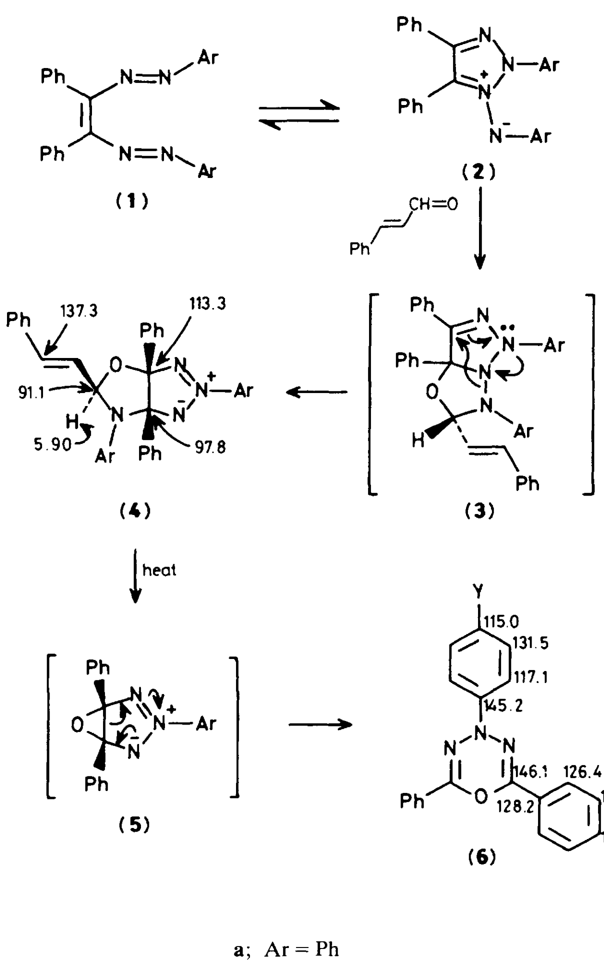
Substituted 1,3,3a,4,5,6a-Hexahydro-oxazolo[4,5-*d*]-1,2,3-triazoles from a Cycloaddition on a Carbonyl Group. Thermal Ring Expansion: A New Route to Substituted 1,3,4,5-Oxatriazenes

Richard N. Butler,* Ann M. Evans, Patrick McArdle, and D. Cunningham
Department of Chemistry, University College, Galway, Ireland

Substituted derivatives of hexahydro-oxazolo[4,5-*d*]-1,2,3-triazoles, a new ring system, are described, and the crystal structure of one derivative is reported; on being heated they undergo a ring expansion providing a simple new route to the rare 1,3,4,5-oxatriazine ring.

While a range of fused azapentalene systems have been described,[1] derivatives of fused oxazolo-1,2,3-triazole systems have not previously been reported. We have encountered the first such compounds from cycloadditions of the 1,2-*cis* bisarylazostilbenes (**1**) with cinnamaldehyde. The compounds (**1**) react *via* formation of a low concentration of the cyclic triazolium imide form (**2**),[2,3] which usually adds to deactivated alkenes at the double bond in an *endo* stereospecific 1,3-dipolar cycloaddition.[3] However, when treated† with cinnamaldehyde the ultimate products of the cycloaddition were the oxazolo[4,5-*d*]-1,2,3-triazole derivatives (**4**). The structure of the compounds (**4**) was indicated by their ^{1}H and ^{13}C n.m.r. spectra which showed the three saturated carbons including the two bridgeheads (Scheme 1). The *X*-ray crystal structure‡ of compound (**4b**) confirmed the ring structure and showed an *exo*-styrenyl substituent (Figure 1). We tentatively suggest that the initial cycloaddition occurred on the carbonyl group giving the unstable *endo*-adduct (**3**) as a reactive intermediate. This sterically unfavoured cycloaddition is probablly facilitated by secondary orbital interactions in the transition state. The species (**3**) rearranged *in situ* by a 1,4-pericyclic N → C migration giving the new hexahydro-oxazolo[4,5-*d*]-1,2,3-triazolo system (**4**) with the styrenyl substituent in an *exo*-position. The *endo* to *exo* change for the styrenyl group on going from (**3**) to (**4**) was confirmed using Dreiding models. No other isomers were encountered and this exclusive stereochemistry supports a 1,3-dipolar cycloaddition rather than a two-step nucleophilic addition to the carbonyl group.

The compounds (**4**) were stable under normal conditions but on being heated† in ethanol or ethanol–HOAc for a short time they underwent an interesting fragmentation and ring expansion giving high yields of the substituted 1,3,4,5-oxatriazenes (**6**). It is likely that this reaction involved the key intermediate (**5**). This is a particularly convenient route from simple precursors to the rare oxatriazene system (**6**). The only compound of this unusual class (a potential 8π planar system)



a; Ar = Ph
b; Ar = *p*-BrC$_6$H$_4$

Scheme 1. Some ^{1}H and ^{13}C n.m.r. shifts are shown for *p*-Br derivatives.

---

† (**1a**) (m.p. 178—179 °C) and (**1b**) (m.p. 197—199 °C, from C$_6$H$_6$) were prepared by oxidising the bis-arylhydrazine of benzil with PbO$_2$ in CH$_2$Cl$_2$ or Pb(OAc)$_4$ in HOAc. A solution of (**1**) (500—700 mg) in pure methyl ethyl ketone (10 ml) was treated with cinnamaldehyde (0.25 ml) and heated under reflux for 8—21 h. Evaporation of the solvent or cooling gave (**4a**) (80 yield; m.p. 177—178 °C, from diethyl ether), and (**4b**) (82% yield; m.p. 182—183 °C, from methyl ethyl ketone). A solution of (**4**) (100 mg) in ethanol (10 ml) (or ethanol containing 2 drops of HOAc) was heated under reflux for 30 min (or 10 min respectively). On cooling, red spindles of (**6a**) (90% yield; m.p. 170—171 °C, from ethanol; lit.[4], 172 °C) and (**6b**) 81% yield (m.p. 179 °C, from ethanol) separated. The ethanol filtrate deposited a yellow gum on evaporation. All compounds gave satisfactory C,H,N elemental analyses. ^{13}C N.m.r. shifts were confirmed by off-resonance decoupling.

‡ *Crystal data for* (**4b**): $C_{35}H_{26}ON_4Br_2$, M = 678.42, triclinic, space group $P\bar{1}$, a = 10.263(2), b = 11.961(3), c = 13.226(3) Å, α = 83.90(2), β = 87.67(2), γ = 73.37(2)°, U = 1546.76 Å^3, Z = 2, $F(000)$ = 684.00, μ = 25.77 cm^{-1}, T = 23 °C, 2291 unique reflections observed with $I > 3\sigma(I)$. (θ–2θ scans over the range $2° < \theta < 24°$, graphite monochromated Mo-K_α radiation, λ = 0.71069 Å, Hilger Y290 diffractometer). The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined using SHELX-76. R = 7.05, R_w = 7.66%, $w = 1/(\sigma^2 F_o + 0.0014\ F^2)$ for 332 refined parameters with hydrogen atoms in calculated positions and all nonhydrogen atoms anisotropic except the atoms of the bicyclic system. $\Delta_{\rho max.}$ = 0.38 e/Å^3, $\Delta_{\rho min.}$ = 0.32 e/Å^3. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

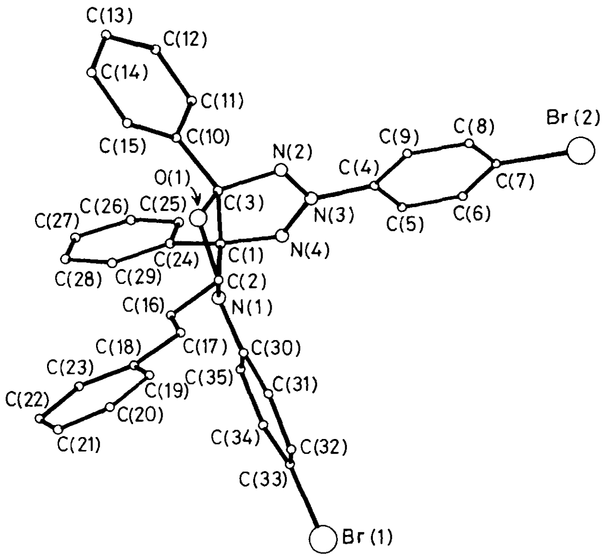


Figure 1. Crystal structure of (**4b**).

known hitherto was prepared in 1980 by photolysis of a relatively inaccessible triazole *N*-oxide.[4] The structures of the compounds (**6**) were established from ^{1}H and ^{13}C n.m.r. spectra (nine carbon signals only) (Scheme 1) and cryoscopic molecular weights. Also compound (**6a**) was identical to a sample obtained from photolysis[4] of 2,4,5-triphenyl-1,2,3-triazole *N*-oxide. The synthetic scope of these reactions is being explored.

A. M. E. acknowledges a State Grant for research.

Received, 16th February 1987; Com. 209

References

1 J. Elguero and R. M. Claramunt, *Adv. Heterocycl. Chem.*, 1978, **22**, 183.
2 R. N. Butler and J. P. James, *J. Chem. Soc., Chem. Commun.*, 1983, 627.
3 R. N. Butler, D. Cunningham, J. P. James, and P. McArdle, *J. Chem. Soc., Chem. Commun.*, 1983, 762.
4 G. J. Gainsford and A. D. Woolhouse, *Aust. J. Chem.*, 1980, **33**, 2447.