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CONVERSION OF ALDEHYDES TO NITRILES VIA PHOTOCHEMICAL REACTION[1]

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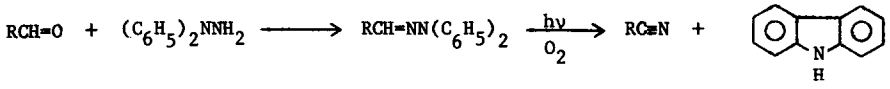
The synthesis of nitriles is a process which, in the past, has frequently required quite vigorous reaction conditions[2]. In recent years, however, interest has arisen in examining milder methods for nitrile synthesis[3-5]. As a contribution to the solution of this problem of reaction conditions, we wish to report our results on a two-step sequence employing a photochemical process which achieves an aldehyde to nitrile conversion under extremely mild conditions[6].

The first part of this sequence is the essentially quantitative non-photochemical reaction between an aldehyde and 1,1-diphenylhydrazine to give the corresponding diphenylhydrazone. This reaction occurs simply upon mixing equal molar amounts of the two reactants at room temperature . The second step, described in detail below, consists of the photochemical decomposition of the diphenylhydrazone in the presence of oxygen to give the corresponding nitrile. This second reaction step, which preceeds in 40-75% yield, is also conducted at room temperature in neutral media.



When one millimole of benzaldehyde diphenylhydrazone (1) in 400 ml of methanol is irradiated under oxygen at room temperature through a Vycor filter with a 450-W Hanovia high-pressure mercury lamp, complete consumption of the starting material occurs in one hour. Chromatography on Florisil separates the reaction mixture into two fractions: benzonitrile (75%) and carbazole (10%)[7]. The four other diphenylhydrazones studied (Table I) exhibit similar photo-

TABLE I. PHOTOCHEMICAL REACTIVITY OF DIPHENYLHYDRAZONES

Diphenylhydrazone	Nitrile Yield (Oxygen Atmosphere)	Nitrile Yield (Nitrogen Atmosphere)
Cinnamaldehyde	43%	none
Phenylacetaldehyde	41%	none
1-Naphthaldehyde	55%	none
Anisaldehyde	49%	25%
Benzaldehyde	75%	40%

chemical behavior. In each case the photoproducts were identified by comparison with independently obtained samples.

The presence of oxygen is critical to the photochemical process as can be seen from comparison of the results from irradiation in nitrogen and oxygen atmospheres (Table I).

REFERENCES

1. Part VIII in a series on the photochemistry of unsaturated nitrogen-containing systems.
2. As noted in ref 4, a large number of examples of nitrile syntheses are cited by W. Theilheimer, "Synthetic Methods of Organic Chemistry," Vol. 1-23, S. Karger, A. G. Basel, Switzerland, 1946-1969.
3. R. F. Smith, J. A. Albright, and A. M. Waring, J. Org. Chem., 31, 4100 (1966).
4. P. J. Foley, Jr., J. Org. Chem., 34, 2805 (1969).
5. J. H. Pomeroy and C. A. Craig, J. Amer. Chem. Soc., 81, 6340 (1959).
6. There is a question whether or not a reaction run in the presence of high intensity ultraviolet radiation can be considered to be run under mild conditions; however, use of such terminology in this case refers simply to low (room) temperature and the absence of acids, bases, and other catalytic or reactive species.
7. Diphenylamine is a possible intermediate in the formation of carbazole since it is known to be converted to carbazole photochemically. K. Grellman, G. M. Sherman, and H. Linschitz, J. Amer. Chem. Soc., 85, 1881 (1963).