

- Raina, A., Jänne, J., Hannonen, P. and Hölttä, E. *Ann. N.Y. Acad. Sci. In press.*
- Pegg, A. E. and Williams-Ashman, H. G. *Arch. Biochem. Biophys.* **137** (1970) 156.
- Tabor, C. W. In Colowick, S. P. and Kaplan, N. O. *Methods in Enzymology*, Academic, New York 1962, Vol. 5, p. 756.
- Pegg, A. E. and Williams-Ashman, H. G. *J. Biol. Chem.* **244** (1969) 682.
- Higgins, G. H. and Anderson, R. M. *Arch. Pathol.* **12** (1931) 186.

Received September 28, 1970.

## Addition of Cyclopentadiene and Indene to 1,3,5-Trinitrobenzene

ROBERT WAHREN and  
OLOF WENNERSTRÖM

Department of Organic Chemistry, Royal  
Institute of Technology, S-100 44  
Stockholm 70, Sweden

The formation of stable  $\sigma$ -complexes — Meisenheimer complexes — in the nucleophilic substitution of aromatic polynitro compounds is well documented.<sup>1,2</sup> Such complexes can be general intermediates in aromatic  $S_N2$  reactions, although the role of  $\sigma$ - and  $\pi$ -complexes is still under discussion.<sup>3</sup>

Meisenheimer compounds can also be regarded as salts of nitronic acids and, if reasonably stable, can be expected to react analogously to other salts of nitronic acids.<sup>4</sup>

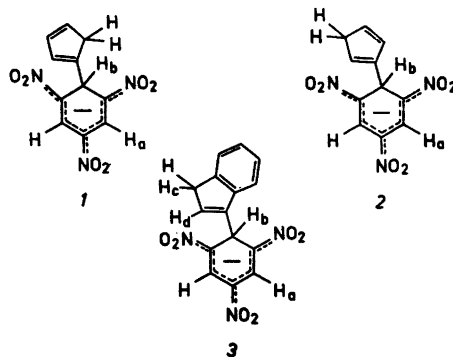
We have recently found new methods for preparing Meisenheimer compounds from phenylethynylcopper<sup>5</sup> or 2,6-dimethoxyphenylcopper<sup>6</sup> and 1,3,5-trinitrobenzene in pyridine.

Cyclopentadienylcopper has been prepared from cyclopentadiene and copper(I) oxide in the presence of suitable phosphines.<sup>7</sup> Organosilver compounds are less reactive (although thermally more labile) than the corresponding copper compounds<sup>8</sup>

and react more slowly with 1,3,5-trinitrobenzene.<sup>5,9</sup>

Cyclopentadiene (or indene), silver oxide [but not copper(I) oxide] and 1,3,5-trinitrobenzene reacted in pyridine to give a beautiful red solution from which a Meisenheimer compound was isolated. Cyclopentadiene and trinitrobenzene also reacted in pyridine in the absence of silver compounds, but more slowly.

Silver oxide possibly facilitates the formation of a cyclopentadienyl anion, a reasonable intermediate in the reaction, besides increasing the electrophilicity of 1,3,5-trinitrobenzene by co-ordination with a nitro group.



Cyclopentadiene (15 mmol), 1,3,5-trinitrobenzene (10 mmol) and silver oxide (5 mmol) were stirred for 24 h in pyridine (100 ml). A red colour developed slowly. Ice and hydrochloric acid (2 M) in slight excess were added. A dark red precipitate formed. A red compound was separated from silver chloride by acetone extraction to give dark red crystals, recrystallised from ethanol (2.8 g, 78%, m.p. 128–33° decomp.). (Found: C 53.5; H 4.0; N 15.5. Calc. for  $C_{16}H_{14}N_4O_8$ : C 53.6; H 3.9; N 15.6.)

The visible spectrum of the product (Fig. 1) is typical for Meisenheimer compounds from 1,3,5-trinitrobenzene.<sup>1</sup>

Monosubstituted cyclopentadienes rearrange under mild conditions to mixtures of the 1- and 2-substituted isomers.<sup>10</sup> The NMR spectra (at 60 MHz and 100 MHz) of the isolated product in pyridine-*d*<sub>5</sub> can best be rationalised on the assumption that the two isomers 1 and 2 are present in approximately equal amounts. The spectrum showed the following charac-

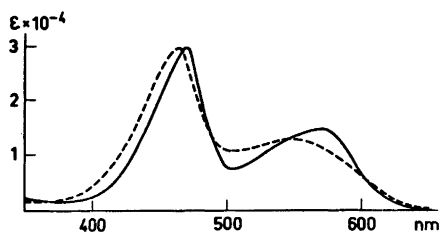


Fig. 1. Visible spectra of the Meisenheimer compounds from cyclopentadiene or indene and 1,3,5-trinitrobenzene in pyridine — and ethanol — — —.

teristics (the spectrum of pyridine has been subtracted; the relative areas and the suggested assignments are shown in brackets):

Doublets at  $\tau=1.18$  and  $1.21$  (2,  $H_a$ ), multiplets at  $4.05$  and  $4.12$  (1,  $H_b$ ), multiplets at  $6.96$  and  $7.33$  (2, methylenic H), multiplets at  $3.76-3.92$  (3, ethylenic H) and singlet at  $-0.56$  (1,  $py-H^+$ );  $J_{H_aH_b}=0.6$  Hz.

The IR spectrum showed the characteristic shift of the asymmetric N—O stretch in 1,3,5-trinitrobenzene to  $1485$   $cm^{-1}$  and a broad, very strong absorption centered at  $1235$   $cm^{-1}$ .

The mass spectrum showed the largest fragment at  $m/e$  277 (=mass of trinitrophenylcyclopentadiene).

Indene reacts with 1,3,5-trinitrobenzene and silver oxide under the same conditions as cyclopentadiene. A dark red compound was isolated and recrystallized from ethanol (yield 90%, m.p.  $165-68^\circ$  decomp.). (Found: C 58.5; H 3.9; N 13.5. Calc. for  $C_{20}H_{16}N_4O_6$ : C 58.8; H 3.9; N 13.7.)

The visible spectrum (Fig. 1) was identical with that of the product from cyclopentadiene.

The NMR spectrum of the indene adduct in pyridine- $d_5$  at 60 MHz showed the following characteristics, consistent with isomer 3: Singlet at  $\tau=1.10$  (2,  $H_a$ ), singlet at  $3.86$  ( $H_b$ ), triplet at  $3.76$  ( $H_d$ , area of  $H_b+H_d$  approx. 2), doublet at  $7.05$  (2,  $H_c$ ) and multiplet at  $2.42$  (approx. 4, aromatic H);  $J_{H_a-H_b}<0.3$  Hz,  $J_{H_c-H_d}=2$  Hz.

The mass spectrum of the indene adduct showed the largest fragment at  $m/e$  327 (=mass of trinitrophenylindene).

Indene reacts more slowly than cyclopentadiene with 1,3,5-trinitrobenzene and silver oxide, while fluorene does not react. The reaction with indene was followed by visible spectroscopy. Initially the solution showed increasing absorptions at  $440$  and  $520$  nm (probably from the attack of pyridine on 1,3,5-trinitrobenzene).<sup>6</sup> These were gradually replaced by absorptions at  $465$  and  $573$  nm (from ion 3).

Products from further reactions of the Meisenheimer compounds are under investigation and will be reported soon.

*Acknowledgements.* We thank Prof. M. Nilsson for his interest and for valuable discussions and criticism. Dr. S. Shvedova took part in the early work. The study has been supported by the Swedish Natural Science Research Council and the Swedish Board of Technical Development. The English was checked by Patrik Hort.

1. Foster, R. and Fyfe, C. A. *Rev. Pure Appl. Chem.* **16** (1966) 61.
2. Servis, K. L. *J. Am. Chem. Soc.* **89** (1967) 1508.
3. de Boer, T. J. and Dirkx, I. P. *The chemistry of the nitro and nitroso groups*, Wiley, New York 1969, Part 1, p. 518.
4. Nielsen, A. T. *The chemistry of the nitro and nitroso groups*, Wiley, New York 1969, Part 1, p. 349.
5. Wennerström, O. *Acta Chem. Scand. In press.*
6. Björklund, C., Nilsson, M. and Wennerström, O. *Acta Chem. Scand. In press.*
7. Wilkinson, G. and Piper, T. S. *J. Inorg. Nucl. Chem.* **2** (1956) 32.
8. Beverwijk, C. D. M., van der Kerk, G. J. M., Leusink, A. J. and Noltes, J. G. *Organometal. Chem. Rev.* **A 5** (1970) 215.
9. Wennerström, O. *To be published.*
10. Mironov, V. A., Sobolev, E. V. and Elizarova, A. N. *Tetrahedron* **19** (1963) 1939.

Received October 16, 1970.