Thermal Cycloaddition on to *N*-Acetyl- and *N*-Dimethylcarbamoyl-azonine

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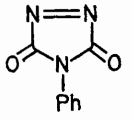
Summary Reaction of *N*-acetyl- and *N*-dimethylcarbamoyl-azonine (**2a,b**) with 4-phenyl-1,2,4-triazoline-3,5-dione (**1**) at −78° leads to unsymmetrical "2 + 4" cycloadducts.

RECENTLY, we reported the ready thermal (−78°) reaction of (**1**) with all *cis*-cyclononatetraene and oxonin to produce cycloadducts.[1] Here we describe the reaction of (**1**) with two typical polyenic azonines, (**2a**) and (**2b**).

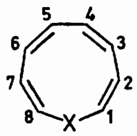
Treatment of (**2a**)† with an equimolar quantity of (**1**) in CH_2Cl_2 at −78° gave (**3a**)‡ (m.p. 111—112°). Similarly (**1**) reacted with (**2b**)[2] to give (**3b**)‡ (m.p. 163—164°).

The n.m.r. spectra show that each cycloadduct has six olefinic and two bridgehead protons all of which are non-equivalent. Analysis of the coupling constants reveals that the bridge-head hydrogens are not coupled to one another but each is coupled (*J ca.* 6—7 Hz) to one of a pair of olefinic protons which are also strongly coupled (*J ca.* 10 Hz) to each other, uniquely consistent with structures (**3a**) and (**3b**).

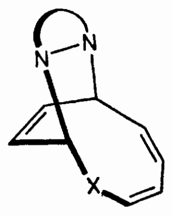
The formation of (**3a**) and (**3b**) clearly entails a symmetry-allowed $[{}_{\pi}2_{s} + {}_{\pi}4_{s}]$ process whereby the C(1)—C(4) segment of the azonine behaves as the ${}_{\pi}4_{s}$ portion. While it is unclear why (**1**) does not add to the remote butadiene segment [C(3)—C(6)] to yield the symmetrical structure (**4**), "Dreiding" molecular models do reveal that any "flattening" of the azonine frame away from the extreme helical shape will be chiefly reflected along the four-carbon array which does indeed react, the two ethylene groups of the remote butadiene group remaining essentially orthogonal during the early stages of this "flattening" process. The C(1)—C(4) segment of (**3a**) and (**3b**) is directly linked to nitrogen and so must be more electron-rich and thus more reactive as a π-donor than the alternate butadiene portion of the molecule. Indeed, the importance of one or both of these factors emerge quite clearly from the fact that (**2a**) which is



(1)



(2a); X=NCONMe$_2$
(2b); X=NCOMe



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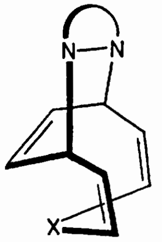

(4)

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† Prepared by treating *NN*-dimethylcarbamoyl chloride with potassium azonide in THF and characterized by spectral and chemical means.

‡ Analysed spectroscopically (including 100 and/or 220 MHz n.m.r. spectra).

believed[3] to possess a frame that is both less distorted and more electron-rich than that of (**2b**) is also the more reactive (*ca.* 18× at −78°) of the two towards (**1**).

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[2] A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *Chem. Comm.*, 1970, 1133.

[3] A. G. Anastassiou, *Accounts Chem. Res.*, in the press.