

Formation and Decomposition of 3,5-Dinitrocyclohexa-2,5- dienenitronic Acid

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Meisenheimer compounds obtained from nucleophilic addition to polynitroarenes have received much attention as such and as intermediates in bimolecular aromatic nucleophilic substitution. Several reviews have appeared lately.¹

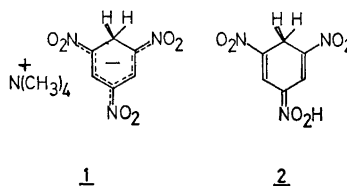
Recently, Taylor reported the formation of stable Meisenheimer compounds from tetramethylammonium tetrahydridoborate² (*I*) or tetramethylammonium tetraalkylborates³ and 1,3,5-trinitrobenzene. The latter compounds were converted by hydrogen chloride to alkyl-2,4,6-trinitrobenzenes.

The conjugate acids of Meisenheimer compounds (nitronic acids) are usually short-lived but have been isolated in some cases.^{4,5} We have investigated the reaction between the Meisenheimer compound (*I*) and sulphuric acid and have found that a nitronic acid, probably 3,5-dinitrocyclohexa-2,5-dienenitronic acid (*2*), is formed initially.

A chloroform suspension of the Meisenheimer compound (*I*) was shaken with

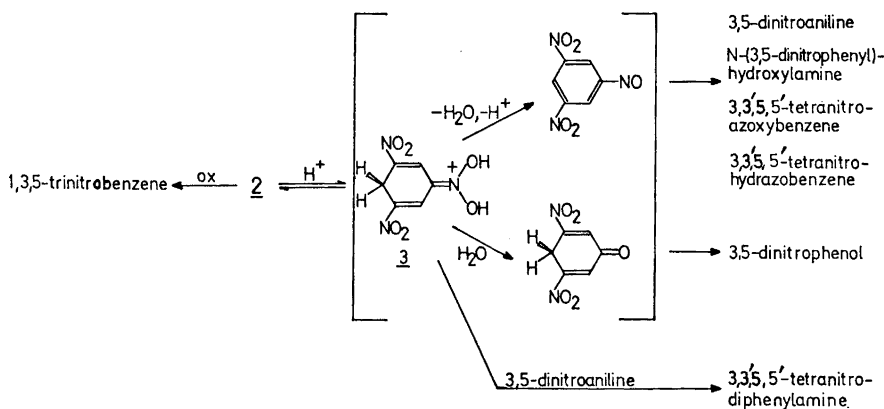
sulphuric acid. The visible spectrum of the resulting chloroform solution showed one strong absorption at 370 nm, the same as that of 4(1-indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid⁴ and 4(2,6-dimethoxyphenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid.^{5,6} When recorded in a polar solvent such as ethanol, the visible spectrum showed the two characteristic absorptions of the Meisenheimer anion (*I*).

The yield of the nitronic acid was at a maximum (60 %) when the Meisenheimer compound was treated with 2–3 M sulphuric acid. The acid is only moderately stable even in dilute solution and has not yet been isolated. It decomposes within a few hours at room temperature and within 48 h at 0° when stored under nitrogen.



The nitronic acid gave a dark red, rather unstable anilinium salt. The ammonium and pyridinium salts were too unstable to be isolated.

The nitronic acid prepared in dichloromethane was decomposed with sulphuric acid. The decomposition was slow with 2–3 M acid (20–30 min) but fast (a few



Scheme 1

seconds) with 6 M acid. Decomposition of the nitronic acid with 2 M sulphuric acid led to the following products: 1,3,5-trinitrobenzene (28 %), 3,3',5,5'-tetranitroazoxybenzene (3.1 %), 3,5-dinitroaniline (4.8 %), *N*-(3,5-dinitrophenyl)hydroxylamine (2.6 %), and traces of three other products which probably were: 3,3',5,5'-tetranitrodiphenylamine, 3,5-dinitrophenol, and 3,3',5,5'-tetranitrohydrazobenzene.

A suggested scheme for the formation of these products (Scheme 1) assumes a nitronic acid as an intermediate. The acid is protonated to give the ion 3 which is the reactive intermediate.⁷ Aromatisation of 3 with elimination of a proton and water gives 3,5-dinitronitrosobenzene, which is immediately reduced to 3,5-dinitroaniline, *N*-(3,5-dinitrophenyl)hydroxylamine, 3,3',5,5'-tetranitroazoxybenzene or 3,3',5,5'-tetranitrohydrazobenzene. Nucleophilic attack on the α -carbon in the protonated nitronic acid (3) by water (Nef reaction) or by 3,5-dinitroaniline gives 3,5-dinitrophenol and 3,3',5,5'-tetranitrodiphenylamine, respectively.

The spectroscopic and the chemical evidence for the structure of the compound formed on treatment of the Meisenheimer compound (1) with sulphuric acid is consistent with a nitronic acid (2).

Experimental. 3,5-Dinitrocyclohexa-2,5-dienenitronic acid. Tetramethylammonium 1,3,5-trinitrocyclohexadienide⁸ (1.5 g) was suspended in chloroform (100 ml), 3 M sulphuric acid (100 ml) was added, the mixture shaken for a few seconds and the chloroform phase filtered through anhydrous magnesium sulphate.

The visible spectrum in chloroform showed one absorption at 370 nm, $\epsilon = 1.8 \times 10^4$ l mol⁻¹ cm⁻¹. After dilution with ethanol the solution showed the spectrum of the Meisenheimer anion. The IR spectrum showed slowly disappearing absorptions at 2800–2200 cm⁻¹ (acid O–H), 1660 sh, 1642 sh and 1635 cm⁻¹, 1525 broad (asym N–O) and 1320 cm⁻¹ (sym N–O).

Anilinium 1,3,5-trinitrocyclohexadienide. Tetramethylammonium 1,3,5-trinitrocyclohexadienide (0.50 g) was suspended in dichloromethane (50 ml), 2 M sulphuric acid (35 ml) was added and the mixture shaken for a few seconds. Freshly distilled aniline (0.19 g) was added to the dichloromethane phase. The precipitate which formed was collected, washed with benzene and dried (0.20 g, 38 %, m.p. 131–137°). The visible spectrum of the compound in acetonitrile showed absorptions at

478 nm, $\epsilon = 2.7 \times 10^4$ l mol⁻¹ cm⁻¹ and 580 nm, $\epsilon = 1.3 \times 10^4$.

Decomposition of 3,5-dinitrocyclohexa-2,5-dienenitronic acid with 2 M sulphuric acid. Tetramethylammonium 1,3,5-trinitrocyclohexadienide (2.5 g) was suspended in dichloromethane (300 ml), 2 M sulphuric acid (150 ml) was added and the mixture vigorously shaken until the dark mixture became yellow (ca. 30 min). The organic phase was collected, the solvent evaporated and the residue chromatographed on silica gel. The first four compounds were eluted with dichloromethane and the last three with dichloromethane mixed with a few per cent acetone giving the following compounds which were characterized by comparison of their mass and infra-red spectra with those of authentic samples, unless otherwise stated: 1,3,5-Trinitrobenzene (m.p. 123–125°, 530 mg, 28 %); 3,3',5,5'-tetranitroazoxybenzene [recrystallized from benzene yielding two fractions, (m.p. 190–191°, 33 mg, 2.0 % and m.p. 180–186°, 18 mg, 1.1 %, respectively) identical with 3,3',5,5'-tetranitroazoxybenzene by UV spectrum.⁸ Mass and infra-red spectra consistent with the suggested structure]; 3,5-dinitroaniline (70 mg, 4.8 % crude product, m.p. after sublimation 145–149°); traces of a compound which probably is 3,3',5,5'-tetranitrodiphenylamine (MS and IR evidence); *N*-(3,5-dinitrophenyl)hydroxylamine (45 mg, 2.6 % crude product); traces of 3,5-dinitrophenol; traces of a compound which possibly is 3,3',5,5'-tetranitrohydrazobenzene (MS evidence).

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