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ORGANIC PHOTOCHEMISTRY WITH 6.7eV PHOTONS: 1,2,5,6-TETRAHYDROPYRIDINES AND TROPIDINE

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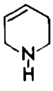
SUMMARY: Irradiation of the title compounds in hydrocarbon solutions with 185nm light leads to retro-Diels-Alder reactions as the principal process. The imine fragment, CH_2=N-CH_3 undergoes efficient trimerization, a process which may be promoted by molecular association of the reactant.

1,2,5,6-Tetrahydropyridine (1) and its alkyl derivatives are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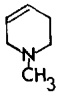
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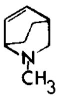
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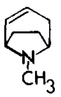
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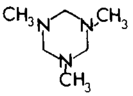
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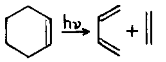
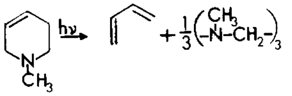

(1)


(2)

bichromophoric systems whose photochemical behavior in the far-ultraviolet can be viewed from the point-of-view of either chromophore. Past work on the photochemistry of aliphatic amines in the condensed phase has been devoted exclusively to saturated amines.[1] When excited by light of wavelength close to 200nm, these compounds tend to lose a H atom preferentially, hydrogen gas and dehydrodimers being the usual products. It will be shown in this work that this behavior is completely modified by the presence of a double bond β to the nitrogen. Irradiation of cyclohexene in the gas phase with photons of energy (8.4eV) less than the ionization potential (8.9eV)[2] leads to a retro-Diels-Alder reaction as shown in Eq. 1 as the major process. Solution-phase irradiation of cyclohexene at 185nm (≡6.7eV) causes no observable fragmentation and leads only to isomerization processes.[3,4] It was suspected that even under these conditions, the cyclohexene ring may undergo a retro-Diels-Alder reaction if a more active dienophile is incorporated in the ring. Such has proved to be the case.

Irradiations of compounds 1 through 4 were carried out in solution (10^{-2} to 10^{-3}M) in spectroscopic-grade pentane or cyclohexane through Suprasil windows. The radiation from a Hanovia mercury resonance lamp was used either unfiltered or filtered by an Acton 185-N filter[5] which transmitted ∿20% at 185nm and <1% at 254nm.

Photolysis of 2 gave 1,3-butadiene and the trimer of CH_2=N-CH_3 (5) as the only isolable products. The latter was identified by comparison of its ir and nmr spectra with those of an authentic sample synthesized from methylamine and formaldehyde.[6] At 10% conversion, the GC yields of 1,3-butadiene and 5 were 74% and 22% (as monomer) respectively. Since there was some inevitable loss of butadiene by evaporation from the photolysis solution, the material balance of the C_4 product according to Eq. 2 should be termed satisfactory. The yield of the trimer, 5, is surprisingly high in view of the dilution at which these experiments were carried out. Since excited electronic states formed at 185nm are relatively short-lived (<1nsec), it was of interest to see if trimerization was promoted by the association of the reactant molecules in the ground state. In Fig. 1, the absorption spectrum of 2 is plotted in the usual way at several concentrations. It can be seen that 2 does not obey Beer's Law which is usually indicative of association. Even the secondary amine 1 was found not to obey Beer's Law, the ε values (solvent:pentane) at 185nm at various concentrations being:

20.10 x 10^{-4}M	8260	all values
10.10 x 10^{-4}M	8910	±3.4%
5.04 x 10^{-4}M	9130	
2.01 x 10^{-4}M	9950	

In a molecule of 2 in its monomeric state, the π electrons of the double bond are separated from the Rydberg (n_N→3s; n_N→3p) transitions of the nitrogen by a methylene group on either side. Both absorptions individually are of comparable intensity and quite strong. In the associated state of the compound, it is questionable whether the photochemistry is from the isolated chromophores or not. It is therefore not surprising that both the retro-Diels-Alder reaction (characteristic of the cyclohexene) and the trimerization of the CH_3-N=CH_2 moiety are observed.

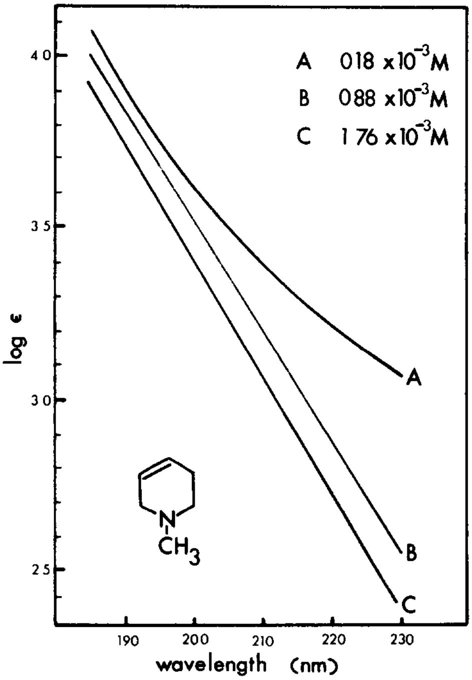
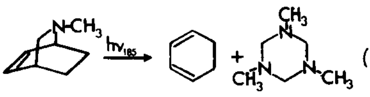


Fig. 1 Plot of Extinction Coefficient vs. Wavelength at Various Concentrations for 2 (solvent:pentane)

The photolysis of 3 which was studied only qualitatively also led to the same kind of photodecomposition to give 1,3-cyclohexadiene and trimer 5 (Eq. 3).



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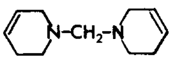


6

The irradiation of 1 was of interest because the amine function is secondary and the cleavage of an N-H bond could compete with a retro-Diels-Alder process. On photolysis to ∿25% conversion, 1,3-butadiene was observed as a major product

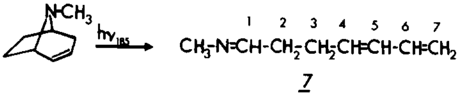
(∿80% - nmr analysis). On work up of the residue a compound of molecular formula $C_{11}H_{18}N_2$ was obtained in 12% yield. Its nmr spectrum was wholly similar to that of 1 except that there was an additional absorption at δ, 3.07 (2H-singlet). It was suspected that this compound was a condensation product having structure 6. This was proved to be the case by its independent synthesis from formaldehyde and 1. The primary products of the photolysis undoubtedly arise according to Eq. 4:

$$1 \xrightarrow{h\nu_{185}} CH_2{=}CH{-}CH{=}CH_2 + HN{=}CH_2 \qquad (4)$$

6 could then be formed during workup by a trace of water hydrolyzing $CH_2{=}NH$ to CH_2O and NH_3, the former leading to 6 by condensation.

It is pertinent to point out that the formation of imines in the photolyses of saturated secondary amines has been reported by Niu and Stenberg[8] in their studies at Ca. 200nm. They have postulated a free-radical mechanism for this process which is initiated by the cleavage of a N-H bond. Hancock and Dickinson[9] have reported that photolysis of dimethylamine in the same wavelength region ultimately gives $(CH_3)_2N{-}CH_2{-}N(CH_3)_2$, a structure which is conceptually very similar to 6. The important difference in photochemical terms between these systems and 1 is that hydrogen is not a product in the latter case whereas it is an important product in the former examples.[10] It follows that cleavage of a N-H or a C-H bond is no longer important when a C=C bond is β to the nitrogen.

The photolysis of tropidine, 4 presents an interesting intramolecular variation of the retro-Diels-Alder reaction. When a solution of tropidine in pentane was photolyzed, only one product was observed to be formed in >90% yield.[11] On a 0.5g scale, secondary photolysis of the product could not be avoided but even so, the product could be isolated in 52% yield (over 95% pure). The product was isomeric to tropidine. In its infrared spectrum (solv:CCl_4) it had absorptions at μ, 5.98(vs), 10.10(m) and 11.05(vs) corresponding to a $-CH{=}CH_2$ group and no N-H absorptions. Its ultraviolet spectrum (solv:pentane) showed a maximum at 227nm, ε>10,000. These data suggested that the retro-Diels-Alder reaction had proceeded according to Eq. 5 to give 7.



$$\xrightarrow{h\nu_{185}} CH_3{-}N{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH{=}CH_2 \qquad (5)$$

7

The nmr spectrum (CCl_4) δ, 7.57 (1H-broad) C_1; 5.0-7.0 (5H-complex) C_4,C_5,C_6,C_7; 3.17 (3H-singlet with fine structure) N-methyl; 2.30 (4H-multiplet) C_2,C_3 was consistent with this structure for 7.

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10. It has been our general observation that photolysis of olefinic compounds at 185nm in solution does not lead to hydrogen as a gaseous product.
11. This process was also photochemically efficient. A quantum yield of 0.8 was estimated. Quantum yields for compounds 1 through 3 were not determined in view of uncertainties concerning the nature of the absorbing species.

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