

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

ETHERS DERIVED FROM THE ADDITION PRODUCTS OF THE NITRO-ANILINES AND CHLORAL.¹

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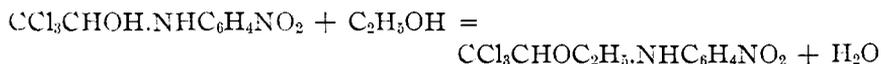
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In our paper on the action of basic reagents on Schiff's bases² we described the action of alcoholic potash, sodium methylate and sodium ethylate on the condensation products of *o*- and *p*-nitro-aniline with chloral, one of the three chlorine atoms being replaced by the hydroxyl, methoxyl or ethoxyl group. Upon turning our attention later to *m*-nitro-aniline certain difficulties arose. In combining *m*-nitro-aniline with chloral a new condensation product, containing one residue of chloral united to two residues of *m*-nitro-aniline, and melting at 130°, was discovered, one melting at 212° having already been described by one of us.³ This new product is obtainable in quantity whereas the one originally observed can be obtained only in small amount. This case of isomerism we have not yet had opportunity to study and at present we see no explanation for it. We also observed a number of times another substance melting at 90°, a special study of which led to the discovery of a class of ethers which are derived from the addition products of the nitro-anilines and chloral.

If *m*-nitro-aniline and chloral in equimolecular quantities are mixed together directly or in ether solution a gummy substance is produced. Upon long standing or upon being heated for several hours at 100° it solidifies and, upon recrystallization from a mixture of chloroform and ligroin, is obtained in bright orange-yellow monoclinic 4-sided plates, melting at 130°. The expected addition product proves to be the condensation product. The following equation expresses the reaction.



If however the gummy mass before being heated is dissolved in hot alcohol a different reaction takes place, since a new product, melting at 90°, is obtained. This reaction may be represented thus:



Turning our attention to other alcohols we obtained a similar reaction with methyl, *n*-butyl and *iso*-amyl alcohols. No crystalline compound

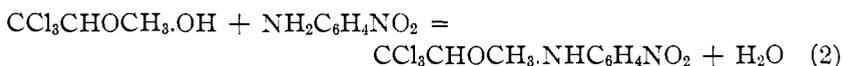
¹ Section II of a thesis presented by Samuel C. Smith to the faculty of the University of North Carolina for the degree of Master of Science. Section I, entitled "The Action of Basic Reagents on Schiff's Bases" was published in (THIS JOURNAL, 41, 1862 (1919)).

² *Ibid.*, 41, 1862 (1919).

³ Wheeler and Weller, *ibid.*, 24, 1063 (1902).

could be obtained with *n*-propyl alcohol but the uncrystallizable syrup gave a satisfactory analysis for an *n*-propyl ether.

The method described above did not work so well with *p*-nitro-aniline but a new method of procedure was found. The alcoholate of chloral was first prepared and this was treated with *p*-nitro-aniline. Thus:



Only the methyl and ethyl ethers have so far been prepared in spite of many attempts to prepare the *n*-propyl, *n*-butyl and *iso*-amyl ethers. Instead of an ether the product was either the condensation product (1 mol. of chloral to 2 mols. of amine) or *p*-nitro-aniline itself.

The new ethers are best recrystallized from ethyl alcohol or the alcohol from which they are made may be used. They crystallize beautifully in large prisms of the monoclinic system or in tables of the orthorhombic system. They are paler in color than the nitro-anilines.

The ethers are insoluble in water but are very slowly decomposed by boiling water. They are insoluble in dil. hydrochloric acid but are slowly dissolved and decomposed by hot conc. hydrochloric acid. They are insoluble in dil. sodium hydroxide but are very slowly decomposed on boiling. The following experiments give a better idea of these relations. One half g. of the ether was boiled in 10 cc. of sodium hydroxide solution of different concentrations and complete decomposition took place as follows: with 5% sodium hydroxide 60 minutes was required; with 10%, 40 minutes; with 25%, 30 minutes; with 50%, 20 minutes. If the period of time is shortened, some of the unchanged ether is recovered, as indicated by its melting point. Boiling water required one and a half hours for complete decomposition. Hot strong acid acted much more rapidly than alkali.

Experimental Part.

The *m*-Nitro-aniline Series.

Addition Product.

N-(α -hydroxy- β -trichloro-ethyl)-*m*-nitro-aniline, $\text{CCl}_3\text{CHOH.NHC}_6\text{H}_4\text{NO}_2$.—This addition product would be named chloral-*m*-nitro-aniline according to the old nomenclature. It is a new compound although not perfectly well defined since we have been unable to crystallize it. If molecular quantities of chloral and *m*-nitro-aniline are mixed together a thick gummy syrup is obtained. All attempts to crystallize it were in vain. If ethereal solutions are brought together and the ether allowed to evaporate slowly the same syrup is obtained. Cooling to -10° was ineffective. On long standing the syrup passes over into the condensation product, $\text{CCl}_3\text{CH(NHC}_6\text{H}_4\text{NO}_2)_2$ which melts at 130° . Heat greatly

hastens the reaction. In order to purify the syrup it was well shaken with water and dried over sulfuric acid.

Subs., 0.1321: AgCl, 0.1963. Calc. for $C_8H_7O_3N_2Cl_3$ (m. w. 285): Cl, 37.19. Found: 36.75.

It is decomposed by strong acids and bases, chloroform being given off with the latter.

The Ethers.

N-(α -methoxy- β -trichloro-ethyl)-*m*-nitro-aniline, $CCl_3CHOCH_3.NH.C_6H_4NO_2$.—The methyl ether was prepared by mixing 5 g. of chloral with 5 g. of *m*-nitro-aniline and dissolving the gummy substance obtained in 20 cc. of methyl alcohol. The solution was heated for a short time on the water-bath and then allowed to evaporate slowly. The yield was 9.5 g. or 87%. The ether, purified by alcohol, melts at 108–109°, and consists of bright yellow elongated monoclinic prisms, readily obtained 1 mm. thick and 5 mm. long. The ether sometimes crystallizes in plates.

Subs., 0.5273: AgCl, 0.7545. Calc. for $C_9H_9O_3N_2Cl_3$ (299): Cl, 35.45. Found: 35.34.

The ether dissolves in methyl and ethyl alcohols, acetone, ether and benzene. It is insoluble in water or ligroin. It is decomposed by hot strong acid and more slowly by hot strong alkali.

N-(α -ethoxy- β -trichloro-ethyl)-*m*-nitro-aniline, $CCl_3CHOC_2H_5.NH.C_6H_4NO_2$.—This ether was prepared in the same manner as the methyl ether. It crystallizes in bright yellow crystals of the monoclinic tabular habit, having a unit prism or ortho dome and clino and ortho pinacoids. Purified from alcohol it melts at 90°. The yield from 5 g. of *m*-nitro-aniline was 9 g. or 79%.

Subs., 0.3029: AgCl, 0.4802. Calc. for $C_{10}H_{11}O_3N_2Cl_3$ (313): Cl, 33.80. Found: 33.69.

N-(α -propoxy- β -trichloro-ethyl)-*m*-nitro-aniline, $CCl_3CHOC_3H_7.NH.C_6H_4NO_2$.—The method of preparation was the same as given above but no crystalline compound could be obtained although many attempts were made. A thick syrup was obtained which could not be recrystallized at -10° or by the use of solvents. For analysis it was well shaken with water and dried over sulfuric acid.

Subs., 0.0903: AgCl, 0.1170. Calc. for $C_{11}H_{13}O_3N_2Cl_3$ (327): Cl, 32.48. Found: 32.05.

N-(α -butoxy- β -trichloro-ethyl)-*m*-nitro-aniline, $CCl_3CHOC_4H_9.NH.C_6H_4NO_2$.—The mixture of equal parts of chloral and *m*-nitro-aniline was dissolved in 15 cc. of *n*-butyl alcohol. After heating for a few minutes the alcohol was allowed to evaporate spontaneously. This ether consists of splendid yellow prisms of the monoclinic system with clino, basal and ortho pinacoids, elongated, 6-sided and occurring in clusters. The pure substance melts at 70°.

Subs., 0.3181: AgCl, 0.4001. Calc. for $C_{12}H_{15}O_3N_2Cl_3$ (341): Cl, 31.08. Found: 31.09.

N-(α -*iso*-amoxy- β -trichloro-ethyl)-*m*-nitro-aniline, $CCl_3CHOC_5H_{11}.NHC_6H_4NO_2$.—The preparation was carried out as above. Recrystallized from alcohol the product melts at 90° . It crystallizes in tables of the orthorhombic system and also in monoclinic prisms, each sort showing 3 pinacoids. This ether is unique in possessing an odor.

Subs., 0.5324: AgCl, 0.6535. Calc. for $C_{13}H_{17}O_3N_2Cl_3$ (355): Cl, 29.86. Found: 30.32.

p-Nitro-aniline Series.

N-(α -methoxy- β -trichloro-ethyl)-*p*-nitro-aniline, $CCl_3CHOCH_3.NHC_6H_4NO_2$.—The condensation product of *p*-nitro-aniline and chloral is formed with so great readiness that the method of making the addition product was abandoned and the chloral was first converted into the alcoholate. The addition product can be employed but it is a tedious process. To a solution of 5 cc. of chloral in 50 cc. of methyl alcohol was added a solution of 5 g. of *p*-nitro-aniline. After heating to boiling, the solution was allowed to evaporate very slowly. A large mass of beautiful yellow monoclinic prisms formed, weighing 9.2 g. These melted at 146 – 147° .

Subs., 0.6408: AgCl, 0.9108. Calc. for $C_9H_9O_3N_2Cl_3$: Cl, 35.45. Found: 35.16.

N-(α -ethoxy- β -trichloro-ethyl)-*p*-nitro-aniline, $CCl_3CHOC_2H_5.NHC_6H_4NO_2$.—The method above employed with ethyl alcohol gave a yield

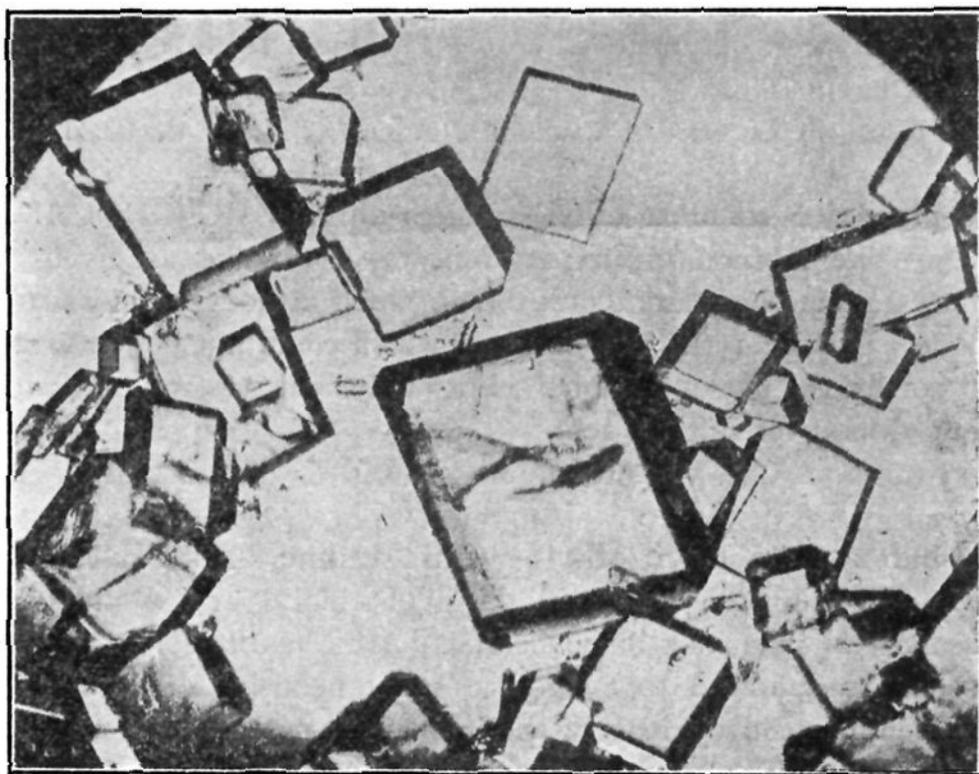


Fig. 1.

of the ethyl ether of 77%, yellow monoclinic prisms, showing a great tendency to form twins and twin clusters. If any condensation product (m. p., 216°) is formed it may be removed by dissolving the ethoxy compound in ether. The pure ether melts at 138°.

The crystals of this ether were examined by Mr. Walter B. Jones of the Geology Department and his report is as follows: photomicrograph $\times 44$; ocular, 2; objective, 3; arc light; exposure 5 seconds through blue glass and through 12 mm. of solution. Triclinic system, tabular habit; basal, macro and brachy pinacoids, usually modified by unit prism, macro and brachy domes. Inclination of angle, $-8^\circ =$.

Subs., 0.5872: AgCl, 0.8015. Calc. for $C_{10}H_{11}O_2N_2Cl_3$: Cl, 33.80. Found: 33.70.

Ethers of the Higher Alcohols.—No ethers could be made with *n*-propyl, *n*-butyl and *iso*-amyl alcohols although both methods of preparation were tried a number of times, and modifications of these methods were resorted to.

Summary.

New ethers are obtained by the action of alcohols upon the addition products of chloral and *meta*- or *para*-nitro-aniline.

The *m*-nitro-aniline product gave ethers with methyl, ethyl, *n*-propyl, *n*-butyl and *iso*-amyl alcohols.

The *p*-nitro-aniline product gave ethers only with methyl and ethyl alcohols. In these cases the amine was made to react with the chloral alcoholate. No ethers of the higher alcohols could be obtained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE.]

THE PREPARATION OF ESTERS BY DIRECT REPLACEMENT OF ALKOXYL GROUPS.

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In a paper on the action of light on esters of α -cyano-cinnamylideneacetic acid,¹ the preparation of a new unstable ethyl ester of this acid was described. The compound was prepared from the methyl ester by direct replacement of the methoxyl by the ethoxyl group, the procedure being that described by Pfannl² in a paper dealing with this replacement action. The fact that an ester too unstable to be prepared by the usual methods could be formed by replacement of one alkoxy group by another, led to the hope that the method might be found of general application in the preparation of a series of esters of unstable, unsaturated acids. It seemed of interest, therefore, as previously stated¹, to study this reac-

¹ Reimer, *Am. Chem. J.*, **45**, 417 (1911).

² Pfannl, *Monats.*, **31**, 301 (1910).