Tetrahedron Letters No. 40, pp 3877 - 3878.
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0040-4039/79/1001-3877$02.00/0

INTRAMOLECULAR THERMAL CYCLOADDITION REACTIONS OF X=Y-ZH SYSTEMS TO NON-ACTIVATED OLEFINS

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Summary Thermal intramolecular cycloaddition of aryl imines of phenyl glycine and of arylhydrazones to non-activated olefins gives fused ring systems probably via a $4\pi + 2\pi$ cycloaddition.

We recently reported examples of what we suggested were a new class of potential 1,3-dipoles involving the tautomeric equilibrium ($1 \rightleftharpoons 2$).[1] Systems where X=CHAr, Y=N, Z=C(R)CO$_2$Me, and X=CHAr, Y=N, Z=NHAr[1] were found to undergo thermal cycloaddition reactions with a range of dipolarophiles bearing electron withdrawing substituents. Intermolecular cycloaddition did not occur to unactivated alkenes. We now report intramolecular examples of the latter type of reaction.

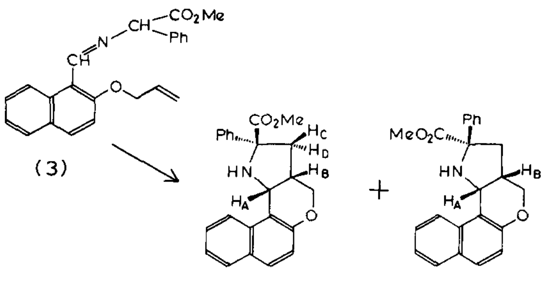
The aldimine (3) on heating in boiling xylene for 3 dy. gave a mixture of (4), m.p. 142-143°,aand (5), m.p. 107-108°, (ratio 47:53) in 71% yield.[3] The coupling constants of the ring junction protons obtained from the nmr of (4) and (5) (J_{AB} = 5.7Hz in both cases) suggested cis fused ring systems.[2] A distinguishing feature in the nmr spectra of (4) and (5) is the chemical shift of the protons H_C and H_D. In (4) these occur at δ 1.79 and 3.37 whilst in (5) they occur as part of a multiplet centred at δ 2.65. The stereochemistry of (5) has been established by an X-ray crystal structure analysis.

Crystal Data: $C_{23}H_{21}NO_3$. M = 359.4. Monoclinic. Space group $P2_1/n$. a = 15.12, b = 10.88, c = 11.24 Å, β = 104.9°. U = 1786.5 Å^3. Z=4. D_c = 1.34g cm^{-3}. 3026 independent diffraction intensities were recorded by automatic diffractometer, using CuKα radiation. The 2257 reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarisation factors. The structure was solved by the direct phasing procedures of MULTAN[4], using 400 high E values. The phased set with the highest figures of merit revealed the 27 C, N and O atoms of the molecule as the 27 largest Fourier peaks.

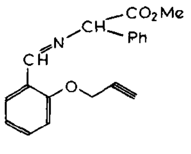
The acetylene (6) undergoes intramolecular cyclisation in boiling xylene to

$$X{=}Y{-}ZH \rightleftharpoons X{=}\overset{+}{\underset{H}{Y}}{-}\overset{-}{Z}$$

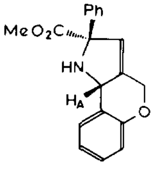
(1) (2)



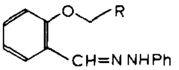
(3) (4) (5)



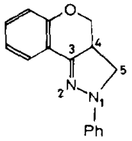
(9)



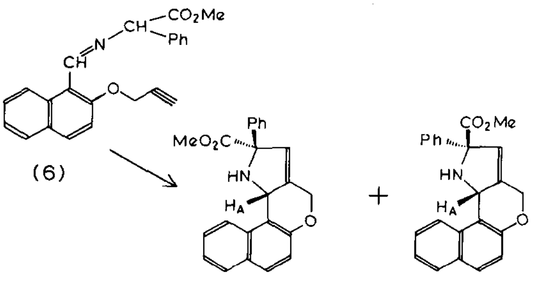
(10)



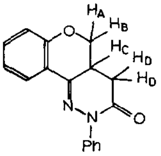
(11) a. R = -C≡CH
b. R = -CH=CHCO$_2$Me



(12)



(6) (7) (8)



(13)

give a 3:1 mixture of (7) and (8) in 93% yield. The stereochemical assignments in (7) and (8) are tentative based on the chemical shifts (CDCl$_3$) of H$_A$ and the ester methyl group, i.e. (7; H$_A$ δ 5.24; Me, δ 3.65), and (8; H$_A$ 5.69; Me, δ 3.82). The phenyl derivative (9) also gave two products (ca. 4:1). The major isomer (50%) is tentatively assigned structure (10) on the basis of its nmr spectrum (CDCl$_3$; H$_A$, δ 4.8 part of a 3H multiplet; Me, δ 3.65). The acetylenic hydrazone (11a) gave a low yield (11%) of the isomerised product (12), on heating in boiling xylene for 3 dy.[5]. In contrast (11b) underwent Michael addition]cyclisation in boiling xylene to give (13; 57%), [δ,CDCl$_3$, 2.63 (m,2H, H$_D$), 3.5 (m, 1H, H$_C$), 3.96 and 4.5 (both m, 2x1H, H$_A$ and H$_B$), and 7-8 (m,9H,Ar)]

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2. W. Oppolzer, Tetrahedron Letters, 1970, 3091.
3. Reactions were carried out under an atmosphere of argon. All new compounds gave satisfactory analytical data.
4. G. Germain, P. Main and M.M. Woolfson, Acta Cryst., 1971, A27, 368.
5. The major product has not yet been obtained pure but its spectral characteristics accord with those expected for the 4,5-double bond isomer of (12).

(Received in UK 23 July 1979)