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THE GENERATION OF A TME BIRADICAL IN THE PHOTOSENSITISED PHOTOLYSIS OF A BI-(1-PYRAZOLIN-4-YLIDENE)

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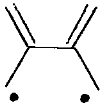
Abstract: The direct photolysis and flash vacuum pyrolysis of 3,3,3',3',5,5,5',5'-octamethyl-bi-(1-pyrazolin-4-ylidene) 4a proceeds via a sequence of TMM intermediates but in the photosensitised photolysis a TME intermediate is formed.

The TME (tetramethylene ethane) biradical 1 is thought to be an intermediate in the dimerisation of allenes.[1] It has also been implicated as an intermediate in the thermal rearrangements of derivatives of 1,2-dimethylenecyclobutane 2,[2] elimination of carbon monoxide or nitrogen from compounds of the type shown in formula 3,[3] and in other reactions.[4]



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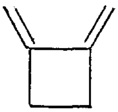

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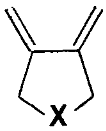
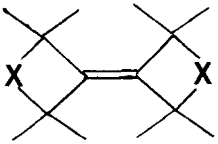
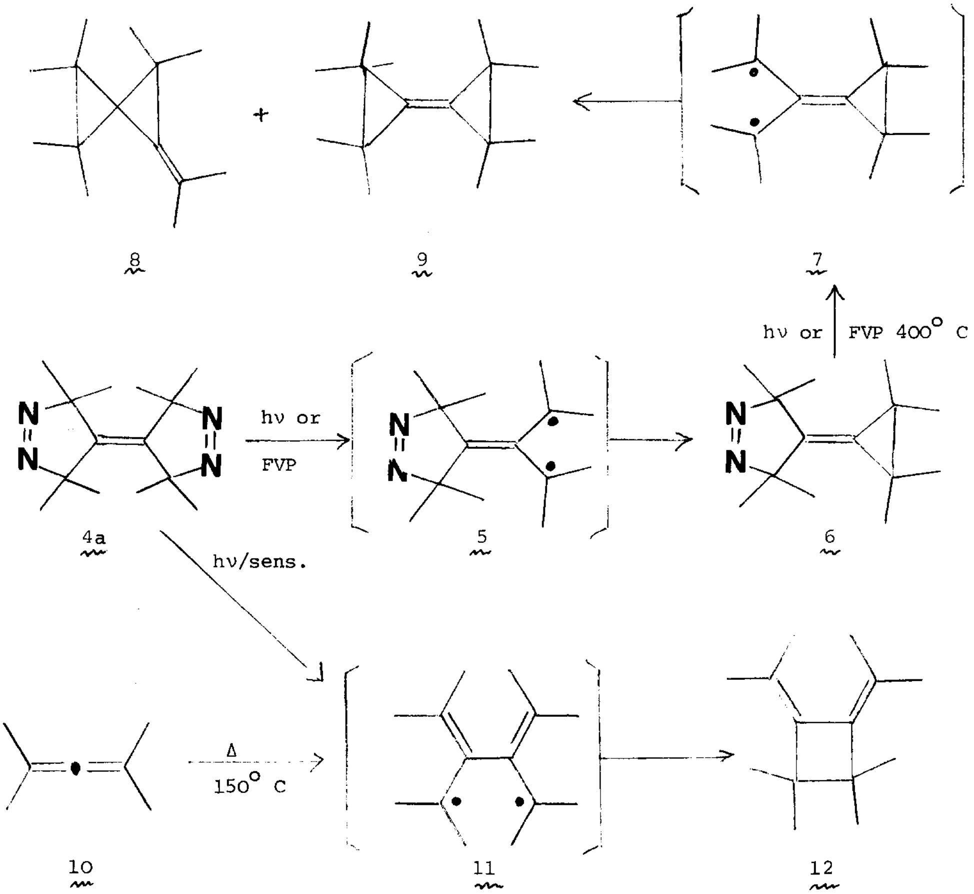


3, X = CO or -N=N-



4, X = SO_2 and/or -N=N-

In connection with earlier work we developed a synthesis of compounds of the type shown in formula 4.[5] In principle these compounds could also be used to generate TME biradicals - provided both leaving groups X could be eliminated at the same time. In practice, from the standpoint of TME generations, our initial studies of the photolysis and pyrolysis of these compounds proved disappointing. The leaving groups are lost sequentially and reactions involving TMM (tetramethylene methane) rather than TME intermediates were observed. For example, the photolysis of the bi-(1-pyrazolin-4-ylidene) 4a involves first an elimination of one molecule of nitrogen to give the pyrazoline 6 which then eliminates the second molecule of nitrogen to give a 55:45 mixture of the hydrocarbons 8 and 9; a reaction sequence involving two TMM biradical intermediates 5 and 7. Flash vacuum pyrolysis of compound 4a[7] follows a similar course. Initially the pyrazoline 6 is formed. At ca. 400° C the spiropentane 8 is obtained (the isomer 9 is not observed since at these temperatures it thermally isomerises to compound 8). However, when benzophenone is added to the photolysis of compound 4a the allene dimer 12 (identical to material independently synthesised from tetramethyl allene 10[8]) becomes the major product (> 90%). The allene dimer 12 apparently arises from 4a itself. It is not formed via sensitised photolysis of compounds 6 or 8. Its formation seems to implicate a TME intermediate 11 and may possibly be the result of a simultaneous elimination of both molecules of nitrogen. It seems more likely, however, that the triplet sensitised reaction, like the direct photolysis, involves initial formation of the TMM biradical 5 but whereas the singlet form of this biradical rapidly closes to give pyrazoline 6 the triplet form is sufficiently long lived to eliminate a second molecule of nitrogen; giving the TME 11.



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