. 104–112° at 760 mm.), and 1,1,3-trichloropropane (b.p. 143° at 760 mm., n_D^{20} 1.4709). 1,3-Dichloropropene was fractionated to give *cis*-1,3-dichloropropene (b.p. 104° at 760 mm., n_D^{20} 1.468). (Lit.:[15] b.p. 103–104°, n_D^{20} 1.4699), and *trans*-1,3-dichloropropene (b.p. 112° at 760 mm., n_D^{20} 1.473). (Lit.:[15] 112.0–112.2°, n_D^{20} 1.4750).

5. *Preparation of 1,1,1,3-tetrachloropropane and 1,1,3-trichloropropene.* The method of Kharasch[16] was used to prepare 1,1,1,3-tetrachloropropane (b.p. 59–60° at 24 mm.). (Lit.:[16] b.p. 155°). Subsequent dehydrohalogenation of tetrachloropropane or isomerization of 3,3,3-trichloropropene in the presence of acid yielded 1,1,3-trichloropropene (b.p. 132° at 760 mm., n_D^{20} 1.497). (Reported: b.p. 132–133°,[15] 131–132°[10]; n_D^{20} 1.4962,[15] 1.4938[10]).

B. *Addition of hydrogen chloride.* Allylic chlorides in the presence of and in the absence of solvent (petroleum ether) were placed in Carius tubes. Anhydrous catalysts, such as $FeCl_3$, $AlCl_3$, and $POCl_3$, were fed into the tube immediately before the tube was connected to the supply line of hydrogen chloride which was dried by passing through a calcium chloride tube. Liquid nitrogen was used to condense the HCl gas. After the required amount of HCl was condensed, the tube was sealed and left standing in the dark at room temperature for about 100 hr. The tube was then opened and the mixture was washed with water and dried over sodium sulfate.

The following table illustrates the quantities of various reagents used in two sets of experiments:

Compounds	Run	Wt. of Compd. (g.)	HCl (g.)	$FeCl_3$ (g.)	Petroleum Ether (ml.)
Allyl chloride	1	3.2	1.6	0.006	—
	2	3.2	1.6	0.400	8
3,3-Dichloropropene	1	4.6	1.6	0.006	—
	2	4.6	1.6	0.400	8
3,3,3-Trichloropropene	1	6.2	1.6	0.006	—
	2	6.2	1.6	0.400	8

C. *Addition of hydrogen iodide.* The appropriate allylic chloride (0.05 mole) was placed in the Carius tube, and the required amount of hydrogen iodide prepared by the method of Ecke, Cook, and Whitmore,[17] was condensed into the tube. After standing for about 100 hr., the tube was opened and the contents washed with water, sodium bisulfite, and potassium carbonate, and dried over sodium sulfate.

1. *3,3-Dichloropropene.* (*a*) Molar ratio (HI:3,3-dichloropropene) = 1:1. Two products were found in the mixture; the major one was 2-iodo-1,1-dichloropropane, $CH_3—CHI—CHCl_2$ (b.p. 43–45° at 30 min., n_D^{20} 1.5621) and the minor one was the substituted product of 1,3-dichloropropene. The iodine atom was probably on carbon 3 giving a structure of $I—CH_2—CH═CHCl$. The identity of the major product was established by infrared and by hydrolysis products.

(*b*) Molar ratio = 3:2. 3-Iodo-1,1-dichloropropane was found in a very small amount in addition to the main product, 2-iodo-1,1-dichloropropane.

(*c*) Molar ratio = 3:1. The products were found to include a very small amount of 1,1-dichloropropane, $CH_3—CH_2—CHCl_2$, in addition to 3-iodo and 2-iodo chlorides.

2. *3,3,3-Trichloropropene.* (*a*) Molar ratio (HI:3,3,3-trichloropropene) = 1:1 and 3:2. The products of the two separate experiments using different molar ratios were identified as the same compound, 3-iodo-1,1-dichloropropene ($CH_2ICH═CCl_2$) (b.p. 45° at 30 mm., n_D^{20} 1.6250).

(*b*) Molar ratio = 3:1. The products were fractionated; the lower fraction contained mainly 1,1,1-trichloropropane (b.p. 40° at 30 mm., $CH_3—CH_2—CCl_3$). The higher fraction (b.p. 56–57° at 18 mm., n_D^{20} 1.5661) contained 3-iodo-1,1,1-trichloropropane and a trace of 1,1,1-trichloropropane. The identity of the major product, $ICH_2—CH_2—CCl_3$, was proved by infrared analysis and hydrolysis.

3. *1,3-Dichloropropene.* (*a*) Molar ratio (HI:1,3-dichloropropene) = 3:2. The products were fractionated; the lower fraction (b.p. 30–40° at 30 mm., n_D^{20} 1.5452) was identified as 1,3-dichloropropane and a very small amount of 1-chloropropane; the higher fraction was shown to be 1-iodo-1,3-dichloropropane ($ClCH_2—CH_2—CHICl$) (b.p. 67° at 3 mm., n_D^{20} 1.5648).

(*b*) Molar ratio = 3:1. The products were mainly 1,3-dichloropropane and 1-iodo-1,3-dichloropropane and a very small amount of 1-chloropropane.

4. *1,1,3-Trichloropropene.* (*a*) Molar ratio (HI:1,1,3-trichloropropene) = 3:2. The products fractionated were: fraction (1) 30–50°, (30 mm.) n_D^{20} 1.489, contained the unreacted chloride; fraction (2) 52–53° (30 mm.) n_D^{20} 1.557 contained 1,1,3-trichloropropane and a very small amount of 1,1-dichloropropane and fraction (3) 46.5–47°, (2 mm.), n_D^{20} 1.5702 was shown to be 1-iodo-1,1,3-trichloropropane, ($ClCH_2—CH_2—CICl_2$). The identity of this compound was proved by infrared analysis and hydrolysis.

(*b*) Molar ratio = 3:1. The products contained mainly 1,1,3-trichloropropane and some 1-iodo-1,1,3-trichloropropane with a very small amount of 1,1-dichloropropane.

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