[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE ADDITION OF NITROGEN TRICHLORIDE TO UNSATURATED HYDROCARBONS. I

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In a recent study[1] of the chlorinating action of nitrogen trichloride on benzene and toluene, it was found that small amounts of chloro-amines were formed, presumably by the addition of nitrogen trichloride to the aromatic nucleus. The products obtained in each case proved to be mixtures of chlorinated amines which could not easily be separated.

The present investigation was undertaken to determine whether such an addition might not occur with hydrocarbons of the ethylene series with the formation of a single product. The hydrocarbons used were 2-butene, 1-butene, and trimethylethylene. The reactions were carried out in carbon tetrachloride solution, well cooled with a freezing mixture.

With 2-butene the reaction takes place fairly rapidly with the formation of a moderate yield of 2-chloro-3-dichloro-amino-butane, $CH_3CHNCl_2CHClCH_3$, considerable free nitrogen, and a small amount of ammonium chloride. The above chloro-amine was not isolated as such, but by treatment with concd. hydrochloric acid was reduced to the corresponding 2-chloro-3-amino-butane, $CH_3CHNH_2CHClCH_3$. A possible explanation of this action of hydrochloric acid has been given by Coleman and Noyes.[1] A similar action of hydrogen chloride on a chloro-amine in ether solution is mentioned by Berg.[2]

With 1-butene the reaction occurs more slowly and a larger excess of the unsaturated hydrocarbon is required. The yield of amine is slightly less than with 2-butene. The amounts of free nitrogen and ammonium chloride are about the same. In this reaction there are, of course, two possible structures for the addition product, $CH_3CH_2CHNCl_2CH_2Cl$ and $CH_3CH_2CHClCH_2NCl_2$. On the basis of Markownikoff's rule[3] for such addition reactions the position taken by the dichloro-amino group might have a bearing on the polarity of the chlorine in nitrogen trichloride. If it is assumed that the chlorine is positive, then according to this rule the dichloro-amino group should be attached to the second carbon atom from the end. This was shown to be the case by reduction of the product to 2-amino-butane. No evidence of the formation of the other possible isomer was obtained.

Racemic *sec*-butyl amine (2-amino-butane) has been prepared by

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[1] Coleman and Noyes, THIS JOURNAL, **43**, 2213 (1921).

[2] Berg, *Chem. Zentr.*, [3] **7**, 542 (1892).

[3] Markownikoff, *Ann.*, **153**, 256 (1870).

Pope and Gibson[4] by the reduction of methylethyl ketoxime. In order to compare this compound with our product the work of these authors was repeated. The melting point of the benzoyl derivative was found to be several degrees higher than that recorded (see Experimental Part), but it agreed exactly with that of our product obtained through the reduction of the chloro-amine. A mixture of these substances melted at the same temperature. The *p*-nitrobenzoyl derivatives prepared by the two series of reactions were also found to be identical.

If in the addition of nitrogen trichloride to 1-butene the dichloro-amino group had added to the end carbon atom, then by reduction *n*-butylamine would be formed. The derivatives of *n*-butylamine do not correspond in physical properties to the same derivatives of the amine obtained in this investigation.

The reaction with trimethylethylene differs from those described above in that it is more rapid, a greater proportion of ammonium chloride is formed, and no amine is obtained from the reaction mixture. In fact, all but a trace of the nitrogen used can be accounted for as ammonium chloride and free nitrogen.

The formation of ammonium chloride in these reactions, and particularly in the last one where the proportion of this compound is considerably greater, is no doubt due to the reaction of nitrogen trichloride with hydrochloric acid, which may split out from the addition product first formed with the unsaturated hydrocarbon. Noyes[5] has shown that nitrogen trichloride and hydrochloric acid yield ammonium chloride and chlorine quantitatively even in the absence of water.

The complete decomposition of the addition product which is probably first formed with trimethylethylene may be connected with the presence of a tertiary carbon atom in this compound and the fact that the nitrogen is very likely attached to this atom. Marvel[6] has recently shown that in dialkyl mercury compounds the carbon-mercury linkage is much more easily broken when mercury is attached to a tertiary alkyl group than when it is attached to a secondary or a primary alkyl group. These facts are in agreement with what is already known concerning alcohols, halides and other compounds. By the action of chlorine on trimethylethylene Hell[7] obtained monochloro-amylene, C_5H_9Cl; amylene dichloride, $C_5H_{10}Cl_2$; and chloro-amylene chloride, $C_5H_9Cl_3$. He concludes that a part of the amylene dichloride first formed must split out hydrochloric acid. The resulting unsaturated monochloro-amylene would then in part react with more chlorine. In the present work both the dichloro and the trichloro com-

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[4] Pope and Gibson, *J. Chem. Soc.*, **101**, 1702 (1912).

[5] Noyes, THIS JOURNAL, **42**, 2173 (1920).

[6] Marvel, *ibid.*, **45**, 820 (1923).

[7] Hell, *Ber.*, **24**, 217 (1891).

pounds were found, but the presence of monochloro-amylene was not definitely proved.

The investigation is being continued in this Laboratory with other unsaturated compounds and also with reference to a possible increase in the yields obtained.

Experimental Part

The Reaction with 2-Butene

The preparation and analysis of nitrogen trichloride was carried out as described by Coleman and Noyes,[1] with some slight modifications. Carbon tetrachloride was used as the solvent for the trichloride. The temperature of the cooling bath was maintained at 0–10°; *N* ammonium nitrate solution was used as the source of the ammonia. After the addition of the chlorine the aqueous solution was removed and the carbon tetrachloride stirred for a short time with a little fresh ammonium nitrate solution. This was repeated a second time to insure the removal of any excess chlorine. Solutions containing as much as 20% of nitrogen trichloride were prepared but, in general, it was found best to use more dilute solutions.

The 2-butene was prepared from *sec*-butyl iodide and alcoholic potassium hydroxide, according to the method described by de Luynes.[8] After it was washed and dried, the gas was passed into dry carbon tetrachloride, surrounded by a cooling bath. The reaction was carried out by adding the nitrogen trichloride solution through a dropping funnel, slowly, to the solution of the unsaturated compound contained in a flask surrounded by a freezing mixture of ice and salt (–10°). The apparatus was so arranged that the solution could be agitated during the addition, and any gas evolved could be collected and measured. When the yellow color of the nitrogen trichloride had completely disappeared, the solution was washed several times with water to remove any ammonium chloride. After it had been carefully separated from the water it was thoroughly shaken with 30–40 cc. of concd. hydrochloric acid. It was found desirable to have enough excess butene present to unite with the chlorine liberated at this point, in the reaction between the acid and the chloro-amine. If necessary, more of the butene solution was added. The hydrochloric acid was diluted with water and separated from the carbon tetrachloride. This acid solution now contained the hydrochloride of 2-chloro-3-amino-butane.

The reduction of the chloro-amine can also be effected by shaking it with an acid sulfite solution, but the reaction is not as complete as with concd. hydrochloric acid. It is interesting to note here that while these aliphatic chloro-amines can be quite easily reduced with an acid sulfite, the chloro-amines obtained by Coleman and Noyes[1] from benzene and toluene were reduced with difficulty, or not at all, by this reagent.

[8] De Luynes, *Ann.*, **132**, 275 (1864).

The amounts used in a typical run were as follows.

One hundred and fifty-six mg. mols. of nitrogen trichloride in 400 g. of carbon tetrachloride; 220 mg. mols of 2-butene (determined by titration with bromine) in 400 g. of carbon tetrachloride. In this run there was formed 11 mg. mols. of ammonium chloride and 45.5 mg. mols. of the amine (isolated as the benzoyl derivative). The remainder of the nitrogen was given off as a gas during the reaction.

***r*-Benzoyl-2-chloro-3-amino-butane.**—The benzoyl derivative of the amine was prepared from the solution of the hydrochloride above, by the usual Schotten-Baumann method; 9.6 g. was obtained, which is 29% calculated from the nitrogen trichloride. This was recrystallized several times from petroleum ether (b. p., 100–110°). Colorless needle-like crystals were formed, melting at 105–106° (uncorr.). The substance was analyzed for nitrogen by the Gunning-Arnold-Dyer modification of Kjeldahl's method, and for chlorine by the sodium peroxide bomb method described by Lemp and Broderson.[9]

Analyses. Subs., 0.1526, 0.2237: 7.25, 10.8 cc. of 0.1 *N* HCl. Calc. for $C_{11}H_{14}ONCl$: N, 6.63. Found: 6.65, 6.76.

Subs., 0.1726, 0.1523: 8.18, 7.21 cc. of 0.1 *N* $AgNO_3$. Calc. for $C_{11}H_{14}ONCl$: Cl, 16.80. Found: 16.83, 16.80.

The Reaction with 1-Butene

1-Butene was prepared from *n*-butyl iodide and alcoholic potassium hydroxide according to the method of Grabowsky and Saytzeff.[10] The apparatus used and the method of carrying out the reaction were the same as given above, for 2-butene. In this case, however, a larger excess of the unsaturated compound was necessary, and a longer time was required for the color of the nitrogen trichloride to disappear. The carbon tetrachloride solution was shaken with water to remove ammonium chloride, then with concd. hydrochloric acid as before. The amounts used in a typical run were the following: 150 mg. mols. of nitrogen trichloride in 400 g. of carbon tetrachloride, 260 mg. mols. of 1-butene in 400 g. of carbon tetrachloride; 11.3 mg. mols. of ammonium chloride was formed, 35.5 mg. mols. of amine, and the remainder of the nitrogen was liberated as a gas.

***r*-Benzoyl-1-chloro-2-amino-butane.**—One-third of the hydrochloric acid solution was used for the preparation of the benzoyl derivative by the Schotten-Baumann method; 2.5 g. of substance was obtained, which is a yield of 23.6%. The product was recrystallized several times from petroleum ether (b. p., 100–110°). Fine, silky needles in small clusters were formed, melting at 91–92° (uncorr.). Careful working up of the mother liquors failed to indicate the presence of more than one compound.

Analyses. Subs., 0.1520, 0.1744: 7.25, 8.36 cc. of 0.1 *N* HCl. Calc. for $C_{11}H_{14}ONCl$: N, 6.63. Found: 6.68, 6.71.

Subs., 0.1670, 0.1504: 7.96, 7.15 cc. of 0.1 *N* $AgNO_3$. Calc. for $C_{11}H_{14}ONCl$: Cl, 16.80. Found: 16.90, 16.87.

***r*-Benzoyl-2-amino-butane.**—The remaining two-thirds of the hydrochloric acid solution described above was cooled and nearly neutralized with sodium hydroxide. An excess of 2.5% sodium amalgam was then slowly added. The solution was stirred with a mechanical stirrer, and kept slightly acid to litmus by the addition of concd. hy-

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[9] Lemp and Broderson, THIS JOURNAL, **39**, 2069 (1917).

[10] Grabowsky and Saytzeff, *Ann.*, **179**, 330 (1875).

drochloric acid as required. The amalgam was made by the modification of Nef's method, described by Raiford and Clark.[11] After separating the solution from the mercury, one-half was used for the preparation of the benzoyl derivative; 1.5 g. was obtained, which after recrystallizing from petroleum ether (b. p., 100–110°), formed colorless needles, melting at 84–85° (uncorr.). The substance was found to contain no chlorine.

Analyses. Subs., 0.2302, 0.0945: 12.9, 5.36 cc. of 0.1 *N* HCl. Calc. for $C_{11}H_{15}ON$: N, 7.92. Found: 7.84, 7.94.

In order to characterize the compound further the other half of the solution described above was used for the preparation of the *p*-nitrobenzoyl derivative. After recrystallizing several times from petroleum ether (b. p., 120–150°), the substance melted at 114.5–115.5° (uncorr.). As mentioned above, Pope and Gibson[4] prepared racemic *sec*-butylamine (2-amino-butane) by the reduction of methylethyl ketoxime with sodium amalgam. The melting point of the benzoyl derivative recrystallized from aqueous alcohol is recorded as 75–76°. This compound was prepared as described by these authors and after recrystallizing several times from petroleum ether (b. p., 100–110°), melted at 84–85° (uncorr.). A mixture of this compound with *r*-benzoyl-2-amino-butane, obtained through the reduction of the chloro-amine, melted at the same temperature.

The *p*-nitrobenzoyl derivative was also prepared from the amine obtained by the reduction of the ketoxime. After recrystallizing from petroleum ether (b. p., 120–150°) this product melted at 114.5–115.5° (uncorr.). When mixed with *r*-(*p*-nitrobenzoyl)-2-amino-butane obtained through the reduction of the chloro-amine no change in melting point was observed.

***p*-Nitrobenzoyl-*n*-butylamine.**—If, as stated above, in the addition of nitrogen trichloride to 1-butene the dichloro-amino group had added to the end carbon atom to form $CH_3CH_2CHClCHNCl_2$, then by reduction *n*-butylamine would be formed. The benzoyl derivative of *n*-butylamine was prepared. This was a clear oil, soluble in hot petroleum ether, and was not obtained in crystalline form. The *p*-nitrobenzoyl derivative was prepared, and after recrystallizing from petroleum ether (b. p., 120–150°) melted at 102.5–103° (uncorr.).

The Reaction with Trimethylethylene

Nitrogen trichloride reacted very rapidly with trimethylethylene. During the addition of the trichloride solution, the yellow color disappeared very quickly as long as there was an excess of the unsaturated compound present, nitrogen gas was given off and a heavy white precipitate of ammonium chloride was formed. The ammonium chloride was filtered off, and the carbon tetrachloride tested for the presence of an amine. None was found. The white precipitate was washed with carbon tetrachloride and dried. Analysis for chlorine showed it to be ammonium chloride.

Analysis. Subs., 0.2102: AgCl, 0.5648. Calc. for NH_4Cl: Cl, 66.33. Found: 66.49.

The following table gives the amounts of the materials used and the products formed in three typical runs. The nitrogen trichloride was in each case dissolved in about 320 g. of carbon tetrachloride and the trimethylethylene in about 240 g. of carbon tetrachloride.

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[11] Raiford and Clark, This Journal, **45,** 1738 (1923).

Table I

Nitrogen Trichloride with Trimethylethylene

	I	II	III
	Mg. mols.		
C_5H_{10}	100	100	100
NCl_3	50.4	55.3	57.7
NH_4Cl	14.5	15.5	16.1
N_2, mg. atoms	35.6	39.2	37.7

Careful fractionation of the carbon tetrachloride solutions from the three runs yielded two very definite fractions with boiling points above that of carbon tetrachloride, one at 130–133° and the other at 174–180°. There was little or no indication of a fraction corresponding to monochloro-amylene. According to Hell[7] monochloro-amylene, C_5H_9Cl, amylene dichloride, $C_5H_{10}Cl_2$, and chloro-amylene chloride, $C_5H_9Cl_3$, boil at 92–93°, 130–133°, and 174–180°, respectively.

Chlorine determinations were made by Carius' method on the two fractions mentioned.

Analyses. Fraction 130–133°. Subs., 0.1662: AgCl, 0.3335. Calc. for $C_5H_{10}Cl_2$: Cl, 50.35. Found: 49.93.

Fraction 174–180°. Subs., 0.2098: AgCl, 0.5127. Calc. for $C_5H_9Cl_3$: Cl, 60.45. Found: 60.66.

Summary

1. Nitrogen trichloride adds to 2-butene to form 2-chloro-3-dichloro-amino-butane. This amine is reduced by concd. hydrochloric acid to 2-chloro-3-amino-butane.

2. Nitrogen trichloride adds to 1-butene to form 1-chloro-2-dichloro-amino-butane. The structure of this product was proved by reduction to 2-amino-butane (*sec*-butylamine).

3. According to Markownikoff's rule, the addition of nitrogen trichloride to 1-butene to form 1-chloro-2-dichloro-amino-butane, agrees with the assumption that the chlorine in nitrogen trichloride is positive.

4. Nitrogen trichloride reacts rapidly with trimethylethylene to form ammonium chloride, nitrogen, and amylene chlorides.

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