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PHOTOREACTIONS OF 2,4-CYCLOHEXADIENONE OXIMES.
HETEROLYTIC α-CLEAVAGE

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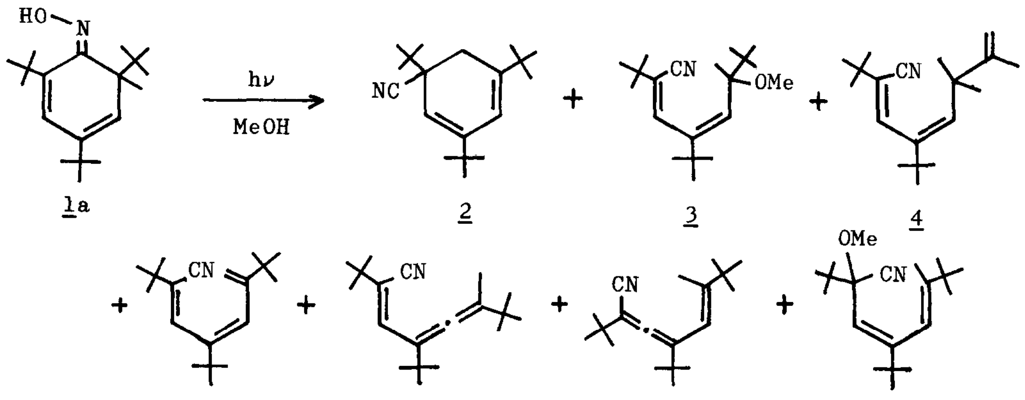
Inspite of numerous studies regarding photo-Beckmann rearrangement,$^{1)}$ there has been no report on photoreactions of an oxime of 2,4-cyclohexadienones; photochemistry of the dienones themselves, by contrast, has been the subject of extensive investigations.$^{2)}$

We now report the photoreaction of 2,4-cyclohexadienone oxime ($\underline{1}$) which reveals a new mode of photoreaction of an oxime, heterolytic α-cleavage.

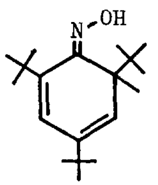
Irradiation of ($\underline{E}$)-oxime ($\underline{1}$a)$^{3)}$ in methanol (high pressure mercury arc, Pyrex-filter, 7.5 h) afforded $\underline{2}$ (19%), $\underline{3}$ (16%), $\underline{4}$ (5%), $\underline{5}$ (1%), $\underline{6}$ (11%), $\underline{7}$ (7%), and $\underline{8}$ (2%) along with some recovered $\underline{1}$a (11%) and the isomer ($\underline{1}$b) (6%).$^{4)}$ When ($\underline{Z}$)-oxime ($\underline{1}$b) was irradiated under identical conditions, isomerization into $\underline{1}$a was observed at first and the final products and their yields were essentially the same as those from $\underline{1}$a. Formation of oxaziridine, which is considered to be an intermediate leading to an amide$^{1)}$ and in some cases characterized in solution,$^{5)}$ was also observed in the reaction of $\underline{1}$a; reaction solution irradiated for 4 h was found to contain about 6% of oxaziridine ($\underline{9}$) by iodometry.$^{6)}$

Acid treatment (trifluoroacetic acid in benzene) of $\underline{3}$ leads to formation of $\underline{5}$ (95%), which undergoes cyclization to give $\underline{2}$ (96%) upon irradiation with Pyrex-filtered light in methanol. This suggests that $\underline{2}$ is a secondary product from $\underline{5}$. Since the ether $\underline{3}$ was found to be stable under the reaction conditions, it is not a precursor of other products.

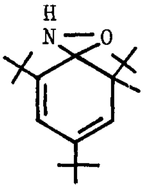


1a 2 3 4

5 6 7 8



1b



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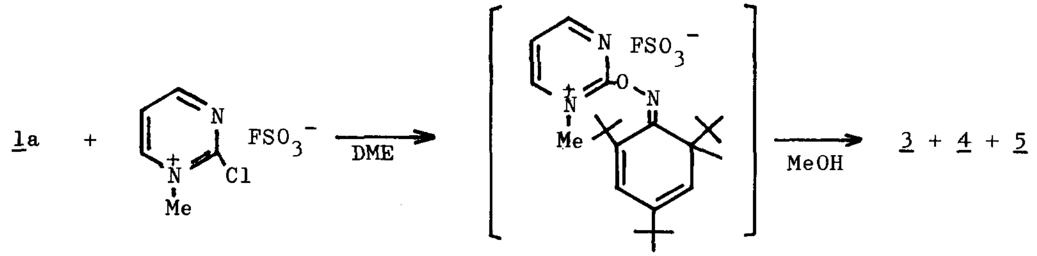
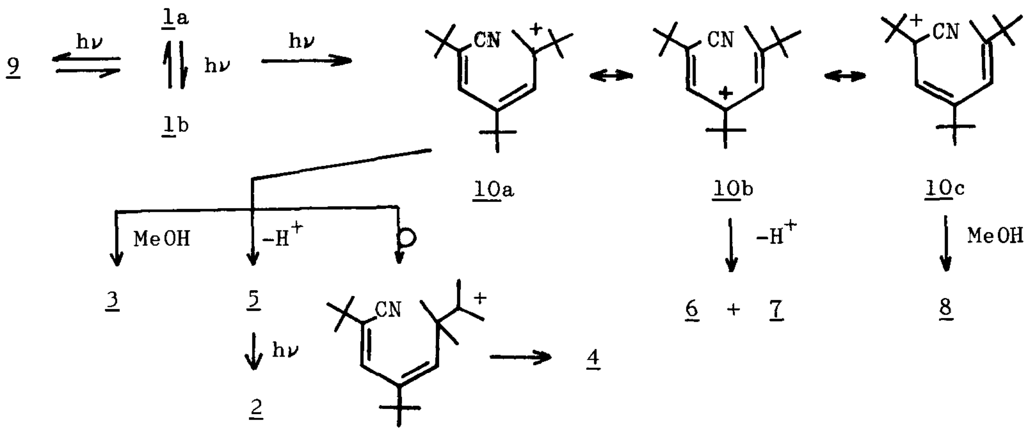
For comparison, thermal Beckmann rearrangement of 1a was conducted using 2-chloro-1-methylpyrimidinium salt.[7)] In this case, the products were only 3 (6%), 4 (9%), and 5 (46%).



Formation of the photoproducts (2-8) is explicable in terms of pentadienyl cation (10) as depicted in Scheme.

The most obvious feature of this photoreaction is that all the products are formed via ionic processes. Contrary to frequent observations of nitrile formation in the ground state Beckmann rearrangement, reluctance to the Beckmann fission is characteristic of photoreactions of oximes[1a)] and, more importantly, formation of nitriles in the excited state reaction has been explained by a

Scheme



homolytic process.[8,9] The present reaction represents the first and unequivocal example of a heterolytic α-cleavage of an oxime. The heterolytic pathway seems to be operative even in non-polar solvent such as pentane although the reaction is apparently more complex; the products identified were 2 (5%), 6 (11%), and 7 (7%).

The discrepancy in the products between the excited and ground state reactions is most likely due to the difference in nature of intermediates in both reactions. The products from the thermal Beckmann fission are only those that are formally derived from canonical structure (10a), suggesting the participation of the solvent (for 3) and neighboring σ bonds (for 4 and 5) in the product forming process. On the contrary, in the photoreaction, the pentadienyl ion (10) appears to be formed as a "free" carbonium ion without such assistance,[10] for the formation of 6, 7, and 8, products characteristic of the excited state reaction, is reasonably explained in terms of canonical structures (10b) and (10c) and this reactivity is most likely accounted for in the light of characteristics of a "free" (or "hot") carbonium ion[11] that reactions occur at a position(s) other than that where a carbonium ion is initially generated. This sort of "free" carbonium ions have recently been invoked in the photoreactions of alkyl and vinyl halides in order to rationalize the difference in reactivity between the photochemical and solvolytic reactions.[12,13]

The present results show that an oxime photochemically undergoes heterolytic α-cleavage if appropriately substituted and add yet another type of reactivity into a list of diverse photoreactions of the carbon-nitrogen double bond.[1b,c]

References and Notes

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4) The sturctures of the products were established by spectral (NMR, IR, MS, and UV) and analytical data.
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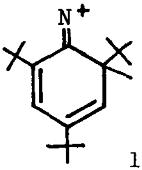
10) We consider that 10 is probably formed by a simultaneous cleavage of the N-O and C-C bonds. Intermediacy of 11 is less likely in view of the known propensity of this kind of nitrenium ion for undergoing intramolecular C-H insertion. P.T. Lansbury, "Nitrenes" ed. by W. Lowski, Chapter 11, Interscience Publishers, New York, 1970. However, the possibility that oxaziridine (9) is a direct precursor of 10, if unlikely, can not be ruled out completely at this time.



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11) For a discussion of the concept of "free" ions, see J.T. Keating and P.S. Skell, "Carbonium Ions" Vol. 2, Chapter 15, Wiley-Interscience, New York, 1970. See also Ref. 12a).
12) a) P.J. Kropp, G.S. Poindexter, N.J. Pienta, and D.C. Hamilton, J. Am. Chem. Soc., 98, 8135 (1976); b) S.A. McNeely and P.J. Kropp, ibid., 98, 4319 (1976).
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