

THE PHOTOCHEMISTRY OF ACYL HYDRAZIDES

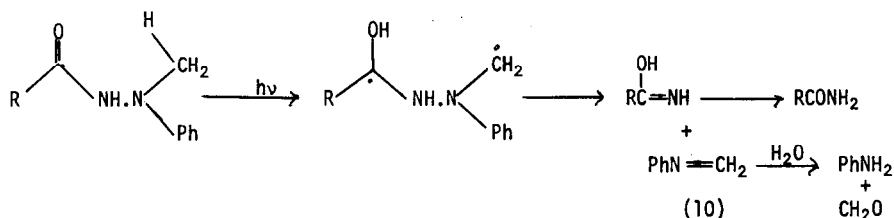
R.S. Davidson* and A. Lewis

Department of Chemistry, The University, Leicester, LE1 7RH.

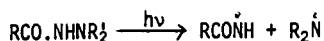
(Received in UK 27 September 1973; accepted for publication 10 October 1973)

Whilst the photochemistry of amides is well documented,¹ there is little information on the photochemistry of the closely related compounds, acyl hydrazides.

Irradiation² of the hydrazides (1) - (6) in acetonitrile solution gave the products shown in the Table. The formation of amides in reactions of (1) and (2) raised the possibility that reaction was occurring via a Norrish Type II process. However, a careful search of the reaction products showed the imine (10) and its

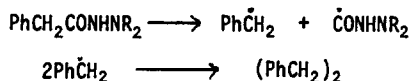


hydrolysis product, aniline, to be absent. The formation of N-methylaniline in the reactions of (1) and (2) and of diphenylamine from (3) can be best accommodated by a mechanism in which the electronically excited hydrazides dissipate their energy by fission of the relatively weak nitrogen-nitrogen bond



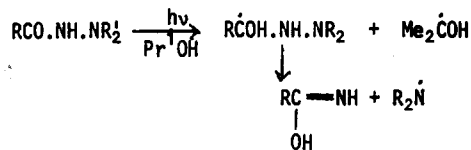
This mode of reaction will be facilitated by R' substituents which stabilise the incipient amino radical. The lack of reactivity of (9) is probably due to the high energy of the incipient phthalimido radical which has the unpaired electron located in an s-orbital.

That hydrazides can undergo homolytic fission on excitation is supported by the finding that (4)-(6) give bibenzyl on irradiation in acetonitrile. The weak benzylic methylene-carbonyl bond will facilitate the process. No products containing



nitrogen were isolated and characterised from these reactions.

The formation of amides and amines in the reactions of (1) and (3) probably results from disproportionation reactions of the initially produced radicals and by reaction of the radicals with the hydrazide. In order to maximise yields, a solvent containing readily abstractable hydrogen atoms, propan-2-ol, was used in the place of acetonitrile. The products of the reactions and their yields are shown in the Table. In the majority of cases the yields were increased but there was one notable exception. The yield of bibenzyl from (4)-(6) was considerably reduced and a new product, phenylacetamide, was formed. This suggests that the hydrazides may have an alternative mode of reaction in powerful hydrogen donating solvents. It is likely that the excited carbonyl group of the hydrazide can abstract a hydrogen atom from the solvent and the



radical so produced fragment.³

In contrast to (4) and (5) the hydrazides (7) and (8) proved to be relatively stable. This stability may be attributed to either, the naphthalene group acting as a sink for triplet energy or, intramolecular exciplex formation between the amino group and the excited hydrocarbon is acting as a sink for singlet energy.⁴ Mechanistic studies, carried out so far, have not indicated the multiplicity of the excited hydrazides which is responsible for reaction and therefore we cannot unequivocally

state the reason for the stability of (7) and (8).

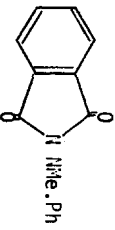
We gratefully acknowledge the award of an S.R.C. studentship to A.L.

References

1. I. Rosenthal in J. Zabicky, *The Chemistry of Amides*, p. 289, Interscience, London, 1970.
2. Irradiations were carried out with Southern New England Ultraviolet Co. Rayonet Reactor fitted with lamps having maximal emission at 254 nm. All solutions were $1 \times 10^{-2}M$ and were purged with dry nitrogen for 15 mins prior to the irradiations and throughout the irradiations. Solutions were contained in quartz tubes. G.l.c. analyses of the reaction products were carried out with a Pye 104 Gas Chromatograph fitted with a flame ionisation detector.
3. The excited carbonyl group of esters undergo hydrogen abstraction reactions to give radicals which fragment. K. Fukui, K. Senda, Y. Shigemitsu, and Y. Odaira, J. Org. Chem., 1972, 37, 3176.
4. These hydrazides have been found to exhibit intramolecular exciplex formation.

TABLE

Products obtained by Irradiation of Acyl Hydrazides in Acetonitrile and Propan-2-ol.

HYDRAZIDE	ACETONITRILE		PROPAN-2-OL	
MeCONHMe.Ph (1)	MeCONH ₂ (20%)	PhNHMe (15%)	MeCONH ₂ (76%)	PhNHMe (41%)
PhCONHMe.Ph (2)	PhCONH ₂ (83%)	PhNHMe (30%)	PhCONH ₂ (70%)	PhNHMe (8%)
PhCONHNPh ₂ (3)	PhCONH ₂ (38%)	Ph ₂ NH (38%)	PhCONH ₂ (80%)	Ph ₂ NH (50%)
PhCH ₂ CONHNMe ₂ (4)	(PhCH ₂) ₂ (21%)		(PhCH ₂) ₂ (Trace)	PhCH ₂ CONH ₂ (70%)
PhCH ₂ CONHNMe.Ph (5)	(PhCH ₂) ₂ (47%)		(PhCH ₂) ₂ (Trace)	PhCH ₂ CONH (61%) PhNHMe (34%)
PhCH ₂ CONHNPh ₂ (6)	(PhCH ₂) ₂ (15%)		(PhCH ₂) ₂ (Trace)	PhCH ₂ CONH ₂ (39%) Ph ₂ NH (26%)
Np. CH ₂ CONHNMe ₂ (7) Mp = 1-Naphthyl		Stable		Stable
Np. CH ₂ CONHNMePh (8) Mp. = 1-Naphthyl		Stable		Stable
 (9)		Stable		Stable

Yields are corrected for amount of starting material consumed in the reaction.

Irradiation time was 4hr. with the exception of 5 in Pr¹OH (2hr.) and 6 in MeCl (20hr.).