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MECHANISM FOR THE FORMATION OF AZINE IN THE DECOMPOSITION OF DIAZO-ALKANES AND DIAZIRINES

MICHAEL T.H. LIU* and K. RAMAKRISHNAN

Department of Chemistry, University of Prince Edward Island
Charlottetown, Prince Edward Island, Canada

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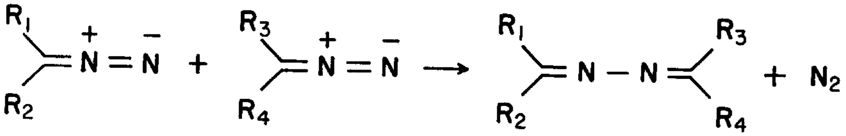
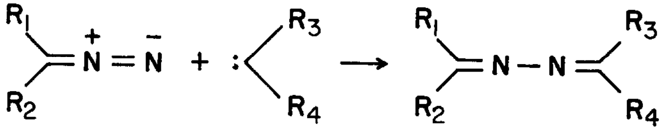
Chemistry of thermal and photochemical decomposition of diazoalkanes and diazirines has been a topic of considerable interest in recent years.[1-11] Many of these decompositions have led to the formation of the corresponding azine and several mechanisms have been proposed for its formation.

The formation of azine can be viewed as the dimerization of two molecules of the diazo compound, followed by the elimination of N_2 as in equation 1.[1,2]



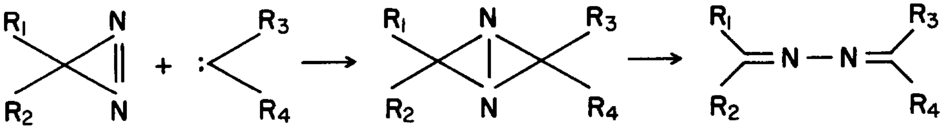
[1]

An alternate mechanism could be the nucleophilic attack of the negatively charged nitrogen on the electron deficient carbene:[3,4]



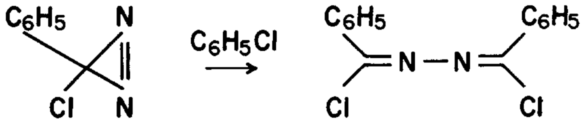
[2]

This compound could also be derived from the addition of carbene into the diazirine double bond as shown in equation 3.[5-7]



[3]

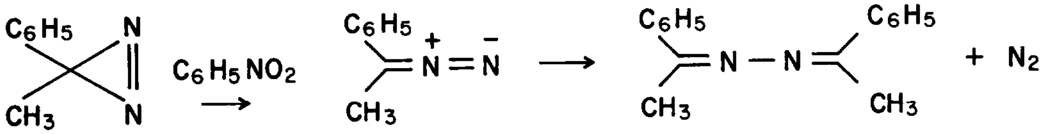
The present study was undertaken with the objective of understanding the mechanism of azine formation. When 0.5M chlorophenyldiazirine 1 was decomposed at 130° in chlorobenzene, the only product isolated was the azine.



1

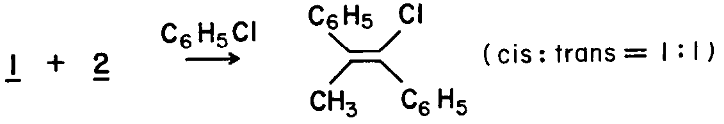
The chlorobenzene solution of 1 was colorless at the beginning but it turned yellow for several seconds before the nitrogen evolution. The transient existence of this yellow hue may be due to the chlorophenyldiazomethane intermediate.[12] In the thermal decomposition of phenyl-n-butyldiazirine[13] and of phenylmethyldiazirine (2),[14] the respective intermediate diazo compounds, 1-phenyl-1-diazopentane and 1-phenyldiazoethane have been detected and isolated.

In the thermolysis of 0.7M phenylmethyldiazirine in nitrobenzene at 130°, the major product was again the azine (95%) which presumably was formed by the dimerization of 1-phenyldiazoethane intermediate.

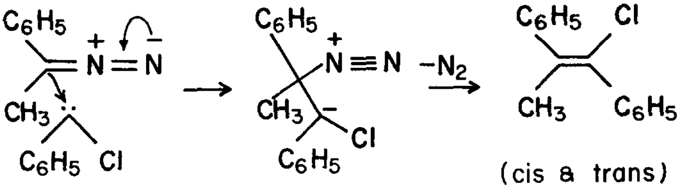


2

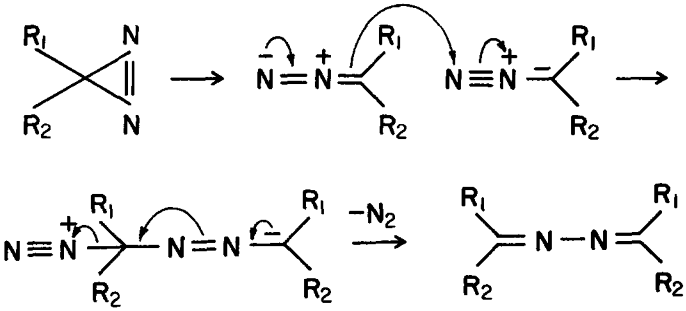
However, when an equimolar mixture (total 0.5M) of 1 and 2 was refluxed in chlorobenzene,[15] two products (1:1) were isolated and identified as cis and trans - - α-chloro- β-methyl stilbene: m/e 228; nmr δ2.25 (s, 3, methyl), 7.0 (m, 4, aromatic), 7.4 (m, 6, aromatic); δ2.27 (s, 3, methyl), 7.0 (m, 4, aromatic), 7.4 (m, 6, aromatic).



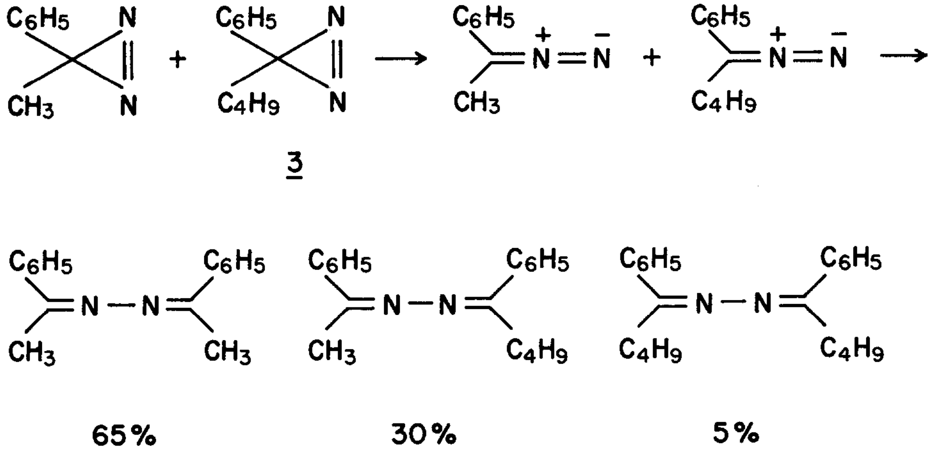
It is interesting to note that no azine was formed although when either 1 or 2 decomposed independently and under similar conditions, the respective azines were observed as major products. It is known that the decomposition of 1[11] and of 2[13] is first-order and the ratio of the rate constants k_1/k_2, is approximately equal to 7 at 100°. This means that while 1 isomerizes to the linear diazo compound and decomposes readily to the phenylchlorocarbene,[12] 2, which is seven times less reactive, remains mostly unchanged and only slowly rearranges to 1-phenyldiazoethane. As there was no azine formed, it could be argued that carbene does not react with diazomethane or diazirine to give the azine as proposed in equation (2) and (3) respectively. The olefin formation resulting from the decomposition of a mixture of 1 and 2 can be rationalized on the basis of nucleophilic attack of the diazo compound on the electron deficient carbene leading to a zwitterion, followed by elimination of N_2.



The formation of this olefin as a result of the reaction between the phenylchlorocarbene and 2 can be ruled out as dichlorostilbene was not formed in the decomposition of 1. Considering all the above facts, the most probable mechanism for the formation of the azine from diazirines appears to be the following:



Further support for the formation of azine from the dimerization of diazomethane intermediate was demonstrated in the decomposition of a mixture of phenylmethyldiazirine (2) and phenyl-n-butyldiazirine (3) in chlorobenzene ($k_2/k_3 = 1$). In this case, the product mixture consisted of all the three possible azines as indicated by the following equation:



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15. The mixture of 1 and 2 was colorless initially and turned red upon heating at 130°. The color persisted for 20-30 minutes.