Photo-induced Decarbonylation of β-Styryl Isocyanates

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Summary Irradiation of a β-styryl isocyanate released the elements of carbon monoxide and gave products formally derived from rearrangement and dimerization of the residue.

Except for the formation of a ketenimine and a nitrile, rearrangements and dimerizations accompanying or following a photoinduced decarbonylation of a β-styryl isocyanate (**1**) are accounted for by assuming the intermediacy of a β-styryl nitrene (**2**) and/or a 2-phenyl-2*H*-azirine (**3**). A rearrangement into a ketenimine concerted with the elimination of carbon monoxide is now proposed.

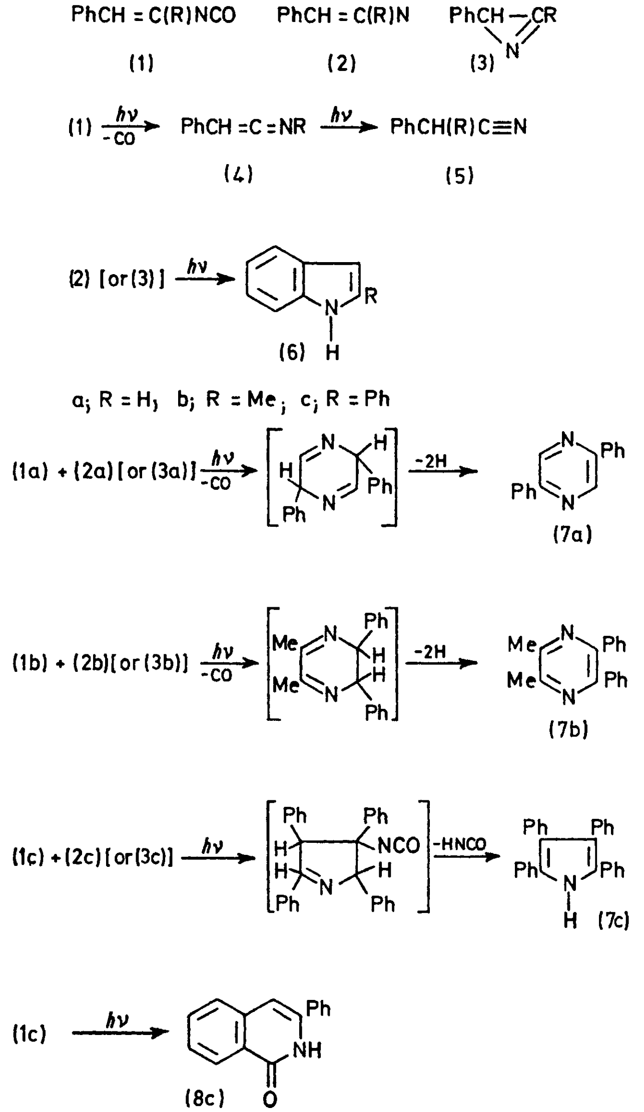
The isocyanate (**1**) in cyclohexane was irradiated (254 nm; low-pressure lamps) for 26 h. The products were identified on the basis of independent syntheses and comparison with authentic samples; satisfactory elemental analytical data were obtained for each new compound, and an unidentified, presumably polymeric, material was obtained as the major product from each irradiation. Traces of benzaldehyde, benzylcyclohexane, stilbene, benzonitrile, and bicyclohexyl were also produced from each of the three isocyanates (**1**).

Since (**5a**) may not be produced by the irradiation of (**3a**),† its formation by a rearrangement of phenylketenimine (**4a**) is proposed. (**4a**) was formed from (**1a**) and (**4b**) from (**1b**) (shown by i.r. and n.m.r. spectroscopy). (**4b**) gave methyl phenylacetate upon treatment with sodium methoxide in methanol followed by aqueous acid hydrolysis, and gave a dimer, $C_{18}H_{18}N_2$, m.p. 191—193°, whose structure has not been assigned.[1] A subsequent photorearrangement of a ketenimine (**4**) would account for the isomeric nitrile (**5**).[2]

Rearrangement attributed to either a styryl nitrene or the corresponding azirine accounts for indole (**6a**) from (**1a**) and (**6b**) from (**1b**). Apparently photo-decarbonylation of (**1c**) did not produce an intermediate nitrene or azirine since the rearrangement products, (**5c**) and (**6c**), were not found.[3]

A dihydropyrazine produced by either the dimerization of an intermediate nitrene or, more likely, by an interaction between the intermediate and its isocyanate precursor, easily gave a pyrazine by dehydrogenation.[4] In either event the formation of 2,5-diphenylpyrazine (**7a**) represented a head-to-tail combination. The formation of (**7b**) from (**1b**) appears to be the first example of 'formal dimerization' of an azirine (or the corresponding nitrene) by a head-to-head reaction. 2,5-Diphenyl-3,6-dimethyl- and 2,6-diphenyl-3,5-dimethyl-pyrazine were not detected. The pyrazine (**7b**), m.p. 97—98°, was prepared independently from benzil and 2,3-diaminobutane.

Irradiation of (**1c**) produced (**7c**) but no pyrazine. Apparently the loss of HCNO during aromatization of a proposed adduct (either head-to-tail or head-to-head) between (**1c**) and (**2c**) gave the pyrrole (**7c**).[5]



Photoisomerization of (**1a**) and (**1b**) was not observed but photocyclization of (**1c**) gave (**8c**) (2·4% by irradiation in cyclohexane at 254 nm, 15·0% by irradiation in cyclohexane at 300 nm, and 29·8% by irradiation in benzene at 254 nm).

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† K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Letters*, 1968, 3499 describe the photogeneration (365 nm) of (**3a**) from β-styryl azide. Diphenylacetonitrile is not produced by irradiation (254 nm) of 2,3-diphenyl-2*H*-azirine in either MeOH or CH_2Cl_2 (our unpublished results).

[1] C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, 1954, **76**, 4398.

[2] L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1964, 1887.

[3] J. H. Boyer, Rearrangements Involving Nitrene Intermediates, in 'Mechanisms of Molecular Migrations,' ed., B. S. Thyagarajan Wiley, New York, vol. 2, p. 267, 1969.

[4] L. Horner, A. Christman, and A. Gross, *Chem. Ber.*, 1963, **96**, 399 describe the photo-conversion of β-styryl azide into (**7a**).

[5] J. H. Boyer, W. E. Krueger, and R. Modler, *Tetrahedron Letters*, 1968, 5979 reported the photogeneration of 2,5-diphenylpyrrole from α-styryl azide.