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PHOTOCHEMICAL REACTIONS OF N',N'-DIALKYL-N-aroylureas

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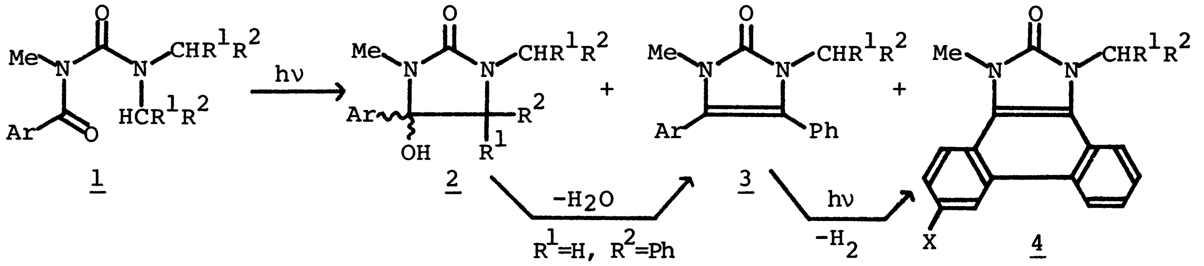
N',N'-Dibenzyl and N',N'-diisopropyl-N-aroylureas undergo cyclization on irradiation to give the corresponding imidazolidin-2-ones via intramolecular hydrogen abstraction by the aroyl carbonyl group.

Amides are photochemically unreactive in comparison with ketones and esters and they usually do not undergo hydrogen abstraction,[1)] whereas imides which have two carbonyl groups and one nitrogen atom exhibit photochemical reactivities similar to those of ketones.[2)] This has been explained in terms of the difference between the π-electron donating effects of nitrogens of amides and those of imides.[2b,d)] Therefore, it is of interest to investigate the photochemical reactions of acyl or aroylureas which have two carbonyl groups and two nitrogen atoms. Although the photochemistry of these ureas has been scarcely studied, it was recently reported that five-membered cyclic acylureas (hydantoins) underwent intramolecular hydrogen abstraction when the reaction was facilitated by substituents.[3)] We now wish to report photocyclization of acyclic aroylureas via intramolecular hydrogen abstraction by the aroyl carbonyl group.

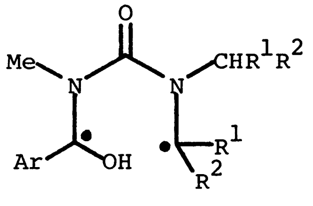
N,N',N'-Trimethyl-N-benzoylurea (1a) was unreactive toward photolysis, and irradiation of N',N'-diethyl-N-benzoyl-N-methylurea (1b) gave an intractable mixture. On the other hand, when an N',N'-diisopropylurea (1c) was irradiated in acetonitrile with a low pressure mercury lamp, 3,5,5-trimethyl-4-hydroxy-1-isopropyl-4-phenylimidazolidin-2-one (2c) was obtained in 38% yield. The structure of 2c was determined on the basis of elemental analysis and spectral data. In the case of an N',N'-dibenzyl derivative (1d), the product (2d) was a mixture of two stereoisomers but they could not be completely purified because they underwent spontaneous dehydration gradually even at room temperature to give 4,5-diphenyl-1-benzyl-3-methyl-2-imidazolone (3d) almost quantitatively. The structure of 3d was confirmed by the independent synthesis.[4,5a)] Photolysis of N',N'-dibenzyl-N-(4-cyanobenzoyl)-N-methylurea (1e) gave a similar result. In the case of 4-methoxybenzoyl and 4-chlorobenzoyl derivatives (1f and 1g), the dehydration took place during irradiation, and the imidazolone (3f and 3g) and phenanthrene derivatives (4f and 4g) were obtained (Table 1). Meanwhile, a 2-naphthoyl derivative (1h) was inert toward photolysis.



a: Ar=Ph, $R^1=R^2=H$
b: Ar=Ph, $R^1=H$, $R^2=Me$
c: Ar=Ph, $R^1=R^2=Me$
d: Ar=Ph, $R^1=H$, $R^2=Ph$
e: Ar=4-CN-Ph, $R^1=H$, $R^2=Ph$
f: Ar=4-MeO-Ph, $R^1=H$, $R^2=Ph$
g: Ar=4-Cl-Ph, $R^1=H$, $R^2=Ph$
h: Ar=2-Naphthyl, $R^1=H$, $R^2=Ph$

Table 1. Photoreaction of 1 (yield/%)

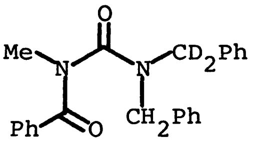
	2	3	4
1c	38	0	0
1d	77	0	0
1e	35	0	0
1f	0	55	13
1g	0	57	10

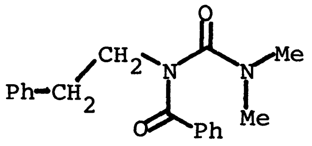


5

The formation of the imidazolidinone (2) is easily explained in terms of δ-hydrogen abstraction by the aroyl carbonyl group via seven-membered cyclic transition states followed by cyclization of the resulting 1,5-diradical (5).[5)] The phenanthrene derivatives (4) is apparently formed by dehydrocyclization of 3 as in the case of the photochemical conversion of stilbenes to phenanthrenes.[6)] This was confirmed by the fact that 4f was produced on irradiation of 3f.

It may be conceivable that the formation of 5 from 1 involves sequential electron-proton transfer rather than one-step hydrogen transfer since it is known that imides bearing nitrogen-containing substituents undergo electron transfer on irradiation.[2a)] However, this mechanism is improbable because of the following reasons. The photoreaction of 1d was effectively quenched by 1,3-pentadiene, while intramolecular photoreactions via electron transfer are usually unquenchable.7) The deuterium isotope effects (Φ_H/Φ_D=4.3) measured by using 1d-d_2 were also inconsistent with the electron transfer mechanism because the isotope effects in photoreactions via electron-proton transfer are usually quite small (<2).8) Thus, the photoreaction of 1 is most reasonably explained in terms of usual hydrogen abstraction from the nπ* triplet states. The inertness of the naphthoyl derivative (1h) is also consistent with the hydrogen transfer mechanism.9) The nonreactivity of 1a is explainable by the strong bond-strength of the methyl C-H bonds.10)


1d-d_2


1i

Finally, photolysis of N',N'-dimethyl-N-benzoyl-N-(2-phenylethyl)urea (1i) was examined. The urea was expected to undergo γ-hydrogen abstraction by the benzoyl group (type II photoprocess) since γ-hydrogen abstraction is sterically more favorable than δ-hydrogen abstraction. Contrary to the expectation, the photoreaction of 1i was sluggish, and the prolonged irradiation resulted in the formation of an intractable mixture. The lower reactivity of 1i might be attributable to the fact that the activation of the γ-hydrogens by phenyl group is significantly weaker than that of δ-hydrogens of 1d-g, where the δ-hydrogens are activated toward abstraction by both the phenyl group and the amide nitrogen.

The results of photoreactions of these acyclic aroylureas together with those of the five-membered cyclic acylureas3a) lead to the conclusion that these ureas undergo photochemical hydrogen abstraction as imides but their reactivities are much lower than those of imides.

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