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NITROGEN TRICHLORIDE AND UNSATURATED HYDROCARBONS. III. NITROGEN TRICHLORIDE AND DIPHENYLKETENE

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Many aliphatic unsaturated hydrocarbons[2] of the olefin series react with nitrogen trichloride to form, among other products, C-chloro-N-dichloro-amines. This is also true for some of the unsaturated ketones.[3] In the present work this reaction was studied with derivatives of ethene in which one or more of the hydrogen atoms of this compound had been replaced by phenyl groups. Diphenylketene was also used since the ketenes undergo addition reactions very readily with ammonia and the amines. It was also thought that the evolution of a large amount of nitrogen which characterizes most addition reactions of nitrogen trichloride might not occur with a highly reactive compound like diphenylketene.

Phenylethene and 1,2-diphenylethene react fairly rapidly with nitrogen trichloride in carbon tetrachloride solution to form nitrogen, the dichloride of the hydrocarbon, a small amount of ammonium chloride and a C-chloro-N-dichloro-amine. These compounds are easily reduced with hydrochloric acid to the corresponding C-chloro-amines, both of which have been previously prepared by other methods.[4] With phenylethene two products are possible. Only one, however, 1-amino-2-chloro-1-phenylethene, was isolated. The reaction rates as well as the products do not differ very greatly from those of the corresponding methyl derivatives, propene and 2-butene.

1,1-Diphenylethene and 1,1-diphenyl-1-propene have reaction rates which are of the same general order as the first two hydrocarbons of this series. Neither of them, however, forms a stable addition product with nitrogen trichloride under the experimental conditions used. Triphenylethene reacts quite slowly, and in this respect differs very decidedly from the corresponding trimethyl derivative, the reaction rate of which is perhaps as rapid as any which has thus far been studied. No amine was isolated. Apparently tetraphenylethene does not react until the mixture is warmed slightly. The slow evolution of nitrogen which then occurs

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[1] This paper is an abstract of the thesis submitted by Arthur W. Campbell in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa.

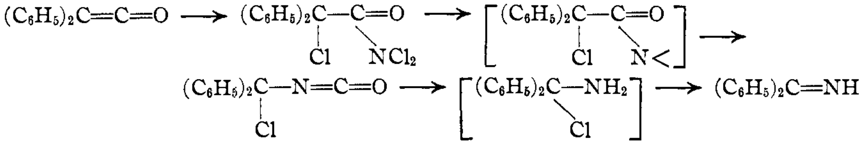
[2] Coleman and Howells, THIS JOURNAL, **45**, 3084 (1923); Coleman, Mullins and Pickering, **50**, 2739 (1928).

[3] (a) Coleman and Craig, *ibid.*, **49**, 2593 (1927); (b) **50**, 1816 (1928).

[4] (a) Gabriel and Colman, *Ber.*, **47**, 1866 (1914); (b) Darapsky and Spannagel, *J. prakt. Chem.*, **92**, 279 (1915).

may be due to reaction with the phenyl groups. Nitrogen trichloride is known to react with benzene and its derivatives.[5] No amine was obtained.

Diphenylketene reacts rapidly with nitrogen trichloride. Practically no nitrogen is evolved and the characteristic odor of nitrogen trichloride disappears if an excess of the ketene is used. On the basis of the addition reactions of nitrogen trichloride with the unsaturated hydrocarbons and the unsaturated ketones, and the well-known reactions of the ketenes, it seems probable that the addition product formed is diphenylchloroaceto-*N*-dichloro-amide. When the reaction mixture is warmed for a short time with a solution of sodium hydroxide and the non-aqueous layer separated, dried and hydrogen chloride passed into it, benzophenone-imide hydrochloride is precipitated. The reaction possibly involves the following steps



$$(C_6H_5)_2C{=}C{=}O \longrightarrow (C_6H_5)_2\underset{Cl}{C}-\underset{NCl_2}{C}{=}O \longrightarrow \left[(C_6H_5)_2\underset{Cl}{C}-\underset{N<}{C}{=}O\right] \longrightarrow$$

$$(C_6H_5)_2\underset{Cl}{C}-N{=}C{=}O \longrightarrow \left[(C_6H_5)_2\underset{Cl}{C}-NH_2\right] \longrightarrow (C_6H_5)_2C{=}NH$$

Experimental Part

The Reaction with Phenylethene (Styrene)

1-Amino-2-chloro-1-phenylethane.—The nitrogen trichloride was prepared and analyzed as described in earlier papers.[3b] The phenylethene was dissolved in carbon tetrachloride. The apparatus was protected from the light and arranged for collecting and measuring the nitrogen evolved. The nitrogen trichloride solution was added slowly through a separatory funnel in the course of one to two hours. During the addition the reaction flask was cooled to $-10°$ or lower and gently shaken. The reaction was fairly rapid and was complete soon after the last of the trichloride had been added. The precipitate of ammonium chloride formed during the reaction was filtered off and dry hydrogen chloride passed into the carbon tetrachloride solution. The amine hydrochloride which precipitated was filtered, dried and weighed.

The amounts used in a typical run were as follows: 71 mg. moles of nitrogen trichloride in 250 g. of carbon tetrachloride, 200 mg. moles of phenylethene in 400 g. of carbon tetrachloride. In this run there were formed 46.4 mg. atm. of nitrogen, 3.2 mg. moles of ammonium chloride and 19.6 mg. moles of the amine, which is 27.6% of the theoretical yield calculated from the nitrogen trichloride.

Benzoyl-1-amino-2-chloro-1-phenylethane.—The benzoyl derivative was prepared from the amine hydrochloride by the Schotten-Baumann method. The product after recrystallization from petroleum ether melted at 133–134° (uncorr.).

Anal. Subs., 0.1553: 5.53 cc. of 0.1076 *N* HCl. Calcd. for $C_{15}H_{14}ONCl$: N, 5.59. Found: 5.36. Subs. 0.1980: 7.70 cc. of 0.0996 *N* $AgNO_3$. Calcd. for $C_{15}H_{14}ONCl$: Cl, 13.66. Found: 13.72.

This compound has been prepared by Gabriel and Colman,[4a] who record a melting point of 137°. The isomeric compound, benzoyl-2-amino-

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[5] Coleman and Noyes, THIS JOURNAL, **43**, 2211 (1921).

1-chloro-1-phenylethane, prepared by Wolfheim[6] has a melting point of 124°.

The Reaction with 1,2-Diphenylethene (Stilbene)

1-Amino-2-chloro-1,2-diphenylethane.—The 1,2-diphenylethene was prepared from benzylmagnesium chloride and benzaldehyde by the method described by Hell.[7] The reaction with nitrogen trichloride was carried out at −14°. The procedure was similar to that with phenylethene. The time of addition was one hour. Nitrogen was evolved for a short time after all of the trichloride had been added. A heavy precipitate of the dichloride of the hydrocarbon and a little ammonium chloride formed during the reaction. This was filtered off and the ammonium chloride separated by solution in water in which the dichloride is insoluble. The amine hydrochloride was obtained as before by treatment with hydrogen chloride. In one run there were obtained from 91.8 mg. moles of nitrogen trichloride, 16.8 mg. moles of the amine, 70.5 mg. atm. of nitrogen and 2.8 mg. moles of ammonium chloride.

Benzoyl-1-amino-2-chloro-1,2-diphenylethane.—The benzoyl derivative was prepared from the hydrochloride of the amine by the Schotten-Baumann method. After recrystallization from alcohol it melted at 192–193° (uncorr.). The compound has been prepared by Darapsky and Spannagel,[4b] who report a melting point of 195°.

The Reaction with 1,1-Diphenylethene

1,1-Diphenylethene was prepared by the method of Allen and Converse.[8] The reaction with nitrogen trichloride was carried out as described for phenylethene. No amine hydrochloride was obtained. In one run there was obtained from 90 mg. moles of nitrogen trichloride, 85 mg. moles of nitrogen and 4.6 mg. moles of ammonium chloride. The reaction rate was much the same as that of 1,2-diphenylethene.

The Reaction with 1,1-Diphenyl-1-propene

The hydrocarbon was prepared from benzophenone and ethylmagnesium iodide by the method of Klages.[9] The reaction was carried out as described for phenylethene. The reaction rate did not differ noticeably from that of the two hydrocarbons just described. Practically all of the nitrogen of the nitrogen trichloride was given off as a gas. No amine was formed.

The Reaction with Triphenylethene

The hydrocarbon was prepared from benzophenone and benzylmagnesium chloride by the method of Hell and Wiegandt.[10] The reaction rate of this compound was much slower than the others thus far described. Ten hours or longer were required for the completion of the reaction. Again practically all of the nitrogen appeared as gas. No amine was formed.

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[6] Wolfheim, *Ber.*, **47**, 1440 (1914).

[7] Hell, *Ber.*, **37**, 453 (1904).

[8] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1926**, Vol. VI, p. 32.

[9] Klages, *Ber.*, **35**, 2646 (1902).

[10] Hell and Wiegandt, *Ber.*, **37**, 1431 (1904).

The Reaction with Tetraphenylethene

The hydrocarbon was prepared from diphenylmethane and dichlorodiphenylmethane by the method of Norris, Thomas and Brown.[11]

At −10° there was apparently no reaction with nitrogen trichloride. When the mixture was warmed to 30°, a slow evolution of nitrogen began and continued for thirty-five to forty hours. A little ammonium chloride formed during the reaction but no amine was obtained.

Diphenylketene and Nitrogen Trichloride.—A solution of diphenylketene was prepared from diphenylchloro-acetyl chloride and zinc by the method described by Staudinger.[12]

In carrying out the reaction with nitrogen trichloride, the apparatus was arranged for collecting any gas which might be liberated. The nitrogen trichloride solution was added to the ketene solution through a separatory funnel in the course of an hour. A slight excess of the ketene was always used. During the addition the ketene solution was kept at −10° and gently shaken. Little or no gas was evolved. The solution was allowed to remain at this temperature for some time after the trichloride had been added. A residue which proved to be largely zinc chloride formed at the bottom of the flask. The solution was poured off and warmed for thirty to forty minutes at about 40° with 6 *N* sodium hydroxide solution. The non-aqueous layer was separated, dried and hydrogen chloride passed into it. A heavy precipitate of benzophenone-imide hydrochloride was formed. This was filtered off. About an equal quantity of benzophenone was obtained from the filtrate by evaporation.

The best yield of benzophenone-imide hydrochloride obtained was 35% calculated from the nitrogen trichloride. A part of this was purified by dissolving in water, adding a slight excess of cold sodium hydroxide solution and extracting with carbon tetrachloride, drying and reprecipitating with hydrogen chloride. This was analyzed for nitrogen by the Kjeldahl method.

Anal. Subs. 0.2037, 0.2006: 7.88, 7.78 cc. of 0.1205 *N* HCl. Calcd. for $C_{13}H_{12}NCl$: N, 6.44. Found: 6.55, 6.56.

A portion of the hydrochloride was heated for a short time with water. The oily product was extracted with ether and the ether evaporated. Benzophenone crystallized on cooling. It was identified by the preparation of the phenylhydrazone.

Summary

1. Nitrogen trichloride reacts with phenylethene and 1,2-diphenylethene to form among other products, C-chloro-N-dichloro-amines. With 1,1-diphenylethene, 1,1-diphenyl-1-propene, triphenylethene and tetraphenylethene no amines are formed under the experimental conditions used.

2. Nitrogen trichloride reacts with diphenylketene. The addition product when warmed with sodium hydroxide solution forms benzophenone imide.

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[11] Norris, Thomas and Brown, *Ber.*, **43**, 2958 (1910).

[12] Staudinger, *Ann.*, **356**, 73 (1907).