

Allenes and 1,3-Dienes from the Photolysis of Pyrazolenines

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THE formation of cyclopropenes by irradiation of pyrazolenines is well established.¹ We have studied the photolysis of pyrazolenine esters of the general type (I)* (*cf.* ref. 2), using the $n \rightarrow \pi^*$ transition at 350 m μ , and have obtained, not the expected cyclopropenes (II), but a mixture of the isomeric allenes (III) and 1,3-dienes (IV) in the ratio *ca.* 3 : 2. [Ester (IIIC) was proved to be free from the isomer with methyl and ethyl groups interchanged.] In contrast, the hydroxy-compound (V) behaved normally, giving the cyclopropene alcohol (VI) [together with the epoxide (VII) as minor product] *via* the red diazo-compound (VIII) [λ_{\max} (Et₂O) 498 m μ], which could be efficiently trapped by acetic acid as the hydroxy-ester (IX).

Similar diazo-compounds could not be detected in the ester photolyses, either spectroscopically or indirectly by trapping with acetic acid as products analogous to (IX). In the presence of acetic acid, the photolysis of the esters (IA) and (IC) was

unaffected, whereas the propionate (IB) was converted into a mixture of the propionates (IIIB) and (IVB) and the corresponding *acetates* (IIIA) and (IVA). Conversely, irradiation of the acetate (IA) in the presence of propionic acid gave a mixture of the same four products. Similar behaviour was observed with (IC). The variation of the ratio acetates:propionates with the ratio added acid:starting material was not concentration-dependent, and was close to that calculated for complete acyloxy-randomization, although some preference (especially in the case of the dienoid products) for the original acyloxy-group was noticed.

Participation of methanol was much less efficient than that of acetic or propionic acid, and for satisfactory conversion into the methoxy-analogues of (III) and (IV) it was necessary to employ toluenesulphonic acid (0.01M in ether-methanol) as catalyst.

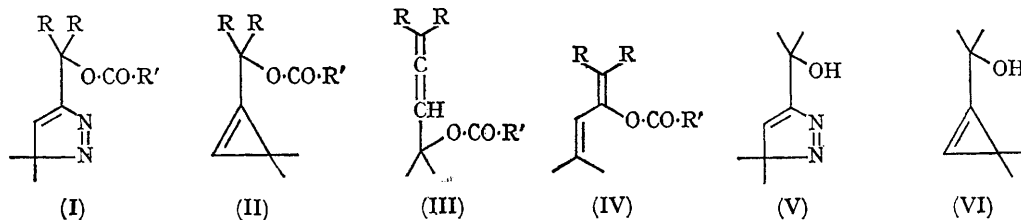
* Readily obtainable from 2-diazopropane and the corresponding ethynylcarbinyl esters.

¹ G. L. Closs and W. A. Böll, *Angew. Chem.*, 1963, **75**, 640; *J. Amer. Chem. Soc.*, 1963, **85**, 3904. *cf.* R. Anet and F. A. L. Anet, *ibid.*, 1964, **86**, 525.

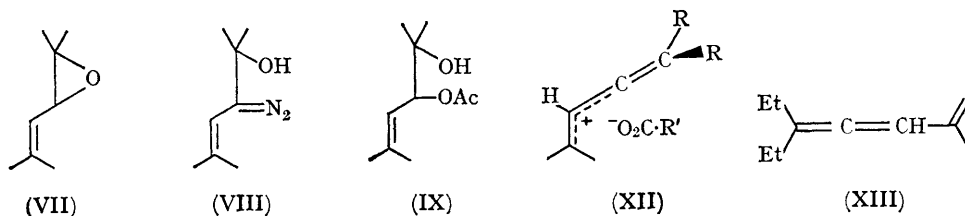
² A. C. Day and M. C. Whiting, *Proc. Chem. Soc.*, 1964, 368.

The intermolecularity of the reaction was demonstrated by the co-irradiation of (IB) and (IC) (each *ca.* 0.05 molar in ether or pentane), which

of cross-over products in the co-irradiation experiment occur *in, and only in,* the photochemical step. Cyclopropene esters (II) could be



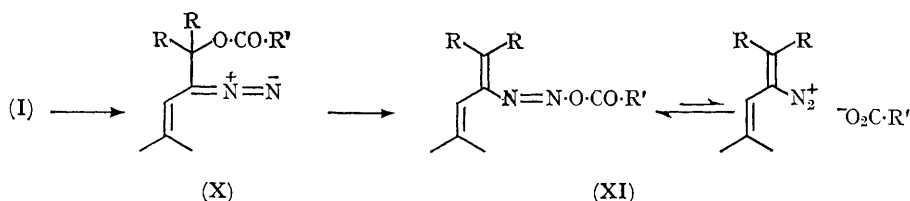
A: R = R' = Me
 B: R = Me; R' = Et
 C: R = Et; R' = Me
 D: R = R' = Et



gave a mixture of the eight possible products, (III, A, B, C, and D) and (IV, A, B, C, and D) in amounts close to those for complete anion-randomization. The proportion of cross-over products was diminished somewhat by irradiation of a more dilute solution (*ca.* 0.02 molar in each reactant).

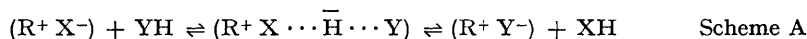
eliminated as possible intermediates, since (IIB) [obtainable by propionylation of the alcohol (VI)] was unaffected under the photolytic conditions.†

Our observations can be rationalized in terms of a diazo-ester (X) (*cf.* ref. 1) which rearranges (too rapidly to react with acid or undergo carbenoid decomposition) to the isomer (XI):

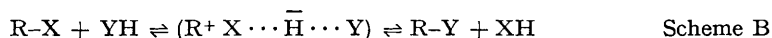


Control experiments showed that the participation of added acid or methanol, and the formation

The latter lives long enough to randomize its anion with added acid according to Scheme A or B:



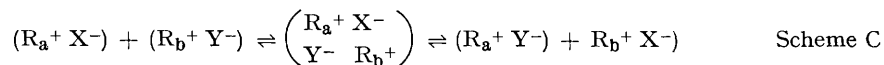
or



† The pyrolysis of this compound (*cf.* ref. 3) will be reported later.

* G. L. Closs, reported in J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, *J. Org. Chem.*, 1965, **30**, 1038, footnote 32.

(the low efficiency of methanol, unless catalyzed by acid, is then understandable) or with a second ion-pair (scheme C).



Decomposition *via* the diazonium ion-pair would then give the allylic system (XII) which could collapse to give either an allene or a 1,3-diene. Additional support for this mechanism was provided by the isolation of a small amount (5%) of

the triene (XIII) in the photolysis of (IC), presumably formed by deprotonation of a cationic species of the type postulated.

Further studies of the reaction, in particular the analogous photolysis of pyrazolenines containing other leaving groups (*e.g.* Cl) in place of acyloxy⁴ will be reported later.

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⁴ A. C. Day and P. Raymond, unpublished work.