ORGANIC AND BIOLOGICAL CHEMISTRY

Pyrolysis of Allyl Chloride

BY L. M. PORTER AND F. F. RUST

The pyrolysis of allyl chloride at about 550° yields biallyl, cyclohexadiene and benzene as well as other compounds. The results are interpreted by assuming an initial dissociation of allyl chloride into a chlorine atom and an allyl radical. The products can be shown to arise as a consequence of association reactions of allyl and chloroallyl radicals followed by cyclization. The alteration of reaction paths and products by adding propylene or toluene to the decomposing allyl chloride is described. The reversible character of association reactions involving allyl radicals has been illustrated by brief decomposition studies of biallyl and 4-phenyl-1-butene.

Introduction

The pyrolysis of allyl chloride in the temperature range 370–475° was concluded by Goodall and Howlett[1] to be complex of chain, non-chain and heterogeneous processes which yielded allene and hydrogen chloride. Allene was not identified, however, presumably because of the rapidity of succeeding reactions. Nevertheless, the correlation of properties of their liquid fractions with those obtained by Meinert and Hurd[2] from the pyrolysis of allene is an important reason for their conclusion that dehydrochlorination is a primary reaction step. The activation energy of 46 kcal. found for the homogeneous component of the allyl chloride decomposition, although well below the estimated C–Cl bond dissociation energy, would suggest an important contribution from a radical-forming dissociation process. Macoll[3] found an activation energy of 45.5 kcal. for the pyrolysis of allyl bromide between 320 and 380° which, related to the C–Br bond strength, led him to conclude that the primary step involved homogeneous dissociation into an allyl radical and a bromine atom.

If it is true that decomposition of allyl chloride in the 370–475° interval has a substantial heterogeneous component and that the homogeneous dissociation is characterized by an activation energy somewhat above 45 kcal., one might reasonably expect to increase considerably at still higher temperatures that fraction of the pyrolysis reaction attributable to the homogeneous allyl chloride dissociation. In fact such a change in mechanism was indicated by the work of Hearne and Groll[4] who found benzene to be a significant product of allyl chloride pyrolysis.
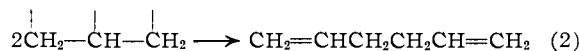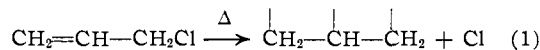
Results and Discussion

In the present investigation reaction products differing substantially from those of Goodall and Howlett were obtained when allyl chloride was pyrolyzed at 540°. Propylene, benzene, 1,3-cyclohexadiene and biallyl are the compounds most suggestive of the reaction processes in the system. However, in all pyrolytic reactions of allyl chloride, tars and carbonaceous deposits on the walls are significant products. The observed products are given in Table I.

(1) A. M. Goodall and K. E. Howlett, *J. Chem. Soc.*, 2596 (1954).

(2) R. N. Meinert and C. D. Hurd. THIS JOURNAL, **52**, 4540 (1930).

(3) A. Macoll, *J. Chem. Phys.*, **17**, 1350 (1949).

(4) G. W. Hearne and H. P. A. Groll, unpublished work.

If, as seems possible, the evolved hydrogen chloride is a fairly good indicator for the degree of allyl chloride decomposition (1), then the input

TABLE I

PYROLYSIS OF ALLYL CHLORIDE—540°

Input allyl chloride: 4.6 moles			10 sec. residence time		
	Moles	G.		Moles	G.
Propylene	0.30	12.6	Biallyl	0.044	3.6
Benzene	.26	20.3	Propane	.010	0.4
1,3-Cyclohexadiene	.085	6.8	C_3H_4	.007	0.3
Hydrogen	.055	0.1	Ethane	.006	0.2
Methane	.048	0.8	Methyl chloride	.003	
Ethylene	.046	1.3	Unidentified (tars, etc.)		26.2
					72.6

Total hydrocarbon as moles $C_3H_4^-$ 1.81
Total hydrogenchloride   1.83

halide was *ca.* 40% reacted. It is proposed that biallyl results from the coupling of allyl radicals formed by the scission of allyl chloride, (2).

$$CH_2\!\!=\!\!CH\!\!-\!\!CH_2Cl \xrightarrow{\Delta} \overset{|}{C}H_2\!\!-\!\!\overset{|}{C}H\!\!-\!\!\overset{|}{C}H_2 + Cl \quad (1)$$

$$2\overset{|}{C}H_2\!\!-\!\!\overset{|}{C}H\!\!-\!\!\overset{|}{C}H_2 \longrightarrow CH_2\!\!=\!\!CHCH_2CH_2CH\!\!=\!\!CH_2 \quad (2)$$

The stoichiometry of allyl chloride conversion to benzene

$$2C_3H_5Cl \longrightarrow C_6H_6 + 2HCl + H_2 \quad (3)$$

requires the formation of a mole of hydrogen for each mole of benzene. The non-appearance of hydrogen in any such quantities, however, indicates that dehydrogenation must be taking place in other ways. The substantial formation of propylene leads to the conclusion that equation 4 illustrates the most important initial step in the mechanism of dehydrogenation wherein cyclohexadiene and probably biallyl must be important hydrogen donors.

$$\overset{|}{C}H_2\!\!-\!\!\overset{|}{C}H\!\!-\!\!\overset{|}{C}H_2 + RH \longrightarrow CH_2\!\!=\!\!CH\!\!-\!\!CH_3 + R \quad (4)$$
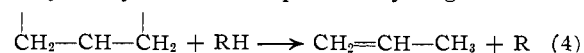
The chlorine atom released from allyl chloride is, of course, a major reactant and in this particular environment will usually remove a hydrogen atom from allyl chloride.

$$Cl + ClCH_2\!\!-\!\!CH\!\!=\!\!CH_2 \longrightarrow HCl + Cl\overset{|}{C}H\!\!-\!\!\overset{|}{C}H\!\!-\!\!\overset{|}{C}H_2 \quad (5)$$
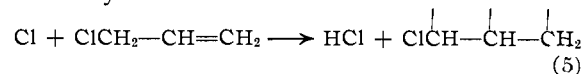
Association of the chloroallyl radical and allyl gives chloro-1,5-hexadienes which should in turn be converted to cyclohexadiene and benzene. This conclusion was checked by passing 1-chloro-1,5-hexadiene through a tube at 450° with a contact time of 11 seconds. Cyclohexadiene was obtained in 57%
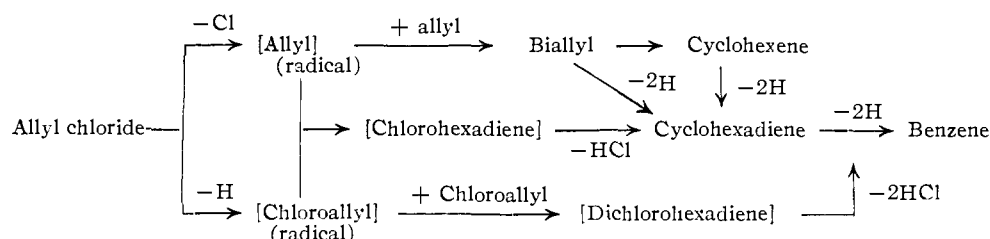
Fig. 1.—Transformation of allyl chloride to benzene.

and benzene in 10% yields. It was further demonstrated that the chlorohexadiene is too unstable to be isolated from the products under these conditions of allyl chloride pyrolysis at 540°.

Besides the associations of two allyl radicals and of an allyl and a chloroallyl, it is probable that the association of two chloroallyls will take place. If this is followed by the loss of two molecules of hydrogen chloride, the stoichiometry indicates that benzene would be the resultant product

$$2ClCH—CH—CH_2 \longrightarrow C_6H_6 + 2HCl \quad (6)$$
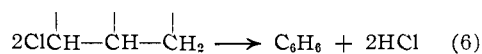
If propylene is included in the allyl chloride stream as an additional object of chlorine atom attack, the number of allyl radicals and, as a consequence, the yield of biallyl should be increased.

$$Cl + CH_3—CH=CH_2 \longrightarrow HCl + CH_2—CH—CH_2 \quad (7)$$
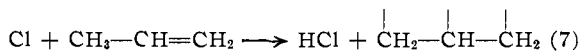
This increase is so great, in fact, that in an experiment with a 12:1 propylene–allyl chloride ratio at 560° in which 30% of the input halide was decomposed, 52.0 moles of biallyl were produced for each 100 moles of allyl chloride pyrolyzed. In the absence of propylene only 2.5 moles of biallyl was produced. As might be expected, either a decrease in the propylene–allyl chloride ratio or an increase in the amount of allyl chloride pyrolyzed brings about a decrease in the yield of biallyl. Thus a drop in the ratio C_3H_6/C_3H_5Cl to 4.2 decreased the biallyl yield to 36% and an increase of the percentage allyl chloride decomposed to 62% (12:1 C_3H_6/C_3H_5Cl) gave a 31% biallyl yield.

These yields would undoubtedly be higher were it not for the fact that the biallyl is itself readily decomposed. The earlier work of Hurd and Bollman,[5] which showed propylene to be the major gaseous decomposition product of this hydrocarbon, has been confirmed. With the aid of infrared spectra and gas–liquid partition chromatography benzene and cyclohexene have been identified as significant liquid products (yields on decomposed bially–benzene 10%; cyclohexene 2%). Cyclohexadiene, although indicated by vapor-phase chromatography, was not positively identified, but, in view of the appearance of both cyclohexene and benzene, cyclohexadiene is certainly the logical precursor of the benzene. This conclusion is somewhat supported, also, by the very small amount of cyclohexadiene appearing in the products of 4-phenyl-1-butene pyrolysis.

The evidence suggests that an unsaturated allylic radical of the type C—C—C—C—C=C can be a forerunner of cyclization. Cyclohexene, for ex-

(5) C. D. Hurd and H. T. Bollman, THIS JOURNAL, 55, 699 (1933).

ample, would be derived from the resulting cyclic isomer

$$\begin{array}{c} C \\ C' \diagup \diagdown C- \\ \| \quad \quad | \\ C \diagdown \diagup C \\ C \end{array}$$
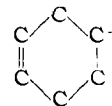
If linear C_6 radicals containing chlorine, such as those derived from allyl chloride, cyclize, further loss of a chlorine atom would lead to cyclohexadiene.

Figure 1 diagrams the routes which appear to be followed when allyl chloride is converted to benzene.

Allyl Chloride–Toluene.—If allyl chloride decomposes into radicals the inclusion of toluene in the reactant stream should provide a source of benzyl radicals. Allyl chloride in toluene (1:4) was 58% decomposed at 560° and gave 4-phenyl-1-butene (0.12 mole), bibenzyl (0.12 mole), stilbene (0.044 mole) and naphthalene (0.055 mole) as products. Only 15% of the potentially available allyl radicals formed coupling products and these were with benzyls to give 4-phenyl-1-butene. The fact that no biallyl was found and that 92% of the remaining allyl fragments were recovered as propylene attests the effectiveness of toluene as a hydrogen donor to allyl.

The reversibility of association of allyl and benzyl is demonstrated by the pyrolysis of 4-phenyl-1-butene at 540° whereby products such as biallyl, cyclohexadiene and benzene suggest allyl radical precursors and bibenzyl suggests a benzyl radical antecedent. The products listed in Table II are, with the exception of the additions of biallyl, bibenzyl, cyclohexene and cyclohexadiene, in essential agreement with those found by Hurd and Bollman for the pyrolysis of this same hydrocarbon.

TABLE II

PYROLYSIS PRODUCTS OF 4-PHENYL-1-BUTENE

10 sec. residence time, 540°

Product	Mole	Gram	Product	Mole	Gram
Toluene	0.18	16.6	Methane	0.013	0.2
Propylene	.16	6.7	Propane	.011	.5
Bibenzyl	.070	12.8	Ethane	.007	.2
Biallyl	.059	4.9	Benzene	.005	.4
Naphthalene	.051	6.5	Butylene	.004	.23
Hydrogen	.029	0.06	Cyclohexene	.002	.15
Ethylene	.027	0.81	Cyclohexadiene	.0015	.12
Styrene	.024	2.5	Bottoms[a]		15.7
			4-Phenyl-1-butene	.51	67.2
			Recovered total		136.5
			Input total		142.0

[a] Contains stilbene and higher molecular weight products.

Experimental

Materials.—Allyl chloride from Shell Chemical Corporation was refractionated prior to use.

Propylene was Phillips pure grade.

1-Chloro-1,5-hexadiene was prepared from allylmagnesium bromide and 1,3-dichloropropane. The distilled product was treated with potassium hydroxide in ethanol for one hour to remove 3% 1,3-dichloropropylene. The redistilled product boiled at 82° at 200 mm. and had a refractive index of n^{20}D 1.4503. Infrared spectra showed all chlorine atoms to be of the type —C=CHCl.

Anal. Calcd. for C_6H_9Cl: Cl, 30.4. Found: Cl, 30.9.

4-Phenylbutene-1 was prepared from benzylmagnesium chloride and allyl bromide; b.p. 107° at 78 mm., n^{20}D 1.5079 (lit.[5] b.p. 175–178°, n^{20}D 1.5090).

Biallyl was purchased from the Farchan Laboratories and had a boiling point of 59.2° and refractive index n^{20}D 1.4034 (lit.[6] b.p. 59.4°, n^{20}D 1.4040).

Procedure and Analyses.—Reactants were passed from calibrated flowmeters through 6 mm. Pyrex preheaters into a 700 ml. Pyrex tube of 40 mm. internal diameter. The temperatures at four evenly spaced thermocouples in a central well were held constant by automatically controlled furnace sections. The effluent was passed through a water-cooled condenser, a water scrubber to remove hydrogen

chloride, and was condensed in a Dry Ice trap. Propylene and other gases were then topped through a short Vigreux column. The residue was washed, dried with calcium chloride and fractionated in a vacuum jacketed column packed with glass helices. Liquid products were usually determined by infrared analyses and gases by mass spectrometry. The identity of significant compounds was confirmed by the following derivatives or constants and in each case was supported by elemental analyses: cyclohexadiene–maleic anhydride adduct, m.p. 147° (lit.[7] 147°); biallyl, b.p. 60°[2]; n^{20}D 1.4041 (lit.[8] 59.6°, 1.4040)[7]; naphthalene, m.p. 79.7 (lit.[9] 80.2°); 4-phenylbutene-1, ultraviolet spectrum, bromine no. calcd. 121, found, 117; bibenzyl, m.p. 53.8° (lit.[10] 52.5°); stilbene, m.p. 123° (lit.[11] 124°).

(7) "Organic Reagents for Organic Analysis," Chemical Publishing Company, New York, N. Y., 1950.

(8) A. Turk and H. Chanan, *Org. Syntheses*, **27**, 7 (1947).

(9) A. Jaquerod and E. Wassmer, *Ber.*, **37**, 2531 (1904).

(10) E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948).

(11) E. Buchta and W. Kallert, *Ann.*, **573**, 220 (1951).

EMERYVILLE, CALIFORNIA

(6) A. L. Henne, H. Chanan and A. Turk, THIS JOURNAL, **63**, 3474 (1941).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF J. T. BAKER CHEMICAL CO.]

Preparation of Esters from the Reaction of Alkyl Orthosilicates with Organic Acids

BY GENE SUMRELL AND GEORGE E. HAM

A convenient new preparative method for aliphatic esters is described, involving the reaction of alkyl orthosilicates with aliphatic acids. Results with certain other acids are also discussed. Improved procedures for preparing methyl and isopropyl orthosilicate are given, and the method extended to the preparation of *t*-butoxytrichlorosilane and di-*t*-butoxydichlorosilane.

It has been noted in the literature[1,2] that ethyl orthosilicate reacts sluggishly with benzoic acid to give ethyl benzoate, and "ethylates" acetic acid, implying the formation of ethyl acetate. However, no data are given and the reaction of alkyl orthosilicates with organic acids as a preparative method for esters does not seem to have been investigated.[3]

During an investigation of the properties of various silicon-containing compounds, it was discovered that methyl orthosilicate reacts readily with several aliphatic acids producing methyl esters in high yield. Since the method seemed to be a convenient means of preparing esters where the desired alkyl orthosilicate is available, the scope of the reaction has been further investigated and the results are reported here.

The reaction seems to be general, and is represented by the equation

$$2RCO_2H + (R'O)_4Si \longrightarrow$$
$$2RCO_2R' + 2R'OH + SiO_2 \quad (1)$$

However, it probably is not as simple as indicated by this equation since distillation of the reaction mixture leaves behind a dry, friable silicious residue which always amounts to more than the theoretical value for silica and evidently still has bound alkoxy groups and probably acyloxy groups (see reference 3). However, in most cases the ester and alcohol are obtained in 85–90% yields as indicated by equation 1 if two moles of acid are used per mole of alkyl orthosilicate. The esters so produced are easily purified by fractional distillation if their boiling points are sufficiently different from that of the alcohol which is formed simultaneously. If the ester is not appreciably soluble in water and the alcohol contains three carbons or less, it is possible to remove the latter by washing with water, as illustrated by the separation of allyl alcohol and allyl acetate in the Experimental Part.

Methyl, ethyl, isopropyl and allyl orthosilicate were allowed to react with various acids. The course of the reaction was easily followed by observing the temperature of the reaction mixture under reflux. As the reaction progressed the temperature of the boiling reaction mixture dropped and finally became constant. The time for complete reaction varied with the alkyl group in the orthosilicate, as well as with the organic acid. For example, methyl orthosilicate (b.p. 121°) and acetic acid (b.p. 118°) react so readily that appreciable reaction evidently occurred during the initial heating period and the mixture initially boiled at about 100°, dropping rapidly to a constant value of about 55° within an

(1) A. W. Dearing and E. E. Reid, THIS JOURNAL, **50**, 3058 (1928).

(2) H. W. Post, "The Chemistry of the Aliphatic Orthoesters," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 120–151.

(3) The authors are indebted to the referee for calling to their attention the disclosure by Langkammer, U. S. Patent 2,490,691 (1949, to du Pont), in which aliphatic acids were heated with various alkyl orthosilicates, yielding a distillate of the appropriate alcohol and ester. The reaction was not taken to completion, however, and the desired product was the residue which is a liquid high molecular weight alkyl polysilicate. The referee also points out that this reaction is used in the formation of silicone-alkyd resins. For a discussion of similar exchange reactions involving alkyl orthosilicates and other alkoxysilanes with carboxylic anhydrides, esters, aldehydes, ketones and alcohols see reference 2 and the references cited therein.