

Borohydride Reduction of 1,3,5-Tricyanobenzene to 1,3,5-Tricyanocyclohex-1-ene

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Summary 1,3,5-Tricyanobenzene (I) was reduced by sodium borohydride to 1,3,5-tricyanocyclohex-1-ene.

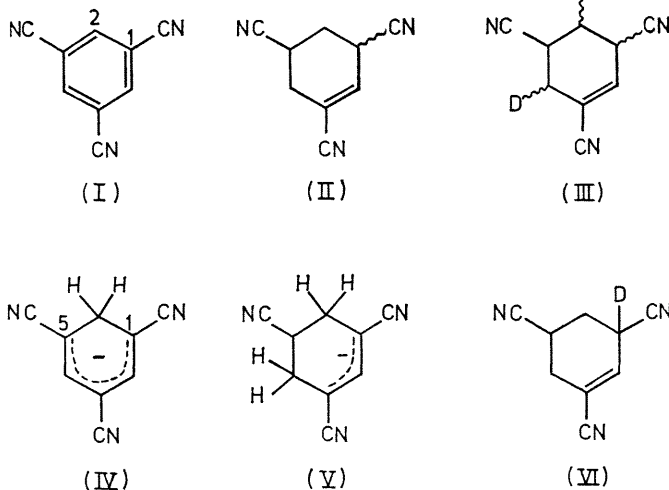
QUANTUM-CHEMICAL calculations^{1,2} using semi-empirical LCAO-MO methods suggest that nucleophilic attack on compound (I) would occur at C-2. To check this prediction we treated an ethanolic solution of (I) with sodium borohydride at room temperature (ca. 20°) for 6 h.

Chromatography of the mixture on silica gel [with benzene-chloroform (1:2) as eluant] afforded starting material (I) (32%); compound (II), † C₉H₇N₃, (45%), m.p. 80–81°, ν_{\max} (CHCl₃) 1650 (C=C), 2230 (conj. C≡N), and 2250 (non-conj. C≡N) cm⁻¹; τ (CDCl₃) ca. 3.4 (m, 1H), ca. 6.2 (m, 1H), ca. 6.9 (m, 1H), ca. 7.2 (m, 2H), ca. 7.8 (m, 2H), and also the 4,6-dideuterio-derivative (III) †, m.p. 73–74°, ν_{\max} (CHCl₃) 2370 (C–D) cm⁻¹, τ (CDCl₃) ca. 3.3 (m, 1H), ca. 6.2 (m, 1H), ca. 6.8 (m, 1H), ca. 7.3 (m, 1H), ca. 7.7 (m, 1H) and deuteriated (I), ν_{\max} (CHCl₃) 2310 (C–D) cm⁻¹.

Reduction of (I) appears to proceed *via* the sigma-complex (IV) which, after protonation at C-1 or C-5, undergoes reduction to ion (V). The conjugated species (V) corresponds to the ionised form of (II), allowing for the ready deuterium-hydrogen exchange at position 3 of (II) by deuterium oxide to give (VI) † τ (CDCl₃) ca. 3.1 (m, 1H), ca. 6.0 (m, 1H), ca. 7.2 (m, 2H), ca. 7.5 (m, 2H). Attempts to prepare (II) from (I) using lithium aluminium hydride failed. Only the air-sensitive red precipitate of (IV) [ν_{\max} (Nujol) 2183 cm⁻¹ (conj. C≡N)] was obtained; its hydrolysis is being studied.

In contrast to the borohydride reduction of 1,3,5-trinitrobenzene to 1,3,5-trinitrocyclohexane,³ in this case the intermediate (V) is stable towards the reducing agent and the reaction stops at the cyclohexene step. Similarly, reduction of 3-nitropyridine affords 3-nitropiperidine⁴ but 3-cyanopyridine gave the corresponding tetrahydro-derivative.⁴

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† Mass spectra of the compounds were consistent with the assigned structures. All n.m.r. measurements were performed at 60 MHz.

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⁴ S. Yamada and Y. Kikugawa, *Chem. and Ind.*, 1966, 2169.