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PHOTOCHEMICAL AND THERMAL DECOMPOSITION OF 2,2-DIPHENYL-5-DIPHENYLMETHYLENE-1,3,4-OXDIAZOLINE.

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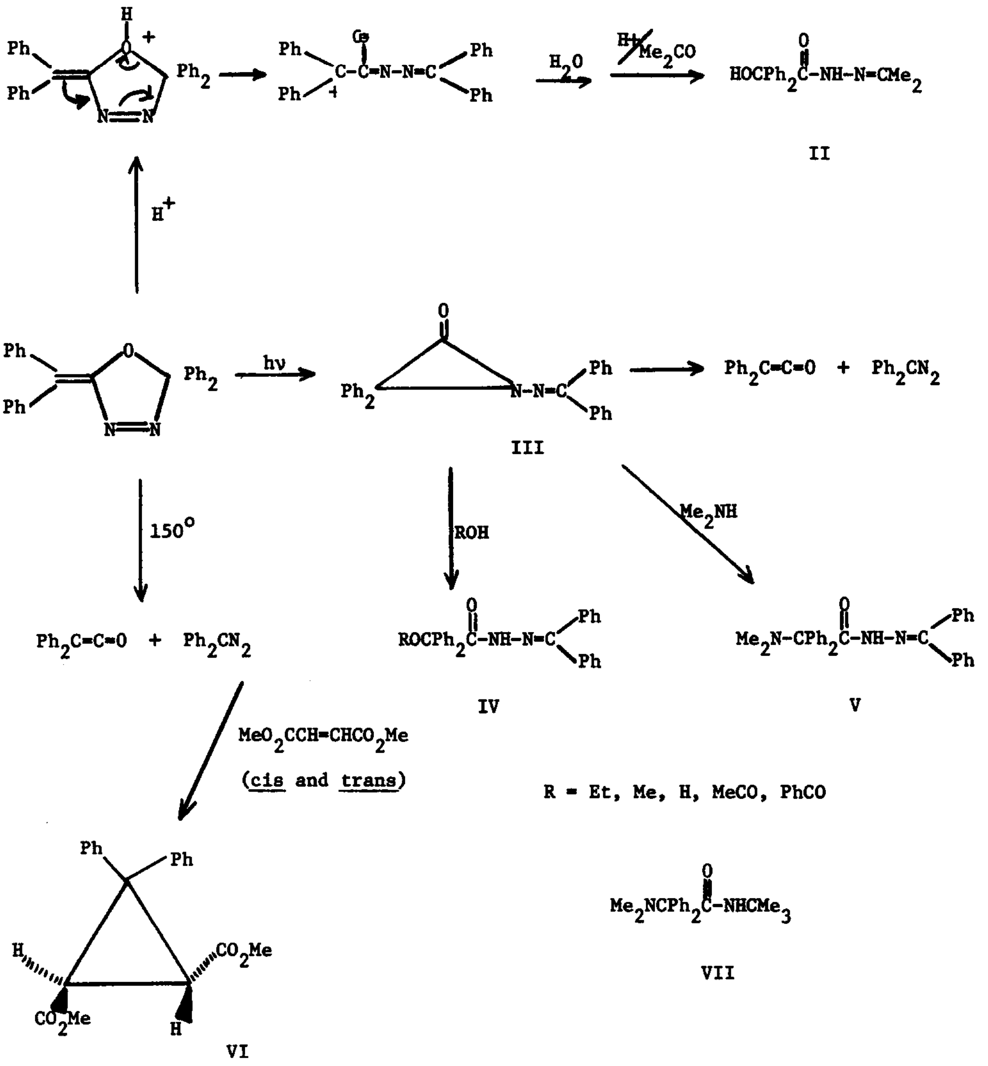
The reaction of diphenylketene with diphenyldiazomethane in ether solution gives 2,2-diphenyl-5-diphenylmethylene-1,3,4-oxdiazoline (I) in good yield.(1,2) The structure of I was established by Kirmse.(2) A further piece of evidence for I is that, being an enol ether, it undergoes facile acid catalyzed hydrolysis in aqueous acetone to give II. Kirmse also reported(2) that the photolysis of I in presence of hydroxylic reagents gave IV (R=Me, MeCO, PhCO and H). Photolysis in benzene solution resulted in the reversal of the cycloaddition reaction because diphenylketene and diphenyldiazomethane were detected as the primary photoproducts. We wish to report some preliminary results which suggest a probable mechanism for the photochemical reaction.

On the basis of the data outlined below we suggest that the primary product of the photolysis[†] of I is the α-lactam III. The lactam, however, is very reactive (and unstable) and undergoes secondary reactions.

Baumgarten and his co-workers(3) found that in general α-lactams react with hydroxylic reagents to break the saturated carbon-nitrogen bond to give compounds analogous to IV. They also found (3b) that when N-*t*-butyl-3,3-diphenylaziridone was treated with dimethylamine the predominant product was VII.

We found that when I was photolyzed in absolute ethanol or in ether containing 20% ethanol the principal product was IV (R=Et). Compound I was recovered unchanged when heated at reflux in ethanol, which precludes any acid catalyzed ring opening under our conditions. Photolysis of I in ether containing a large excess of dimethylamine produced a mixture from which V was obtained in 61 per cent yield. The other major product was N,N-dimethyldiphenylacetamide. The latter probably arises from the reaction of diphenylketene with dimethylamine.

These data, together with the data of Kirmse, strongly suggest the -lactam intermediate III in the photolysis of I. We have as yet been unable to observe III directly but experiments



II

III

IV

V

VI

VII

R = Et, Me, H, MeCO, PhCO

to that end are now in progress. We have repeated Kirmse's photolysis in benzene (also in ether and acetonitrile) and confirm that in absence of a trapping agent diphenylketene and diphenyldiazomethane are formed. We suggest that the α-lactam III is unstable with respect to those compounds and rearranges to them if it is not trapped first. It seems highly unlikely that in this case the photochemical reaction would follow the same course as a thermal reaction. When I was heated at 150° in bromobenzene solution containing an equivalent of either dimethylfumarate or dimethyl maleate the cyclopropane VI was formed. This result can be explained in terms of formation of diphenyldiazomethane which then adds to the unsaturated esters. The resulting pyrazolines lose nitrogen under the conditions of the reaction to give VI. The loss of nitrogen gives the <u>trans</u> product irregardless of whether dimethylfumarate or maleate is used.(4)

We are examining further aspects of this photochemical rearrangement. This work has been supported by a grant from the Petroleum Research Fund and the University of Nebraska Research Council.

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† The photolysis experiments were carried out at room temperature using a Hanovia 450 watt medium pressure Hg arc. Pyrex was used to filter out light below 3000 Å. The samples were not degassed.

1. H Staudinger and T. Reber, Helv. Chemica Acta, 1921, <u>4</u>, 1.
2. W. Kirmse, Ber., 1960, <u>93</u>, 2357.
3. (a) H. E. Baumgarten, J. Am. Chem. Soc., 1962, <u>84</u>, 4975.
   (b) Private communication from Prof. Baumgarten. The data are taken from a paper being prepared for publication.
4. W. M. Jones, J. Am. Chem. Soc., 1959, <u>81</u>, 3776.