

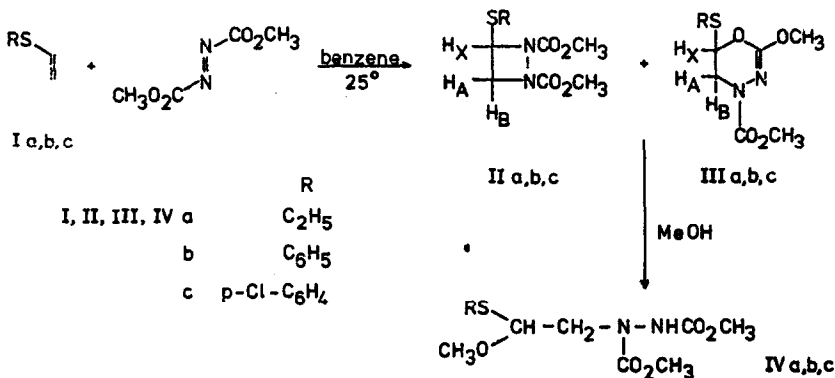
ADDITION OF AZODICARBONYL COMPOUNDS TO MONOOLEFINS VI.  
 $\alpha,\beta$ -UNSATURATED SULFIDES.

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Enolethers (1,2) and enamines (3,4) are able to yield two different cyclo-adducts - 1,2-diazetidines or 5,6-dihydro-1,3,4-oxadiazines - in the reaction with azodicarbonyl compounds. While the mechanism of the 2+2-addition leading to the diazetidine derivatives is still a matter of debate (1,5), one is tempted to assume a priori the 2+4-addition to be a concerted  $\pi^2_s + \pi^4_s$ -process. This view is supported by experimental results obtained with enolethers (1,2). However in view of the inherent polarity of both components, the possibility of a multi-step reaction must also be considered. We wish to present some examples which indicate that the 2+4-adducts from azodicarbonyl compounds and monoolefins can indeed be formed in a multi-step reaction.



Azodicarboxylic acid dimethylester (ADM) reacts with ethylvinylsulfide (Ia) or arylvinylsulfides (Ib,c) forming a mixture of the 2+2- and the 2+4-

cycloadducts II and III in overall yields of more than 80%. Elemental analysis and the molecular weights determined by mass spectrometry are in accord with the 1:1 composition of the adducts IIa-c and IIIa-c. The latter exhibit spectral features characteristic for such compounds reported in previous communications (2,3). On solvolysis with methanol corresponding adducts II and III yield the same thioacetal IV, indicating that of the two possible orientational isomers of the six-membered ring only III is formed.

	NMR <sup>a)</sup>						IR ν -C=N (cm <sup>-1</sup> )
	H <sub>X</sub> <sup>b)</sup>	H <sub>A</sub>	H <sub>B</sub>	J <sub>AB</sub> <sup>c)</sup>	J <sub>AX</sub>	J <sub>BX</sub>	
IIa	5.48	4.62	4.03	9.1	8.2	6.0	---
IIIa	5.48	3.93	3.93	e)	8.6 <sup>d)</sup>		1675 (KBr)
IIb	5.51	4.50	3.48	9.2	8.1	5.7	---
IIIb	5.68	4.08	3.75	13.4	3.7	5.1	1669 (KBr)
IIc	5.49	4.52	3.50	9.2	8.1	5.5	---
IIIc	5.61	4.04	3.71	13.5	3.6	4.8	1675 (KBr)
VI	5.64	4.47	---	---	8.0	---	---
VII	5.40	4.60	---	---	2.3	---	1660 (film)
VIII	5.45	4.54	---	---	1.2	---	1660 (film)

a) in CDCl<sub>3</sub>, b) ppm, c) Hz, d) J<sub>AX</sub> + J<sub>BX</sub> e) not measured

Under the reaction conditions neither of the cycloadducts II or III can be interconverted. The isomeric ratio II/III is therefore kinetically controlled. As can be seen from table II, the product composition is only slightly affected by varying the substituent R on sulfur, suggesting that the product determining transition states of both reactions possess similar polarity.

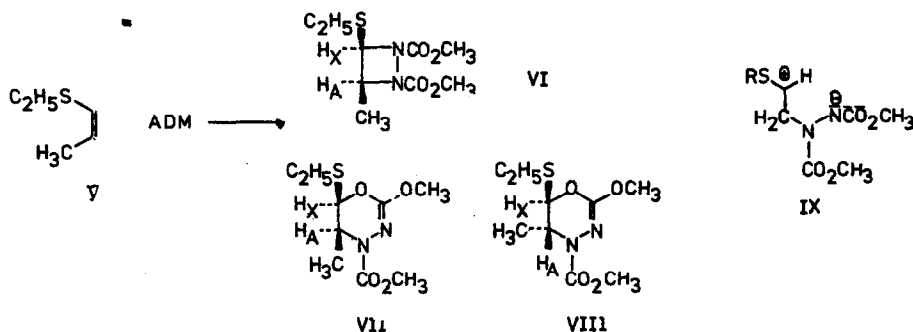
**Tab. II** Product composition in the addition of the vinylsulfides Ia-c to ADM in benzene

	R	% II x)	% III
Ia	C <sub>2</sub> H <sub>5</sub>	35 ± 3	65 ± 3
Ib	C <sub>6</sub> H <sub>5</sub>	34	66
Ic	p-Cl-C <sub>6</sub> H <sub>5</sub>	28	72

x) relative yield determined by NMR-spectroscopy

More information about the mechanisms of both cycloadditions can be derived from stereochemistry. Cis-1-thioethylpropylene V (purity 95%) yields three different 1:1-adducts in the reaction with ADM, which are identified by their spectral data to be the cis-substituted diazetidene VI and the stereo-

isomeric oxadiazines VII and VIII which are formed in comparable amounts (VI:VII:VIII  $\approx$  3:1:1) in benzene solution.



Neither the unsaturated sulfide V nor the oxadiazines VII or VIII are isomerized when exposed to the reaction conditions. Therefore, the formation of both stereoisomers indicates an intermediate in the 2+4-cycloaddition, identifying this reaction as a nonconcerted cycloaddition process. In view of the polarity of the  $\alpha,\beta$ -unsaturated sulfides, the most reasonable structure for the intermediate seems to be that of a more or less free rotating dipole, schematically represented as IX.

Such a dipole of course could be the common intermediate of both cycloaddition reactions. In this case however, the exclusive formation of the cis-isomeric diazetidine VI in the addition of V to ADM would be somewhat surprising, since the formation of trans-isomeric diazetidine can be expected to be more favourable for stereochemical reasons when starting from the ionic intermediate. On the basis of this result it seems more likely that the ionic precursor of the 2+4-adducts is not simultaneously an intermediate in the formation of the four-membered ring.

The dipole IX should be trapped partially or completely by suitable agents such as methanol. Running the addition of phenylvinylsulfide Ib to ADM in methanol, a 1:1-mixture of the diazetidine IIb and the thioacetal IVb, but no trace of the oxadiazine IIIb is obtained. IVb cannot arise from a solvolytic cleavage of the cycloadducts, because IIb and IIIb are not solvolyzed to a significant extent when exposed to the reaction conditions for several reaction half-times of the addition. The formation of IVb therefore confirms the existence of a polar intermediate.

Tab. III

Ib + ADM	<u>methanol</u> →	IIb (ca 50%) + IVb (ca 50%)
	<u>benzene</u> →	IIb ( 34%) + IIIb ( 66%)
	<u>acetonitrile</u>	IIb ( 48%) + IIIb ( 52%)
	<u>tert.butanol</u> →	IIb (ca 50%) + IIIb (ca 50%)

As can be seen from table III, neither polar aprotic solvents as acetonitrile nor the polar protic solvent tert. butanol - which because of steric hindrance is less apt to trap the intermediate - reduce the amount of the oxadiazine IIIb to less than 50%. Since about the same amount of the acetal IVb is found in methanol, it seems to arise essentially from the 2+4-addition. In agreement with the zwitterionic structure proposed for the intermediate IX, it is trapped completely by methanol. On the other hand, the presence of methanol does not prevent the formation of the four-membered ring, confirming the suggestion that the dipole IX is not an intermediate of the 2+2-addition as well.

The experimental facts strongly suggest, that the 2+4-cycloaddition of ADM with  $\alpha, \beta$ -unsaturated sulfides is a multi-step reaction proceeding via a more or less free rotating dipole. No details can be derived from these results concerning the mechanism of the 2+2-cycloaddition, except that it presumably does not proceed via an open dipole.

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