

1,4-CYCLOADDITION OF NITROSOBENZENE TO N-ETHOXYCARBONYLAZEPINE

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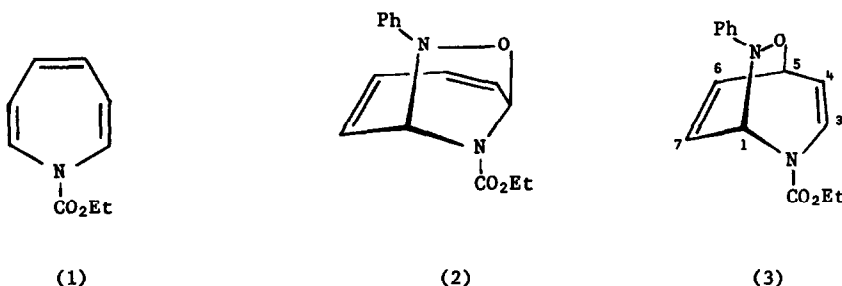
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A new stable product from the reaction of nitrosobenzene and N-ethoxycarbonylazepine is shown to be a 1,4-cycloadduct.

The cycloadduct of nitrosobenzene and N-ethoxycarbonylazepine (1) has been shown by us¹ to have the structure (2). No other product was detected. If concerted, the cycloaddition



must be an unprecedented $\pi 6s + \pi 2a$, since a ground state $\pi 6s + \pi 2s$ mode is forbidden.² Accordingly, the mechanism of formation of (2) is of interest and the possibility of a rearrangement of an initially formed 1,4-cycloadduct arises.

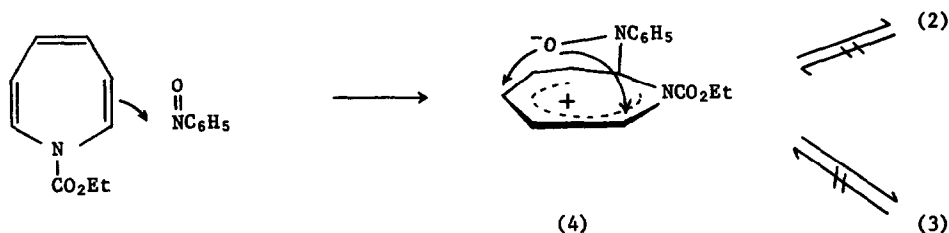
The reaction of (1) with nitrosobenzene was followed at room temperature in C_6D_6 by n.m.r. in situ. Within 2h the adduct (2) was observable together with another product of identical R_F .³ During an eight week period adduct (2) had completely decomposed probably to polymer. The second product was then readily isolable (p.t.l.c.,⁴ 17%) as a pale yellow oil. Comparison of its spectra with other 1,4-cycloadducts⁵ permitted assignment of structure (3) to this product: λ_{max} (ethanol) 220 nm (ϵ 4,060) and 255 nm (ϵ 5,440); ν_{max} , 1705, 1635 and 1593 cm^{-1} ; τ 2.9(5H, m, Ph), 3.3(2H, m, H-1 + H-3), 3.5-4.0(2H, 2xt, J 8Hz, H-6 (upfield) + H-7 (downfield)), 4.7(1H, t, J 8Hz, H-4), 5.5(1H, m, H-5), 5.8(2H, q, J 8Hz, CH_2) and 8.7(3H, t, J 8Hz, CH_3); m/e 272 (M^+), 165, 156, 107, 92.

The thermal stability of the cycloadducts (2) and (3) at room temperature in C_6D_6 was separately investigated over eight weeks by n.m.r. in situ. Neither rearranged. The separate addition of catalytic quantities of (1), CF_3COOD , and NaOD to (2) and to (3) did

not cause rearrangement of either.

The formal 1,6-addition of chlorosulphonyl isocyanate to cycloheptatriene⁶ has been shown⁷ to be a rearrangement product of an initially formed $\pi 2s + \pi 2a$ cycloadduct. However, a related mechanism for the formation of the 1,6-cycloadduct (2) involving rearrangement of the 1,4-cycloadduct (3) can now be discounted on the basis of our results.

It has been established that nitrosobenzene also forms a 1,6-cycloadduct with cycloheptatriene.⁸ Narita and coworkers⁹ ruled out both a concerted and a radical mechanism for this reaction. They proposed a two step ionic mechanism on the basis of the effects of substituents on the rates of reaction. The following mechanism is proposed by analogy and as an alternative to one involving a concerted $\pi 6s + \pi 2a$ cycloaddition. A zwitterionic intermediate (4) is suggested which collapses irreversibly to a mixture of (2) and (3).



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(Received in UK 16 November 1979)