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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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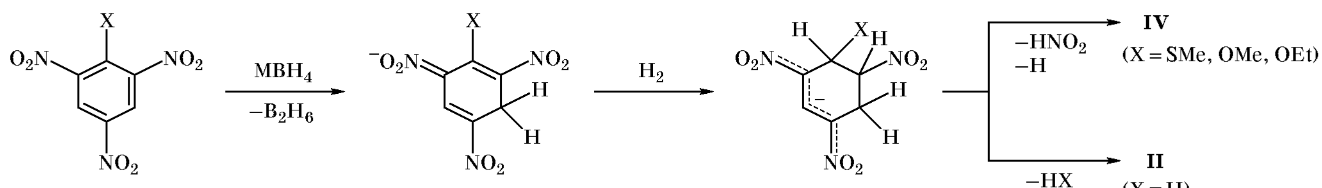
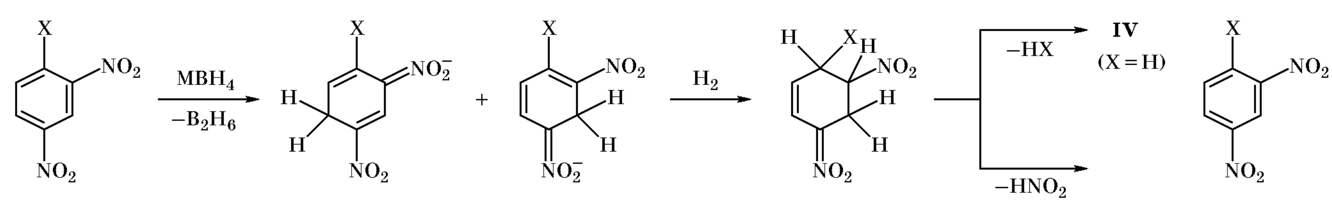
Reactions of 1-substituted 2,4,6-trinitrobenzenes with hydridoborate complexes characteristically result in replacement of the 1-substituent by hydrogen [1, 2], whereas 1-X-2,4-dinitrobenzenes react with $NaBH_4$ to give products of hydrogenolysis of the 2-nitro group [3]. By studying the reactions of potassium (sodium) tetrahydridoborate with a series of 1-X-2,4,6-trinitrobenzenes and 1-X-2,4-dinitrobenzenes in DMSO-d_6 by ^{1}H NMR spectroscopy (in some cases, by ^{13}C 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-σ_3-complexes of trinitro compounds (Scheme 1) or isomeric H-σ_3/H-σ_5-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 ^{1}H NMR spectrum belongs to

Scheme 1.



X = H (**a**), OH (**b**), OMe (**c**), OEt (**d**), NHMe (**e**), NMe_2 (**f**), CO_2H (**g**), CO_2Me (**h**), Cl (**i**), SMe (**j**), $SC_6H_2(NO_2)_3$-2,4,6 (**k**), $SC_6H_3(NO_2)_2$-2,4 (**l**), NH_2 (**m**), CH_3 (**n**), CH_2COCH_3 (**o**).

Scheme 2.



M = K, Na; X = H (**a**), OK (**b**), OMe (**c**), OEt (**d**), OCH_2CH_2Cl (**e**), Cl (**f**), Br (**g**), NMe_2 (**h**), SMe (**i**), SPh (**j**), $SC_6H_4NO_2$-4 (**k**), SOMe (**l**), Me (**m**), CH_2COMe (**n**), NH_2 (**o**), NHMe (**p**), NHPh (**q**), NHCOMe (**r**), $NHNH_2$ (**s**), NHCOPh (**t**), $NHCOC_6H_4NO_2$-4 (**u**), $SC_6H_3(NO_2)_2$-2,4 (**v**), SOPh (**w**), $SOC_6H_4NO_2$-4 (**x**), SO_2Me (**y**), SO_2Ph (**z**), $SO_2C_6H_4NO_2$-4 (**z1**), $SO_2C_6H_3(NO_2)_2$-2,4 (**z2**).

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Scheme 3.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

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 C^1 in σ-adduct **II** (X = NH_2) is deactivated due to donor effect of the amino group; therefore, molecular hydrogen adds at the double bond at C^4 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 ^{13}C NMR spectra of the same adducts, the signal from the sp^3-carbon atom attached to the nitro group (C^2 and C^4, respectively) is observed at δ_C ~78 ppm; in the off-resonance spectrum it is split into a doublet, indicating that there is a proton attached thereto.

Adducts **IIIb**–**IIIl** 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 HNO_2 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 = NH_2) [4] and **V** (X = H) to 1,3,5-trinitrobenzene.

Adducts **VIIc**–**VIIl** derived from dinitrobenzenes undergo aromatization to mononitro compounds **VIIIc**–**VIIIl** through elimination of HNO_2 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 = SO_2Me, SOMe, $SOC_6H_4NO_2$-4, and $NHCOC_6H_4NO_2$-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 $S_NAr(AA_2E)$, 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 $NaBH_4$.

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