N-Aryl-*C*-nitroso-imines

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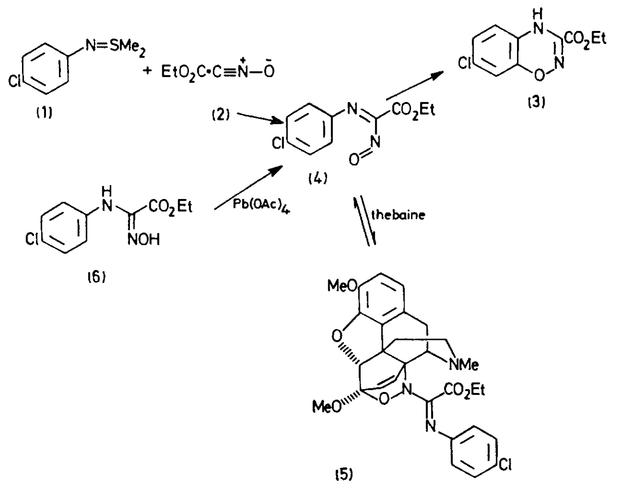
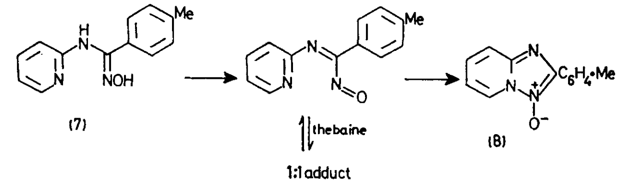
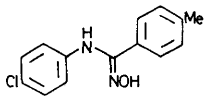
Summary Reaction of 4-chlorophenyl-*SS*-dimethylsulphimide (**1**) with ethyl cyanoformate *N*-oxide, or oxidation of the amidoxime (**6**) with lead tetra-acetate, gives the nitroso-imine (**4**), which cyclises spontaneously to the 1,2,4-benzoxadiazine (**3**), but which can be reversibly intercepted in a Diels–Alder reaction with thebaine.







(9)

IN an earlier communication we described the preparation of 1,2,4-benzoxadiazines from *N*-arylsulphimides and nitrile oxides, and suggested that the reactions might involve the unknown *C*-nitroso-imines as intermediates.[1] Following the observation of Kirby and Sweeny that nitrosocarbonyl compounds undergo Diels–Alder reaction with dienes,[2] we carried out the reaction between 4-chlorophenyl-*SS*-dimethylsulphimide (**1**) and ethyl cyanoformate *N*-oxide, generated from ethyl chloroglyoxylate 2-oxime and triethylamine, in the presence of 1 mol of the nucleophilic diene thebaine at −20 °C. The products were 7-chloro-3-ethoxycarbonyl-1,2,4-benzoxadiazine (**3**) (13%, m.p. 130—131 °C) and a 1:1 adduct (**5**) of the nitroso-imine (**4**) with thebaine (44%, m.p. 158—160 °C). The same products were formed when 2 mol of thebaine were used, to liberate the nitrile oxide from the chloro-oxime and to intercept the nitroso-imine. When the adduct (**5**) was heated in benzene at 80 °C for 3 h, the benzoxadiazine (**3**) (62%) and thebaine (90%) were isolated. Thus the nitroso-imine (**4**) can be reversibly intercepted by thebaine, and readily undergoes electrocyclic ring closure to the benzoxadiazine (**3**).

An alternative method of generating the nitroso-imine (**4**) was investigated: oxidation of the amidoxime (**6**), m.p. 131—132 °C, with lead tetra-acetate in dichloromethane at −20 °C gave the benzoxadiazine (**3**) in 88% yield. Oxidation of the amidoxime in the presence of thebaine gave the Diels-Alder adduct (**5**) (53%).

Oxidation of the pyrido-amidoxime (**7**) with lead tetra-acetate in the presence of thebaine at −78 °C also gave a Diels–Alder adduct (68%), m.p. 105—108 °C (decomp.). When this adduct was heated in benzene, it gave the *N*-oxide (**8**) in quantitative yield. As was shown earlier, this *N*-oxide is formed by oxidation of the amidoxime (**7**) in the absence of a trapping agent.[3] Oxidation of the amidoxime (**9**) in the presence of thebaine also gave an adduct, but this was unstable and could not be characterised.

These experiments provide the first direct evidence for the generation of *C*-nitroso-imines. Boyer and Frints investigated the oxidation of *N*-phenylbenzamidoxime and suggested that the subsequent complex reactions were consistent with the presence of a nitroso-imine intermediate, but no monomeric products were isolated.[4]

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[1] T. L. Gilchrist, C. J. Harris, and C. W. Rees, *J.C.S. Chem. Comm.*, 1974, 485.
[2] G. W. Kirby and J. G. Sweeny, *J.C.S. Chem. Comm.*, 1973, 704.
[3] T. L. Gilchrist, C. J. Harris, C. J. Moody, and C. W. Rees, *J.C.S. Chem. Comm.*, 1974, 486.
[4] J. H. Boyer and P. J. A. Frints, *J. Org. Chem.*, 1968, **33**, 4554.