an approximately 50% yield of dark red, cottony needles, m.p. 191–192°.

Anal. Calc'd for $C_{21}H_{18}N_2O$: C, 80.3; H, 5.73; N, 8.92. Found: C, 80.4; H, 5.68; N, 8.80.

2-Nitro-7-acetoxyfluorene. (*a*). A mixture of 0.45 ml. of nitric acid (*d.* 1.42) and 1 ml. of acetic anhydride was added to 0.45 g. of 2-acetoxyfluorene[13] at 60°. The solution was warmed to 80° and held at that temperature for 5 minutes. The solid was separated and washed with acetic acid, water, and then with methanol. It melted at 191–192°. Crystallization from alcohol gave about 0.4 g. (75%) of lustrous, yellow, thread-like needles, m.p. 194–195°.

(*b*). Excess acetic anhydride and 1.14 g. of 7-hydroxy-2-nitrofluorene, m.p. 248–250°, were vigorously refluxed for 1 hour. The mixture was poured into water. Two crystallizations from kerosene and two from alcohol gave feathery yellow crystals, m.p. 191–192°. The mixture melting point with product (*a*) was 191–195°. The infrared spectra of (*a*) and (*b*) in chloroform were identical.

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(13) Claborn and Haller, *J. Am. Chem. Soc.*, 59, 1055 (1937).

A Novel Condensation of Benzonitrile Catalyzed by Mercuric Acetate

YOSHIRO OGATA AND MASARU TSUCHIDA

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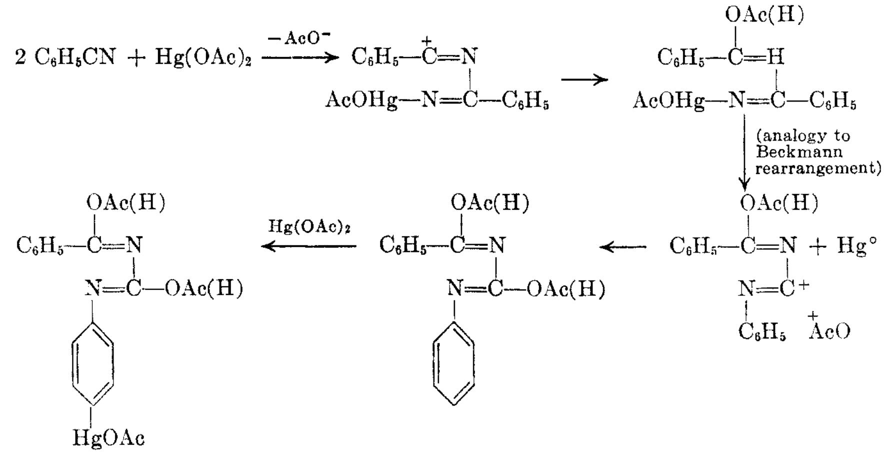
In the course of our investigation on a peculiar orientation in the mercuration of various aromatic compounds in acetic acid,[1] it was noted that no mercuration occurred on the benzene nucleus of benzonitrile. However, the mercurating agent attacked the cyano group, giving a phenyl-rearranged condensate which contained mercury and which on bromination gave N-benzoyl-N′-(*p*-bromophenyl)-urea.

It is of interest to note that this reaction involves a rearrangement of a phenyl group. A plausible course for this rearrangement is assumed tentatively to be that shown in the diag;om below.

The amount of mercury liberated is in agreement with the above stoichiometry. If a sufficient amount of mercuric acetate is used, mercurous acetate is produced instead of mercury.



EXPERIMENTAL

N-Benzoyl-N′-(p-bromophenyl)urea. In a flask provided with a ground glass reflux condenser, there was placed a solution of freshly distilled benzonitrile (7 g.) and commercial mercuric acetate (10 g.) in glacial acetic acid (50 ml.). This was boiled for 7 hours. Deposition of metallic mercury (2.1 g.) was recognized in the reaction mixture. The cooled mixture was poured into a concentrated aqueous solution (200 ml.) of sodium chloride; a small amount of unreacted benzonitrile (*ca.* 2.5 g.) was removed by extraction with ether. An aqueous solution of sodium hydroxide was added with ice-cooling to the clear salt solution until the solution became slightly alkaline. The resulting voluminous white precipitate of the mercuric compound was filtered. The product, suspended in an aqueous solution of potassium bromide, was treated dropwise with bromine. After the gradual disappearance of the solid material, a new precipitate appeared. The precipitate, after recrystallization from aqueous methanol, gave white crystals (m.p. 233°); the yield was 3.8 g. (27%). No melting point depression was observed on admixture with an authentic sample of N-benzoyl-N′-(*p*-bromophenyl)urea prepared by the benzoylation of N-(*p*-bromophenyl)urea.[2]

The yield was somewhat improved to *ca.* 32% by the use of an increased amount of mercuric acetate (1.5 moles per mole of benzonitrile). On addition of aqueous sodium chloride to this reaction mixture, there was obtained a certain amount of a precipitate of mercurous chloride.

Hydrolysis of the mercuration product. Another crop of the mercuric compound was hydrolyzed with 6 *N* sodium hydroxide to yield benzoic acid (m.p. and mixture m.p. 121°), aniline (m.p. of acetanilide and mixture m.p. 115°), and mercuric oxide.

Other related condensations. The reaction did not occur with benzamide or with an equimolar mixture of benzamide and benzonitrile in the presence of a mercuric salt. The same reaction was attempted with the addition of a small amount of acetic anhydride or water, but the condensation was not recognized in either experiment; *i.e.*, the solution containing

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(1) Ogata and Tsuchida, *J. Org. Chem.*, 20, 1637, 1643 (1955).

(2) Moore and Cederholm, *J. Am. Chem. Soc.*, 28, 1191 (1906).

water gave benzamide, and from the solution containing acetic anhydride the benzonitrile was recovered.

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Conversion of a 1,4-Diol to a Lactone by Raney Nickel[1]

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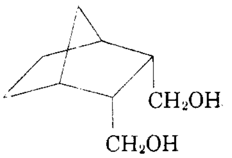
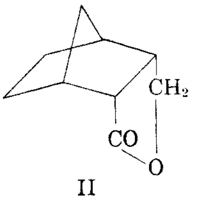
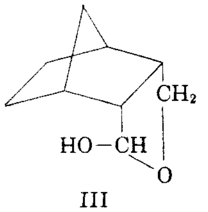
As an incidental observation in another study, we have found that the diol I is converted to the lactone II in excellent yield by a large excess of Raney nickel in boiling benzene. The structure of II is established by its empirical composition, molecular weight (Rast), and properties. Compound II is insoluble in cold alkali, dissolves slowly in hot alkali, and re-precipitates upon acidification. In the infrared spectrum of II, the O—H stretching region is clear, but a single strong absorption in the C=O region occurs at 5.68 μ, whereas I shows strong O—H absorption and no C=O absorption. Compound II is reduced by lithium aluminum hydride to I, and is also found among the neutral products of the controlled oxidation of I with cold potassium permanganate. The latter reaction constitutes an independent synthesis of II.



I



II



III

The dehydrogenation of I to II finds analogies in the nickel-catalyzed conversions of primary and secondary alcohols to aldehydes and ketones,[3] and in the conversion of diols to lactones by copper or copper-chromium oxide.[4] It should be noted that the previous dehydrogenations[3,4] were carried out at high temperatures (usually above 170° and sometimes as high as 300°). The smooth dehydrogenation under much milder conditions in our work may be a consequence of the use of large excesses of nickel, although we made no attempt to establish this point.[4a]

By analogy to the mechanism proposed by Reppe,[4] the formation of II from I would involve formation of a γ-hydroxyaldehyde, of which the cyclic hemiacetal III is a tautomer, and dehydrogenation of the latter.

EXPERIMENTAL[5]

Preparation of 2,3-di-(hydroxymethyl)norbornane (I). The diol has been prepared by Alder and Roth[6] by lithium aluminum hydride reduction of the corresponding dimethyl ester. We have prepared it by lithium aluminum hydride reduction of *endo*-norbornane-2,3-dicarboxylic anhydride. A mixture of 10 g. of lithium aluminum hydride and 250 cc. of anhydrous ether was stirred and heated at reflux. The condensate was passed through a Soxhlet apparatus containing 28.5 g. of the anhydride.[7] When all of the anhydride had dissolved, the mixture was cooled and treated dropwise with 81 cc. of isopropyl alcohol and then with 66 cc. of a saturated sodium chloride solution.[8] The mixture was stirred an additional 30 minutes, the inorganic salts were filtered off, and the filter cake was washed with 2:3 isopropyl alcohol-ether. Evaporation of the filtrate left 21 g. of gummy solid. This material was distilled at 148–150°/1.5 mm. and recrystallized from benzene-hexane to give 9.5 g. of pure I, m.p. 61–62°, reported[6] m.p. 62°.

The *di-p-toluenesulfonate* melted at 128–129°, reported[6] m.p. 131°.

Action of Raney nickel on I. Raney nickel was prepared according to Mozingo.[9] Most of the water was removed by decantation and washing with absolute ethanol. Ethanol and traces of water were removed immediately prior to use by azeotropic distillation with benzene. A mixture of 10 g. of Raney nickel thus prepared, 50 cc. of benzene, and 1.0 g. of diol I was heated at reflux for three hours. The nickel was removed by filtration, the filter cake washed well with benzene, and the filtrate evaporated. Crystallization of the

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)1544.

[2] Present address: Department of Chemistry, University of Florida, Gainesville, Florida.

(3) *Cf. inter alia* borneol or isoborneol → camphor (a) M. M. Korotaeva and M. P. Kochneva, *J. Chem. Ind.* (*U.S.S.R.*), 52 (1933); *Chem. Abstr.*, **28**, 138 (1934). (b) *Elsevier's Encyclopedia of Organic Chemistry*, edited by E. Josephy and F. Radt, Elsevier Publishing Co., New York, N. Y., 1948, Vol. **12A**, p. 745. See also (c) L. Palfray and S. Sabatay, *Compt. rend.*, **208**, 109 (1939). (d) L. Palfray, S. Sabatay, and A. Halasz, *Compt. rend.*, **208**, 1654 (1939). (e) A. Halasz, *Ann. chim.*, **14**, 318 (1940).

(4) W. Reppe and co-workers, *Ann.*, **596**, 158 (1955).

(4a) A referee has pointed out the possibility that benzene may act as a hydrogen acceptor in this reaction.

(5) Melting points are corrected. The microanalyses are by Dr. Adalbert Elek, Elek Microanalytical Laboratories, 4763 W. Adams Blvd., Los Angeles, Calif.

(6) K. Alder and W. Roth, *Ber.*, **87**, 161 (1954).

(7) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(8) This elegant method of decomposing lithium aluminum hydride reduction mixtures to facilitate isolation of water-soluble products was devised by R. F. Brown and N. M. van Gulick, *J. Am. Chem. Soc.*, **77**, 1079 (1955).

(9) R. Mozingo, *J. Am. Chem. Soc.*, **65**, 1013 (1943).