

SHORT
COMMUNICATIONS

Mechanism of Hydrogenation of 1,3,5-Trinitrobenzene and 1,3-Dinitrobenzene Derivatives in Reactions with Alkali Metal Tetrahydridoborates

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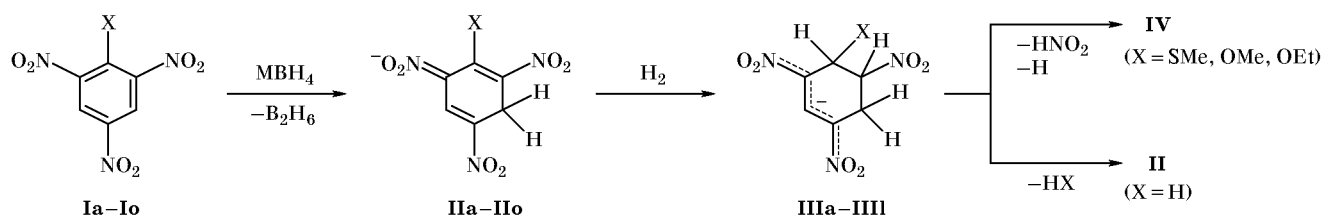
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Reactions of 1-substituted 2,4,6-trinitrobenzenes with hydridoborate complexes characteristically result in replacement of the 1-substituent by hydrogen [1, 2], whereas 1-X-2,4-dinitrobenzenes react with NaBH₄ to give products of hydrogenolysis of the 2-nitro group [3]. By studying the reactions of potassium (sodium) tetrahydridoborate with a series of 1-X-2,4,6-trinitrobenzenes and 1-X-2,4-dinitrobenzenes in DMSO-*d*₆ by ¹H NMR spectroscopy (in some cases, by ¹³C NMR) we revealed a general mechanism of the process which was different from the direct [1] or vicinal [3]

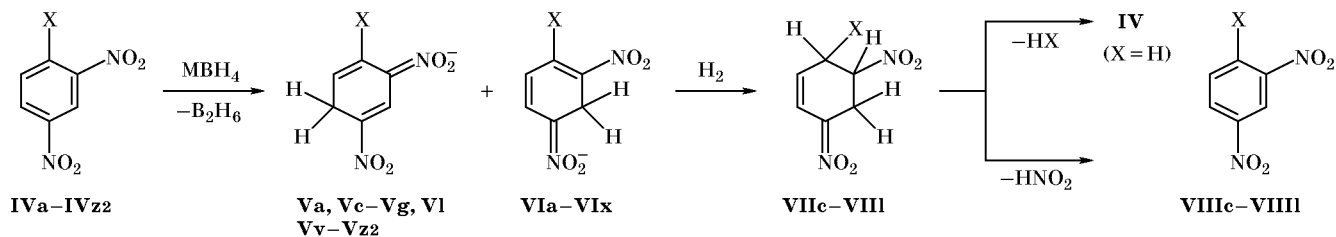
attack by hydride ion on the leaving group. In both series, the initial stage was addition of hydride ion at unsubstituted carbon atom of the aromatic ring to give H-σ₃-complexes of trinitro compounds (Scheme 1) or isomeric H-σ₃/H-σ₅-adducts with *m*-dinitrobenzene derivatives (Scheme 2); here, the subscript at σ denotes the site of nucleophile addition to the substrate. In DMSO-*d*₆ containing traces of moisture and absorbed oxygen, the next stage is formation of molecular hydrogen according to Scheme 3. The signal at δ 4.615 ppm in the ¹H NMR spectrum belongs to

Scheme 1.



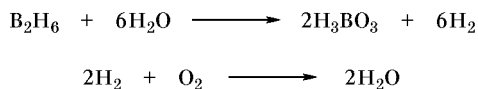
X = H (a), OH (b), OMe (c), OEt (d), NHMe (e), NMe₂ (f), CO₂H (g), CO₂Me (h), Cl (i), SMe (j), SC₆H₂(NO₂)₃-2,4,6 (k), SC₆H₃(NO₂)₂-2,4 (l), NH₂ (m), CH₃ (n), CH₂COCH₃ (o).

Scheme 2.



M = K, Na; X = H (a), OK (b), OMe (c), OEt (d), OCH₂CH₂Cl (e), Cl (f), Br (g), NMe₂ (h), SMe (i), SPh (j), SC₆H₄NO₂-4 (k), SOMe (l), Me (m), CH₂COMe (n), NH₂ (o), NHMe (p), NHPh (q), NHCOME (r), NHHNH₂ (s), NHCOPh (t), NHCOC₆H₄NO₂-4 (u), SC₆H₃(NO₂)₂-2,4 (v), SOPh (w), SOC₆H₄NO₂-4 (x), SO₂Me (y), SO₂Ph (z), SO₂C₆H₄NO₂-4 (z1), SO₂C₆H₃(NO₂)₂-2,4 (z2).

Scheme 3.



molecular hydrogen absorbed by the solvent. The energy released in reactions outlined in Scheme 3 promotes hydrogen addition at the most activated double bond in the ring of H- σ_3 -complexes, which involves the substituent X and nitro group (Schemes 1 and 2). The double bond at C¹ in σ -adduct **II** (X = NH₂) is deactivated due to donor effect of the amino group; therefore, molecular hydrogen adds at the double bond at C⁴ to form 1-amino-2-*aci*-nitro-4,6-dinitro-5-cyclohexene potassium (or sodium) salt **IX**. In the ¹H NMR spectra of compounds **III** (X = H) and **IX** the signal of the proton neighboring to the nitro group appears as a quintet ($J \approx 5.5$ Hz) in the region δ 5.2–5.0 ppm, and signals from nonequivalent axial and equatorial protons in positions 3 and 5 are doublets of doublets ($J_{ax-eq} \approx 16$ Hz) in the region δ 3.7–2.7 ppm. In the ¹³C NMR spectra of the same adducts, the signal from the sp^3 -carbon atom attached to the nitro group (C² and C⁴, respectively) is observed at $\delta_C \sim 78$ ppm; in the off-resonance spectrum it is split into a doublet, indicating that there is a proton attached thereto.

Adducts **IIIb–III** undergo decomposition by the action of unreacted trinitro compound, resulting in 1,2-elimination of HX molecule provided that X is a readily leaving group. Elimination of HNO₂ was observed for X = SMe, OMe, and OEt; in the ¹H NMR spectra we observed *ABM* patterns from the corresponding dinitro compounds **IV** (X = SMe, OMe, OEt). Their precursors are σ -complexes **V**

(X = SMe, OMe, OEt); in the presence of the corresponding trinitro compounds adducts **V** act as donors of hydride ion. This scheme is supported by hydride ion transfer from σ -adducts **VI** (X = NH₂) [4] and **V** (X = H) to 1,3,5-trinitrobenzene.

Adducts **VIIc–VIII** derived from dinitrobenzenes undergo aromatization to mononitro compounds **VIIc–VIII** through elimination of HNO₂ molecule and hydride ion. The products are identified via *AA'BB'* patterns in the ¹H NMR spectra. In the series of 1-X-2,4-dinitrobenzenes, hydrogenolysis of the 1-substituent was observed for X = SO₂Me, SMe, SOC₆H₄NO₂-4, and NHCOC₆H₄NO₂-4; the reaction gave initial *m*-dinitrobenzene and products of its further transformations.

The proposed mechanism of hydrogenolysis of 1,3,5-trinitrobenzene and 1,3-dinitrobenzene derivatives can be denoted as S_NAr(AA₂E), i.e., nucleophilic aromatic substitution via addition–addition–elimination. We believe that this mechanism deserves specific attention, for it also applies to hydrolysis reactions: for example, it explains formation of 3,5-dinitrophenol in the initial stage of the reaction of 2,4,6-trinitrobenzoic acid with NaBH₄.

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