[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, FACULTY OF ENGINEERING, KYÔTO UNIVERSITY]

The Organic Reactions with Aluminum Chloride. XX. The Action of Aluminum Chloride upon Ethylene Chloride

BY KEIITI SISIDO AND YOSIO YOSIKAWA

In our previous communications[1] in which the Friedel–Crafts reaction of dihalogenoalkanes with benzene were investigated, many anomalies, particularly shifts and splitting off of halogen atoms, were observed. During these researches we were impressed with the need for the fundamental studies of the behavior of these alkylene dichlorides alone in the presence of aluminum chloride, in order to clarify our understanding of the complicated reaction of condensation. The present paper deals with the change of ethylene chloride, one of the simplest homologs of the series, in the absence of an aromatic hydrocarbon, under the ordinary conditions of the Friedel–Crafts reaction.

It was astonishing that, when we treated ethylene chloride with 15% of its weight of aluminum chloride at 80°, a violent reaction ensued and the whole reactant, after only four hours of heating, solidified. In order to study the mechanism of the formation of solid material, it was decided to carry out the experiments under milder conditions. The reaction was now carried out with ethylene chloride and 10% of aluminum chloride at 26 ± 1°, and it was interrupted when the greater part of the dichloride still remained unreacted, so that the distillable intermediate products could be obtained. The reaction was continued for seventy-five minutes and the mass was poured into iced water to decompose aluminum chloride; after recovering the unchanged material, the products were fractionated in the usual way. By this procedure we have isolated the same compounds as the intermediates of a polycondensation product of benzene and ethylene chloride,[2] which we have described in a previous paper,[3] namely, bibenzyl and *m*-bis-(β-phenylethyl)-benzene were identified by analyses and by mixed melting points with authentic specimens. It should be noted that the latter substance was a new compound which we had found just before the War among the intermediates of the above mentioned high molecular material; the constitution was ascertained by the decomposition[3] as well as by the synthesis.[4] The mechanism of the formation of these substances from benzene and ethylene chloride as well as the *meta*-orientation of the reaction were discussed in the previous papers.

The present facts are explained only by the assumption that benzene was formed from ethylene chloride by the action of aluminum chloride; this benzene condenses with the excess of ethylene chloride in the presence of aluminum chloride in the same way as the synthesis of the elastomer by the Friedel–Crafts reaction. During the reaction a considerable amount of hydrogen chloride was liberated, but it was not accompanied by acetylene, ethylene, vinyl chloride or any other unsaturated compound according to qualitative analyses. As these compounds are therefore not regarded as stable intermediates, the route from ethylene chloride to benzene is not certain. It is easy to surmise that an elimination of two moles of hydrogen chloride from ethylene chloride produces a free radical —CH=CH—, three moles of which form a benzene molecule by cyclization. But rigorous proof is lacking.

The formation of benzene from ethylene chloride during the Friedel–Crafts reaction was not observed previously by us, although many investigations were carried out on the condensations of ethylene chloride and aromatic hydrocarbons other than benzene by the action of aluminum chloride. Particularly, we could not find benzene derivatives among the reaction products of ethylene chloride and toluene,[5] ethylbenzene,[6] chlorobenzene,[7] bromobenzene,[8] cymene,[8] biphenyl,[8] naphthalene,[8] phenol,[9] anisole,[9] diphenyl ether,[9] etc., respectively.

Experimental[10]

Ethylene chloride used in this investigation was carefully redistilled and the fraction boiling at 82–83° was submitted to the reaction.

In an ordinary three-necked flask 1190 g. of ethylene chloride was maintained at 25° and 119 g. of newly pulverized anhydrous aluminum chloride was thrown in at once. During the addition, which required one minute, scarcely any elevation of the temperature was remarked. The mixture was stirred for seventy-five minutes at 26 ±

Fraction	Boiling range, °C.	Yield, g.
I	80–140	4.0
II	140–180	3.2
III	180–230	6.7
IV	230–270	3.4
V	270–295	3.0
VI	295–320	4.0
Residue	.....	13.0

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[1] Sisido and Nozaki, THIS JOURNAL, **69**, 961 (1947), etc.

[2] Shinkle, U. S. Patent 2,016,026; *C. A.*, **29**, 8175 (1935); etc.; Shinkle, Brooks and Cady, *Ind. Eng. Chem.*, **28**, 275 (1936); Sisido and Katô, *J. Soc. Chem. Ind., Japan*, **43**, 232B (1940); *C. A.*, **35**, 1026 (1941); Klebanskii and Mironenko, *J. Applied Chem., U. S. S. R.*, **14**, 618 (1941).

[3] Sisido and Katô, *J. Soc. Chem. Ind., Japan*, **44**, 25B (1941); *C. A.*, **35**, 4369 (1941).

[4] Sisido, *J. Soc. Chem. Ind., Japan*, **44**, 55B (1941); *C. A.*, **35**, 4370 (1941).

[5] Sisido and Kanari, *J. Soc. Chem. Ind., Japan*, **44**, 170B (1941); Sisido and Siihara, *ibid.*, **45**, 62B (1942).

[6] Sisido and Katô, *ibid.*, **44**, 148B (1941).

[7] Sisido, *ibid.*, **44**, 463B (1941).

[8] Not yet published.

[9] Sisido and Huruya, *J. Soc. Chem. Ind., Japan*, **46**, 674 (1943), (in Japanese).

[10] Microanalyses by Miss Yasuko Meizyô of our Laboratory.

1°, and then was poured into iced water acidified with hydrochloric acid. The organic layer was separated and after drying over calcium chloride the unchanged ethylene chloride, which weighed 755 g., was removed by distillation. The residue was now fractionally distilled under vacuum of 10 mm. and several fractions were obtained.

The fractions I and III crystallized after a day.

The crystals obtained from fraction I were recrystallized three times from alcohol until the melting point was fixed at 51.7–52.0°. This compound was proved to be identical with bibenzyl by a mixed melting point with a known sample.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.87.

The repeated recrystallizations of the crystals from the fraction III afforded a sample of a melting point of 56.7–57.4°. This agrees in properties with *m*-bis-(β-phenylethyl)-benzene and, when admixed with an authentic specimen, did not depress the melting point, thus proving the identity.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.49.

Summary

By the action of anhydrous aluminum chloride ethylene chloride yields bibenzyl, *m*-bis-(β-phenylethyl)-benzene and finally a polycondensation product.

This phenomenon is explained that at first benzene is formed from ethylene chloride. The resultant benzene then condenses with the excess of ethylene chloride in the sense of the Friedel–Crafts reaction.

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The Organic Reactions with Aluminum Chloride. XXI. The Cycli-alkylation of Benzene with 1,4-Dibromo-2-butene and the Disproportionation of Hydrogen Atoms

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The Friedel–Crafts reactions of poly-functional alkylating agents with benzene are often associated with various anomalies, for example, the "cycli-alkylation"[1] and the shift or reduction of halogen atoms.[2] The former reaction may be of unusual interest as a simple method of synthesizing the compounds of polynuclear structures. In continuation of the studies in this field, we have investigated the condensation of 1,4-dibromo-2-butene with benzene.

The dibromobutene dissolved in a large excess of benzene was treated with aluminum chloride at ordinary temperature. Upon fractional distillation of the reaction products, tetralin and 2-phenyl-1,2,3,4-tetrahydronaphthalene were found to have been formed along with a considerable amount of tarry matter. Neither naphthalene nor dihydronaphthalene was produced. Phenyl-substituted butanes which might be expected as a result of the ordinary Friedel–Crafts reaction also failed to be detected.

These observations may indicate that the first stage of the reaction consists in the condensation of one mole of benzene with one mole of the dibromobutene forming 1,4-dihydronaphthalene under the cyclization by the 2-butene residue. As 1,4-dihydronaphthalene rearranges, however, easily into 1,2-dihydro-compound, for example, by the action of sodium ethylate,[3] the hydrogen atoms at the 1,4-position are supposed to be labile. It seemed to us, therefore, necessary to examine the action of aluminum chloride upon 1,4-dihydronaphthalene in order to clarify the mechanism of this condensation.

To a solution of the dihydronaphthalene in benzene was added aluminum chloride and the mixture was allowed to react at ordinary temperature. It was noted that only small quantities of 2-phenyl-1,2,3,4-tetrahydronaphthalene were produced. The main product was found to be a mixture of about equal amounts of naphthalene and tetralin. We have repeated the same experiment introducing hydrogen chloride gas into the reaction mixture and achieved the same result. Treating 1,4-dihydronaphthalene alone with aluminum chloride we obtained also naphthalene and its tetrahydride.

We have also investigated the reaction of aluminum chloride with 1,2-dihydronaphthalene. In addition to considerable amounts of higher-boiling substances there resulted also in this case naphthalene and tetralin in almost equal quantities. Scott and Walker,[4] who studied the nature of the polymerized dihydronaphthalene as a synthetic resin, stated that 1,2-dihydronaphthalene gave, upon treatment with aluminum chloride, a red brittle resin having a molecular weight of 388 as well as a viscous oil, apparently a dihydronaphthalene dimer. We have found that the 1,2-isomer gives more resinous matter than the 1,4-compound.

Among the reaction products of the 1,4-dihydronaphthalene was a higher-boiling fraction, whose elementary analysis indicated the formula $C_{20}H_{20}$, from which, after a week, crystals of composition $C_{20}H_{18}$ separated. As the original fraction upon sulfur-dehydrogenation, gave 2,2′-binaphthyl in a good yield, it is supposed that the fraction consists of a mixture of 1,2,3,4-tetrahydro-2,2′-binaphthyl, $C_{20}H_{18}$, and 1,2,3,4,1′,2′,3′,4′ - (or 1,2,3,4,5′,6′,7′,8′) - octahydro - 2,2′ - bi-

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(1) Bruson and Kroeger, THIS JOURNAL, **62**, 36 (1940); see also Price, Chapin, Goldman, Krebs and Shafer, *ibid.*, **63**, 1857 (1941).

(2) Sisido and Nozaki, *ibid.*, **69**, 961 (1947).

(3) Straus and Lemmel, *Ber.*, **54**, 25 (1921).

(4) Scott and Walker, *Ind. Eng. Chem.*, **32**, 312 (1940).