finery of the Standard Oil Co. (N. J.) and separated as crystals of a high degree of purity.

2. The compound is undoubtedly an octane-sultone, since its behavior is strictly analogous to that of sultones in the aromatic and camphene series.

3. On refluxing with alkalies various alkaline salts are obtained whose different chemical properties are explained by a shifting of the double bond generated from the hydroxyl group.

4. Attempts are now being made to synthesize sultones in the aliphatic series.

5. The compound is interesting to the petroleum technologist as it is volatile in steam; hence aliphatic sultones may be partly responsible for the sulfur content of refined gasolines.

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[Contribution from the Department of Chemistry of the University of Pittsburgh]

REACTIONS OF VINYL CHLORIDE AND BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

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The purpose of this investigation has been to study the reactions of vinyl chloride and benzene in the presence of aluminum chloride, under variable conditions, in order to determine the course of the reactions and to study the products formed. These reactions seemed important since vinyl chloride has recently been prepared in large quantities.

Böeseken and Bastet[1] found that vinyl chloride and benzene condensed in the presence of a catalyst made from aluminum and mercuric chloride, and produced chiefly unsymmetrical diphenylethane and a small quantity of 9,10-dimethyldihydro-anthracene. Vinyl bromide and benzene were found to react in the presence of aluminum chloride by Angelbis and Anschütz,[2] and Anschütz,[3] and yielded the identical products described by Böeseken and Bastet. Hanriot and Guilbert[4] obtained products believed to have been β-bromo-ethylbenzene and *p*-di-(β-bromo-ethyl)-benzene in the same reaction.

From the nature of the Friedel–Crafts reaction, styrene would be expected as an intermediate in the reaction under consideration. Schramm[5] obtained unsymmetrical diphenylethane from the reaction between styrene, benzene and aluminum chloride, but Böeseken and

[1] J. Böeseken and M. C. Bastet, *Rec. trav. chim.*, **32**, 184 (1913).

[2] A. Angelbis and R. Anschütz, *Ber.*, **17**, 165, 167 (1884).

[3] R. Anschütz, *Ann.*, **235**, 159, 299 (1886).

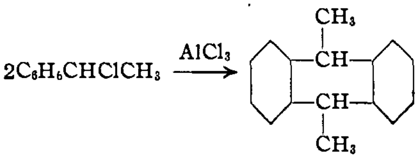
[4] Hanriot and Guilbert, *Compt. rend.*, **98**, 525 (1884).

[5] J. Schramm, *Ber.*, **26**, 1709 (1893).

Bastet described polymerization of styrene under these conditions. The present investigation showed that styrene did polymerize in the presence of benzene and aluminum chloride, and could not have been an intermediate in the reaction between vinyl chloride, benzene and aluminum chloride. Unsymmetrical diphenylethane and an anthracene-type resin were the main products isolated and under special conditions 9,10-dimethyldihydro-anthracene was also obtained. In previous work no mention has been made of this resin.

The following schematic outline substantiated the reactions given by Böeseken and Bastet, in which they used the Al–$HgCl_2$ catalyst

$$C_6H_6 + CH_2 = CHCl \xrightarrow{AlCl_3} C_6H_5CHClCH_3 \xrightarrow[C_6H_6]{AlCl_3} (C_6H_5)_2CHCH_3$$



The reactions, as carried out at 0–5°, tended to produce only traces of 9,10-dimethyldihydro-anthracene and relatively large amounts of unsymmetrical diphenylethane and resinous substances. Both of the latter substances were found to decrease if the temperature was maintained at 60–70°, and appreciable amounts of 9,10-dimethyldihydro-anthracene were formed. Similar results were obtained when 0.1 g. of iodine, originally used to prevent the polymerization of styrene, was present.

Experimental

Considerable preliminary experimental work was done to study the rate of addition of vinyl chloride, the temperature effects, and the variation of addition of components to the reaction mixture.

Description of a Typical Experiment.—Fifty grams of anhydrous aluminum chloride and 300 cc. of benzene (thiophene free, dried over sodium) were agitated in a one-liter three-necked flask, provided with an upright condenser, thermometer, gas inlet tube and a stirrer run at 1000–1400 r.p.m., until the aluminum chloride was in a finely divided state. Vinyl chloride gas, supplied in small cylinders by the Carbide and Carbon Chemicals Corporation, was passed into the flask, kept at 0–5°, at such a rate that only a few bubbles of gas escaped from an alkali trap connected to the condenser. No evolution of hydrogen chloride was observed until after an initial period of fifteen to twenty minutes. After 90 g. of gas had been added, all of the hydrogen chloride apparently had been evolved.

The reaction mixture was poured into ice, acidified with hydrochloric acid and, after the heavy black layer had completely disappeared, the fluorescent brown top layer was separated, washed with water and steam distilled. The distillate, consisting chiefly of unreacted benzene, was dried and fractionated. Besides benzene, some ethylbenzene was obtained in the fraction boiling at 130–135°. In no case was a styrene fraction (140–145°) obtained.

The residue from the steam distillation was a very viscous, fluorescent, greenish oil. This was distilled under reduced pressure in a 500-cc. Claisen flask. Water was removed first at 50-mm. pressure, after which unsymmetrical diphenylethane distilled at 130–140° under 12-mm. pressure. The latter was a nearly colorless oil, but possessed a strong violet fluorescence. On redistillation most of the fraction boiled at 134–136° (12 mm.). Above 140° the pressure was reduced to 0.5 mm., and traces of 9,10-dimethyldihydro-anthracene sublimed from 180–200°. The residue was poured into a beaker and solidified on cooling to a dark green resin having a reddish fluorescence when in solution.

Occasionally the residue from the steam distillation crystallized on standing. In this event the solid was filtered and crystallized from alcohol. It was identified as 9,10-dimethyldihydro-anthracene, and possessed the following characteristics: yellow platelets, melting at 179–181°, purplish fluorescence in solution. The oily filtrate was distilled as described above.

The following table outlines the purpose, details and results obtained in experiments performed under variable conditions.

Table of Results

Purpose of expt.	Reagents		Temp., °C.	Time, hrs.	Products[a]			
	$AlCl_3$, g.	Vinyl chloride, g.			A, g.	B, g.	C, g.	D, cc.
Variation of reagents	2	90	0–5	2	4	10	tr.	50
	50	90	0–5	2	3	46	tr.	40
	133.5 (1 mole)	90	0–5	2	4	35	tr.	60
	267 (2 moles)	90	0–5	2	7	32	tr.	15
	133.5	60	0–5	1.5	6	23	tr.	20
Effect of heat	50	90	0–5	1.5				
			then 60–70	2	4	32	tr.	60
	50	90	60–70	2	4	13	17	33
Addn. of 0.1 g. of iodine	133.5	90	0–5	1.5	4	10	20	25
Addn. of 1 g. of Hg	50	90	0–5	1.5	..	..	..	..
			then 60–70	2	15	17	tr.	20

[a] A, Ethylbenzene; B, unsymmetrical diphenylethane; C, 9,10-dimethyldihydro-anthracene; D, resin. 300 cc. of benzene was used in each of the above experiments.

Discussion of Results

A maximum quantity of unsymmetrical diphenylethane was obtained with 50 g. of aluminum chloride. Very small amounts of aluminum chloride gave smaller yields of all the products, while larger amounts of this reagent tended to diminish the yield of unsymmetrical diphenylethane. Holding the aluminum chloride constant and diminishing the amount of vinyl chloride added reduced the quantities of products formed, as expected. Larger amounts of vinyl chloride could not be absorbed by the reaction mixture.

When the reacting compounds were heated from the start, a relatively large amount of 9,10-dimethyldihydro-anthracene was obtained. This could not have been a product at the lower temperature, since heating of the cold reaction product did not cause the formation of this compound.

The amounts of resin and unsymmetrical diphenylethane were decreased in the first instance, but the amount of resin increased at the expense of the unsymmetrical diphenylethane after the reaction products formed in the cold had been heated. This seemed to indicate that the resin was formed by the action of aluminum chloride upon unsymmetrical diphenylethane.

The presence of a trace of iodine was sufficient to accelerate the reaction, for hydrogen chloride was evolved immediately. At the same time there was a relatively large amount of 9,10-dimethyldihydro-anthracene formed and the amounts of resin and unsymmetrical diphenylethane were reduced.

Mercury caused the reduction of α-phenylchloro-ethane, probably formed as an intermediate, to ethylbenzene. The amounts of resin and unsymmetrical diphenylethane were also reduced. The reducing power of mercury accounted for the formation of large quantities of ethylbenzene and polyethylated benzenes obtained during a preliminary experiment, when a mercury-seal stirrer was used.

Effect of Carbon Disulfide.—Carbon disulfide was used as a solvent or diluent in one experiment. Sulfur-containing oils, formed probably by the condensation of vinyl chloride and carbon disulfide, were obtained, but they were not related to the products of the normal reaction.

Study of the Resin.—The resin, which was a brittle, dark green solid possessing a reddish fluorescence in solution, melted at 50–65°. It was soluble in benzene, acetone and glacial acetic acid, slightly soluble in alcohol, but insoluble in water, acids or alkalies. It contained no halogen and therefore was not a vinyl chloride-type resin.

On heating the resin formed a dark green, fluorescent liquid which was very viscous. Although heated to 300°, no traces of 9,10-dimethyldihydro-anthracene were observed. Instead of sublimation, there was a noticeable decomposition. When heated to 220° under 0.5-mm. pressure, small amounts of 9,10-dimethyldihydro-anthracene were obtained. Continued heating caused decomposition.

A benzene solution of styrene, when treated with aluminum chloride under the normal experimental conditions, yielded a resin different from those obtained with vinyl chloride, since styrene was obtained by heating it.

Oxidation of a solution of the resin in glacial acetic acid and benzene with chromium trioxide produced anthraquinone, indicating an anthracene-type resin. No crystalline picrate could be obtained from the resin and the exact identity of the hydrocarbon constituent of the resin could not be learned.

Summary

1. The reaction of vinyl chloride and benzene in the presence of aluminum chloride took place with the formation of unsymmetrical diphenylethane, 9,10-dimethyldihydro-anthracene and an anthracene-type resin. No styrene or metastyrene was formed. α-Phenylchloro-ethane has been considered as the most probable intermediate.

2. Increased amounts of aluminum chloride at low temperatures decreased the amounts of unsymmetrical diphenylethane.

3. The amounts of 9,10-dimethyldihydro-anthracene were increased by using a higher temperature, or by the presence of iodine.

4. Mercury caused the formation of ethylbenzene and considerably reduced the amount of resin formed.
5. Certain physical and chemical properties of the resin have been studied.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S COLLEGE]

THE BECKMANN REARRANGEMENT IN THE PRESENCE OF FREE RADICALS

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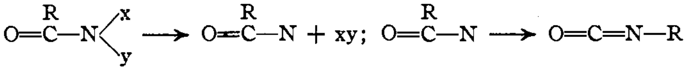
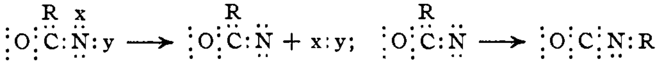
Of the several theories that have been advanced to explain the rearrangement of hydroxamic acids, halogen amides, acyl azides and other similar classes of compounds, the most successful has been the interpretation by Stieglitz.[2] Assuming the intermediate formation of a univalent nitrogen derivative, he proposed that all rearrangements of this character take place as follows



$$\mathrm{O{=}\overset{R}{C}{-}N}\Big\langle\begin{matrix}\mathrm{x}\\ \mathrm{y}\end{matrix} \longrightarrow \mathrm{O{=}\overset{R}{C}{-}N + xy};\ \mathrm{O{=}\overset{R}{C}{-}N} \longrightarrow \mathrm{O{=}C{=}N{-}R}$$

Jones and Hurd,[3] suggesting an interpretation of the mechanism of these rearrangements based upon the modern conception of chemical bonds and electrons, formulated the rearrangement thus



$$\vdots\mathrm{O}\vdots\overset{\mathrm{R}}{\ddot{\mathrm{C}}}:\overset{\mathrm{x}}{\underset{..}{\ddot{\mathrm{N}}}}:\mathrm{y} \longrightarrow \vdots\mathrm{O}\vdots\overset{\mathrm{R}}{\ddot{\mathrm{C}}}:\underset{..}{\ddot{\mathrm{N}}} + \mathrm{x}:\mathrm{y};\ \vdots\mathrm{O}\vdots\overset{\mathrm{R}}{\ddot{\mathrm{C}}}:\underset{..}{\ddot{\mathrm{N}}} \longrightarrow \vdots\mathrm{O}\vdots\mathrm{C}\vdots\underset{..}{\mathrm{N}}:\mathrm{R}$$

Their interpretation, which excluded the oximes, assumed that the radical, R, in its wandering from the carbon atom to the nitrogen atom existed momentarily as a free radical, and that the relative ease of rearrangement of such types of compounds depended upon the tendency of the radical, R, in the univalent nitrogen derivative to exist as a free radical. This hypothesis was tested by studying the rearrangement of monophenyl-, diphenyl- and triphenylacethydroxamic acids and their derivatives.

Hurd[4] also found further evidence in support of this hypothesis in his study of certain derivatives of N-diphenylhydroxyurea, $(C_6H_5)_2N\text{-}CO\text{-}NHOH$.

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[1] Some of the preliminary experiments in this investigation, including the preparation of materials, etc., were carried out with the help of Mr. Howard W. Gilbert, a graduate assistant in the department.

[2] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); *ibid.*, **29**, 49 (1903); Stieglitz and Earle, *ibid.*, **30**, 349, 412 (1903); Stieglitz and Slossen, *Ber.*, **28**, 3265 (1895); **34**, 1613 (1901); Stieglitz and Leech, THIS JOURNAL, **36**, 272 (1914).

[3] Jones and Hurd, *ibid.*, **43**, 2422 (1921).

[4] Hurd, *ibid.*, **45**, 1472 (1923).