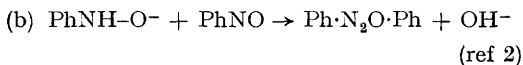
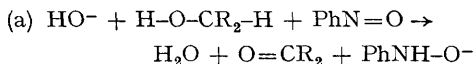


## A 1,6-Addition of Nitrosobenzene to Cycloheptatriene

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KINETIC and product studies<sup>1</sup> in this laboratory indicate that in alkaline solution nitrosobenzene readily oxidises alcohols by hydride transfer and thereby is reduced to azoxybenzene.

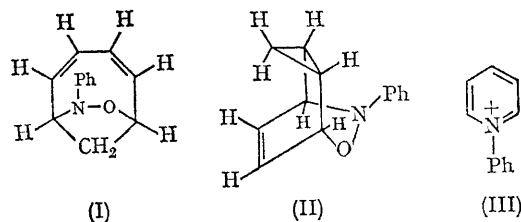


Since hydride transfer from cycloheptatriene to yield the tropylium cation is easy, its interaction with nitrosobenzene has been studied, under nitrogen in *t*-butyl alcohol, ether, and nitromethane as solvents. A slow reaction occurs even at room temperature to give a brown product which can be separated chromatographically into azoxybenzene (40–60%) and 12–20% of a white crystalline adduct, C<sub>13</sub>H<sub>13</sub>NO, m.p. 106–107°, which from its spectroscopic properties appears to be a 1,6-adduct (I) and not a 1,4-adduct (II) similar to that formed between cycloheptatriene and maleic anhydride,<sup>3</sup> with which we have made a direct comparison.

The i.r. spectrum of our adduct (in CS<sub>2</sub> at 20°) showed the absence of either OH or NH stretching vibrations and its u.v. spectrum (λ<sub>max</sub> at 2370 Å, ε 11,500 shoulder at 2600 Å, ε 6400) was closely additive of that of phenylhydroxylamine and cycloheptatriene and consistent with diene conjugation. Its n.m.r. spectrum (60 Mc./sec. in

CCl<sub>4</sub> at 34°) showed a multiplet of five benzenoid protons (τ 2.6–3.3), four vinyl protons as a slightly deformed singlet (τ 4.0), two single protons showing in broad bands centred at τ 5.25 and 5.8 and two methylenic protons split to a quadruplet at τ 7.4–7.9, whereas the maleic anhydride adduct of cycloheptatriene<sup>3</sup> (type II) clearly shows the cyclopropane protons near τ 10. The mass spectrum showed the sequential loss of O, CH, and CH<sub>2</sub> from the parent ion, leading to a strong peak at *M* = 156 corresponding to the phenylpyridinium cation (III). Peaks were also found at *M* = 107 (PhNO)<sup>+</sup>, 92 (C<sub>7</sub>H<sub>8</sub>)<sup>+</sup> and 91 (C<sub>7</sub>H<sub>7</sub>)<sup>+</sup>. This sequence of degradations is consistent with structure (I) but not with (II) or any other 1,4-adduct.

In view of the paucity of examples of 1,6 additions in chemical literature we consider that these observations deserve placing on record.



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<sup>1</sup> J. Hutton and W. A. Waters, to be published.

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<sup>3</sup> K. Alder and F. G. Jacobs, *Chem. Ber.*, 1953, **86**, 1528; K. Alder, K. Kaiser, and M. Schumacher, *Annalen*, 1957, **602**, 80.