

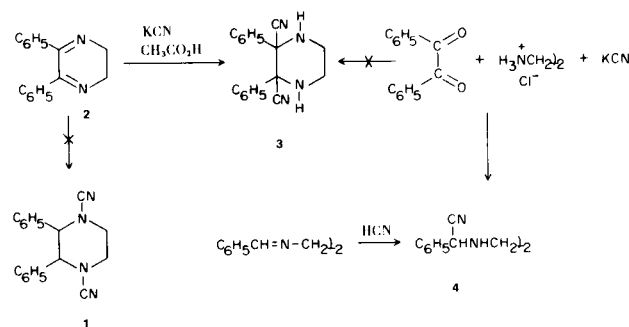
The Formation of 2,3-Dicyano-2,3-diphenylpiperazine from 2,3-Diphenyl-5,6-dihydropyrazine and Hydrogen Cyanide.

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Received August 10, 1971

The recent report (1) confirming an earlier assignment (2) that 1,4-dicyano-2,3-diphenylpiperazine (**1**) is the product of the reaction of 2,3-diphenyl-5,6-dihydropyrazine (**2**) with hydrogen cyanide attracted our attention because if the assignment is correct, the reaction would be an example of heterophilic addition (3) to an imine bond. The principal evidence supporting the structure as **1** is the fact that the product is different from that of the expected product 2,3-dicyano-2,3-diphenylpiperazine, (**3**) (1). The structure of **3** in turn is based largely on its synthesis from benzil, ethylenediaminedihydrochloride and potassium cyanide (4). We have found that the products of these reactions have structures different from those previously assigned. The dihydropyrazine **2** gives the expected adduct **3** and the material previously assigned the structure **3** is, in fact, *N,N'*-bis-(α -cyanobenzyl)ethylenediamine (**4**).



The structure of **3** follows from its method of preparation from **2** and its analytical and spectral properties. The ir spectrum establishes the presence of C \equiv N and NH functionality while the nmr spectra shows ten aromatic hydrogens, four methylene protons adjacent to nitrogen, and two protons bound to nitrogen.

The nmr spectrum obtained after shaking the deuteriochloroform solution with deuterium oxide is especially informative as the protons bound to nitrogen have been exchanged and the methylene proton remaining constitute a fourteen line AA'BB' multiplet. Assignment of the structure of the material from the reaction of benzil, ethylenediaminedihydrochloride, and potassium cyanide

as **4** is consistent with its spectral properties and established by its identity with the product of the reaction of dibenzalethylenediamine and hydrogen cyanide. The mechanism for the formation of **4** has not been elucidated. However, the fragmentation of the dicyanohydrin of benzil into benzoyl cyanide and benzaldehyde cyanohydrin can be envisioned with the latter serving as a source of benzaldehyde (**5**) to give **4** by condensation routes.

EXPERIMENTAL

Melting points are corrected. The nmr spectra were obtained on a Varian A-60A spectrometer and the chemical shifts are reported in δ (ppm) relative to TMS as an internal standard. Infrared spectra were measured on Perkin-Elmer model 137, 237B or 521 spectrometers. Mass spectra were obtained by Mr. J. C. Cook and associates on an Atlas CH5 mass spectrometer. Microanalyses were carried out by Mr. J. Nemeth and associates.

2,3-Dicyano-2,3-diphenylpiperazine (**3**).

Potassium cyanide (**1**) and acetic acid in ethanol gave **3** in 52% yield (1,2), m.p. 205-206° (lit. (1), 203-204°); ir (Nujol) 3311 (NH) and 2237 cm⁻¹ (C \equiv N); nmr (deuteriochloroform) δ 7.32 (m, 10, C₆H₅), 3.4 (m, 4, -N-CH₂-CH₂-N-), 2.30 (br. s, 2, NH); mass spectrum (70 eV) *m/e* (rel. intensity) 288 (57.7, m⁺), 158 (57.2), 157 (38.2) 104 (100.0), 103 (61.1).

Anal. Calcd. for C₁₈H₁₆N₄: C, 74.97; H, 5.59; N, 19.43. Found: C, 74.92; H, 5.82; N, 19.64.

N,N'-Bis-(α -cyanobenzyl)ethylenediamine (**4**).

Dibenzalethylenediamine and hydrogen cyanide gave **4** in 27% yield (1), m.p. 120-122° (lit. (1) 128°); ir (Nujol) 3279 (NH) and 2227 cm⁻¹ (C \equiv N); nmr (deuteriochloroform) δ 7.45 (m, 10, C₆H₅), 4.85 (s, 2, -CH-N-), 2.97 (s, 4, -N-CH₂CH₂-N-), 2.30 (s, 2, NH).

Anal. Calcd. for C₁₈H₁₈N₄: C, 74.46; H, 6.25; N, 19.29. Found: C, 74.39; H, 6.24; N, 19.20.

Reaction of benzil, potassium cyanide and ethylenediamine-hydrochloride in methanol (2,4) gave **4** in 17% yield; m.p. 118-119° (lit. 123° (2), 128° (1)) mixed m.p. with authentic material 118-119°. The ir and nmr were identical with authentic material but the sample from the benzil reaction was faintly brown, whereas the authentic material was white.

Acknowledgment.

We are grateful to the National Institutes of Health (GM-12595) for partial support of this work.

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