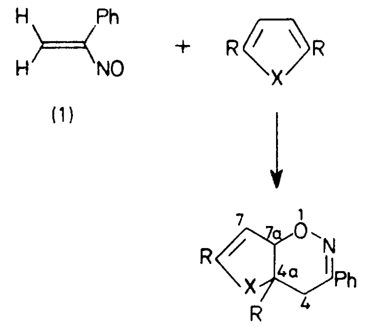
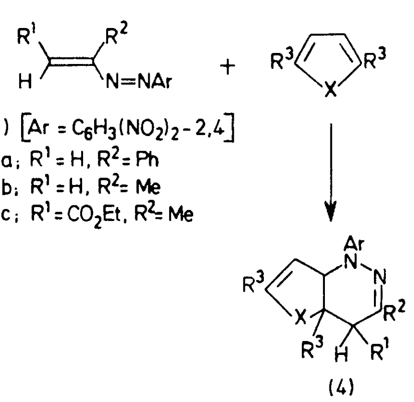
Cycloaddition of Dienes to Nitroso- and Azo-alkenes

By ROY FARAGHER and THOMAS L. GILCHRIST
(*The Robert Robinson Laboratories, University of Liverpool, P.O. Box* 147, *Liverpool* L69 3BX)

Summary Furan, 2,5-dimethylfuran, and cyclopentadiene add to the nitroso- and azo-alkenes (**1**) and (**2**) to give the oxazine and pyridazine derivatives (**3**) and (**4**); a mechanism involving Diels–Alder addition followed by rapid [3,3] rearrangement is proposed.



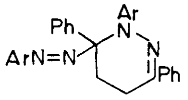
a; X = O, R = H (45%) m.p. 71–72 °C
b; X = O, R = Me (44%) m.p. 62–64 °C
c; X = CH_2, R = H (90%) m.p. 79–80 °C



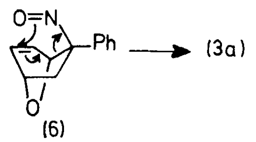
(2) [Ar = $C_6H_3(NO_2)_2$-2,4]
a; R^1 = H, R^2 = Ph
b; R^1 = H, R^2 = Me
c; R^1 = CO_2Et, R^2 = Me

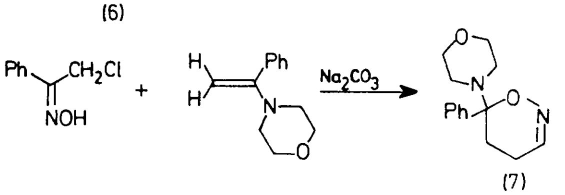
X	R^1	R^2	R^3	Yield (%)	m.p. (°C)
O	H	Ph	H	89	177–179
O	H	Ph	Me	87	190–194
CH_2	H	Ph	H	96	172–173
O	H	Me	H	22	192 (decomp.)
CH_2	H	Me	H	78	168–169
CH_2	CO_2Et	Me	H	83	175 (decomp.)

CONJUGATED nitroso- and azo-alkenes could participate in the Diels–Alder reaction either as 2π-electron components, *via* the carbon–carbon or heteroatom double bonds, or as 4π-electron components. Recent studies of nitrosocarbonyl compounds[1] and of *C*-nitrosoimines[2] have shown that they react as 2π-electron components, *via* the nitroso group, in Diels–Alder reactions. We find that α-nitrosostyrene (**1**) and structurally related azoalkenes (**2**) also react with dienes, but in a different manner to that of other nitroso and azo compounds, giving cycloadducts (**3**) and (**4**).



(5)





(92%) m.p. 187–188 °C

α-Nitrosostyrene was generated by the reaction of α-chloroacetophenone oxime with anhydrous sodium carbonate in dichloromethane at room temperature. In the presence of an excess of furan, a 1 : 1 adduct was formed, and was isolated (45%) by layer chromatography. The adduct was assigned structure (**3a**) on the basis of its ^{1}H n.m.r. spectrum: δ (100 MHz) 2·78 and 3·08 (both 1H, dd, *J* 14, 4 Hz, 2H on C-4), 5·08—5·20 (3H, m, H on C-4a, -7, and -7a), 6·50 (1H, d, *J* 3 Hz, H on C-6), and 7·32—7·74 (5H, m). Similar adducts (**3b**) and (**3c**) were obtained from 2,5-dimethylfuran and from cyclopentadiene. The ^{1}H n.m.r. spectrum of the adduct (**3b**) contains doublets (both 1H, *J* 14 Hz) at δ 2·57 and 3·00, and no signal in the region δ 6—7, indicating that positions 4a and 6 are occupied by methyl groups; the spectrum of the cyclopentadiene adduct (**3c**) contains three multiplets, each equivalent to one hydrogen, at δ 4·95, 5·81, and 6·03, which are assigned to the hydrogen atoms at C-7a, C-7, and C-6. Support for the formulation of the furan adduct as (**3a**) was obtained by its conversion in boiling dioxan containing a trace of HCl into α-(2-furyl)acetophenone oxime (36%), m.p. 90 °C,[3] identical to an authentic specimen.

The azoalkenes (**2**) were generated in a similar way, from the appropriate α-halogeno-ketone 2,4-dinitrophenylhydrazones and sodium carbonate in tetrahydrofuran, and gave the corresponding adducts (**4**). Compound (**2a**) failed to give adducts with cyclopentene, dimethyl acetylenedicarboxylate, anthracene, and 1,3-diphenylisobenzofuran; a cyclic dimer of the azoalkene, which was assigned structure (**5**) (*cf.* ref. 4) was isolated instead.

We consider that these results are best explained by a mechanism involving Diels–Alder addition of the dienes to the carbon–carbon double bonds of the nitroso- and azoalkenes, giving *endo* adducts (*e.g.*, **6**) which then undergo rapid [3,3] sigmatropic rearrangement to the observed products. The failure to isolate an adduct of (**2a**) with diphenylisobenzofuran or anthracene may be due to the fact that the primary Diels–Alder adducts cannot readily undergo this rearrangement, and so they revert to starting materials. An alternative formulation of the reaction sequence would require the dienes to add as 2π-electron components in a regiospecific manner; this appears to be unlikely because simple monoenes such as cyclopentene failed to react. Enamines do give cycloadducts (*e.g.*, **7**) with α-chloroacetophenone oxime in the presence of sodium carbonate, but, as an earlier study has shown,[5] enamines react rapidly with α-halogeno-ketoximes even in the absence of base to give salts which can then be cyclised to oxazines such as (**7**); it is therefore unlikely that α-nitrosostyrene is an intermediate in the formation of (**7**).

(*Received*, 26*th May* 1976; *Com.* 603.)

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