

REACTION OF 1,3,5-TRICYANOGENE WITH COMPLEX HYDRIDES*

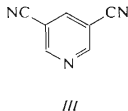
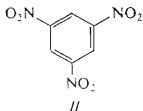
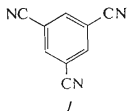
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1,3,5-Tricyanobenzene (*I*) affords with complex hydrides in aprotic media a stable σ -complex *VII*. In protic media, one part of this complex is reconverted to the starting compound *I* while the other part undergoes reduction to 1,3,5-tricyanocyclohexene (*IV*). The reactivity of compound *I* and the assumed reduction intermediate is discussed in terms of a simple HMO theory.

The quantum chemical calculations of cyano derivatives of the benzene and pyridine series¹⁻³ led to conclusions that positions 2, 4, or 6 in 1,3,5-tricyanobenzene (*I*) should be highly reactive towards nucleophilic agents^{1,2}. As shown by experiments of Severin and coworkers^{4,5}, the electronically similar 1,3,5-trinitrobenzene (*II*) reacts readily with sodium borohydride and Grignard reagents with the formation of the corresponding cyclohexane derivatives. It appeared of interest to verify the validity of the so called Ehrlich rule⁶; according to this rule, the tricyano derivative *I* should display similar properties as the analogous heterocycle carrying a heterocyclic nitrogen atom instead of the original cyano group, namely, 3,5-dicyanopyridine (*III*). Since compound *III* virtually undergoes an easy reduction with complex hydrides⁷⁻⁹, we have now examined such a reduction also in the case of the benzene derivative *I*.

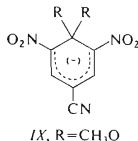
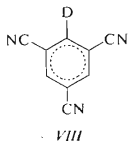
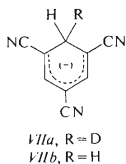
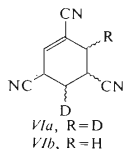
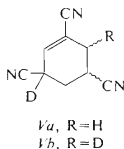
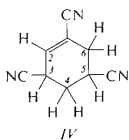


The reaction of compound *I* with sodium borohydride occurs at room temperature. The resulting red-orange precipitate, somewhat soluble in water, loses the colour and is decomposed by the addition of dilute aqueous acetic acid. The reaction mixture affords 32% by weight of the starting compound *I* and 45% by weight of a crystalline compound $C_9H_7N_3$ which was ascribed the structure of 1,3,5-tricyanocyclohexene

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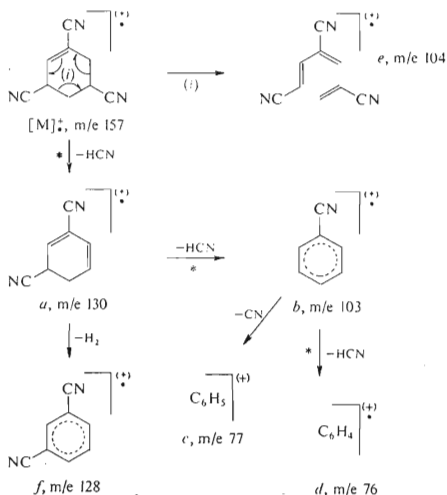
(IV). The IR spectrum of compound IV displays absorption bands corresponding to stretching vibrations of the C=C bond, conjugated and nonconjugated C≡N group, and aliphatic CH bonds; absorption bands of stretching vibrations of the aromatic CC bonds (1500–1600 cm⁻¹) and NH bonds (3100–3600 cm⁻¹) are absent. The PMR spectrum (at 60 MHz) exhibits five multiplets, namely, of an olefinic proton at position 2 (at 3.4τ), methine protons at positions 3 and 5 (at 6.2τ and 6.9τ), and methylene protons at positions 6 and 4 (at 7.2τ and 7.8τ). These data confirm the constitution IV but do not allow to determine the relative configuration of the two cyano groups at positions 3 and 5. As indicated by the sharp melting point and the homogeneous behaviour in thin-layer chromatography, one of the two possible racemates is obviously involved. This assumption is in accord with disappearance of the 6.9τ signal in PMR spectrum when compound is refluxed with deuterium oxide. In view of the ready exchange of the hydrogen atom at position 3 with the primary formation of the monodeuterio compound Va, an epimerisation could take place at the reaction center mentioned during chromatography on silica gel with the exclusive formation of the energetically more advantageous diastereoisomer. The assignment of the 6.9τ signal to the hydrogen proton at position 3 is also in accordance with the higher multiplicity of the 6.2τ signal in the PMR spectrum of the nondeuterated compound IV when compared with the signal at 6.9τ. The methylene multiplet at 7.8τ may be ascribed to hydrogen protons at position 4. According to the more rigorous mass-spectrometrical analysis of products, compound Va undergoes an additional deuteration at position 6; after a prolonged treatment with deuterium oxide, the reaction mixture thus consists from the deuterated derivatives Va and Vb.

To obtain more detailed informations on the mechanism of the borohydride reduction of compound I, we have also examined products of the sodium borodeuteride treatment of compound I. After this treatment, both 1,3,5-tricyanocyclohexene



and 1,3,5-tricyanobenzene contain deuterium. The IR spectrum of the deuterated compound *IV* exhibits bands of the CDH stretching vibration at 2310 cm^{-1} and the intensities of bending and stretching vibrations of CH_2 groups at 1440, 1455, and 2975 cm^{-1} are decreased in comparison with the IR spectrum of the original compound *IV*. In the PMR spectrum of the deuterated compound *IV*, there are decreased multiplet intensities at 7.2τ and 7.7τ ; the ratio of integral intensities paraffinic/olefinic protons is changed from the original value of about 6.6 with compound *IV* to about 5.4 in the case of the deuterated product. As shown by quantitative evaluation of mass spectra in the molecular ion region, the primarily formed dideuterio derivative *VIa* undergoes partially a protodeuteration at the "allylic" position 6 by the action of ethanol serving as solvent, with the formation of the monodeuterio derivative *VIb*.

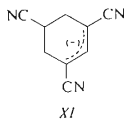
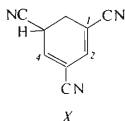
The structure of compounds *IV–VI* was confirmed by mass spectra. The main fragmentation paths of compound *IV* at 70 eV are shown in Scheme 1. The molecular ion $[\text{M}]^+$ of m/e 157 (r.i. 38%) splits off hydrogen cyanide with the formation of the *a*-ion, m/e 130, which represents the most abundant species. Elimination of another molecule of hydrogen cyanide from the particle *a* leads to the *b*-ion of m/e 103, the additional fragmentation of which affords the *c*- and *d*-ions of 77 and 76 m/e , resp. (metastable ions of m/e 107.5, 81.8, and 57.4). In the retro-Diels-Alder fragment-



ation of the molecular ion, acrylonitrile is split off with the formation of the e -ion of m/e 104. The relatively abundant ionic species of m/e 129 (r.i. 47%) is formed either by expulsion of a hydrogen atom from the a -ion or from the M-1 ion by elimination of hydrogen cyanide. The ionic species of m/e 128 (r.i. 42%) of the probable structure f is obviously formed by a similar mechanism. The spectra of the deuterated analogues V and VI confirmed the proposed fragmentation mechanisms of compound IV with respect to the expected mass shift of some ionic species. With the mixture of compounds Va and Vb or VIa and VIb , the masses are gradually degraded in the sequence m/e 159, 158, 157 \rightarrow m/e 132, 131, 130 \rightarrow m/e 104, 103 \rightarrow m/e 79, 78, 77, 76 with the corresponding metastable m^* 108.5 and 82.5 ions, and finally the ionic species of m/e 105 formed by the retro-Diels-Alder degradation of the molecular monodeuterated ion of m/e 158. Increase of peaks in the above-mentioned spectral regions of the deuterio derivatives V and VI with respect to the spectrum of the nondeuterated compound IV results, however, in a negligible change of the $\sum_{128}^{133}/\sum_{40}$, $\sum_{103}^{107}/\sum_{40}$, and \sum_{75}^{79}/\sum_{40} values; consequently, the charge in these regions is transferred by analogous ionic species.

The presence of deuterium in 1,3,5-tricyanobenzene isolated after the reaction with sodium borodeuteride indicates that a nucleophilic exchange of the hydrogen atom at position 2 of compound I also takes place. It is most probable that a proton of the primarily formed σ -complex $VIIa$ undergoes under the reaction conditions a rearomatisation with the formation either of compound I (e.g., $VIIa + C_2H_5OH \rightarrow I + C_2H_5O^- + HD$) or the deuterio derivative $VIII$ (e.g., $VIIa + C_2H_5OH \rightarrow VIII + C_2H_5O^- + H_2$). From relative intensities of molecular ions of compounds I and $VIII$ (m/e 153 and 154) in the resulting product there was estimated the molar ratio $VIII/I$ as about 2.2; elimination of deuterium from the anion $VIIa$ thus appears somewhat more difficult than that of hydrogen.

In the reaction of compound I with lithium aluminumhydride, in ether, a red-brown precipitate is immediately formed. In the IR spectrum of this precipitate, the band of one absorption maximum of $C\equiv N$ bonds (2185 cm^{-1}) is markedly decreased in contrast to that of compound I (2254 cm^{-1} ; cf.²) but corresponds to that of the Meisenheimer complex IX (2198 cm^{-1} ; cf.¹⁴). A primary product of the nucleophilic attack on compound I is obviously involved and its structure might be expressed by the formula $(VIIb)_n AlH_{4-n}Li$. A mixture of compounds is obtained by hydrolysis of the intermediary precipitate; we did not succeed, however, in proving the presence



of the cyclohexene derivative *IV* in the resulting mixture of compounds. A lesser amount of compound *I* was isolated after decomposition of the precipitate with iodine. The treatment with lithium aluminodeuteride afforded the expected mixture of compound *I* and the monodeuterio derivative *VIII* in the molar ratio of about 1.5, *i.e.*, in a similar ratio as in the case of the borodeuteride reduction.

The results of reductions of compound *I* with complex hydrides may be concluded as follows. In an aprotic medium (the aluminohydride reduction), the reaction is interrupted at the stage of the σ -complex *VII*, while in ethanol, the intermediate *VII* is reduced to compounds *IV* or *VI*.

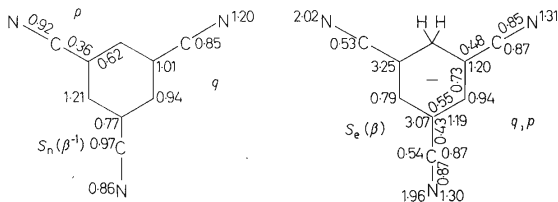


FIG. 1
HMO Molecular Diagrams Calculated for *I* and *VII*

Fig. 1 shows molecular diagrams calculated by the simple HMO method for compound *I* and the anion *VII* which is in the first approximation identical with the Wheland activated complex for the nucleophilic attack of the molecule *I* at position 2. The magnitude of the CN π -bond orders are in the case of the compound *I* model higher, *i.e.*, in accordance with the above mentioned shift of the stretching vibration wavenumbers in the IR spectrum, and indicate thus a higher conjugation of nitrile groups in the anion *VII*. The experimental behaviour is also in accord with dynamic indices of chemical reactivity. The nucleophilic superdelocalizability S_n for compound *I* shows the highest value in the virtually attacked position 2 ($1.21\beta^{-1}$) and in the same position, the analogous atomic localization energy L_n is considerably lower (2.11β) than in position 1 (2.92β). Furthermore, the corresponding Wheland complex contains in the latter case a nonbonding HMO (0.00β) indicating instability and a low formation probability of this intermediate. From the HMO molecular diagram of the anion *VII*, the probable subsequent course of the borohydride reduction of the aromatic nucleus may also be inferred. The unusually high S_e electrophilic superdelocalizabilities at positions bearing the nitrile groups ($3.07\beta^{-1}$ and $3.25\beta^{-1}$, resp.) may be taken as indices expressing the ready protonation of the anion *VII* by the protic solvent (*e.g.*, ethanol) with the intermediary formation of the dihydro

derivative *X*. The subsequent nucleophilic attack of the BH_4^- reagent at position 4 of the dihydro derivative *X* affords the anion *XI* (resistant towards any additional reduction) from which the product *IV* is finally formed.

EXPERIMENTAL

Temperature data are uncorrected. Melting points were taken on a heated microscope stage (Boetius block). The IR spectra were measured on a Zeiss (Jena) Model UR 10 spectrometer in chloroform solutions or by the KBr technique. The UV spectra were recorded on an Optica Milano Model CF 4 NI apparatus (ethanol as solvent). The PMR spectra were taken on a Tesla BS 477 spectrometer (in CDCl_3 ; stable frequency 60 MHz). The mass spectra were measured on an AB Stockholm Model LKB 9000 apparatus. Chromatography was performed on silica gel, particle size 0.07–0.20 cm (Lachema, Brno, Czechoslovakia). The HMO calculations were carried out by means of a standard program (author, Dr V. Kvasnička) on a NE 803b computer with $h_{\text{N}} = 0.5$ and $k_{\text{C}\equiv\text{N}} = 1.4$ empiric parameters¹⁰. For the other atomic centers and bonds, the following parameter values were used: $h = 0$ for the coulombic integral and $k = 1$ for the exchange integral.

1,3,5-Tricyanobenzene (*I*)

The reported² procedure afforded compound *I*, m.p. 210–214°C (after sublimation in vacuum) in accordance with reported^{2,11} data; after repeated crystallisations from benzene, m.p. 257–258°C reported^{12,13}, m.p. 254–263°C). The solutions of both modifications exhibit identical spectra. Mass spectrum, m/e (r.i., %): 154 (11), 153 (100), 127 (6), 126 (13), 101 (7), 100 (9), 76 (9), 75 (24), 64 (6), 51 (10), and 50 (8).

Reaction with sodium borohydride. A mixture of compound *I* (2 g), sodium borohydride (2.5 g), and ethanol (125 ml) was stirred at room temperature for 6 h, concentrated under diminished pressure to half of its original volume, the concentrate decomposed with a 5 : 1 mixture of water and acetic acid (150 ml) (the original orange colour disappeared), extracted with five portions of chloroform (total, 150 ml), the extract dried over anhydrous magnesium sulfate, and evaporated to dryness. The residue (2.36 g) was dissolved in a little benzene–chloroform (1 : 1) and chromatographed on a column of silica gel (115 g). About 5 ml fractions were taken and their content checked by thin-layer chromatography on silica gel in 2 : 1 chloroform–benzene; the spots were detected by iodine vapours and viewed under UV light. Fractions 1–49 contained 253 mg of a mixture of compounds, m.p. 110–230°C; IR spectrum: 2250 and 2240 cm^{-1} , $\nu(\text{C}\equiv\text{N})$; 1730 cm^{-1} , $\nu(\text{C}=\text{O})$; 1635 cm^{-1} ($\text{C}=\text{C}$); this mixture was not investigated in detail. Fractions 50–87 afforded 635 mg (32%) of compound *I*. Fractions 88–121 (a strong chromatographic spot after treatment with iodine vapours) contained 925 mg (45%) of compound *IV*, m.p. 80–81°C (benzene). For $\text{C}_9\text{H}_7\text{N}_3$ (157.2) calculated: 68.77% C, 4.49% H, 26.74% N; found: 68.70% C, 4.71% H, 26.69% N. IR spectrum: 3030 cm^{-1} , $\nu(\text{HC}=\text{C})$; 2950, 2920, and 2880 cm^{-1} , $\nu(\text{CH}_2, \text{CH})$; 2250 and 2230 cm^{-1} , $\nu(\text{C}\equiv\text{N})$; and 1650 cm^{-1} , $\nu(\text{C}=\text{C})$. PMR spectrum: multiplets centered at 3.4 τ (1 H), 6.25 τ (1.1 H), 6.87 τ (1.1 H), 7.25 τ (2.2 H), 7.77 τ (2.2 H). Mass spectrum, m/e (r.i., %): 157 (38), 130 (100), 129 (46), 128 (42), 104 (35), 103 (40), 76 (38), 75 (15), 65 (12), 55 (30), 52 (26), 51 (20).

Reaction with sodium borodeuteride. The reaction of compound *I* (0.8 g) with sodium borodeuteride (1 g) in ethanol (50 ml) was performed analogously to the preceding paragraph and the crude product (860 mg) was chromatographed on silica gel (193 g). Elution with 1 : 1 benzene–

—chloroform afforded 499 mg of a mixture of compounds *I* and *VIII*; m.p. 238–251°C; IR spectrum: 3080 cm^{-1} , $\nu(\text{CH arom.})$; 2310 cm^{-1} , $\nu(\text{CD arom.})$; 2250 cm^{-1} , $\nu(\text{C}\equiv\text{N})$; 1855 cm^{-1} 2 γ (CH arom.); 1430 cm^{-1} , $\nu(\text{CC arom.})$; mass spectrum, m/e (r.i., %): 155 (12), 154 (100), 153 (43), 127 (8), 126 (8), 76 (10), and 75 (17). Elution with chloroform afforded 118 mg of a mixture of the deuterio derivatives *Va* and *Vb*; m.p. 73–75°C (after washing with light petroleum and drying in the vacuum of an oil pump; IR spectrum: 3060 cm^{-1} , $\nu(\text{HC}\equiv)$; 2955, 2925, and 2875 cm^{-1} , $\nu(\text{CH}_2, \text{CH})$; 2370 cm^{-1} , $\nu(\text{CDH})$; 2250 and 2230 cm^{-1} , $\nu(\text{C}\equiv\text{N})$; and 1645 cm^{-1} , $\nu(\text{C}=\text{C})$; PMR spectrum: five multiplets at 3.35 τ (1 H), 6.20 τ (1.1 H), 6.83 τ (1.1 H), 7.26 τ (1.7 H), and 7.70 τ (1.5 H); mass spectrum, m/e (r.i., %): 159 (11), 158 (35), 157 (12), 132 (33), 131 (100), 130 (51), 105 (41), 104 (57), 103 (18), 79 (11), 78 (33), 77 (41), 76 (21), 64 (31), 52 (40), 27 (26); calculated: 10% d_0 , 70% d_1 , and 20% d_2 .

Reaction with lithium aluminohydride. To a stirred suspension of lithium aluminohydride (100 mg) in ether (50 ml) there was added dropwise a solution of compound *I* (100 mg) in ether (100 ml); a red-brown precipitate was formed. The whole mixture was refluxed for 2 h and then kept overnight. Attempts to obtain the primary product by filtration under nitrogen and drying in the vacuum of an oil pump resulted in a spontaneous exothermic destruction of the sample; the precipitate was therefore in another experiment collected by centrifugation and transferred into a paraffin oil suspension to make possible spectral measurements. The IR spectrum of this suspension exhibited absorption maxima at 2185 and 2240 cm^{-1} , $\nu(\text{C}\equiv\text{N})$, and at 1520 and 1595 cm^{-1} , $\nu(\text{C}=\text{C}$ and $\text{Al}-\text{H}$, resp.). Decomposition of the precipitate with dilute aqueous acetic acid in an ethanolic suspension affords (as shown by thin-layer chromatography) a mixture of several compounds of a similar R_f value, including compound *I*. In another experiment, the precipitate was not separated, but its ethereal suspension was treated dropwise under stirring with a solution of iodine (1.34 g) in ether (30 ml). The mixture was stirred for 8 h, kept at room temperature for 48 h, and decomposed under stirring by the addition of water (100 ml). The ethereal layer was washed with water, 1% aqueous sodium hydride (50 ml), and 10% aqueous sodium thiosulfate (50 ml), dried, and evaporated. The residue was sublimed at 100–110°C/1.2 Torr to afford 10 mg of compound *I*, m.p. 238–240°C, identified by comparison of the mass spectrum with that of the authentic specimen.

Reaction with lithium aluminodeuteride. The reaction of compound *I* (100 mg) with lithium aluminodeuteride (100 mg) and treatment of the reaction mixture with iodine (see the preceding paragraph) afforded (after repeated sublimations of the reaction product at 100–120°C/1.5 Torr) 17 mg of a mixture (m.p. 215–220°C) of compounds *I* and *VIII* (2 : 3), identified by mass spectrum (m/e 154, 100%; m/e 153, 67%).

Reaction with methylmagnesium iodide. A solution of compound *I* (110 mg) in benzene (50 ml) and ether (18 ml) was added with stirring to the title Grignard reagent ($2.88 \cdot 10^{-3}$ mol) in ether (30 ml), and the mixture kept at room temperature for 20 min. The resulting orange precipitate was filtered off under nitrogen and the solvent removed under diminished pressure (found: 12.37% Mg and 42.60% *I*); the nujol suspension was prepared by the earlier reported¹⁵ technique. IR spectrum: 435 and 490 cm^{-1} , $\nu(\text{Mg}-\text{C})$; 1049 cm^{-1} ; 1506 and 1605 cm^{-1} , (C=C conj.); 2183 and 2280 cm^{-1} , $\nu(\text{C}\equiv\text{N})$. The hydrolytical decomposition of the precipitate affords a mixture of unidentified products.

Reaction of Compound *IV* with Deuterium Oxide

A mixture of compound *IV* (50 mg) and deuterium oxide (30 ml) was refluxed for 3.5 h under exclusion of atmospheric moisture, the solvent evaporated, and the whole process repeated once more. The residue was then washed with light petroleum and dried in the vacuum of an oil pump

to afford 48 mg of a mixture of the deuterio derivatives *Va* and *Vb*. PMR spectrum: four multiplets centered at 3.1 τ (1 H), 6.0 τ (0.9 H), 7.18 τ (2.1 H), and 7.52 τ (2 H). Mass spectrum, *m/e* (r.i., %): 159 (13), 158 (37), 157 (18), 132 (18), 131 (100), 130 (63), 104 (57), 103 (21), 79 (21), 78 (22), 77 (48), 76 (21); calculated: 20% *d*₀, 60% *d*₁, 20% *d*₂.

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