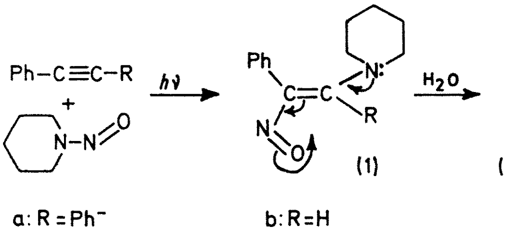
C-Nitroso-enamines

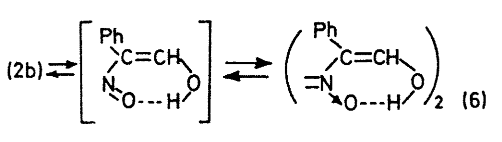
By Y. L. CHOW* and D. W. L. CHANG

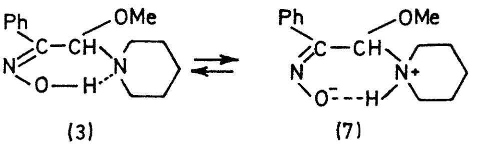
(*Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada*)

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 conditions[1] 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 phenylgloxal 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; αα-dimethoxyacetophenone[3] (**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**) tautomerises[4] 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.