Photochemistry of α-Diketones in Amines

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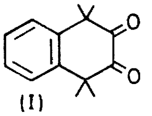
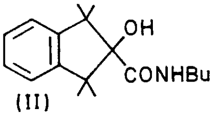
Summary Two six-membered-ring non-enolisable α-diketones (I), and to a very minor extent (VI), undergo a novel benzilic amide type rearrangement when irradiated in n-butylamine.

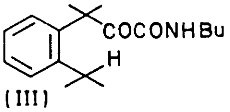
THE photochemical behaviour of some monoketones, in particular aryl ketones, in amines has received considerable attention,[1] though the corresponding behaviour of α-diketones has been almost neglected.† We report the photochemical behaviour of several α-diketones when irradiated in aliphatic amines.

Prolonged irradiation‡ (120 hr) of (I)[2] in n-butylamine gave a neutral fraction from which, among other substances, the compounds (II) (47%), m.p. 140—141°, (III) (7%), m.p. 78—79°, and (IV) (6%), m.p. 112·5—114° and 2-hydroxy-1,1,4,4-tetramethyl-3-oxotetralin (5%) were isolated. Compound (II) was shown to be 2-n-butylcarbamoyl-2-hydroxy-1,1,3,3-tetramethylindane on the basis of analytical and spectral data,§ and by synthesis. Compound (V), prepared from 2-carboxy-2-hydroxy-1,1,3,3-tetramethylindane[3] by treatment with acetic anhydride in pyridine (m.p. of acetyl derivative 189—190°) followed by thionyl chloride, yielded (II) on being warmed with an excess of n-butylamine. The structure of (III)¶ was assigned on the basis of analytical and spectral data§ only, while (IV), which probably arose from oxidation of an initially neutral substance during isolation was identical with the compound formed by the action of n-butylamine on αα′-*o*-phenylenedi-isobutyric anhydride.[4]

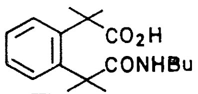

(I)



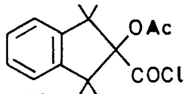
(II)



(III)

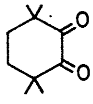


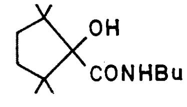
(IV)



(V)

Since the formation of (II) represents a photo-induced benzilic amide-type rearrangement, 3,3,6,6-tetramethyl-1,2-dioxocyclohexane (VI),[5] 3,3,5,5-tetramethyl-1,2-dioxocyclopentane,[6] phenanthrene-9,10-quinone (purified commercial sample), 3,3-dimethylindanedione,[6] benzil (purified commercial sample), 1,2-dioxocyclodecane,[7] and 6,7-dioxo-n-dodecane[6] were irradiated in n-butylamine to determine whether the rearrangement was characteristic of α-diketones. Only (VI) (irradiated for 20 hr), however, underwent the rearrangement but the yield of (VII), m.p. 118—118·5°, was very low (4%). The major product (20%) from (VI) was the acyloin 2-hydroxy-3,3,6,6-tetramethylcyclohexanone.

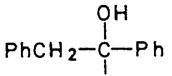

(VI)



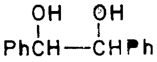
(VII)

When (I) was irradiated in diethylamine, reduction was the predominant reaction with the acyloin 2-hydroxy-1,1,4,4-tetramethyl-3-oxotetralin (67%) being the major product. A minor product (4%) has been identified as 2-ethylcarbamoyl-2-hydroxy-1,1,3,3-tetramethylindane (II; Et in place of Bu). 2-Diethylcarbamoyl-2-hydroxy-1,1,3,3-tetramethylindane (II; NEt_2 in place of NHBu) was not detected in the reaction mixture.

Irradiation (52 hr) of benzil in n-butylamine gave a neutral fraction from which *N*-n-butylbenzamide (19%), deoxybenzoin (5%),†† and the diastereoisomers [*meso*, 4%; (±), 6%] of the pinacol (VIII).[8] That the diastereoisomers were derived, at least in part, from deoxybenzoin was shown when irradiation (10 hr) of the last mentioned compound in n-butylamine yielded the two pinacols [*meso*, 41%; (±), 38%). The only compound that could be identified in the basic fraction obtained from irradiation of benzil in n-butylamine was *N*-2-butylidene-2-butylamine (IX).


$\mathrm{PhCH_2C(OH)(Ph){-}C(OH)(Ph)CH_2Ph}$
(VIII)

PrCH=N—Bu
(IX)


$\mathrm{PhCH(OH){-}CH(OH)Ph}$
(X)

When benzil was irradiated (30 hr) in diethylamine, benzoin (trace), benzaldehyde (trace), *NN*-diethylbenzamide (42%), and a mixture of *meso*- and (±)-hydrobenzoin (X)[9] (combined yield 2%) were the products. Under the same

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† In a recent report (N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, 1969, **91**, 7113) on the quenching of biacetyl fluorescence and phosphorescence, it was mentioned that biacetyl is reduced to the pinacol 3,4-dihydroxy-3,4-dimethylhexane-2,5-dione on irradiation in tripropylamine.

‡ The irradiations were carrried out with 1% solutions of the α-diketones under nitrogen in a Pyrex reactor equipped with a Philips 125w mercury–quartz high-pressure lamp cooled by a water jacket. "Dark" reactions have been carried out to establish that the transformations were light-induced.

§ Satisfactory analyses and spectral data (i.r., n.m.r., and mass) in complete accord with assigned structures have been obtained for all new compounds except (V) which was used without purification.

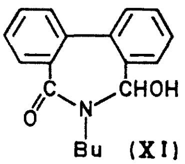
¶ In our extensive investigations[2] on the photochemistry of (I), compound (III) provides the first positive evidence that bond cleavage between C-1 and C-2, rather than between the two carbonyl groups, can occur in (I).

†† Of the α-diketones which have been irradiated in n-butylamine, 1,2-dioxocyclodecane, besides benzil, is the only one in which one of the carbonyl groups was reduced to a methylene group. After irradiation in n-butylamine for 105 hr, 1,2-dioxocyclodecane gave cyclodecanone (10%).

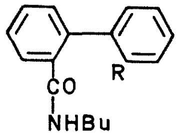
conditions of irradiation, benzoin yielded *NN*-diethylbenzamide (33%) and the two hydrobenzoins (combined yield 16%).

With triethylamine as the solvent, irradiation (18 hr) of benzil yielded *NN*-diethylbenzamide (19%) and a mixture of the two hydrobenzoins (combined yield 7%).

Irradiation (27 hr) of phenanthrene-9,10-quinone in n-butylamine yielded (XI) (53%), m.p.150·5—152·5°, and (XII; R = CO_2H) (16%), m.p. 101—103°. The structures of both compounds were determined from analytical and spectral data and confirmed by synthesis as follows. Diphenic acid mono-n-butylamide (XII; R = CO_2H) was prepared by heating diphenic anhydride (from diphenic acid and acetic anhydride) in n-butylamine, and its methyl ester (XII; R = CO_2Me), m.p. 42—44° was readily reduced with lithium borohydride in tetrahydrofuran to (XII; R = CH_2OH), m.p. 92—93°. Oxidation of the last mentioned compound with chromic anhydride in pyridine yielded (XI), the cyclic tautomer of (XII; R = CHO).



(XI)



(XII)

When phenanthrene-9,10-quinone was irradiated in diethylamine, complex mixtures, from which no pure products could be isolated, were formed.

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[2] For previous work, G. E. Gream and J. C. Paice, *Austral. J. Chem.*, 1969, **22**, 1249; and references therein.

[3] H. A. Bruson, F. W. Grant, and E. Bobko, *J.Amer. Chem. Soc.*, 1958, **80**, 3634.

[4] A. W. Burgstahler and M. O. Abdel-Rahman, *J. Amer. Chem. Soc.*,1963, **85**, 173.

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[6] J. H. Bowie, R. G. Cooks, G. E. Gream, and M. H. Laffer, *Austral. J. Chem.*, 1968, **21**, 1247.

[7] A. T. Blomquist, and A. Goldstein, *Org. Synth., Coll. Vol. IV*, 1963, 838.

[8] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, 1968, **33**, 1271.

[9] J. Dale, *J. Chem. Soc.*, 1961, 210.