

C-Nitroso-enamines

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Summary C-Nitroso-enamines are unstable intermediates generated during the photoaddition of *N*-nitrosopiperidine to an acetylene.

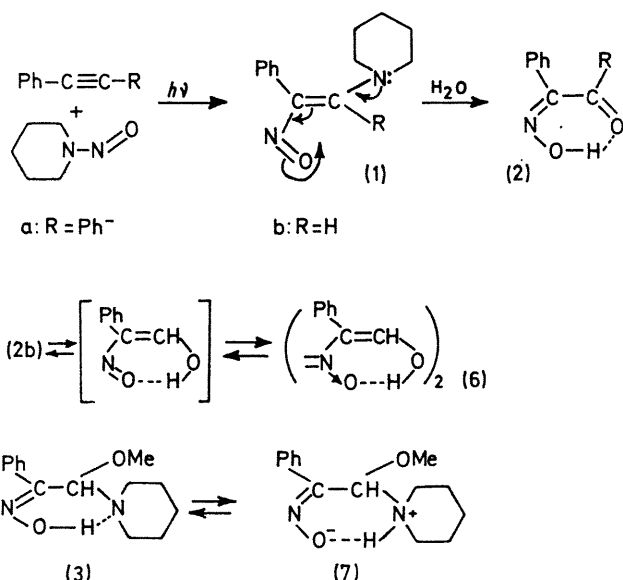
When an acidic solution (0.2–0.3 *N*-HCl) of *N*-nitrosopiperidine and an acetylene was irradiated in methanol the reaction proceeded in a manner apparently similar to that observed in nitrosamine photoaddition to an olefin.¹ If the mode of photoaddition were in fact the same, then compound (1) would be the expected adduct, possessing an extended conjugated system between the enamine and the nitroso-group. Such conjugated systems may hydrolyse under the photolysis condition in the expected manner to give an α -diketone oxime (2). Indeed, photoaddition of *N*-nitroso-piperidine to diphenylacetylene under the usual

photoaddition conditions¹ gave benzil mono-oxime (2a), m.p. 136–138°, lit.² 137°, in 61% yield.

Photoaddition to phenylacetylene was, however, more complicated, demonstrating a more complex behaviour of nitroso-enamine (1b). When the photolysate was evaporated in the presence of hydrochloric acid, in addition to the expected phenylglyoxal ketoxime (2b), 27%, m.p. 48–50°, ν_{\max} 2840 and 1700 cm^{-1} in chloroform solution, n.m.r. singlet at τ 0.20, the following three compounds were isolated: α -piperidino- α -methoxyacetophenone oxime (3), 24%, n.m.r. singlets at τ 2.58 and 6.17 in a ratio of 1:3; $\alpha\alpha$ -dimethoxyacetophenone³ (4), 22%, ν_{\max} 1695, 1122, and 1070 in Nujol, n.m.r. singlets at τ 4.85 and 6.55 in a ratio of 1:6; and phenylglyoxal dioxime (5), 9%, m.p. 163–165°, lit.² 168°. In the presence of an excess of phenylacetylene, (1b) apparently reacted preferentially with the acetylene to give mainly high-melting amorphous products; taken together, phenylglyoxal derivatives (2b–5) were produced in only about 10% yield. However, when the photolysate was made alkaline and worked-up, (2b) was obtained in 65% yield. The structures of the new compounds† were supported by appropriate i.r., n.m.r., and mass spectral data. Oxime (2b) tautomerises⁴ reversibly to the corresponding C-nitroso-compound which crystallizes readily as the dimer (6), m.p. 113–115°, ν_{\max} 1590 and 1210 cm^{-1} in Nujol mull. The dimer (6) reverts to (2b) on dissolution in a solvent or on sublimation at 110°. Oxime (3) exhibits an unusually low chemical shift for the methine proton (τ 2.58 buried in the aromatic proton signal) probably due to intramolecular protonation (7) at the amine centre.

The results demonstrate that hydrochloric acid efficiently catalyses the addition of methanol and phenylacetylene to nitroso-enamines (1). Since under the reaction conditions (2b) is not hydrolysed to phenylglyoxal or its acetal, it is suspected that acetal (4) is derived directly from (1) without using (2b) as an intermediary.

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† The molecular formulae of the new compounds were determined by elemental analysis or high-resolution mass spectroscopy.

¹ Y. L. Chow, C. J. Colon and S. C. Chen, *J. Org. Chem.*, 1967, **32**, 2109; Y. L. Chow and C. J. Colon, *Canad. J. Chem.*, 1967, **45**, 2559.

² R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th edn., Wiley, New York, 1964, p. 337.

³ J. Houben and W. Fischer, *Ber.*, 1932, **64B**, 2636.

⁴ Cf. J. J. Norman, R. M. Heggie, and J. B. Larose, *Canad. J. Chem.*, 1962, **40**, 1547; J. J. Norman, *ibid.*, p. 2033.