the presence of hydroxyl groups. The expected absorption for a mesityl group and a phenyl group is shown.

Isomerization was observed when the tetraketone was recrystallized repeatedly from ethanol or 1-propanol. When 0.5 g. of the compound was boiled with ethanol for a few minutes it was converted to a colorless powder which still melted at 133–134°. When the contact with boiling ethanol was prolonged, the product was a colorless powder melting at 199–200° (corr.). Under the same conditions the sample described earlier[2] was found to melt at 199–200° (corr.). A mixture of the two samples melted at 199–200° (corr.).

Anal. Calcd. for $C_{38}H_{38}O_4$: C, 81.69; H, 6.86. Found: C, 81.44; H, 7.18.

The infrared spectrum is identical to that obtained for the low-melting product.

The isomerization was accomplished also by use of sodium methoxide. The reagent was made by shaking 0.5 g. of the methoxide with 10 ml. of methanol and removal of undissolved methoxide by filtration. The reagent was added to a methanolic solution of 0.1 g. of the tetraketone (m.p. 133–134°). The solution, which immediately became pale yellow, was allowed to stand for 15 min. at room temperature. Dilute hydrochloric acid was added until a permanent turbidity was produced. The product, which separated during 2 hr. of refrigeration, crystallized from ethanol as a colorless powder melting at 199–200° (corr.). A mixture melting point with the sample described above was not depressed.

The same two tetraketones were obtained by oxidation of the cyclic glycol III with periodic acid. When the oxidation product was recrystallized from an ether–petroleum ether mixture, pale yellow crystals melting at 133–134° were obtained. When the recrystallization solvent was ethanol, however, the product separated as a colorless powder. This product and its mixture with the high-melting tetraketone from the linear glycol melted at 199–200° (corr.).

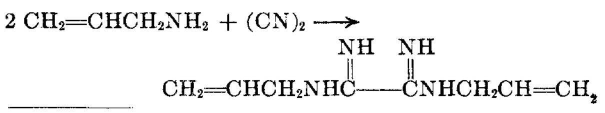
THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILL.

Reaction of Cyanogen with Organic Compounds. IX. Allyl Amines

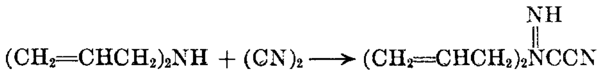
HENRY M. WOODBURN, CHEN MING CHIH,[1] AND DONALD H. THORPE[2]

Received December 6, 1956

Several years ago it was shown in this laboratory[3,4] that saturated primary and secondary aliphatic amines react with cyanogen at low temperature and atmospheric pressure to yield oxamidines and cyanoformamidines. We report here the similar behavior of the unsaturated compounds allylamine and diallyl amine:



$$2\,\mathrm{CH_2{=}CHCH_2NH_2} + \mathrm{(CN)_2} \longrightarrow \mathrm{CH_2{=}CHCH_2NH}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{NHCH_2CH{=}CH_2}$$



$$\mathrm{(CH_2{=}CHCH_2)_2NH} + \mathrm{(CN)_2} \longrightarrow \mathrm{(CH_2{=}CHCH_2)_2N}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{CN}$$

These compounds are important in our current study of the chemistry of oxamidines because they possess nitrogen-free reactive centers somewhat removed from the $C{=}NH$ and $C{\equiv}N$ groups.

Physically the allyl derivatives are quite similar to their saturated analogs.[3,4] The oxamidine is a white, crystalline solid, soluble in water, ethanol, carbon tetrachloride, acetone, and ether, and insoluble in petroleum ether. It quickly turns brown in air, but forms a stable, crystalline dihydrochloride. The cyanoformamidine is a colorless liquid when freshly distilled but darkens on standing, even in the ice chest. Its hydrochloride is a stable, white solid.

The behavior of the new compounds toward bromine was investigated. From *sym*-diallyloxamidine, or better from its hydrochloride, was obtained a white, crystalline compound which gave the correct analysis for

$$\mathrm{CH_2BrCHBrCH_2NH}\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NH}}{\overset{\|}{\mathrm{C}}}\mathrm{NHCH_2CHBrCH_2Br\cdot 2HCl}$$

Both diallylcyanoformamidine and its hydrochloride decolorized bromine solutions readily but the gummy products could not be purified. A quantitative bromination with $KBr\text{-}KBrO_3$ solution indicated that four equivalents of bromine reacted with one mole of cyanoformamidine.

Difficulty was experienced in determining the chlorine content of *N*-diallylcyanoformamidine hydrochloride. Both Mohr and Volhard methods gave consistent results about 3% higher than theoretical. However, titration of the hydrochloride with standard sodium hydroxide gave an equivalent weight corresponding to the calculated value. It is conceivable that the cyanoformamidine forms a complex with $AgNO_3$ thus consuming part of the precipitant.

Although *sym*-diallyloxamidine can be obtained by the conventional method of cyanogenating an aqueous solution,[3] the most successful method employs petroleum ether, from which the product precipitates as formed.

EXPERIMENTAL

Cyanogen was prepared, purified and dried by the method described by Woodburn, Morehead, and Bonner.[4]

sym-Diallyloxamidine dihydrochloride. A solution of 10 g. of allylamine in 25 g. of petroleum ether was placed in an ice bath and maintained at 0° while cyanogen gas was bubbled in. After some time light-colored crystals of product appeared. Cyanogenation was discontinued soon thereafter, since experience showed that further cyanogenation converted the crystals to a brown liquid.

The crystals were filtered, dissolved in diethyl ether, and the solution saturated with dry hydrogen chloride. The precipitated hydrochloride was purified by dissolving it in ethanol and reprecipitating with ether. White crystals, melt-

---

[1] Present address: Foramino, Inc., Kenova, W. Va.

[2] Present address: Durez Plastics Division, Hooker Electrochemical Co., Walck Road, North Tonawanda, N. Y.

[3] Woodburn, Morehead, and Chen, *J. Org. Chem.*, **15**, 535 (1950).

[4] Woodburn, Morehead, and Bonner, *J. Org. Chem.*, **14**, 555 (1949).

ing with decomposition at 260° were obtained. The yield (based on amine) was 39%.

Anal. Calcd. for $C_8H_{14}N_4 \cdot 2HCl$: C, 40.3; H, 6.7; N, 23.5; Cl, 29.8. Found: C, 40.5; H, 7.2; N, 23.7; Cl, 29.8.

Crystals of *the free base* could be kept for a short time at room temperature in a tightly stoppered bottle. Exposed to air they turned brown in a few hours. They melted between 65–75°, were very soluble in water, ethanol, acetone, carbon tetrachloride, and ether, but insoluble in petroleum ether.

N-diallylcyanoformamidine. A solution of 20 g. of diallyl amine in 40 ml. of anhydrous ethyl acetate was cooled to 40° and treated with cyanogen until the mixture turned yellow. After standing in the ice chest for 2 days, it was heated to 75° in a water bath under the hood to remove any unreacted cyanogen. Ethyl acetate was distilled off at atmospheric pressure and the remaining mixture was fractionated at 16 mm. pressure. Unreacted diallylamine weighing 9.8 g. was recovered. The yield of diallylcyanoformamidine boiling at 102–104°/16 mm. was 9.5 g. which on the basis of the diallylamine which reacted was 66.9%. The liquid was colorless and had a refractive index, n_D^{20}, of 1.4903.

The *hydrochloride* was prepared by saturating an ether solution of diallylcyanoformamidine with dry hydrogen chloride. The white solid was filtered, washed with cold ether, and dried in a vacuum desiccator over concentrated sulfuric acid. The crystals melted at 136–138° with decomposition.

Anal. Calcd. for $C_8H_{11}N_3 \cdot HCl$: C, 51.8; H, 6.52; N, 22.6; equiv. wt., 185.5. Found: C, 52.0; H, 6.95; N, 22.2; equiv. wt. (by NaOH titration), 186.4.

It was also possible to prepare the hydrochloride by cyanogenating diallylamine in petroleum ether. The cyanoformamidine, which settled out as an insoluble layer, was separated, washed with petroleum ether, dissolved in diethyl ether, and saturated with dry hydrogen chloride. This procedure eliminated the time-consuming distillation of the cyanoformamidine involved in the other procedure.

sym-Bis(2,3-dibromopropyl)oxamidine dihydrochloride. To 1 g. of *sym*-diallyloxamidine dihydrochloride dissolved in water was added bromine water until a yellow color persisted. Sufficient normal NaOH solution was added to remove excess bromine and to liberate the free base of the brominated product. The solution was extracted with ether, the extract dried, and saturated with gaseous hydrogen chloride. The crystalline product was recrystallized from ethanol. It melted at 212°.

The same product was obtained by adding a carbon tetrachloride solution of bromine to a carbon tetrachloride solution of *sym*-diallyloxamidine. The gummy precipitate was dissolved in ethanol and saturated with hydrogen chloride. Cooling in a dry ice chest caused the separation of crystals which melted at 212°.

Anal. Calcd. for $C_8H_{14}N_4Br_4 \cdot 2HCl$: C, 17.2; H, 2.9; N, 10.0; Br, 57.2; Cl, 12.7. Found: C, 17.5; H, 3.2; N, 10.3; Br, 57.0; Cl, 13.0.

The hydrochloride neutralized with dilute sodium hydroxide gave a solid presumed to be the *free base* which melted at about 112°.

Bromination of N-diallylcyanoformamidine. (a) Attempts to isolate the product of the bromination of *N*-diallylcyanoformamidine in carbon tetrachloride, ether, or ethanol solution produced only a gummy material. This, dissolved in ethanol and saturated with hydrogen chloride likewise failed to produce crystals. (b) *N*-diallylcyanoformamidine hydrochloride, dissolved in water, decolorized bromine water readily but gave a gummy product on which no analysis was attempted. (c) Two samples of *N*-diallylcyanoformamidine, quantitatively brominated with KBr-$KBrO_3$-HCl mixture, consumed respectively 3.90 and 3.89 equivalents of bromine per mole.

Acknowledgment. Acknowledgment is made to The Edwal Laboratories, Inc., Ringwood, Ill., for their gift of diallylamine.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BUFFALO
BUFFALO, N. Y.

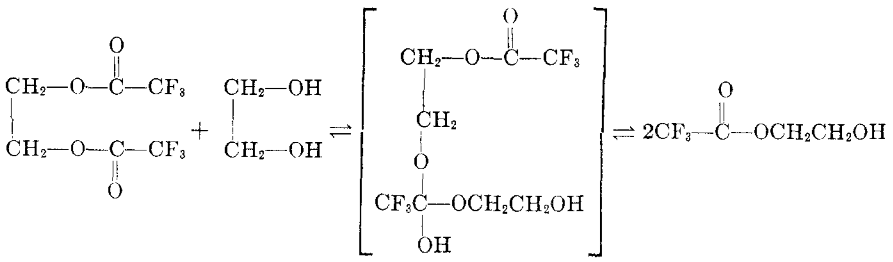
Trifluoroacetates of Ethylene Glycol

SIDNEY D. ROSS AND MANUEL FINKELSTEIN

Received February 14, 1957

When an excess of ethylene glycol is reacted with either trifluoroacetic acid or trifluoroacetic anhydride and the reaction mixture is distilled at atmospheric pressure, an apparently homogeneous product is obtained. This product has a constant boiling point of 151–152°; n_D^{25} 1.3450. If this product is arbitrarily divided during distillation into successive fractions, all of the fractions have the same index of refraction and the same infrared spectrum.

Nevertheless, this product gives a saponification equivalent of 144, a value intermediate between those calculated for 2-trifluoroacetoxyethanol (158) and 1,2-bis(trifluoroacetoxy)ethane (127). It may be shown that this product is, in fact, a mixture by subjecting it to vapor phase chromatography at 145°, whereby it is separated into its two components, initially present in a ratio of 1.33 to 1 and having retention times of 10.5 min. and 7.6 min. respectively. This product is a mixture of 2-trifluoroacetoxyethanol and 1,2-bis(trifluoroacetoxy) ethane and results from an equilibration, at the temperature of distillation, according to the following equation:



$$CF_3C(=O)OCH_2CH_2OC(=O)CF_3 + HOCH_2CH_2OH \rightleftharpoons \left[CF_3C(=O)OCH_2CH_2OC(OH)(CF_3)OCH_2CH_2OH \right] \rightleftharpoons 2CF_3C(=O)OCH_2CH_2OH$$