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THE PHOTOCHEMISTRY OF HYDRAZONES: A PHOTOCHEMICAL WOLFF-KISHNER REDUCTION (1)

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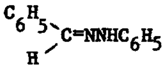
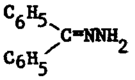
As a result of an interest in the photochemistry of unsaturated systems containing nitrogen (2,3), we have investigated the light induced transformations of a group of hydrazones (I-III).



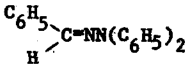
$(C_6H_5)(H)C=NNHC_6H_5$

I



$(C_6H_5)_2C=NNH_2$

II

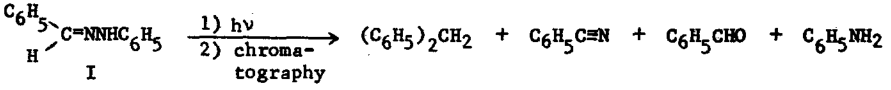


$(C_6H_5)(H)C=NN(C_6H_5)_2$

III

Products from the photochemical reactions of these molecules indicate that the processes initiated by excitation of these systems are of the following two types: a) nitrogen-nitrogen bond cleavage; b) hydrogen migration from nitrogen to carbon. In the case of the unsubstituted hydrazone II, this second process results in a photochemical reaction analogous to the Wolff-Kishner reduction.

When 1.00 millimole of benzaldehyde phenylhydrazone (I) in 400 ml of methanol was irradiated under nitrogen through a vycor filter using a 450 watt Hanovia high pressure quartz mercury-vapor lamp, the reaction mixture changed from yellow to brown after two hours and the uv spectrum indicated that essentially all of the starting material had reacted. The following four products were obtained after solvent removal[+] and chromatographic separation of Florisil: diphenylmethane (14%), benzaldehyde (9%), benzonitrile (8%), and aniline (12%). The bulk of the material could not be eluted from the chromatography column but remained as an immobile brown band at the top. The same reaction with slightly improved yields occurred with benzene as the reaction solvent. Con-



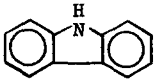
$$\underset{\text{I}}{(C_6H_5)(H)C=NNHC_6H_5} \xrightarrow[\text{2) chromatography}]{\text{1) } h\nu} (C_6H_5)_2CH_2 + C_6H_5C\equiv N + C_6H_5CHO + C_6H_5NH_2$$

[+] A uv spectrum of the distilled solvent indicated the presence of small amounts of benzene and toluene.

trol runs showed that no dark reaction was taking place. The product identity and yield from this and the other two hydrazones studied (irradiation and isolation procedures were identical to those described for compound I) are given in Table I.

TABLE I

Product Identity and Yield From Hydrazone Irradiations

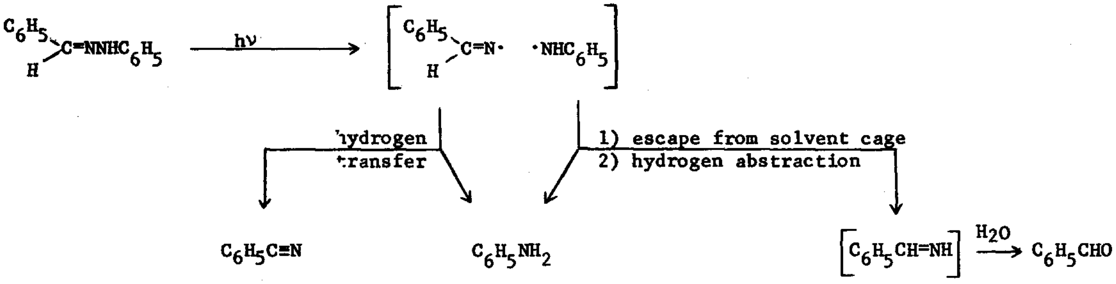
Compound Irradiated	$(C_6H_5)_2CH_2$	$C_6H_5C\equiv N$	C_6H_5CHO	$C_6H_5NH_2$	$(C_6H_5)_2C=O$	$(C_6H_5)_3CH$	 +
$C_6H_5CH=NNHC_6H_5$	14%	8%	9%	12%	---	---	---
$(C_6H_5)_2C=NNH_2$	25%	---	---	---	33%	---	---
$C_6H_5CH=NN(C_6H_5)_2$	---	30%	18%	---	---	---	56%

+Carbazole is known to result from photolysis of diphenylamine (4).

With the exception of diphenylmethane it is postulated (Scheme I) that the products from these reactions result from an initial nitrogen-nitrogen bond cleavage in the hydrazone system. This first step is followed by either a hydrogen transfer within the solvent cage to give benzonitrile and aniline or escape from the solvent cage by the radicals produced. Once the radical pair has separated, each member can then abstract a hydrogen atom from either the solvent or another molecule of I leading to aniline and benzaldimine. Benzaldimine is known (2) to be transformed into benzaldehyde under the isolation conditions. This proposed process (Scheme I) is directly analogous to the photochemical nitrogen-nitrogen bond cleavage and subsequent reactions found in the photolysis of benzalazine (IV) to produce benzonitrile and benzaldimine (2,3).

SCHEME I

Reactions Initiated by Nitrogen-Nitrogen Bond Cleavage in Benzaldehyde Phenylhydrazone (I)

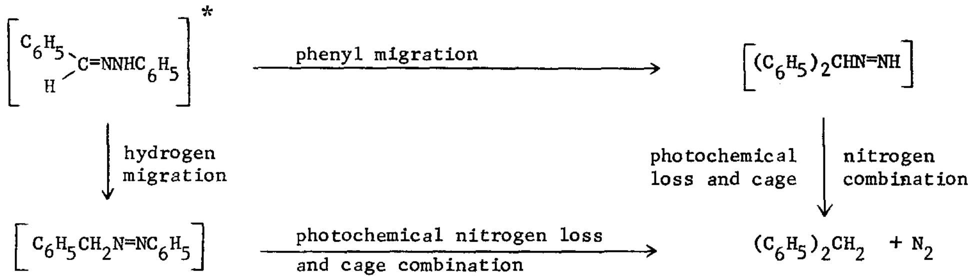


$$\underset{\text{IV}}{C_6H_5CH{=}NN{=}CHC_6H_5} \xrightarrow[CH_3OH]{h\nu} \left[C_6H_5CH{=}N\cdot \quad \cdot N{=}CHC_6H_5\right] \longrightarrow C_6H_5CH{=}NH + C_6H_5C{\equiv}N$$

The formation of diphenylmethane is pictured as arising *via* one or both of the mechanisms shown in Scheme II. These two processes differ only in that one postulates an initial phenyl migration to produce an azo system while the other suggests an hydrogen migration. A photochemical 1,3-hydrogen migration of the type proposed here has recently been observed in a series of related immines (5). The second step in each case is the expulsion of molecular nitrogen from the compound formed and combination of the radicals produced. Such nitrogen loss is known (6) to be the most important reaction of aliphatic azo compounds; it is also observed in aralkyl systems (7).

SCHEME II

Formation of Diphenylmethane From Excited Benzaldehyde Phenylhydrazone (I)



A clear choice between the two alternate mechanisms shown in Scheme II is not at present possible, although the available evidence clearly favors the hydrogen migration pathway. The fact that diphenylmethane is formed when compound II is irradiated demonstrates that a hydrogen migration process does exist‡; in addition, the lack of hydrocarbon formation upon irradiation of III argues against the phenyl migration option. It is also conceivable, however, that since the stability of the radicals formed by nitrogen-nitrogen bond cleavage increases in the series II, I, III, this type of cleavage may progressively dominate over the migration reaction. In Compound III the cleavage process may be completely dominant.

We are now studying the mechanisms of these reactions, in particular the reaction leading to diphenylmethane. Also being investigated is the extension of these reactions to other systems.

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‡ It is assumed in this discussion that the "hydrogen migration process" is an internal hydrogen transfer. The fact that it is internal remains to be proven.

It is especially of interest to know if the observed photochemical Wolff-Kishner reduction is a general reaction process of hydrazones.

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