The Photochemistry of Aliphatic Azomethines

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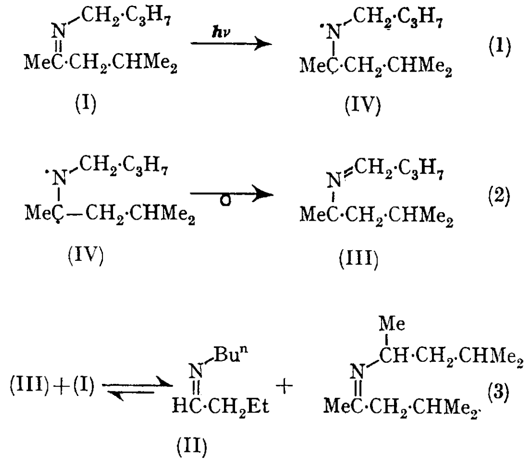
SINCE aliphatic azomethines have a weak $n \rightarrow \pi^*$ transition occurring around 230—250 mμ,[1] they might be expected to show photochemical reactions similar to those of ketones. We report the first example of the photochemistry of this class of compounds.[2]

The two major products of irradiation of a 0·66 M solution of *N*-(1,3-dimethylbutylidene)-butylamine (I) in pentane using a 450 w Hanovia L medium pressure mercury arc were isolated by preparative gas chromatography. One of these, obtained in 6·1% yield, was shown to be identical by its n.m.r., mass, u.v., and i.r. spectra to a synthetic sample of *N*-butylidenebutylamine (II). The second product (3·1%) was likewise shown to be *N*-butylidene-1,3-dimethylbutylamine (III). These products are rationalized as resulting from a di-radical intermediate (IV), generated from the excited azomethine. A 1,3-hydrogen rearrangement of (IV) gives (III). Exchange of (III) with unreacted (I) forms (II) and a second product, (V).

In support of this mechanism, we have found that (I) and (III) do exchange in a dark reaction to form (II) and (V), and that the exchange favours the formation of (II) and (V).



A variety of other *N*-alkylidenebutylamines have also been photolyzed, and the results are given in the Table.

As required by the proposed mechanism, the major photo-product isolated in each case was *N*-butylidenebutylamine. Rearrangement products

TABLE

$\mathrm{R^1R^2C{=}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me}$

	$\mathrm{R^1}$	$\mathrm{R^2}$	Irradiation time (hr.)	M in pentane	% Yield of (II)
(VI)	Me	Me	120	0·53	12·3
(VIII)	Me	Et	100	0·56	10·1
(VIII)	Me	Pr	150	0·66	8·4
(IX)	Me	$\mathrm{Bu^s}$	100	0·56	6·1
(X)	Me	$\mathrm{Bu^t}$	200	0·65	16·1
(XI)	Et	Et	110	0·49	9·8

analogous to (III) have not been isolated from these photolyses, since they appear to be present in much smaller amounts than (III). This fact is presumably due to the increased rate of exchange of the rearranged product with the starting azomethines. In fact, it was fortuitous that (III) was isolated at all, since on prolonged standing of this photolysate the exchange proceeds essentially to completion. The second product of the exchange (V), was not observed in the original photolysate due to its nearly identical retention time with the unreacted starting compound (I).

Our initial observations indicate the photochemistry of aliphatic azomethines is not analogous to that of aliphatic ketones. We can find no evidence for products corresponding to a Norrish Type II cleavage, a reaction shown by essentially all aliphatic ketones with a hydrogen γ to the carbonyl,[3] or to a type (1) process. The observed reaction would appear more analogous to olefin isomerization.[4]

This research was supported by funds from U.S.P.H.S., and from the Graduate Research Council and Division of Basic Research of the University of Wyoming, and from a National Science Foundation Research Participation for High School Teachers Grants to one of us (G.L.C.).

(*Received, February* 19*th*, 1968; *Com.* 202.)

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[1] R. Bonnet, M. J. David, J. Hamlin, and P. Smith, *Chem. and Ind.*, 1963, 1836.

[2] M. Fischer (*Chem. Ber.*, 1967, **100**, 3599) has reported the photoreduction of benzophenone methyl imine by isopropyl alcohol.

[3] J. G. Calvert and J. N. Pitts, jun., "Photochemistry", John Wiley, New York, 1966, p. 382.

[4] P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, 1967, **89**, 5199.