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Cycloaddition of Azo-dienophiles to *N*-Ethoxycarbonylazepine

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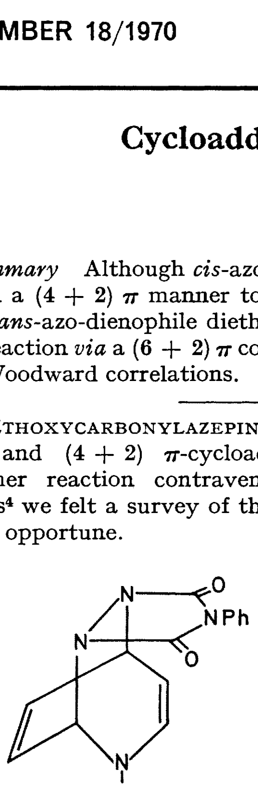
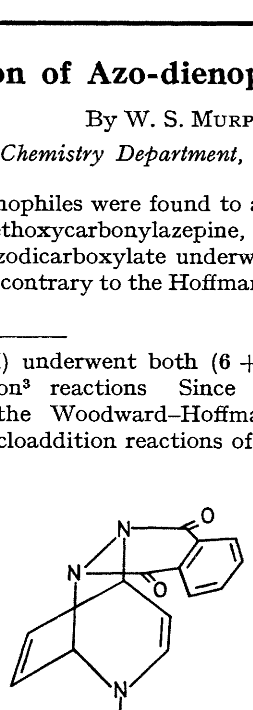
Summary Although *cis*-azo-dienophiles were found to add in a (4 + 2) π manner to *N*-ethoxycarbonylazepine, the *trans*-azo-dienophile diethyl azodicarboxylate underwent reaction *via* a (6 + 2) π course contrary to the Hoffmann–Woodward correlations.

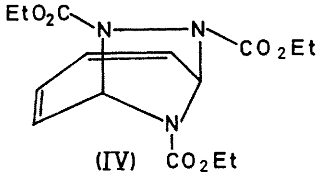
N-ETHOXYCARBONYLAZEPINE[1] (I) underwent both (6 + 2) π[2] and (4 + 2) π-cycloaddition[3] reactions Since the former reaction contravened the Woodward–Hoffmann rules[4] we felt a survey of the cycloaddition reactions of (I) was opportune.



(II)



(III)



(IV)

Both 4-phenyl-1,2,4-triazoline-3,5-dione[5] and 1,4-phthalazinedione[5] (each have *cis*-configuration about the nitrogen double bond) reacted rapidly with (I) in methylene chloride at 0—5° as indicated by the rate of disappearance of the red colour. 1 : 1 Adducts (II)† m.p. 132—133° and (III)† m.p. 216—217°, respectively, were formed.

Reaction of diethyl azodicarboxylate (*trans*-configuration about the nitrogen double bond[5b]) reacted very slowly with (I) in the absence of solvent (10 weeks at 20°) to yield the 1 : 1 adduct (IV)† quantitatively as a viscous oil (t.l.c.). The structures of (II) (52% yield), (III) (46%), and (IV) were established by chemical and spectroscopic means. Our method for establishing structure (II) confirmed its recent[3e] structural assignment. The n.m.r. splitting pattern agrees closely with that expected[3d] for structure (II). The u.v. spectrum (cyclohexane) exhibited maxima at 223 (ϵ 19,400) and 237 nm (ϵ 13,000). Both the u.v. and n.m.r. spectra of (III) were similar to that of (II). Hydrogenation of (II) and (III) in a Parr hydrogenator at 50 lb./in.^{2} pressure with a Pt catalyst for 100 hr. afforded the tetrahydro-adducts (V)† (89% yield, m.p. 158—159°) and (VI)† (87%, m.p. 150—151°), respectively. The u.v. spectrum of (V) had maxima at 218 (ϵ 19,200) and 236 nm (ϵ 10,200). The u.v. difference curve between that of (II) and (V) which consisted of maxima at 236 (ϵ 3800) and 246 nm (ϵ 3200) is consistent only with a non-conjugated diene structure[3e,7] (II). The structure of (III) was similarly determined. The u.v. difference curve between the u.v. spectra of (III) and (VI) consisted of a maximum at 241 (ϵ 3800) with a shoulder at 246 nm (ϵ 3200).

The assignment of a 1,6-type structure to (IV) is based on the close similarity between its n.m.r. spectrum and that of the (6 + 2)π-cycloadduct of nitrosobenzene and (I).[2] The n.m.r. of (IV) consisted of absorptions at τ 2·6 (4H,s), 3·3 (2H, s), 5·7 (6H, q), 8·7 (9H, m). The simplicity of the vinylic region strongly indicates the symmetrical structure (IV).[6] Further indication of a conjugated diene chromophore was obtained from the u.v. spectrum, which consisted of maxima at 253 (ϵ 8800) and 258 nm (ϵ 6600). An

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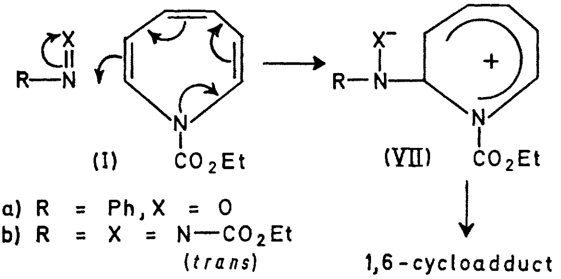
† Elemental analysis was satisfactory. Molecular weight was determined ebullioscopically. Molecular weight of (II) determined from the mass spectrum.

u.v. difference curve between (IV) and its tetrahydro-derivative was not obtainable. Attempted hydrogenation of (IV) failed. Hydrogenolysis occurred with the formation of diethyl hydrazodicarboxylate. A similar degradation in a related system has been reported.[7]



(a) R = Ph, X = O
(b) R = X = N—CO$_2$Et
(*trans*)

The success of the Woodward–Hoffmann rules[4] has been notable. It would appear probable then that $(6 + 2)\pi$-cycloadditions to *N*-ethoxycarbonylazepine, *i.e.* (IV) and the nitrosobenzene adduct, occur by a two-step[6c,d] mechanism. Both of these reactions are slow relative to the formation of (II) and (III) which are probably formed by a concerted mechanism. We suggest initial attack at the 2-ring position followed by ring closure of the intermediate dipolar ion (VII) to give the more stable 1,6-product.

Nitrosobenzene is known to be susceptible to nucleophilic attack,[8] whereas steric factors may inhibit a concerted attack on diethyl azodicarboxylate.

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