4. Benzyl alcohol reduced the nitro compound to azoxybenzene and was fully oxidized to benzaldehyde and benzoic acid.
5. The aliphatic alcohols were oxidized to acids of less carbon content, among them formic.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

NITROGEN TRICHLORIDE AND UNSATURATED HYDROCARBONS. II

BY GEORGE H. COLEMAN, G. M. MULLINS AND ELIZABETH PICKERING

RECEIVED JUNE 20, 1928 PUBLISHED OCTOBER 6, 1928

The reaction of nitrogen trichloride with the unsaturated hydrocarbons,[1] 1-butene, 2-butene and trimethylethylene has been reported in a previous communication, as has also its reaction with the unsaturated ketones,[2] benzalacetophenone and benzalacetone.

The reaction has now been studied with ethene, propene, methylpropene, 2-pentene and cyclohexene. There is a wide difference in the reaction rates of these hydrocarbons. Ethene reacts most slowly and methylpropene most rapidly. The degree of difference is indicated by the fact that at 20–25° two weeks or longer is required for the completion of the reaction with ethene, while with methylpropene the reaction, even at −45 to −50° is complete within two to three hours. The reaction rates of the other hydrocarbons fall between these two extremes.

The products of the reaction with ethene are nitrogen, ammonium chloride, ethylene chloride and 2-chloro-1-dichloro-amino-ethane. This compound was not isolated but was converted by hydrochloric acid to 1-amino-2-chloro-ethane. On further reduction with sodium amalgam ethylamine was obtained.

With propene, which reacts more rapidly than ethene but more slowly than the others, the products are similar to those obtained with ethene. Of the two possible addition products, $CH_3CHNCl_2CH_2Cl$ and $CH_3CHClCH_2NCl_2$, only the first was definitely shown to be formed. Attempts to prove the presence of the other isomer were not successful.

With methylpropene, although the products were much the same, the reaction differed in some respects from the others. In nearly all of the reactions thus far studied of nitrogen trichloride with unsaturated hydrocarbons, all or at least the greater part of the stable addition product remains in solution in the carbon tetrachloride as the dichloro-amino compound and is obtained as the hydrochloride of the corresponding amine by treatment with hydrochloric acid. In this case, however, most of the

---

[1] Coleman and Howells, THIS JOURNAL, **45**, 3084 (1923).

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

amine was precipitated as the hydrochloride along with the ammonium chloride during the reaction. A similar precipitation of the amine hydrochloride occurs with benzalacetone.[2b] This may be due to a greater reactivity toward hydrochloric acid of the dichloro-amino group in these compounds. Again only one addition product $(CH_3)_2CNCl_2CH_2Cl$ was found. The formation of a moderate yield of the amine in this reaction, although the dichloro-amino group is attached to a tertiary carbon atom, may be due to the very low temperature at which the reaction was carried out. Experience with similar compounds in reactions at higher temperatures has indicated that little or none of the amine is usually formed. In general the lower the temperature at which the reaction is carried out the better the yield of the amine.

The reactions with 2-pentene and cyclohexene are quite similar to those already described. Stable addition products are obtained in each case.

Experimental Part

The unsaturated hydrocarbons used were prepared by well-known methods. Ethene was obtained from ethyl alcohol and sulfuric acid. Propene was prepared from *iso*propyl iodide and alcoholic potassium hydroxide. Ethene and propene were collected and measured over water. Methylpropene was prepared by adding *iso*butyl iodide slowly to warm alcoholic potassium hydroxide. The gas was passed through a 30cm. water-jacketed fractionating column and subsequently through a concentrated solution of calcium chloride. The amount obtained was determined by titration with bromine in carbon tetrachloride solution. 2-Pentene was prepared from diethyl carbinol and sulfuric acid by the method of Norris and Joubert.[3] Cyclohexene was prepared from cyclohexanol by the method given in "Organic Syntheses."[4] The hydrocarbons were all dried with fused calcium chloride and dissolved in cold carbon tetrachloride.

Nitrogen trichloride was prepared and analyzed as described in earlier papers.[1,2b]

The method of carrying out the reaction was essentially the same as that previously used.[5] The highest yields of addition products were obtained when at least two moles of the hydrocarbon for each mole of nitrogen trichloride were used. With methylpropene, when the reaction was carried out at a low temperature, a little chloroform was added in order to keep the reaction mixture liquid. In every case except with methylpropene the dichloro-amino chloro compound was changed to a chloro-amine by dry hydrogen chloride. With methylpropene, as already mentioned, the chloro-amine hydrochloride was obtained during the initial

---

[3] Norris and Joubert, THIS JOURNAL, **49**, 885 (1927); "Organic Syntheses," **7**, 76 (1927).

[4] Coleman and Johnstone, "Organic Syntheses," **5**, 33 (1925).

[5] Ref. 1, p. 3086.

addition reaction. A small amount of chloro-amine hydrochloride was obtained in each instance by final treatment with aqueous hydrochloric acid. Benzoyl derivatives of the chloro-amines were prepared, and usually the Schotten-Baumann method was used. However, in the case of the chloro-amine from methylpropene, the hydrochloride was suspended in benzene, a little concentrated potassium hydroxide solution added and the mixture shaken until all the hydrochloride had reacted. The benzene solution of the amine was separated and dried with solid potassium hydroxide. To this after filtering was added a little less than the calculated amount of benzoyl chloride and the mixture was allowed to stand for one or two hours. It was then filtered and the benzene was evaporated nearly to dryness on the water-bath. The residue solidified on cooling. It was crystallized from petroleum ether (b. p. 40–60°). Table I summarizes the results.

TABLE I

YIELDS OF CHLORO AMINES AND ANALYSES OF THEIR BENZOYL DERIVATIVES

Hydrocarbon	Prep. of amine hydrochloride Temp., °C.	Yield, %	M. p., °C.	Formula of benzoyl derivative	Nitrogen, % Calcd.	Found		Chlorine, % Calcd.	Found	
Ethene	20 to 25	13.7	104–105	$C_9H_{10}ONCl$	7.63	7.82	7.70	...	...	...
Propene	−10	19.5	74–75	$C_{10}H_{12}ONCl$	7.09	6.93	7.01	17.97	18.27	18.04
Pentene	0 to 10	10–21	106–107	$C_{12}H_{16}ON_2Cl$[a]	10.35	10.33	10.31	13.10	13.16	13.20
Cyclohexene	−19	23	162–163	$C_{13}H_{16}ONCl$	5.89	5.82	5.91	14.95	15.10	15.11
Methylpropene	−50	12.2	83–84	$C_{11}H_{14}ONCl$	6.62	6.69	6.74	...	...	...

[a] *p*-Nitrobenzoyl derivative. The corresponding benzoyl derivative is an oil.

The chloro-amines obtained from ethene and propene were reduced with sodium amalgam in acid solution to the corresponding amines, ethylamine and *iso*propylamine. The benzoyl derivatives of these were prepared and identified by mixed melting points with the known compounds. No depression was observed in either case. Attempts to reduce the chloro-amines obtained from methylpropene and 2-pentene were not entirely successful. This was also true of the benzoyl derivative obtained from methylpropene. However, when the benzoyl derivative was tested with alcoholic silver nitrate for the presence of chlorine attached to a tertiary carbon atom, no precipitate was obtained until the solution was warmed. A control test with a known tertiary chloride formed a precipitate immediately. This test indicated that the compound was benzoyl-2-amino-1-chloro-2-methylpropane, since the isomer would contain chlorine attached to a tertiary carbon atom.

Summary

Nitrogen trichloride reacts with ethene, propene, methylpropene, 2-pentene and cyclohexene.

Nitrogen, ammonium chloride, the dichloride of the hydrocarbon and a C-chloro-N-dichloro-amine are formed with each.

IOWA CITY, IOWA