thalene in the 1,4 manner yielding the corresponding enols. The enols absorb oxygen to yield enol peroxides or, if allowed to stand in the absence of oxygen, rearrange to the corresponding ketones. In the case of 2-mesitoylnaphthalene the yield of the 1,4 addition product was 74% of the theoretical.

URBANA, ILLINOIS RECEIVED DECEMBER 4, 1944

[CONTRIBUTION FROM ROHM AND HAAS CO., INC., AND RESINOUS PRODUCTS & CHEMICAL CO.]

The Chemistry of Acrylonitrile. VI. · Cyanoethylation of the Haloforms

BY HERMAN A. BRUSON, WARREN NIEDERHAUSER, THOMAS RIENER AND WILLIAM F. HESTER

The behavior of acrylonitrile with compounds possessing labile hydrogen atoms[1] suggested the possibility that chloroform, if suitably activated, might add to acrylonitrile in the following manner

$$Cl_3CH + CH_2{=}CH{-}CN \longrightarrow Cl_3C{-}CH_2CH_2CN$$

It has now been found that this reaction does occur in the presence of strongly basic catalysts at low temperatures, for example, finely powdered potassium hydroxide, or aqueous 40% trimethylbenzylammonium hydroxide preferably at 0–25°. The γ-trichlorobutyronitrile obtained is a crystalline solid. Its structure follows from the fact that it yields γ-trichlorobutyric acid[2] on mild acid hydrolysis, and succinic acid upon more vigorous alkaline hydrolysis. With alkaline hydrogen peroxide it yields γ-trichlorobutyramide.

In a similar manner acrylonitrile reacted with bromoform to yield γ-tribromobutyronitrile, from which the corresponding acid and amide were in turn prepared. Although the yields are not high, due probably to the poor solubility of the catalysts in the haloforms, the γ-trichloro and γ-tribromobutyronitriles are obtained in very pure form. The reaction affords a simple method for preparing these otherwise relatively inaccessible compounds.

The reaction of iodoform with acrylonitrile in the presence of trimethylbenzylammonium hydroxide yielded a crystalline addition product of iodoform and trimethylbenzylammonium iodide, $C_6H_5CH_2N(CH_3)_3I{\cdot}CHI_3$ instead of the desired γ-tri-iodobutyronitrile. A splitting out of iodine also occurred when KOH was used as a catalyst.

Experimental

γ-Trichlorobutyronitrile.—Forty grams of a 40% aqueous solution of trimethylbenzylammonium hydroxide at 2° was mixed with 447 g. of chloroform previously cooled to 2°, and to the ice-cooled mixture at a temperature not above 5° there was added dropwise with rapid mechanical stirring 202 g. of acrylonitrile during the course of two hours. The mixture was stirred for eight hours longer at 0–5°, at the end of which time an additional 10 g. of 40% aqueous trimethylbenzylammonium hydroxide was added, and the mixture stirred sixteen hours longer at 0–5°. The reaction product was washed twice with water and then distilled. A mixture of 474 g. of chloroform and acrylonitrile boiling between 60 and 80° was recovered. The residual oil was distilled in vacuum to yield 75 g. of γ-trichlorobutyronitrile boiling at 91–103° at 16 mm., which solidified in the receiver; yield 11% based on the acrylonitrile employed. Upon redistillation the compound boiled at 90–95° (12 mm.) or 214–216° at 760 mm. After recrystallization from petroleum ether it formed colorless needles melting at 41° (uncor.). It possesses a pleasant odor and is very soluble in methanol, acetone, benzene, and carbon tetrachloride, but is insoluble in cold water. *Anal.* Calcd. for $C_4H_4Cl_3N$: C, 27.86; H, 2.32; Cl, 61.70; N, 8.12. Found: C, 27.50; H, 2.30; Cl, 60.89; N, 8.16.

An alternative procedure is to gradually add 27 g. of acrylonitrile at 0–5° to a stirred mixture of 10 g. of finely powdered potassium hydroxide and 62 g. of chloroform.[3] After stirring for four hours at 0–5° the product is washed with water and dilute hydrochloric acid. The chloroform layer is then distilled to yield 10.5 g. of γ-trichlorobutyronitrile, b. p. 95–105° (17–18 mm.); yield, 12%.

Hydrolysis of γ-Trichlorobutyronitrile.—A mixture of 8.6 g. of γ-trichlorobutyronitrile, 110 g. of water, and 12 g. of sodium hydroxide was boiled under reflux for eleven hours. The product was acidified to congo red with concentrated hydrochloric acid and evaporated to dryness *in vacuo* on a steam-bath. The residue was extracted with acetone. Upon evaporation of the acetone extract a partially solid, dark material was obtained. This was extracted several times with boiling nitroethane and the extract cooled to 5°. The crystals which separated were recrystallized again from nitroethane to yield colorless crystals, m. p. 188–189°, which gave no depression in melting point when mixed with an authentic sample of pure succinic acid.

γ-Trichlorobutyramide.—A mixture of 8.6 g. γ-trichlorobutyronitrile, 50 g. of water, 0.4 g. of sodium hydroxide and 25 g. of 27% hydrogen peroxide solution was stirred rapidly at 40–45° for five hours, and allowed to stand overnight. The crystalline product was filtered off, washed with a little water, then air-dried and washed with petroleum ether. The compound was purified by recrystallization from toluene. The analytical sample formed colorless crystals, m. p. 89–90° (uncor.).

Anal. Calcd. for $C_4H_6Cl_3NO$: C, 25.20; H, 3.17; Cl, 55.81; N, 7.35. Found: C, 25.50; H, 3.35; Cl, 55.90; N, 7.28.

γ-Trichlorobutyric Acid.—A mixture of 8.6 g. of γ-trichlorobutyronitrile and 50 g. of concentrated hydrochloric acid was heated at 60° for six hours with rapid stirring. The mixture was then cooled and the crystalline product filtered off. The crude compound was recrystallized from 400 cc. of hot water from which it separated in colorless needles, m. p. 55°. (uncor.).[4] *Anal.* Calcd. for $C_4H_5Cl_3O_2$: C, 25.07; H, 2.63; Cl, 55.57. Found: C, 24.70; H, 2.72; Cl, 55.30.

γ-Tribromobutyronitrile.—Ten grams of aqueous 40% trimethylbenzylammonium hydroxide was added to 126 g. of bromoform at 10°. Acrylonitrile (27 g.) was added

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[1] Bruson and Riener, THIS JOURNAL, **66**, 56 (1944); **65**, 23 (1943); **65**, 18 (1943); **64**, 2850 (1942).

[2] Baroni, *Gazz. chim. ital.*, **63**, 23 (1933).

[3] Since chloroform reacts with powdered potassium hydroxide at room temperature it is advisable to add the powdered potassium hydroxide to the previously chilled chloroform at 0–5° when preparing the mixture.

[4] Baroni ref. 2 reported a m. p. 57° for this compound.

dropwise while the mixture was stirred and the temperature maintained at 5–10°. The mixture was stirred for three hours at 5–10° and three hours at 25°. It was then washed with water and distilled under reduced pressure to give 74 g. of bromoform and 7 g. of product, b. p. 126–128° (6 mm.), which solidified in the receiver. Upon recrystallization from petroleum ether the γ-tribromobutyronitrile formed colorless needles melting at 98° (uncor.).

Anal. Calcd. for $C_4H_4Br_3N$: C, 15.71; H, 1.31; Br, 78.41; N, 4.58. Found: C, 15.80; H, 1.38; Br, 77.90; N, 4.65.

The compound is soluble in alcohol, ether, acetone, benzene, and ethylene dichloride, and is slightly soluble in cold petroleum ether.

γ-Tribromobutyramide.—A mixture of 13 g. of 30% hydrogen peroxide, 25 g. of water, 0.2 g. of sodium hydroxide and 5 g. of γ-tribromobutyronitrile was stirred at 40–45° for five hours and allowed to stand overnight. The white solid material (3 g.) was filtered off, dried and recrystallized from petroleum ether. It formed colorless crystals, m. p. 102–103° (uncor.). *Anal.* Calcd. for $C_4H_6Br_3NO$: C, 14.82; H, 1.87; Br, 74.04; N, 4.32. Found: C, 15.00; H, 1.90; Br, 73.70; N, 4.21.

γ-Tribromobutyric Acid.—A mixture of 7 g. of γ-tribromobutyronitrile and 40 g. of concentrated hydrochloric acid was heated at 60–65° for six hours with rapid stirring. The mixture was allowed to stand overnight. The crystalline product consisting of a mixture of the amide and the acid was washed with water and shaken with a 10% sodium carbonate solution to extract the acid, leaving 2 g. of the insoluble amide. The sodium carbonate extract was acidified with hydrochloric acid to yield 3 g. of γ-tribromobutyric acid which separated in the form of colorless crystals. The analytical sample upon recrystallization from petroleum ether melted at 94–95°. *Anal.* Calcd. for $C_4H_5Br_3O_2$: C, 14.78; H, 1.55; Br, 73.82. Found: C, 14.90; H, 1.60; Br, 73.50.

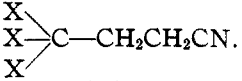
Reaction of Iodoform with Acrylonitrile.—Five grams of aqueous 40% trimethylbenzylammonium hydroxide was added at 20° to a solution of 39.4 g. of iodoform in 50 g. of dioxane. Acrylonitrile (11 g.) was added dropwise while the mixture was stirred at 18–23°. After stirring for twenty-four hours the product was filtered and the yellow solid (6 g.) recrystallized first from nitromethane and then from alcohol to give yellow needles m. p. 132–133°. It is only slightly soluble in benzene, alcohol and acetone. The product is an addition compound $C_6H_5CH_2N(CH_3)_3I \cdot CHI_3$ instead of γ-tri-iodobutyronitrile. *Anal.* Calcd. for $C_{11}H_{17}NI_4$: C, 19.68; H, 2.56; N, 2.09; I, 75.67. Found: C, 19.80; H, 2.64; N, 2.05; I, 75.70. The filtrate did not yield γ-tri-iodobutyronitrile.

The same addition product can be obtained by mixing alcoholic solutions of iodoform and trimethylbenzylammonium iodide.

Acknowledgment.—The analyses of the above compounds were made by Mr. C. W. Nash of these laboratories.

Summary

1. Acrylonitrile reacts in the presence of alkaline catalysts with chloroform and with bromoform to yield γ-trihalo-butyronitriles,



$X_3C—CH_2CH_2CN$. Iodoform did not react with acrylonitrile under the same conditions.

2. From γ-trichlorobutyronitrile and γ-tribromobutyronitrile the corresponding γ-trihalobutyramides and γ-trihalobutyric acids were prepared.

PHILADELPHIA, PA.

RECEIVED DECEMBER 30, 1944

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

2,4:3,5-Dimethylene-L-iditol and Some of its Derivatives

BY RAYMOND M. HANN AND C. S. HUDSON

There is an uncertainty in the literature concerning formaldehyde acetals of iditol. Lobry de Bruyn and Alberda van Ekenstein[1] prepared from L-iditol,[2] formalin and concentrated hydrochloric acid a crystalline acetal which was first designated (p. 8) a trimethylene-L-iditol and later (p. 180) shown to be a dimethylene-iditol; its melting point was 262° and they reported that it was sufficiently soluble in chloroform to permit a reading of its rotation, which was [α]D −8° (*c*, 0.2). They also prepared the enantiomorphous dimethylene-D-iditol. Six years later Bertrand and Lanzenberg[3] prepared an acetal which they reported to be a trimethylene-D-iditol by heating D-iditol, formaldehyde and fuming hydrochloric acid in a sealed tube at 100°; it was not sufficiently soluble in chloroform to permit a reading of its rotation, but the value in glacial acetic acid was "about −35°." It began to sublime on the "bloc Maquenne" at 250° and the crystals hardly melted until about 300–305° ("les cristaux ne fondant guère que vers 300–305°"). It is evident from their statements on p. 1079 that they were not acquainted with Lobry de Bruyn and Alberda van Ekenstein's analysis (p. 180 of reference 1) which showed the composition of a dimethylene acetal of iditol, because they regarded their substance as identical with the "trimethylene" acetal which those workers had made. We have recently had occasion to study the formation of an acetal from L-iditol, 37% aqueous formaldehyde and concentrated hydrochloric acid under various conditions of temperature. Only one acetal has been found and it is readily produced in high yield. The best conditions seem to be slow evaporation of the reactants at room temperature; the yield was 97%. Its melting point is 264–266° in a capillary tube and its $[\alpha]^{20}D$ in glacial acetic acid is +37°; in water the $[\alpha]^{20}D$ value is +39.2°. Its solubility in

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(1) Lobry de Bruyn and Alberda van Ekenstein, *Rec. trav. chim.*, **19**, 8, 180 (1900).

(2) Rosanoff's D and L nomenclature for the iditols is used throughout this article; the letters are the reverse of those used in references 1 and 3.

(3) Bertrand and Lanzenberg, *Bull. soc. chim.*, [3] **35**, 1078 (1906).