The Cycloaddition of Diazoalkanes to Conjugated Allenes

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IN the 1,3-dipolar addition of diazoalkanes to alkenes, reactivity increases with increasing electrophilicity of the ethylenic bond. With $\alpha\beta$-unsaturated carbonyl compounds, the nucleophilic diazocarbon atom generally becomes bonded to the carbon β to the carbonyl group,[1] although cases are known where for steric reasons diazoalkanes add in the reverse sense to conjugated ethylenic[2] and acetylenic[3] esters. Similar reversals have been observed with $\alpha\beta$-unsaturated sulphones[4] and nitro-compounds.[5] We have studied the reaction between 2-diazopropane and a series of conjugated allenic esters (I; R = H, Me)† and found that, whilst in all cases cycloadditions occurs at the most electrophilic ($\alpha\beta$) double bond, the orientation is dependent in a very clear-cut way on the substitution at the γ-carbon atom.

Thus, as predicted on electronic grounds, adducts of type (II) are the sole products obtained from the allenic esters (I; R^3 = Me), when at least one of the groups R^1 and R^2 is hydrogen. Esters (I; R^1 = R^3 = H) which lack the α-methyl group behave similarly, but in such cases the reaction is complicated somewhat by the very ready tautomerisation of the initial adduct (II; R^3 = H). Thus methyl butadienoate rapidly forms 4-methylene-Δ^2-pyrazoline (IV) with 2-diazopropane. In the presence of an excess of the diazo-compound, further attack at the *exo*-double bond (activated by conjugation with C=N) occurs and the spiro-system (V) is obtained.

In contrast, the $\gamma\gamma$-disubstituted allenes (I; R^1 = R^2 = Me; R^3 = H and Me) give not (II) but the isomeric 3-alkylidenepyrazolines (III; R^1 = R^2 = Me), in which 2-diazopropane has added to the $\alpha\beta$-double bond in the opposite sense.

Formula (VI) illustrates the very severe crowding of alkyl groups which must occur in the transition state for formation of an adduct of type (II) when R^1 = R^2 = Me. Apparently this situation is very

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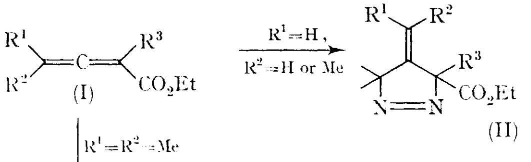
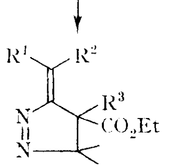
† The literature on allene–diazoalkane cycloadditions is surprisingly sparse (see ref. 6).

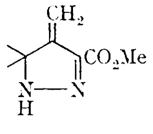
much worse than that (VII) leading to a 3-alkylidenepyrazoline (III) even in the case of the tetra-substituted allene (I; $R^1 = R^2 = R^3 = Me$), for which transition state (VII) contains two eclipsing interactions. The eclipsing interactions in this particular example are however reflected in the low reactivity of the allene towards 2-diazopropane: no better yield of adduct than 5% has been achieved with the compound. (The other allenes gave adducts in essentially quantitative yields.)



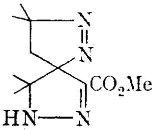
(I) (II)



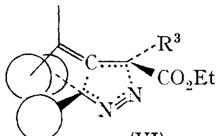
(III)



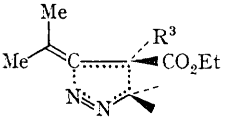
(IV)



(V)



(VI)



(VII)

Transition states of type (VI) are relatively uncongested for esters (I; $R^1 = H$; R^2 and $R^3 = H$ or Me), so electronic control of orientation prevails. Also, allenes with a single γ-methyl group would be expected to give a single adduct (as found) having the geometry (II; $R^1 = H$; $R^2 = Me$).

Identical effects have been observed with the series of cyanoallenes analogous to the esters (I). A more general survey of allene–diazoalkane cycloadditions is currently under way.

A similar kind of steric argument has been used by Farnum *et al.*,[7] for the dimerisation of ketens, and related considerations may apply to the reaction of secondary amines with cyanoallenes.[8]

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