

examples of this oxidation reaction¹⁶ are known.¹⁷ Further, the hydrogen bromide generated during the condensation of ethyleneimine with 1-bromo-2-chloroethane may be expected to produce a transient ethyleneimmonium intermediate (*e.g.*, VI) which might then dimerize to the stable piperazine (IV).

In summary, under essentially neutral conditions N,N'-bis(2-chloroethyl)piperazine is one of the most important transformation products of bis(2-chloroethyl)amine. The facile production of this substance (IV) should now be considered when evaluating reactions of nitrogen mustard.

(16) Oxidative cleavage of vicinal amines by manganese dioxide has recently been described by E. F. Curragh, H. B. Henbest, and A. Thomas, *J. Chem. Soc.*, 3559 (1960). See also, H. S. Mosher, "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 686.

(17) For example, see L. Knorr, *Ber.*, **37**, 3516 (1904).

Symmetrical Tricyanobenzenes

CLAUS D. WEIS

*Explosives Department, Experimental Station Laboratory,
E. I. du Pont de Nemours & Company,
Wilmington, Delaware*

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The cumbersome preparation of symmetrical tricyanotrimethylbenzene (I) (tricyanomesitylene) by a stepwise introduction of three cyano groups has been reported.¹ We deemed it of interest to attempt a more facile synthesis of this type of compound.

The Rosenmund-von Braun reaction generally proceeds well with halogen compounds bearing the halogen atoms on nonadjacent carbon atoms. The method is satisfactory even under sterically unfavorable conditions.² Therefore, simultaneous substitution of all three halogens in the 1, 3, 5-positions of substituted benzene derivatives appeared to be quite feasible.

It has now been prepared by the action of the pyridine-copper cyanide adduct on tribromomesitylene. Apparently the reaction proceeded stepwise, since at 170° a small yield (31%) of dicyanobromomesitylene (V) was formed and at 205° I was obtained in 46–56% yield. The crude reaction product could be readily separated from highly colored by-products by filtration of its solution in chloroform through a column of activated alumina. This procedure eliminated the yellow by-products which otherwise could only be removed by repeated recrystallizations involving considerable loss of material. Since the melting point was found to be slightly different from the reported one, the

structure was further supported by the n.m.r. spectrum.

Upon heating I in a mixture of concentrated sulfuric acid and fuming nitric acid symmetrical trinitromesitylene (III) was obtained. This was probably formed from I by successive saponification decarboxylation and subsequent nitration.

Symmetrical tricyanotriethylbenzene (IV) was similarly obtained in 81% yield from symmetrical tribromotriethylbenzene.³

Experimental⁴

Symmetrical Tricyanotrimethylbenzene (I).—Copper cyanide (220 g., 2.46 moles) and pyridine (254 g., 3.30 moles; 260 ml.) were converted into the copper-pyridinium salt. The crude salt was thoroughly mixed with symmetrical tribromotrimethylbenzene (266 g., 0.74 mole) and the mixture in two equal portions heated in a steel autoclave to 205° for a period of 80 min.

The solid material was discharged and heated with hydrochloric acid to remove the pyridine. The mixture was filtered, and the residue heated in dilute nitric acid (1:5) for 5 hr. on a steam bath. After cooling, the black mixture was filtered and the residue dried and extracted with chloroform in a Soxhlet apparatus. The chloroform solution was concentrated and filtered through a column of neutral alumina (Woelm, 1500 mm. × 45 mm.).

Evaporation of the solution to dryness gave almost white crystals (82 g., 56%). Recrystallization from butanol yielded colorless crystals, m.p. 182° (lit. 165°), which started to sublime slowly at about 130°. The compound was soluble in most organic solvents except petroleum ether, hexane, and carbontetrachloride.

Anal. Calcd. for C₁₂H₆N₃: C, 73.84; H, 4.65; N, 21.53. Found: C, 73.77; H, 4.60; N, 21.44.

Absorption in the nitrile band region occurred at 4.50 μ (KBr wafer).

Dicyanobromomesitylene (II).—A mixture of tribromomesitylene (5 g., 0.014 mole), copper cyanide (4.5 g., 0.5 mole), and pyridine (25 ml.) was heated in a sealed tube to 190° for a period of 45 min. The product was heated with an excess of dilute nitric acid (1:5) for 3 hr. on a steam bath. The black residue was filtered off and extracted with ethanol (25 ml.). Concentration and cooling of the solution yielded white crystals, m.p. 189–190° (from ethanol) (1.1 g., 31%).

Anal. Calcd. for C₁₁H₆N₂Br: C, 53.03; H, 3.64; N, 11.24; Br, 32.09. Found: C, 53.24; H, 3.80; N, 11.09; Br, 32.18.

Trinitromesitylene (III).—Tricyanomesitylene (1.0 g., 0.005 mole) was dissolved in a mixture of fuming sulfuric acid (20% oleum) (25 ml.) and fuming nitric acid (30 ml.) and the mixture refluxed for 1 hr. It was then poured onto ice and the colorless crystals (0.71 g., 54.5%), m.p. 233–235° (from chloroform) identified by mixed melting point, m.p. 233–234°, with an authentic specimen of trinitromesitylene.

Symmetrical Tricyanotriethylbenzene (IV).—Tribromotriethylbenzene (142 g., 0.356 mole) was thoroughly mixed with pyridine-copper cyanide (255 g., 1.51 moles). The mixture was divided into two equal parts, pyridine (30 ml.) added to each one, and each heated in a steel autoclave for a period of 70 min.

The solid powdered reaction product was treated with an excess of dilute hydrochloric acid and the solid filtered off and heated with dilute nitric acid (1:5) on a steam bath for 5 hr. The mixture was then filtered and the residue washed with water and dried. The crystalline solid was dissolved

(1) F. W. Küster and A. Stallberg, *Ann.*, **278**, 207 (1887).

(2) R. C. Fuson *et al.*, *J. Am. Chem. Soc.*, **68**, 533 (1946).

(3) M. Markarian, Sydney D. Ross, and Mathew Nazzewska, U. S. Patent 2,695,900 (1954).

(4) All melting points are uncorrected.

in chloroform (200 ml.) and purified by filtration through an alumina column. Evaporation of the chloroform yielded crude IV (70 g., 81%), m.p. 162–164°.

Recrystallization from ethanol gave the pure compound as white crystals, m.p. 165–166°.

Anal. Calcd. for $C_{15}H_{15}N_3$: C, 75.88; H, 6.37; N, 17.71. Found: C, 75.68; H, 6.56; N, 17.67.

Absorption in the nitrile region occurred at 4.49 μ (KBr wafer).

Reaction of *trans*-2-Aminocyclohexanol and Formaldehyde

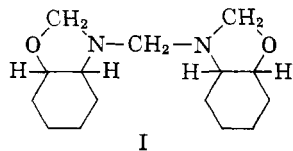
ELBERT W. CRANDALL AND WILLIAM R. VAN HOOZER^{1,2}

Department of Physical Science,
Kansas State College, Pittsburg, Kansas

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Blaha and Kovar³ have suggested that the product from the reaction of *trans*-2-aminocyclohexanol and formaldehyde is bis(4,5-tetramethylene-oxazolid-3-yl)methane (I). Gil-Av⁴ obtained a product from the same reagents, having a molecular weight of 300 and showing no oxazolidine triplet in the infrared. On this basis Gil-Av concluded that 2-aminocyclohexanols do not form oxazolidines.

Because of the discrepancy between these two reports we have studied this reaction further. Blaha and Kovar obtained their product by treating the aminocyclohexanol and formaldehyde in alcoholic potassium carbonate for 24 hours. We have found that the reaction can be carried out by treating *trans*-2-aminocyclohexanol with 37% aqueous formaldehyde at 25°. The reaction was complete after one-half hour to give a white crystalline product melting at 157–158° as compared to 148–150° for the product of Blaha and Kovar. This product was found to have a molecular weight of 266 and elemental analysis gave a molecular formula of $C_{15}H_{26}O_2N_2$.



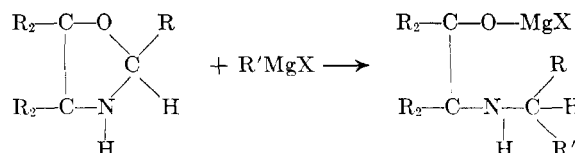
The infrared spectrum of I shows no bands for $C=N$ ($1630\text{--}1670\text{ cm.}^{-1}$ or OH (3650 cm.^{-1}).⁵ Neither is there an oxazolidine triplet at 1100, 1155, and 1190 cm.^{-1} .⁶ An aliphatic ether band is present at 1125 cm.^{-1} . The absence of OH and

$C=N$ bands would eliminate a Schiff base as a possible structure.

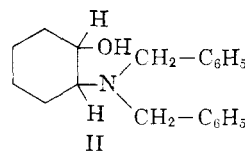
Because of lack of definite evidence for the structure of I by infrared, we have determined the n.m.r. spectrum for this compound.⁷ This spectrum shows five singlet bands at τ values of 5.47, 5.67, 5.76, 5.87, and 6.07 as compared to the protons of tetramethylsilane at a τ value of 10.00. In addition there are two low intensity, broad multiplets with the highest peaks at 6.67 and 7.22, respectively, and a higher intensity broad multiplet with its most intense peaks at 8.26 and 8.73. The four bands at τ values of 5.47, 5.67, 5.87, and 6.07 can be assigned to the hydrogens of a $O-CH_2-N$ structure in which the chemical difference of the two protons gives two resonance lines which are further split by spin-spin coupling. Integration of the area under the curve shows four hydrogens of this type.

The singlet at 5.76 can be assigned to the protons of a $N-CH_2-N$ structure and integrates as two protons. The multiplet at 6.67 and 7.22 can be assigned to the protons of the tertiary carbons in the cyclohexyl ring, the low field multiplet is the signal from the proton adjacent to the oxygen of the oxazolidine ring and the high field multiplet is due to the proton adjacent to the nitrogen. The broad multiplet with the most intense band at 8.73 is assigned to the remaining protons of the two cyclohexyl rings.⁸ These values are in good agreement with the proposed structure I.

Because of the possible oxazolidine structure in I, it was subjected to ring opening by means of Grignard reagent. Senkus⁹ has shown that Grignard reagents will cause ring openings of the following type



Compound I was treated with phenylmagnesium bromide and gave an 86% yield of *N,N*-dibenzyl-2-aminocyclohexanol (II), based on the formation of one mole of II from one mole of I.



Experimental

The Reaction of *trans*-2-Aminocyclohexanol with Formaldehyde.—A solution of 21.4 g. of *trans*-2-aminocyclohexanol in 150 ml. of water was stirred with 22.6 ml. of 37%

(7) The authors wish to express their appreciation to Dr. P. W. K. Flanagan of Continental Oil Co., Ponca City, Oklahoma, for the preparation and interpretation of the n.m.r. spectrum of I.

(8) A. C. Huitric and J. B. Carr, *J. Org. Chem.*, **26**, 2648 (1961).

(9) M. Senkus, *J. Am. Chem. Soc.*, **67**, 1515 (1945).

(1) Present address: Continental Oil Co., Ponca City, Oklahoma.

(2) From the M.S. thesis of William R. Van Hoozer.

(3) R. Blaha and J. Kovar, *Chem. Vesty*, **52**, 77 (1958).

(4) E. Gil-Av, *J. Am. Chem. Soc.*, **81**, 1602 (1959).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, 1954.

(6) E. D. Bergmann, E. Zimkin, and S. Pinchas, *Rec. trav. chim.*, **71**, 168 (1952).