Photochemical Transformations of 1,2-Diketones and Benzhydrylamine

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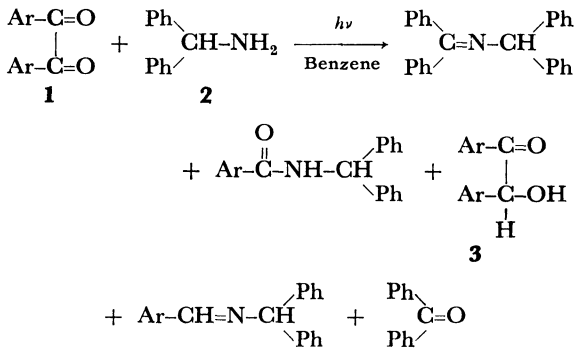
Photolysis of a mixture of substituted 1,2-diketones and benzhydrylamine (in 1:2 mole ratio) in benzene gave *N*-benzhydrylidenebenzhydrylamine, *N*-(diarylmethyl)benzamides, acyloins (**3**), *N*-(arylmethylene)benzhydrylamines, and benzophenone separated by fractional crystallization and column chromatography. The products have been characterised by analytical and spectral (IR, UV, and NMR) data and the structural assignments confirmed by the comparison (IR spectra and undepressed mixed mp) with authentic samples. Acyloins (**3**) are precursors for *N*-(diarylmethyl)benzamides and *N*-(arylmethylene)benzhydrylamines. A tentative mechanistic route for the formation of products has been suggested.

Irradiation of aromatic ketones and aliphatic amines (primary as well as secondary) in nonpolar media leads to a high yield of pinacols and substituted imines initiated by hydrogen abstraction from amine by the triplet-excited state of the ketone.[1] It has been observed that the presence of a hydrogen atom to the heteroatom in amine enhances its reactivity towards photoreduction of ketones.[2] Hydrogen abstraction by an excited state of benzil from 2-propanol and subsequent α-cleavage has been known to form benzoin, 2,3-dihydroxy-1,2,3,4-tetraphenyl-1,4-butanedione, small amount of benzoic acid, benzaldehyde, α-benzoylbenzylbenzoate, and 1,2-dibenzoyl-1,2-diphenylethylene dibenzoate.[3] Irradiation of benzil in butylamine has been reported to give *N*-butylbenzamide, deoxybenzoin, *dl* and *meso* forms of 1,2-dibenzyl-1,2-diphenyl-1,2-ethanediol and *N*-butylidine-2-butylamine.[4] In the present paper we describe the isolation of *N*-benzhydrylidenebenzhydrylamine, *N*-(diarylmethyl)benzamides, acyloins (**3**), *N*-(arylmethylene)benzhydrylamines, and benzophenone from the irradiation of 1,2-diketones and benzhydrylamine in benzene with UV light. The formation of *N*-(diarylmethyl)benzamides and *N*-(arylmethylene)-benzhydrylamines has been shown to occur through acyloins.

Results and Discussion

Irradiation of benzil (**1a**) and benzhydrylamine (**2**), in 1:2 mole ratio, in thiophene free benzene under nitrogen atmosphere by UV light for 32 h gave *N*-benzhydrylidenebenzhydrylamine, *N*-benzhydrylbenzamide, benzoin, *N*-benzylidenebenzhydrylamine, and benzophenone. These products were separated by fractional crystallization and column chromatography. The irradiated solution gave a positive Nessler's spot test for the presence of ammonia.[5] Similar results were obtained on irradiation (21—48 h) of a mixture of other diketones (**1b—d**) and benzhydrylamine. In each case the time of irradiation for complete disappearance of diketone (TLC) has been found to depend on the nature of substituents on the phenyl rings of the diketone (Table 1). It has been observed that the irradiation time increased and total yields of the products decreased as the diketone (**1**) was changed from **a** to **b** to **c**. The excited state reactivity of the diketones has been known to decrease with the presence of electron-donating groups on the *para* position of the phenyl rings of benzil,[6] the order of reactivity, H>CH_3>OCH_3, is in agreement with the observed behaviour of the diketones **1a—c** (Table 1). The reaction can be shown as



These products were not formed when a mixture of benzil and benzhydrylamine in benzene was heated to reflux for 24 h confirming the photochemical nature of the above reaction.

Irradiation of a mixture of benzoin and benzhydryl-

TABLE 1. PRODUCTS DISTRIBUTION OBTAINED ON IRRADIATION OF 1,2-DIKETONES AND BENZHYDRYLAMINE (in 1:2 mole ratio)

1,2-Diketones	Ar	Time of Irradiation / h	Ph(Ph)C=N-CH(Ph)Ph yield/%	Ar-C(=O)-NH-CH(Ph)Ph yield/%	Ph(Ph)C=O yield/%	Ar-CH=N-CH(Ph)Ph yield/%	Ar-CH(OH)-C(=O)Ar yield/%
1a	C_6H_5	32	34	28	7	9	5
1b	C_6H_4·CH_3-*p*	36	30	19	10	9	4
1c	C_6H_4·OCH_3-*p*	48	21	15	8	11	6
1d		21	16	8	—	6	a)

a) Could not be isolated but its presence was detected by TLC.

amine (in 1 : 2 mole ratio) in benzene for 21 h in a similar manner as described above gave *N*-benzhydrylbenzamide and *N*-benzylidenebenzhydrylamine. This observation supports the view that acyloins (**3**) could be intermediates in the formation of *N*-(diarylmethyl)-benzamides and *N*-(arylmethylene)benzhydrylamines from the irradiation of diketones **1a**—**d**.

The photoreaction is initiated by an abstraction of a hydrogen α to the amino group in benzhydrylamine by an excited triplet state of the diketone leading to the α-aroyl-α-hydroxybenzyl radical (**a**) and α-aminobenzhydryl radical (**b**). This step is similar to the one given in the photoreduction of benzil in 2-propanol[3] and also in the photoreduction of benzophenone in primary amines[1,2] in which the initial step involves a hydrogen atom abstraction.

$$Ph_2C{=}O^{*3} + RR'CHNH_2 \longrightarrow Ph_2\dot{C}OH + RR\dot{C}NH_2$$

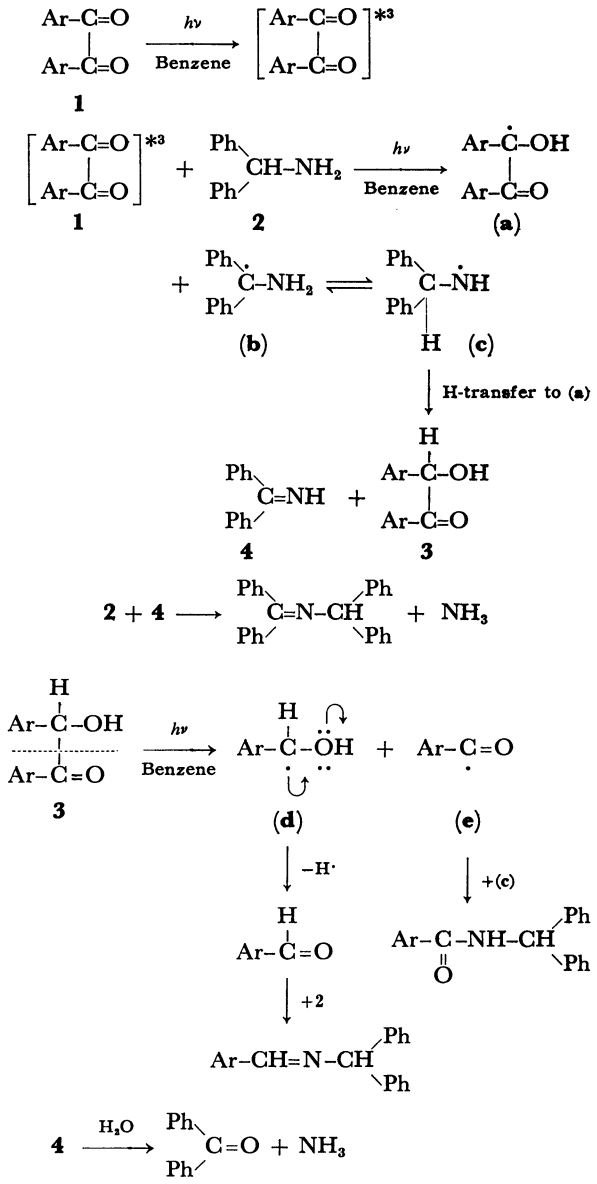
In deuterated amines, where electron release is more efficient, an electron transfer has been suggested to occur in the initial step.[2]

$$Ph_2C{=}O^{*3} + R_2CHND_2 \longrightarrow [Ph_2\dot{C}{-}O^- \quad R_2\overset{+}{C}H\dot{N}D_2]$$

Such electron transfer initiation has also been known to occur in photoreduction of aromatic ketones in tertiary amines.[7] Hydrogen abstraction by one of the carbonyl groups in 1,2-diketones[6] has been known to occur through an excited triplet state *via* a $^3(n\rightarrow\pi^*)$ excitation.[8] It has been observed that the presence of a hydrogen atom α to the amino group increases the hydrogen donating capability of amines in the photoreduction of ketones.[2] Rearrangement of **b** to **c** and subsequent hydrogen transfer to **a** may lead to the formation of acyloin (**3**) and diphenylmethanimine (**4**). The reaction between **4** and benzhydrylamine (**2**) may give rise to *N*-benzhydrylidenebenzhydrylamine and ammonia in a manner already reported.[9] The formation of *N*-benzhydrylidenebenzhydrylamine in each case, irrespective of the nature of the aryl group present in 1,2-diketones, strongly suggests that it must be arising from benzhydrylamine only which is in agreement with the step given in Scheme. The proposed Scheme also explains the requirement of two moles of benzhydrylamine per mole of the diketone in the reaction.

A photolytic carbon-carbon bond cleavage in acyloin (**3**) may give rise to radicals **d** and **e** in an analogous manner as proposed in the case of irradiation of benzoin ethers.[10] Recombination of the radicals **c** and **e** may form *N*-(diarylmethyl)benzamides and loss of hydrogen from radical **d** may lead to aldehydes which on reaction with benzhydrylamine form *N*-(arylmethylene)benzhydrylamines. Irradiation of benzoin with UV light has been known to give benzaldehyde.[11] Hydrolysis of diphenylmethanimine (**4**) may result in the formation of benzophenone and ammonia.

On the basis of the above observations a tentative mechanistic route can be shown as follows:



Experimental

General. Melting points have been determined in capillaries on Buchi melting point apparatus and are uncorrected. The IR spectra were measured in Nujol mull on a Perkin-Elmer 720 spectrophotometer and the UV in ethanol on a Cary-14 spectrophotometer. The NMR spectra were recorded on a Varian A-60 Hz spectrometer in $CDCl_3$ with TMS as the internal standard.

Materials. The 1,2-diketones were obtained from Ega Chemie, Germany and benzhydrylamine was prepared according to the reported method.[12]

General Irradiation Procedure. A solution containing 1,2-diketones (0.005 mol) and benzhydrylamine (0.010 mol) in 350 ml of benzene (thiophene free) was irradiated with UV light from a 200 W Hanovia lamp. Pre-purified nitrogen was bubbled into the solution prior to irradiation and a slow stream was continued during the course of photolysis. The progress of reaction was monitored by TLC. The irradiated solutions gave a positive Nessler's test for ammonia.[5] Irradiation was discontinued when the starting diketone had appreciably diminished. The solvent was evaporated under reduced pressure. The products were separated by fractional crystallization and column chromatography and were characterised on the basis of analytical and spectral (IR, UV, and NMR) data. The structural assignments were further confirmed by the comparison (IR spectrum and mixed mp) with authentic samples.

Irradiation of Benzil (1a) and Benzhydrylamine. Irradiation of a mixture of benzil and benzhydrylamine in benzene for 32 h and evaporation of the solvent gave a thick pasty mass which on treatment with ethanol afforded a white crystalline solid (34%), identified as *N*-benzhydrylidene benzhydrylamine, mp and mixed mp 149—151 °C (lit,[13] mp 152 °C); UV (EtOH, nm): 252; IR (Nujol, cm^{-1}): 1620 ($\nu_{C=N}$); NMR ($CDCl_3$, δ ppm): 5.60 (s, 1H, $CHPh_2$), 7.35 (m, 16H, arom.), and 7.90 (m, 4H, arom.). Found: C, 90.01; H, 6.20; N, 3.89%. Calcd for $C_{26}H_{21}N$: C, 89.91; H, 6.05; N, 4.03%.

Fractional crystallization of the mother liquor from benzene–hexane (1: 1) gave 28% of white needle shaped crystals which were shown to be *N*-benzhydrylbenzamide, mp and mixed mp 169—172 °C (lit,[14] mp 172—174 °C). UV (EtOH): end absorption; IR (Nujol, cm^{-1}): 3300 (ν_{NH}), 1640 ($\nu_{C=O}$); NMR ($CDCl_3$, δ ppm): 1.65 (bs, 1H, NH, exchangeable on deuteration), 6.39 and 6.53 (d, 1H, J=8.4 Hz, $CHPh_2$, doublet due to spin-spin coupling with NH[15]), 7.41 (m, 13H, arom.), and 7.75 (m, 2H, arom.). Found: C, 83.24; H, 5.51; N, 5.07%. Calcd for $C_{20}H_{17}NO$: C, 83.62; H, 5.92; N, 4.87%. The IR spectrum was superimposable with that of an authentic sample.[16]

The mother liquor was concentrated and subjected to column chromatography over neutral alumina (60 g, 2.5×45 cm) to give the following products by using hexane, hexane–benzene (7: 3), and hexane–benzene (1: 1) as eluants:

(*i*). Benzophenone (7%), identified as 2,4-dinitrophenylhydrazone derivative mp 229 °C.

(*ii*). *N*-Benzylidenebenzhydrylamine (9%), mp and mixed mp 98—99 °C (lit,[17] mp 98—100 °C). UV (EtOH, nm): 252; IR (Nujol, cm^{-1}): 1620 ($\nu_{C=N}$); NMR ($CDCl_3$, δ ppm): 5.58 (s, 1H, $CHPh_2$), 7.40 (m, 13H, arom.), 7.90 (m, 2H, arom.), and 8.34 (s, 1H, formyl). Found: C, 88.58; H, 6.35; N, 4.98%. Calcd for $C_{20}H_{17}N$: C, 88.56; H, 6.27; N, 5.17%.

(*iii*). Benzoin (5%), mp and mixed mp 136—138 °C. The IR spectrum was superimposable with that of an authentic sample.[18]

Irradiation of 4,4'-Dimethylbenzil (1b) and Benzhydrylamine. Irradiation of a mixture of 4,4'-dimethylbenzil (**1b**) and benzhydrylamine in benzene for 36 h and similar work up as described above gave the following products:

(*i*). *N*-Benzhydrylidenebenzhydrylamine (30%), mp and mixed mp 149—151 °C.

(*ii*). *N*-Benzhydryl-4-methylbenzamide (19%), mp and mixed mp 182—184 °C (lit,[14] mp 183—184 °C). UV (EtOH): end absorption; IR (Nujol, cm^{-1}): 3300 (ν_{NH}), 1640 ($\nu_{C=O}$); NMR ($CDCl_3$, δ ppm): 1.59 (bs, 1H, NH, exchangeable on deuteration), 2.30 (s, 3H, CH_3), 6.45 and 6.31 (d, 1H, J= 8.4 Hz, doublet due to spin-spin coupling with NH[15]), 7.26 (m, 12H, arom.), and 7.68 (m, 2H, arom.). Found: C, 83.78; H, 6.46; N, 4.72%. Calcd for $C_{21}H_{19}NO$: C, 83.85; H, 6.31; N, 4.65%. The IR spectrum was superimposable with that of an authentic sample.[16]

(*iii*). Benzophenone (10%), identified as 2,4-dinitrophenylhydrazone derivative, mp 229 °C.

(*iv*). *N*-(4-Methylbenzylidene)benzhydrylamine (9%), mp and mixed mp 103—105 °C. UV (EtOH, nm): 254; IR (Nujol, cm^{-1}): 1620 ($\nu_{C=N}$); NMR ($CDCl_3$, δ ppm): 2.40 (s, 3H, CH_3), 5.60 (s, 1H, $CHPh_2$), 7.38 (m, 12H, arom.), 7.80 (m, 2H, arom.), and 8.50 (s, 1H, formyl). Found: C, 88.52; H, 6.82; N, 5.01%. Calcd for $C_{21}H_{19}N$: C, 88.42; H, 6.66; N, 4.92%.

(*v*). 4,4'-Dimethylbenzoin (4%), mp and mixed mp 85—86 °C. The IR spectrum was superimposable with that of an authentic sample.[18]

Irradiation of 4,4'-Dimethoxybenzil (1c) and Benzhydrylamine. Irradiation of a mixture of 4,4'-dimethoxybenzil and benzhydrylamine in benzene for 48 h and separation of the components in a similar manner as described above gave the following products:

(*i*). *N*-Benzhydrylidenebenzhydrylamine (21%), mp and mixed mp 149—151 °C.

(*ii*). *N*-Benzhydryl-4-methoxybenzamide (15%), mp and mixed mp 198—199 °C (lit,[14] mp 198—200 °C). UV (EtOH, nm): 250; IR (Nujol, cm^{-1}): 3300 (ν_{NH}), 1640 ($\nu_{C=O}$); NMR ($CDCl_3$, δ ppm): 1.83 (bs, 1H, NH, exchangeable on deuteration), 3.76 (s, 3H, OCH_3), 6.53 and 6.39 (d, 1H, J= 8.4 Hz, $CHPh_2$, doublet due to spin-spin coupling with NH[15]), 6.83 (A_2B_2, 2H, J=9 Hz, arom.), 7.28 (m, 10H, arom.), and 7.75 (A_2B_2, 2H, J=9 Hz, arom.). Found: C, 79.43; H, 6.18; N, 4.51%. Calcd for $C_{21}H_{17}NO_2$: C, 79.49; H, 5.99; N, 4.41%. The IR spectrum was identical with that of an authentic sample.[16]

(*iii*). Benzophenone (8%), identified as 2,4-dinitrophenylhydrazone derivative mp 229 °C.

(*iv*). *N*-(4-Methoxybenzylidene)benzhydrylamine (11%), mp and mixed mp 108—110 °C (lit,[17] mp 110 °C). UV (EtOH, nm): 272; IR (Nujol, cm^{-1}): 1620 ($\nu_{C=N}$); NMR ($CDCl_3$, δ ppm): 3.70 (s, 3H, OCH_3), 5.43 (s, 1H, $CHPh_2$), 6.80 (A_2B_2, 2H, J=9 Hz, arom.), 7.23 (m, 10H, arom.), 7.70 (A_2B_2, 2H, J=9 Hz, arom.), and 8.27 (s, 1H, formyl). Found: C, 84.01; H, 6.52; N, 4.58%. Calcd for $C_{21}H_{19}NO$: C, 83.85; H, 6.30; N, 4.64%.

(*v*). 4,4'-Dimethoxybenzoin (6%), mp and mixed mp 115—117 °C. The IR spectrum was superimposable with that of an authentic sample.[18]

Irradiation of 2,2'-Furil (1d) and Benzhydrylamine. Irradiation of a solution containing 2,2'-furil and benzhydrylamine in benzene for 21 h and separation on a column packed with alumina gave the following products:

(*i*). *N*-Benzhydrylidenebenzhydrylamine (16%), mp and mixed mp 149—151 °C.

(*ii*). *N*-Benzhydryl-2-furamide (8%), mp and mixed mp 161—162 °C. UV (EtOH): end absorption; IR (Nujol, cm^{-1}): 3290 (ν_{NH}), 1650 ($\nu_{C=O}$); NMR ($CDCl_3$, δ ppm): 1.82 (bs, 1H, NH, exchangeable), 6.30 and 6.16 (d, 1H, J=8.4 Hz, $CHPh_2$[15]), and 6.25 (m, 13H, aromatic and 2-furoic). Found: C, 78.38; H, 5.32; N, 5.20%. Calcd for $C_{18}H_{15}NO_2$: C, 77.97; H, 5.41; N, 5.05%. The IR spectrum was superimposable with that of an authentic sample.[16]

(*iii*). *N*-(2-Furfurylidene)benzhydrylamine (6%), mp and mixed mp 104—106 °C. UV (EtOH, nm): 272; IR (Nujol, cm^{-1}): 1640 ($\nu_{C=O}$); NMR ($CDCl_3$, δ ppm): 5.58 (s, 1H, $CHPh_2$), 6.43 (m, 1H, furan CH_a), 6.46 (d, 1H, J=3 Hz, furan CH_b), 7.33 (m, 11H, 10 arom+1 furan CH_c), and 8.20 (s, 1H, formyl). Found: C, 83.03; H, 5.37; N, 5.45%. Calcd for $C_{18}H_{15}NO$: C, 82.75; H, 5.74; N, 5.36%. The IR spectrum was superimposable with that of an authentic sample prepared by following the method of Michaelis.[17]

In this case 2,2'-furoin could not be isolated although its presence was detected on TLC.

Irradiation of Benzoin and Benzhydrylamine. Irradiation of a mixture of benzoin and benzhydrylamine in a similar manner as described earlier gave *N*-benzhydrylbenzamide (28%) and *N*-benzylidenebenzhydrylamine (21%) identified on the basis of comparison (IR spectra and undepressed mixed mp) with authentic samples.

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