

2,4,6-Trinitrophenylcyclopentadiene and 2,4,6-Trinitrophenylindene from 1,3,5-Trinitrobenzene and Cyclopentadiene or Indene

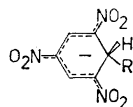
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Silver oxide catalyses the formation of a Meisenheimer compound from pyridine and 1,3,5-trinitrobenzene. This is probably an intermediate in the formation of the Meisenheimer compound from indene and 1,3,5-trinitrobenzene in pyridine but not, however, in the corresponding reaction with cyclopentadiene.

The Meisenheimer compounds from cyclopentadiene and indene are oxidized, by *p*-benzoquinone or hydrogen peroxide, to 2,4,6-trinitrophenylcyclopentadiene and to 1-(2,4,6-trinitrophenyl)indene, respectively. The Meisenheimer compound from indene and 1,3,5-trinitrobenzene, on treatment with strong acid, is transformed into a nitronic acid - 4-(1-indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid. On oxidation with *p*-benzoquinone or hydrogen peroxide, the nitronic acid gives 1-(2,4,6-trinitrophenyl)indene.

1,3,5-Trinitrobenzene reacts with a wide variety of nucleophiles to form σ -complexes,^{1,2} usually called Meisenheimer compounds (*I*). These are important for the understanding of aromatic nucleophilic substitution.^{3,4}



I

Recently, Taylor reported the addition of hydride ion (from borohydride anion) to 1,3,5-trinitrobenzene ($R = H$).⁵ Analogous reactions with tetra-alkylboron anions have also been successful ($R = \text{methyl, butyl}$).⁶ We have prepared Meisenheimer compounds from 1,3,5-trinitrobenzene and organocopper^{7,8} or organosilver compounds⁹ ($R = 2,6\text{-dimethoxyphenyl, phenylethynyl}$) or from

acidic hydrocarbons such as cyclopentadiene or indene (R = cyclopentadienyl, indenyl) in the presence of silver oxide.¹⁰

The Meisenheimer compounds from 1,3,5-trinitrobenzene can be regarded as salts of substituted dinitrocyclohexadienenitronic acid – *aci*-dihydrotrinitrobenzene. Such an acid was prepared from the Meisenheimer compound from 2,6-dimethoxyphenylsilver.⁹

Oxidation of Meisenheimer compounds from 1,3,5-trinitrobenzene give 2,4,6-trinitrophenyl derivatives.^{4,9,11} We have studied the corresponding oxidation of the Meisenheimer compounds from cyclopentadiene and indene.

RESULTS

In order to study the influence of the solvent and that of the metal on the formation of Meisenheimer compounds, 1,3,5-trinitrobenzene was dissolved in pyridine and silver oxide was added. The reaction was followed by visible spectroscopy. Increasing absorptions at 437 and 520 nm were observed due to the formation of a Meisenheimer complex with pyridine (Fig. 1). The same

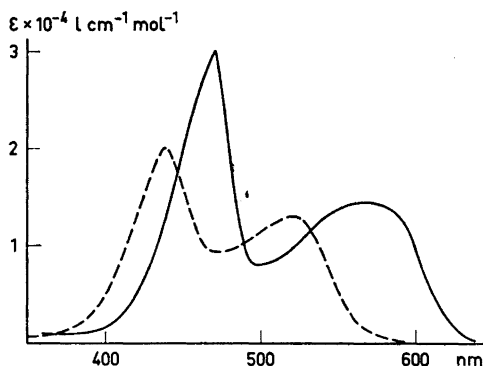


Fig. 1. Visible spectra of 4(1-indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid in pyridine —, of the Meisenheimer complex between 1,3,5-trinitrobenzene and indene in pyridine —, and of the Meisenheimer complex between 1,3,5-trinitrobenzene (10^{-4} M) and pyridine - - -.

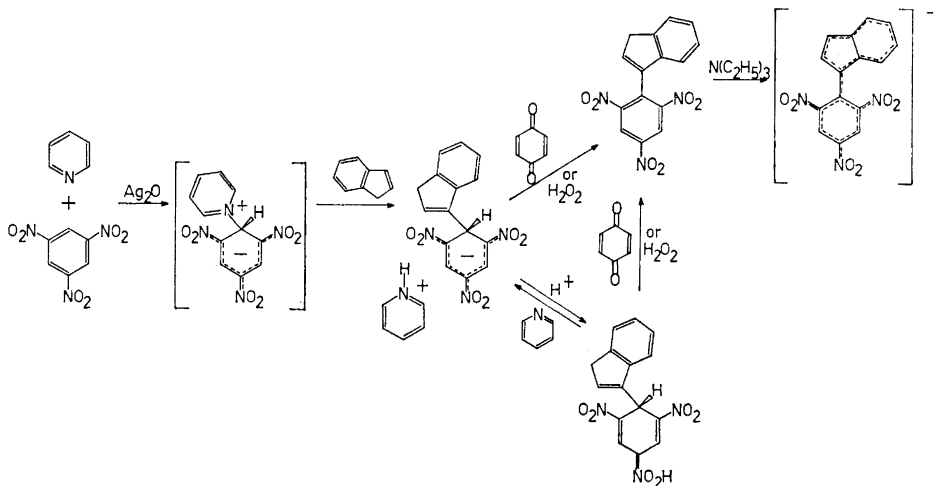
compound was initially formed in the reaction between indene and 1,3,5-trinitrobenzene in pyridine. The rate of formation of the indene adduct was roughly proportional to the concentration of the pyridine adduct.

Cyclopentadiene under the same conditions reacts about 16 times faster than does indene. The addition of cyclopentadiene is also faster (about five times) than the addition of pyridine.

Upon treatment with strong acid, the Meisenheimer complex from 1,3,5-trinitrobenzene and indene gives the yellow 4(1-indenyl)3,5-trinitrocyclohexa-2,5-dienenitronic acid (74 %). On addition of pyridine to the acid, the pyridinium salt of the nitronic acid, *i.e.* the Meisenheimer compound, is reformed (Scheme 1). The nitronic acid is oxidized to 1-(2,4,6-trinitrophenyl)indene by

p-benzoquinone (80 %), acidic hydrogen peroxide (46 %), slowly by air (IR evidence), or on standing in acetone solution (NMR evidence).

The Meisenheimer complex between 1,3,5-trinitrobenzene and indene is oxidized by *p*-benzoquinone or acidic hydrogen peroxide to 1-(2,4,6-trinitrophenyl)-indene, the yields being 52 and 25 %, respectively (Scheme 1).



Scheme 1

Treatment of a suspension of the Meisenheimer complex from 1,3,5-trinitrobenzene and cyclopentadiene with sulphuric acid in chloroform gives a yellow chloroform solution. The visible spectrum of the solution, diluted with chloroform, showed the same absorptions as that of 4-(1-indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid (Fig. 2). The visible spectrum of the chloroform phase diluted with pyridine was the same as that of the Meisenheimer complex between cyclopentadiene and 1,3,5-trinitrobenzene (Fig. 1). Assuming quantita-

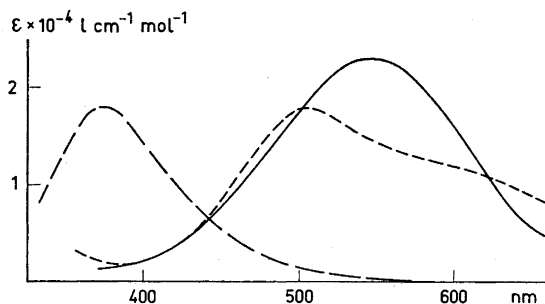
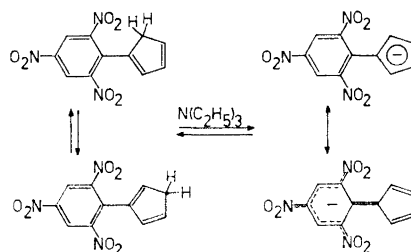


Fig. 2. Visible spectra of 4-(1-indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid in chloroform —, of the anions from 2,4,6-trinitrophenylcyclopentadiene — — —, and from 2,4,6-trinitrophenylindene - - - in acetone with excess triethylamine.

tive formation of the Meisenheimer complex from the acid in pyridine, the conversion to the nitronic acid was 67 %.

Oxidation of the Meisenheimer complex from cyclopentadiene with benzoquinone affords an isomeric mixture of 1- and 2-(2,4,6-trinitrophenyl)cyclopentadiene in 25 % yield (see Discussion).

Trinitrophenylcyclopentadiene (Scheme 2) and trinitrophenylindene both form blue solutions with bases. The visible spectra of the compounds in acetone with 5 % triethylamine showed strong absorptions at 542 and 504 nm, respectively (Fig. 2).



Scheme 2

DISCUSSION

Solvent participation. The Meisenheimer complex between pyridine and 1,3,5-trinitrobenzene has been suggested as an intermediate in the addition of certain nucleophiles to 1,3,5-trinitrobenzene.⁹ Metallic copper and silver oxide¹⁰ catalyse the formation of this complex presumably by co-ordination to a nitro group in the nitrobenzene. Analogous co-ordination between copper compounds and electron withdrawing *ortho* substituents in iodoarenes have been suggested to cause the unusually high reactivity of these iodoarenes in copper-promoted reactions.^{12,13}

The Meisenheimer complex between pyridine and 1,3,5-trinitrobenzene is not necessarily an intermediate in nucleophilic addition to trinitrobenzene. The rate of addition of cyclopentadiene is greater than the rate of addition of pyridine (about 5:1). The pyridine complex, however, probably is an intermediate in the addition of indene to trinitrobenzene (Scheme 1). If so, the pyridine complex is more reactive towards nucleophiles than is trinitrobenzene. The difference in reactivity between cyclopentadiene and indene (about 16:1) is much less than the difference in acidity ($> 10^4$:1).¹⁴ This could be explained by assuming different reaction paths such as those suggested above. However, it may be irrelevant to compare kinetic data such as reaction rates, with thermodynamic data such as acidity constants.

The nitronic acid. Most Meisenheimer compounds are unstable towards acid and decompose to a polynitroarene and the protonated nucleophile.⁹ However, the Meisenheimer complexes from cyclopentadiene or indene and 1,3,5-trinitrobenzene are stable towards weak acids. They can be protonated by sulphuric acid analogously to the Meisenheimer complex from 2,6-dimethoxy-

Table 1. Assignment of the NMR data. The chemical shifts are given in τ values. s, singlet; d, doublet; t, triplet.

Compound	Solvent	H _a	H _b	H _c	H _d	H _e
	Pyridine- <i>d</i> ₆ ^a	1.18d and 1.21d	4.05 and 4.12	6.96 and 7.33	3.76–3.92	
	Acetone- <i>d</i> ₆	1.45	4.25	6.89 and 7.04	3.36–3.86	
	Dimethyl sulphoxide- <i>d</i> ₆	1.60	4.38	6.94–7.06	3.57–3.93	
	Acetone- <i>d</i> ₆	0.84s		6.52 and 6.66	3.24	
	Dimethyl sulphoxide- <i>d</i> ₆	0.79s		6.67	3.25	
	Pyridine- <i>d</i> ₆ ^a	1.10s	3.86s	7.05d	3.76t	~2.4
	Acetone- <i>d</i> ₆	1.34s	3.92s	6.65	3.47	~2.6
	Acetone- <i>d</i> ₆	0.82s		6.32	3.22t ^b	2.4–3.0
	Acetone- <i>d</i> ₆	1.71s	3.89	6.57	3.29	2.0–2.8

^a See Ref. 10. ^b $J_{\text{Hc-Hd}} = 2$ Hz.

phenylsilver and trinitrobenzene.⁹ The yellow product is believed to be a nitronic acid (Scheme 1). This assumption is based on NMR, visible and IR spectra (Table 1, Figs. 1 and 2, and Experimental). In solution, a rapid proton exchange between the nitro groups is expected.

Isomerization. It is previously known that substituted cyclopentadienes rearrange under mild conditions to an equilibrium mixture of the 1- and 2-substituted isomers. The 5-substituted isomer is present in minor amounts only.¹⁵ The NMR spectrum of the Meisenheimer complex between cyclopentadiene and trinitrobenzene in pyridine showed the presence of the 1- and 2-isomers in approximately equal amounts.¹⁰ The solvent has a large effect on the spectrum (Table 1). The assignment of the spectrum of 2,4,6-trinitrophenylcyclopentadiene in acetone and in dimethyl sulphoxide is shown in Table 1. The isomers (Scheme 2) are present in an approximate ratio of 3:7. Assuming a strong shielding of methylenic hydrogens by appropriately situated nitro groups, one concludes that the 1-substituted isomer dominates.

Anions. The visible spectra of the Meisenheimer anions from cyclopentadiene or indene and 1,3,5-trinitrobenzene are identical within the experimental error.¹⁰ The visible spectra of the anions from trinitrophenylcyclopentadiene and trinitrophenylindene differ and absorb at 542 nm ($\epsilon = 2.3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 504 nm ($\epsilon = 1.8 \times 10^4$), respectively (Fig. 2). In the anion from trinitrophenylindene, the two aromatic systems cannot be co-planar due to steric crowding. As expected, this anion absorbs at shorter wavelength than does that from trinitrophenylcyclopentadiene.

EXPERIMENTAL

Formation of Meisenheimer complexes from 1,3,5-trinitrobenzene and pyridine, cyclopentadiene or indene. 1,3,5-Trinitrobenzene (0.5 mmol) was dissolved in pyridine (50 ml), and silver oxide (0.25 mmol) was added under stirring in the dark at room temperature. At intervals, small samples were removed and diluted with pyridine and their visible spectra recorded. Two increasing absorptions were observed, at 437 and at 520 nm. Assuming $\epsilon = 3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the pure complex,² the yield was 75 %. The time for the formation of 50 % of this yield was 7.7 h.

The same reaction was repeated with addition of cyclopentadiene (0.5 mmol). Absorptions corresponding to a quantitative yield of the Meisenheimer complex between cyclopentadiene and 1,3,5-trinitrobenzene (Fig. 1) were observed; 50 % of the total yield was formed within 90 min.

The reaction was repeated with the addition of indene (0.5 mmol) instead of cyclopentadiene. Absorptions from the pyridine complex were first observed. These were slowly replaced by absorptions from the Meisenheimer complex between indene and 1,3,5-trinitrobenzene (yield 87 %); 50 % of the total yield was formed within 24.2 h.

4-(1-Indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid. The Meisenheimer complex from 1,3,5-trinitrobenzene and indene (2.5 g) was suspended in 5 M sulphuric acid (50 ml), chloroform (200 ml) was added, and the mixture was vigorously shaken for 10 min. The chloroform phase was collected, the solvent evaporated, and the residue recrystallized from a mixture of dry methylene chloride and cyclohexane to give a bright yellow compound, m.p. 120–124°, believed to be 4-(1-indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid (1.5 g, 74 %). The compound is sensitive to moisture.

The visible spectrum of the acid in chloroform showed an absorption at 368 nm with $\epsilon = 1.8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ (Fig. 2), and in pyridine an absorption identical to that of the Meisenheimer complex (Fig. 1). The suggested assignment of its NMR spectrum is shown in Table 1.

The IR spectrum of the nitronic acid in potassium bromide showed the same characteristics as the spectrum of 4-(2,6-dimethoxyphenyl)-3,5-dinitrocyclohexa-2,5-diene nitronic acid.⁵ The nitronic acid (0.062 g) was dissolved in ether (100 ml), and pyridine (0.10 g) mixed with ether (5 ml) was added. The pyridinium salt of the nitronic acid precipitated instantly in a quantitative yield (0.077 g). The IR spectrum of the salt was identical with that of the Meisenheimer complex.

1-(2,4,6-Trinitrophenyl)indene. The Meisenheimer complex from 1,3,5-trinitrobenzene and indene (0.5 g) was suspended in 5 M sulphuric acid (15 ml), chloroform (50 ml) was added and the mixture was vigorously shaken for 10 min. The chloroform phase was collected and excess *p*-benzoquinone (0.26 g) was added. The solvent was evaporated and the residue chromatographed on silica gel with methylene chloride as mobile phase. A yellow compound was collected and recrystallized from ethanol. The compound was identified as 1-(2,4,6-trinitrophenyl)indene (m.p. 174–175°, 206 mg, 52%). (Found: C 54.9; H 3.2; N 12.7; O 29.3. Calc. for C₁₅H₉N₃O₆: C 55.1; H 2.8; N 12.8; O 29.3.) The mass spectrum showed the parent ion at *m/e* 329 (base peak). The IR spectrum of 1-(2,4,6-trinitrophenyl)indene in potassium bromide was consistent with the suggested structure. The assignment of the NMR spectrum is shown in Table 1. The visible spectrum of 1-(2,4,6-trinitrophenyl)indene in acetone with excess trimethylamine added is shown in Fig. 2.

The Meisenheimer compound from 1,3,5-trinitrobenzene and indene (0.5 g) was suspended in a mixture of sulphuric acid (1 M, 10 ml) and hydrogen peroxide (35%, 10 ml). The product was extracted with methylene chloride (20 ml), the solvent evaporated, and the residue chromatographed on silica gel with methylene chloride as mobile phase. The yield of 1-(2,4,6-trinitrophenyl)indene was 25% after recrystallization from ethanol.

4-(1-Indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid (0.050 g) was dissolved in chloroform (50 ml) and excess *p*-benzoquinone (0.032 g) was added. After 20 min, the solvent was evaporated and the residue chromatographed on silica gel with methylene chloride as mobile phase. The compound collected was identified as 1-(2,4,6-trinitrophenyl)indene (0.04 g, 80%). The oxidation of the nitronic acid was also performed with acidic hydrogen peroxide to form 1-(2,4,6-trinitrophenyl)indene in 46% yield (after recrystallization from ethanol).

1- and 2-(2,4,6-Trinitrophenyl)cyclopentadiene. The Meisenheimer complex from 1,3,5-trinitrobenzene and cyclopentadiene (1.0 g) was suspended in a mixture of 5 M sulphuric acid (25 ml), chloroform (100 ml) was added and the mixture was vigorously shaken for 10 min. The chloroform phase was collected and excess benzoquinone (0.60 g) was added.

The solvent was evaporated and the residue chromatographed on silica gel with methylene chloride as mobile phase. A yellow compound was collected and identified as an isomeric mixture of 1- and 2-(2,4,6-trinitrophenyl)cyclopentadiene (m.p. 125–128°, 196 mg, 25%). (Found: C 47.8; H 2.8; N 15.0. Calc. for C₁₁H₇N₃O₆: C 47.7; H 2.6; N 15.2.) The mass spectrum showed the parent ion at *m/e* 279 (base peak). The IR spectrum was consistent with the suggested structure. NMR data are shown in Table 1. Oxidation of the Meisenheimer complex with acidic hydrogen peroxide affords the same compound in a lower yield (11%).

The visible spectrum of 1- and 2-(2,4,6-trinitrophenyl)cyclopentadiene in acetone with excess triethylamine added is shown in Fig. 2.

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