Photocyclization of β-Oxo-amides. Possible Electron Transfer from Amide Nitrogen to Excited Ketone Carbonyl

By **Tadashi Hasegawa**, Department of Chemistry, Tokyo Kyoiku University, Otsuka, Bunkyo-ku, Tokyo, Japan
Hiromu Aoyama * and **Yoshimori Omote**, Department of Chemistry, Tsukuba University, Sakuramura, Niiharigun, Ibaraki 300–31, Japan

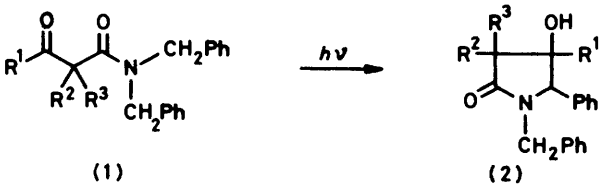
Benzoylacetamide (1a) undergoes unquenchable photocyclization to give pyrrolidin-2-one (2a) in benzene. Upon irradiation *p*-phenylbenzoylacetamide (1d) and 2-naphthoylacetamide (1e) also undergo cyclization to give the pyrrolidin-2-ones (2d) and (2e), respectively. The quenchable portion of the photoreaction of (1a) is greater in methanol than in benzene. Benzoylacetamides having a 2-methyl substituent exhibit similar behaviour although the quenchable portion of the reaction increases with an increase in the number of the 2-methyl substituents. The photoreaction of 2,2-dimethylbenzoylacetamide (1c) is completely quenched by piperylene in methanol. Quantum yields also increase with introduction of a substituent into β-oxo-amides except in the photocyclization of 2-naphthoylacetamides. Irradiation of *N*-benzyl-*N*-methyl-β-oxo-amides (1g—i) affords, predominantly, 1-benzylpyrrolidin-2-ones, which are produced *via* methyl hydrogen abstraction; 2-methyl-β-oxo-amide (1j) however gives 1-methylpyrrolidin-2-one (2j) exclusively, which is formed *via* benzylic hydrogen abstraction. It is concluded that β-oxo-amides which have no substituents on the 2-position undergo photocyclization mainly through electron transfer from amide nitrogen to singlet-excited ketone carbonyl followed by δ-proton transfer, while β-oxo-amides which carry two methyl substituents on the 2-position undergo the cyclization *via* normal δ-hydrogen abstraction from the n,π* triplet state. The enol form of β-oxo-amides acts as internal filter in the photoreactions.

AROMATIC ketones generally undergo a Norrish Type II reaction from their n,π* triplet states [1] and amino-ketones, the subject of current interest,[2,3] behave similarly although the mechanism of hydrogen abstraction by the carbonyl oxygen in the latter is strikingly different from that in the former. The excited carbonyl group of amino-ketones interacts with the amino-group, and electron transfer from nitrogen to the carbonyl group occurs prior to hydrogen shift.[3] The efficiency of electron transfer is influenced by the ionization potential of the amines.[4] The charge-transfer interaction between nitrogen and the carbonyl group in the excited state becomes less efficient upon introduction of an electron-withdrawing group on the nitrogen.[3e] Gold suggested that the Type II cyclization of α-amido-ketones to 3-azetidinols proceeded not from the charge-transfer state but through normal hydrogen abstraction by carbonyl in analogy with the Type II reaction of α-alkoxy-ketones.[5] We have previously reported photocyclization of β-oxo-amides to pyrrolidin-2-ones in high yields,[6] and now wish to report that charge-transfer interaction between amide nitrogen and excited ketone carbonyl is presumed to play an important role in the cyclization. Furthermore, 2-methyl substituents in β-oxo-amides remarkably affect the reaction path; the substituents make the direct hydrogen abstraction process predominant and change the regioselectivity in the hydrogen abstraction of *N*-benzyl-*N*-methyl-β-oxo-amides.

RESULTS AND DISCUSSION

Quenching Studies.—Irradiation of the benzoylacetamides (1a—c) in benzene or methanol under nitrogen with a high-pressure mercury lamp gave the corresponding pyrrolidin-2-ones (2a—c) respectively, in high yields.[6] The quantum yields at 3 130 Å for the production of (2a) and (2b) in benzene were 0.008 and 0.26, respectively.

Quenching of the photocyclization of the β-oxo-amide (1a) by 0.15M-piperylene (penta-1,3-diene) ($E_T = 57$ kcal) [7] was not observed in benzene, while the reaction in methanol was partially quenched ($\phi_q/\phi = 0.57$) by the same concentration of piperylene. Such solvent dependence of sensitivity to quencher molecule was significantly



(1) (2)

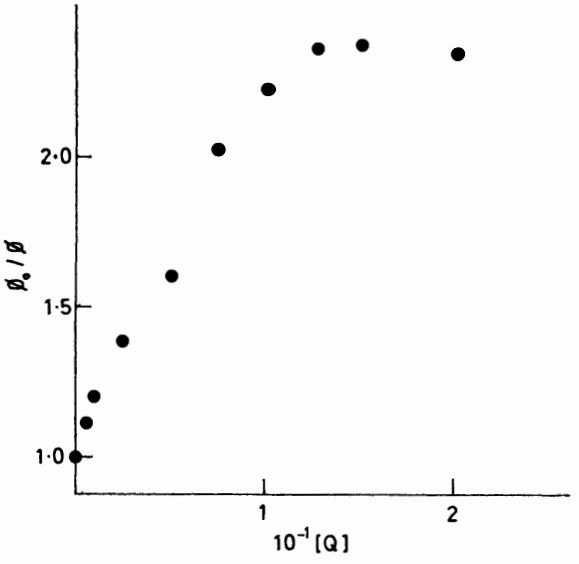
	R^1	R^2	R^3	Yield(%)
a;	Ph	H	H	80 [6]
b;	Ph	Me	H	90 [6]
c;	Ph	Me	Me	65 [6]
d;	*p*-PhC_6H_4	H	H	25
e;	2-Naphthyl	H	H	50
f;	2-Naphthyl	Me	H	50

different from that in the photoreactions of usual ketones,[8] and was quite similar to that reported in the case of amino-ketones.[3b,h] The failure to quench the reaction and the solvent effect suggest intervention of a zwitterion intermediate (3) produced through the charge-transfer interaction between amide nitrogen and ketone carbonyl in the photoreaction of the β-oxo-amides.

It is well known that photochemical hydrogen transfer to carbonyl oxygen from the charge-transfer state occurs even if the lowest triplet state of ketones is unreactive π,π* state.[3a,h] Accordingly, we investigated the photoreactions of *p*-phenylbenzoylacetamide (1d) and 2-naphthoylacetamide (1e).

Irradiation of (1d) and (1e) in benzene gave pyrrolidin-2-one (2d) and (2e) in 25 and 50% yield, respectively. The quantum yields for the production of (2d) and (2e)

were *ca.* 0.0002 and *ca.* 0.001 respectively.†,[9] The production of the pyrrolidin-2-ones (2d) and (2e) seems to support the idea that β-oxo-amides undergo photocyclization through the charge-transfer mechanism. An alternative mechanism, which involves hydrogen abstraction from the n,π* singlet state, may be considered in the cases of the photoreactions of (1d) and (1e) because of the low quantum yields for the formation of (2d) and (2e). However the latter mechanism can be excluded at least in the case of the unquenchable reaction of (1b) for the following reason. The amide (1b) photocyclized in



benzene with a quantum yield of 0.26, of which three-fifths was quenchable (as Table 1 and Figure). The

TABLE 1

Quantum yields for product formation from β-oxo-amide (1a), (1b), and (1c) [a]

Product	Quantum yields
(2a)	$\phi_{benzene} = 0.008$
	$\phi^{q}_{benzene}/\phi_{benzene} = 1.0$
	$\phi^{q}_{MeOH}/\phi_{MeOH} = 0.57$ [b]
	$\phi_{MeOH}/\phi_{benzene} = 1.4$
(2b)	$\phi_{benzene} = 0.26$
	$\phi^{q}_{benzene}/\phi_{benzene} = 0.41$ [b]
	$\phi^{q}_{MeOH}/\phi_{MeOH} = 0.12$ [b]
	$\phi_{MeOH}/\phi_{benzene} = 0.70$
(2c)	$\phi^{q}_{benzene}/\phi_{benzene} < 0.1$ [c]
	$\phi^{q}_{MeOH}/\phi_{MeOH} = 0$

[a] Production of the pyrrolidinones (2a), (2b), and (2c) was measured by n.m.r. spectroscopy. The quantum yields were determined by using a benzophenone–diphenylmethanol actinometer. An Ushio 100 W high-pressure mercury lamp was used as irradiation source. A Pyrex and a coloured glass filter were used to isolate the 3 130 Å region. [b] Nearly constant values were obtained by use of more than 0.1M-piperylene. In these experiments 0.15M-piperylene was used. [c] The determination is poor because of difficulty of measurement of product formation.

quantum yield for the unquenchable reaction of (1b) is, therefore, 0.11. Since the rate of intersystem crossing of phenyl ketones is very rapid (*ca.* 10^{11} s^{-1}), it is quite improbable that δ-hydrogen abstraction from the n,π* singlet can compete with intersystem crossing. Therefore, the unquenchable (singlet) reaction of (1b) can be most reasonably explained in terms of the charge or electron-transfer mechanism.

The quenchable (triplet) reaction of (1b) was then studied. An estimate value of $k_q\tau$ obtained from the low concentration quenching points for (1b) is 20 l mol^{-1}. Although the $k_q\tau$ value is much smaller than that for δ-hydrogen abstraction of β-ethoxypropiophenone (360 l mol^{-1}),[9] such a small value is not unreasonable for the structure of (1b). The δ-hydrogens of (1b) are activated both by a nitrogen and a phenyl group.[10] Since rotation of CO–N bond of amides is slow, the CO–N bond of (1b) is sure to be fixed planar during the photoprocess.[11] The frozen rotation should further enhance the rate of δ-hydrogen transfer.[12] The triplet reaction can be explained in terms of direct hydrogen abstraction from the n,π* state. An alternative mechanism which involves proton transfer from the charge-transfer state may be considered for the triplet reaction. However, the latter mechanism is less probable because photocyclization of *N*-benzyl-*N*-methyl-β-oxo-amide (1j) showed normal regioselectivity as predicted for hydrogen abstraction from the n,π* triplet state of phenyl ketones[10] (see the third section).

Solvent dependence of sensitivity to quencher was also found in the case of the β-oxo-amide (1b). Photocyclization of the amide (1b) was much more efficiently quenched by piperylene in methanol than in benzene. The quenchable portion of photocyclization of β-oxo-amides increased with introduction of a methyl substituent on the 2-position of the amides and the photoreaction of (1c) in methanol was completely quenched by piperylene (see Table 1).

Consequently, the reaction efficiency of 2-naphthoylacetamides was expected to become low by introduction of the 2-methyl substituent, because the substituent increases the contribution of the triplet state and the triplet state of 2-naphthyl ketones is unreactive for hydrogen abstraction.[13]

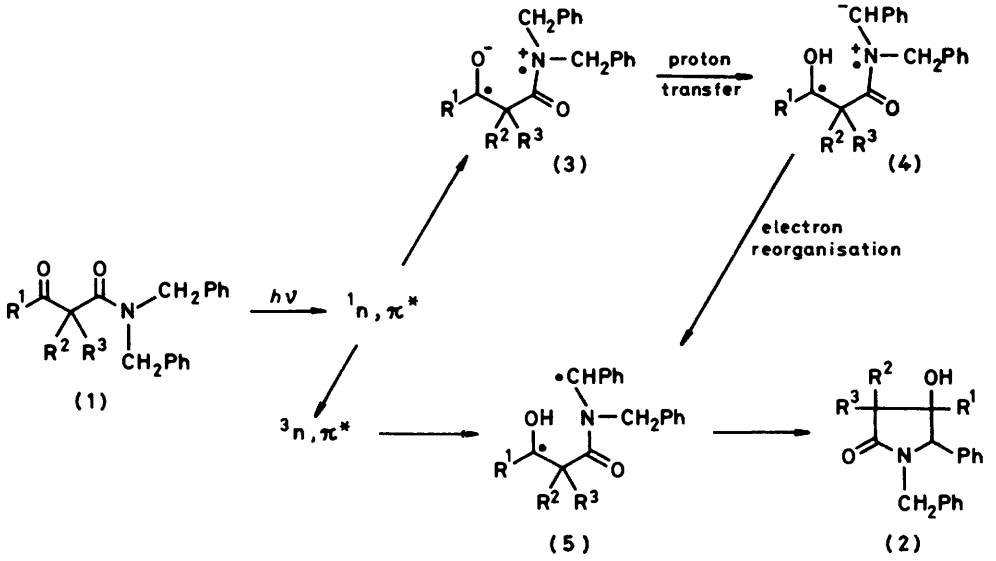
Irradiation of 2-methyl-(2-naphthoyl)acetamide (1f) in benzene also gave pyrrolidin-2-one (2f) in 50% yield. The photoreaction of (1f) was much more inefficient than that of (1e) (ϕ_{1f}/ϕ_{1e} = *ca.* 0.5) in spite of the fact that (1f) is completely in the reactive keto-form and (1e) contains *ca.* 50% of an enol form (see the following section). On the other hand, (1b) reacted much more efficiently than (1a) ($\phi_{1b}/\phi_{1a} = 33$). These results also support the above explanation that the methyl substituents on the 2-position of β-oxo-amides control the charge-transfer interaction. The substituent on the 2-position might destabilize the conformation which suitable for the charge-transfer interaction between excited carbonyl oxygen and amide nitrogen. However, examination of molecular models did not give a strong support for this explanation.

The smaller contribution of the charge-transfer process in methanol compared with benzene can be explained in terms of solvation. The solvation of the amide and

† The determination is poor because of difficulty in the measurement of product formation.

ketone groups by methanol should impede close approach of the lone pair on the amide nitrogen to the ketone carbonyl, and make the charge-transfer interaction inefficient.

The formation of the pyrrolidin-2-ones from the β-oxo-amides can be explained by the following mechanism. A



β-oxo-amide which has two methyl substituents on the 2-position undergoes photocyclization *via* hydrogen abstraction from the n,π* triplet state, *i.e.* excited carbonyl abstracts δ-hydrogen directly to give the 1,5-biradical (5). In contrast for a β-oxo-amide which carries no 2-substituents, in nonpolar solvents, singlet-excited carbonyl interacts with an electron or the nitrogen to give a zwitterion intermediate (3) *via* electron transfer from amide nitrogen to the ketone carbonyl group. Transfer of a proton from the benzylic carbon to the ketyl radical and electron reorganization produce the same 1,5-biradical (5) as would be obtained by direct hydrogen abstraction. Both processes would occur for a β-oxo-amide which has one 2-methyl substituent, the former process predominating in polar solvents.

Role of An Enol Form.—β-Oxo-amides exhibit keto–enol tautomerism and a u.v. spectrum of the amide (1a) in ethanol showed a high-intensity band at 301 nm (ε 18 500) which is attributable to an enol form, by analogy to the assignment of the corresponding peak for benzoylacetone.[14] The n.m.r. spectrum of (1a) in carbon

TABLE 2

Light absorption properties of β-oxo-amides

Compound	Solvent	$\lambda_{max.}$/nm (ε/l mol^{-1} cm^{-1})
(1a)	EtOH	301 nm (18 500)
(1b)	EtOH	245.5 (11 700), *ca.* 280 (1 200)
	n-Hexane	243 (11 200), *ca.* 280 (1 100)
(1c)	EtOH	248.5 (11 600), *ca.* 280 (1 300)
	n-Hexane	246 (11 700), *ca.* 280 (1 300)
(1e)	EtOH	242 (32 500), 250.5 (31 000), 275 sh (19 300), 284 (21 200), 316.5 (25 300)
(1f)	EtOH	243 (sh) (28 800), 250.5 (31 900), 285 (6 400), 293 (5 900), 337 (1 000)

tetrachloride shows that the amide contains 82% of an enol form. However, its homologue, the amide (1b) exhibited absorption identical with that of the amide (1c) which carries no enolizable hydrogen atom (see Table 2). The enol content of the amide (1a) decreased with an increase in solvent polarity. The n.m.r. spectrum in deuteriochloroform showed 60% of the amide present in the enol form; a similar result has been reported for benzoylacetanilides.[15] Photocyclization of the β-oxo-amides would be expected to occur only from the keto-isomer.

Photocyclization of (1a) was much more inefficient than that of (1b) and quenching of the reaction of (1a) by piperylene was not observed in benzene. These results may be explained in terms of the quenching effect of the enol form of (1a). Thus, the enol form of (1a) may act as the quencher for the reactive keto-form triplet so that the cyclization may proceed only from the singlet state of the keto-form. However, this possibility was excluded by the following experiments.

Irradiation of a mixture of the amide (1a) and (1b) in benzene gave (2b) exclusively in a short reaction period; the conversion of (1a) into (2a) was negligible during this period. Although the efficiency of photocyclization of (1b) was lower than that for the irradiation of (1b) alone, quenching of the reaction by 0.15M-piperylene showed $\phi_q/\phi = 0.40$; this value was in accord with that for the irradiation of (1b) alone ($\phi_q/\phi = 0.41$). These results indicate that the enol form of (1a) does not quench the triplet state of the reactive keto-form of (1b). Since the triplet energy of the keto-form of (1a) is presumed to be closely similar to that of (1b), we can safely conclude that the enol form of (1a) does not quench the triplet state of the reactive keto-form of (1a).

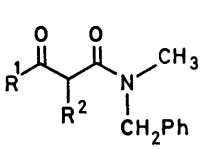
Oliver and Hamilton suggested that the triplet energy of the enol form of benzoylacetanilides was greater than that of the keto-form,[15] so that it is quite conceivable that the keto-form of the β-oxo-amides was not quenched by the enol form.

In conclusion, the enol form of the β-oxoamides did not act as a triplet quencher but, rather, an internal

filter. The low efficiency of the photoreaction of the β-oxo-amides (1a), (1d), and (1e) is attributable mainly to the internal filter effect of the enol form. The solvent dependence of sensitivity to quencher molecule is not due to the presence of the enol form.

Regioselectivity of δ-Hydrogen Abstraction in Photolyses of N-*Benzyl*-N-*methyl* β-*Oxo-amides*.—Finally we describe photochemical reactions of β-oxo-amides which carry different *N*-alkyl substituents.

Irradiation of *N*-benzyl-*N*-methylacetoacetamide (1g) in methanol gave 1-benzyl-4-hydroxy-4-methylpyrrolidin-2-one (2g), which is produced through methyl hydrogen transfer, in 78% yield. No 1-methylpyrrolidinones, which are formed through benzylic hydrogen abstraction, were detected. Similarly, irradiation of the amide (1h) and (1i) in methanol gave predominantly 1-benzylpyrrolidin-2-one (2h) (67%) and (2i) (31%) respectively. In these cases 1-methylpyrrolidin-2-one (2h') and (2i') were obtained in 22% and 13% yield respectively. The structures of the pyrrolidinones were elucidated on the basis of spectral evidence and elemental analyses.



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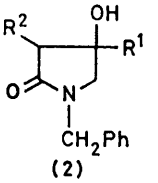
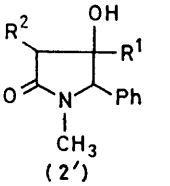


(2)

(produced through methyl hydrogen abstraction)

and / or



(2′)

(produced through benzylic hyrogen abstraction)

	R¹	R²	Yield of (2)(%)	Yield of (2′)(%)
g;	Me	H	78	*a*
h;	Ph	H	67	22
i;	2-Naphthyl	H	31	13
j;	Ph	Me	*a*	75

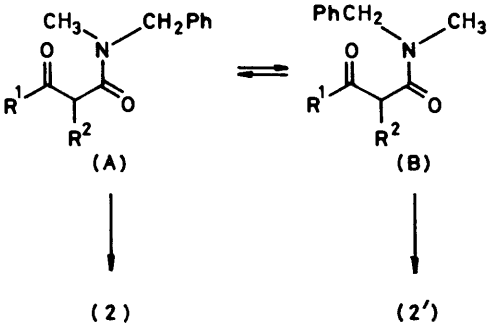
[a] Not detected.

In contrast, the distribution of cyclization products was dramatically changed in the case of 2-methylbenzoylacetamide (1j). Irradiation of (1j) in methanol gave two stereoisomers of 4-hydroxy-1,3-dimethyl-4,5-diphenylpyrrolidin-2-ones (2j'–a) and (2j'–b) in 75% total yield; any 1-benzylpyrrolidin-2-one (2j) formed through methyl hydrogen abstraction was not detected.

The product distribution in the photolysis of (1j) can be reasonably explained in terms of preferential hydrogen abstraction by ketone carbonyl from the benzylic position rather than the methyl position *viz* a biradical process; this occurs because benzylic hydrogen is much more reactive than methyl hydrogen toward abstraction by radicals.[10a] On the other hand, the product distribution in photolyses of the amides (1g), (1h), and (1i) is not explained by the customary hydrogen abstraction by ketone carbonyl.

Davidson and Lambeth reported that the benzylic C–H bond was less reactive than the methyl C–H bond in the photoreduction of ketones by amines,[16] a phenomenon which arose because the nitrogen atom activated adjacent C–H bonds in the amine cation radical to such an extent that the stabilization afforded by a phenyl group in benzylic compounds was negligible. Similar behaviour was reported by Berry *et al.* in the anodic oxidation of amines.[17] They reported that the methyl hydrogens in an *NN*-dimethylbenzylamine cation radical were much more reactive than the methylene hydrogen, a result of more positive charge density on the methyl hydrogens of the cation radical than on the methylene hydrogens. These results seem to support the idea that photocyclization of the β-oxo-amides (1g), (1h), and (1i) proceeds *via* a charge-transfer mechanism.

The regioselectivity in the photoreactions of (1g), (1h), and (1i) may be ascribable to the isomer composition of these oxo-amides. The percentage of the isomer (A) should be greater than that of the isomer (B) because of reduced steric hindrance [in the case of *N*-benzyl-*N*-methylacetamide, the percentage of the isomer corresponding to (A) is 69%].[18] The structure of the isomer (A) is favourable to methyl hydrogen abstraction. On the other hand, the percentage of isomer (A) in (1j)



should be larger than that in (1h) because the α-benzoylethyl group of (1j) is bulkier than the benzoylmethyl group of (1h). However, (1j) gave (2j'), which was formed by benzylic hydrogen abstraction, exclusively. Consequently, it is obvious that the reactivity of the methyl hydrogens of (1g), (1h), and (1i) is at least comparable with that of the benzylic hydrogens, and that the methyl hydrogens of (1j) are much less reactive than

the benzylic hydrogens. The lack of specificity of attack of the excited carbonyl group upon the C–H bonds of alkylated amines has been reported in the photoreduction of ketones by the amines *via* charge-transfer interaction.[19] These results indicate that photocyclization of (1j) proceeds mainly through normal hydrogen abstraction from the n,π* triplet state and that of (1g), (1h), and (1i) involves proton transfer from the charge-transfer state.

EXPERIMENTAL

I.r. absorption spectra were determined on a Hitachi EPI-2 spectrometer. U.v. absorption spectra were measured with a Hitachi EPS–033 spectrometer. N.m.r. spectra were determined at 60 MHz with a Hitachi R–20 spectrometer. Tetramethylsilane was used as an internal standard. An Ushio 450 W high-pressure mercury lamp was used as irradiation source in preparative photolyses of β-oxo-amides.

Starting Materials.—The β-oxo-amides were prepared according to previously described methods.[20]

NN-Dibenzylbenzoylacetamide (1a): m.p. 79—80 °C (lit.,[21] 79—80 °C).

NN-Dibenzyl-2-methylbenzoylacetamide (1b): m.p. 125—126 °C; i.r. (KBr) $\nu_{max.}$ 1 695 and 1 620 cm^{-1}; n.m.r. ($CDCl_3$) δ 1.52 (d, 3 H, J = 6.8 Hz, CH_3), 4.38 (s, 2 H, N–CH_2), 4.40 (s, 2 H, N–CH_2), 4.47 (q, 1 H, J = 6.8 Hz, methine), 7.0—7.5 (m, 13 H, aromatic), and 7.7—7.9 (m, 2 H, aromatic) (Found: C, 81.0; H, 6.55; N, 3.85. Calc. for $C_{24}H_{23}NO_2$: C, 80.65; H, 6.5; N, 3.9%).

NN-Dibenzyl-2,2-dimethylbenzoylacetamide (1c): m.p. 100—101 °C; i.r. (KBr) $\nu_{max.}$ 1 670 and 1 630 cm^{-1}; n.m.r. ($CDCl_3$) δ 1.65 (s, 6 H, CH_3), 4.15 (s, 2 H, N–CH_2), 4.47 (s, 2 H, N–CH_2), 6.7—7.5 (m, 13 H, aromatic), and 7.8—8.0 (m, 2 H, aromatic) (Found: C, 81.3; H, 6.9; N, 3.65. Calc. for $C_{25}H_{25}NO_2$: C, 80.85; H, 6.8; N, 3.75%).

NN-Dibenzyl-*p*-phenylbenzoylacetamide (1d): m.p. 145—147 °C; i.r. (KBr) $\nu_{max.}$ 1 690, 1 640, and 1 620 cm^{-1}; n.m.r. ($CDCl_3$). The n.m.r. spectrum shows that the amide (1d) contains 40% of an enol form. Keto-form: δ 4.22 (s, 2 H, CH_2), 4.70 (bs, 4 H, N–CH_2), and 7.05—8.0 (m, 19 H, aromatic). Enol form: δ 4.55 (bs, 4 H, N–CH_2), 5.95 (s, 1 H, olefinic), and 7.05—8.0 (m, 19 H, aromatic) (Found: C, 82.2; H, 5.95; N, 3.45. Calc. for $C_{29}H_{25}NO_2$: C, 83.0; H, 6.0; N, 3.35%).*

NN-Dibenzyl-2-naphthoylacetamide (1e): m.p. 101—103 °C; i.r. (KBr) $\nu_{max.}$ 1 675, 1 635, and 1 625 cm^{-1}; n.m.r. ($CDCl_3$). The spectrum shows that the amide (1e) contains 50% of an enol form. Keto-form: δ 4.30 (s, 2 H, CH_2), 4.70 (bs, 4 H, N–CH_2), and 6.8—8.4 (m, 17 H, aromatic). Enol form: δ 4.56 (bs, 4 H, N–CH_2), 6.00 (s, 1 H, olefinic), and 6.8—8.4 (m, 17 H, aromatic) (Found: C, 81.9; H, 5.7; N, 3.7. Calc. for $C_{27}H_{23}NO_2$: C, 82.4; H, 5.9; N, 3.55%).

NN-Dibenzyl-2-(2-naphthoyl)propionamide (1f): m.p. 94—94.5 °C; i.r. (KBr) $\nu_{max.}$ 1 680 and 1 625 cm^{-1}; n.m.r. ($CDCl_3$) δ 1.58 (d, 3 H, J = 7.4 Hz, CH_3), 4.42 (bs, 4 H, N–CH_2), 4.62 (q, 1 H, J = 7.4 Hz, methine), and 7.8—8.3 (m, 17 H, aromatic) (Found: C, 82.25; H, 6.1; N, 3.65. Calc. for $C_{28}H_{25}NO_2$: C, 82.5; H, 6.2; N, 3.45).

* The analyses are poor because these amides are not crystalline but amorphous powder.

N-Benzyl-*N*-methylacetoacetamide (1g): b.p. 110—120 °C/5 mmHg; i.r. (liq. film) $\nu_{max.}$ 1 725 and 1 640 cm^{-1}; n.m.r. ($CDCl_3$) the spectrum shows that the amide (1g) contains 27% of an enol form, and reveals the presence of stereoisomers of a keto-form. Keto-form: δ 1.21 (s, 3 H, CH_3), 2.82 and 2.86 (each s, 3 H, N–CH_3), 3.52 and 3.55 (each s, 2 H, CH_2), 4.50 and 4.54 (each s, 2 H, N–CH_2), and 7.0—7.3 (m, 5 H, aromatic). Enol form: δ 1.90 (s, 3 H, CH_3), 2.87 (s, 3 H, N–CH_3), 4.44 (s, 2 H, N–CH_2), 5.18 (s, 1 H, olefinic), and 7.0—7.3 (m, 5 H, aromatic) (Found: C, 70.05; H, 7.35; N, 7.0. Calc. for $C_{12}H_{15}NO_2$: C, 70.2; H, 7.35; N, 6.8).

N-Benzyl-*N*-methylbenzoylacetamide (1h): b.p. 100—110 °C/10^{-3} mmHg; i.r. (film) $\nu_{max.}$ 1 690 and 1 630 cm^{-1}; n.m.r. ($CDCl_3$) the spectrum reveals the presence of an enol form (40%) and stereoisomers of a keto-form. Keto-form: δ 2.92 and 2.98 (each s, 3 H, CH_3), 4.08 and 4.12 (each s, 2 H, CH_2), 4.59 (s, 2 H, N–CH_2), and 7.2—8.1 (m, 10 H, aromatic). Enol form: δ 2.88 (s, 3 H, CH_3), 4.55 (s, 2 H, N–CH_2), 5.79 (s, 1 H, olefinic), 7.2—8.1 (m, 10 H, aromatic), and 15.8 (bs, 1 H, OH) (Found: C, 76.15; H, 6.3; N, 5.2. Calc. for $C_{17}H_{17}NO_2$: C, 76.4; H, 6.4; N, 5.25%).

N-Benzyl-*N*-methyl-2-naphthoylacetamide (1i): the amide (1i) was not completely purified because it was an amorphous powder; i.r. (KBr) $\nu_{max.}$ 1 680 and 1 630 cm^{-1}; n.m.r. ($CDCl_3$) the spectrum shows the presence of an enol form (40%) and stereoisomers of a keto-form. Keto-form: δ 1.88 and 1.94 (each s, 3 H, CH_3), 4.14 and 4.16 (each s, 2 H, CH_2), 4.55 (bs, 2 H, N–CH_2), and 6.9—8.4 (m, 12 H, aromatic). Enol form: δ 1.84 (s, 3 H, CH_3), 4.50 (s, 2 H, N–CH_2), 5.87 (s, 1 H, olefinic), and 6.9—8.4 (m, 12 H, aromatic).

N-Benzyl-*N*,2-dimethylbenzoylacetamide (1j): b.p. 90—110 °C/10^{-3} mmHg; i.r. (film) $\nu_{max.}$ 1 690 and 1 640 cm^{-1}; n.m.r. ($CDCl_3$) δ 1.52 (d, 3 H, J = 7.0 Hz, CH_3), 2.90 (s, 3 H, N–CH_3), 4.37 (q, 1 H, J = 7.0 Hz, methine), 4.39 (s, 2 H, N–CH_2), 7.0—7.6 (m, 8 H, aromatic), and 7.6—8.0 (m, 2 H, aromatic) (Found: C, 76.75; H, 6.7; N, 5.1. Calc. for $C_{18}H_{19}NO_2$: C, 76.85; H, 6.8; N, 4.95%).

Irradiation of N,N-*Dibenzyl*-p-*phenylbenzoylacetamide* (1d)—A solution of (1d) (200 mg) in benzene (70 cm^3) was irradiated for 205 h. The solvent was removed under reduced pressure and the resulting residue was chromatographed on silica gel Elution with 20% ethyl acetate–benzene afforded 49 mg (25%) of white solid which was recrystallized from benzene–n-hexane and identified as 1-benzyl-4-biphenyl-4-hydroxy-5-phenylpyrrolidin-2-one (2d): m.p. 172—173 °C; i.r. (KBr) $\nu_{max.}$ 3 400 and 1 680 cm^{-1}; n.m.r. ($CDCl_3$) δ 2.0 (bs, 1 H, OH), 3.05 (s, 2 H, 3-CH_2), 3.60 (d, 1 H, J = 14.0 Hz, N–CH_2Ph), 4.72 (s, 1 H, 5-H), 5.30 (d, 1 H, J = 14.0 Hz, N–CH_2Ph), and 7.0—7.6 (m, 19 H, aromatic) (Found: C, 83.15; H, 6.05; N, 3.2. Calc. for $C_{29}H_{25}NO_2$: C, 83.05; H, 6.0; N, 3.35%).

Irradiation of NN-*Dibenzyl*-2-*naphthoylacetamide* (1e).—A solution of (1e) (100 mg) in benzene (70 cm^3) was irradiated for 50 h. The reaction mixture was concentrated under reduced pressure and chromatographed on silica gel. Elution with 20% ethyl acetate–benzene afforded 50 mg (50%) of white solid which was recrystallized from benzene–n-hexane and identified as 1-benzyl-4-hydroxy-4-(2-naphthyl)-5-phenylpyrrolidin-2-one (2e): m.p. 169—170 °C; i.r. (KBr) 3 350 and 1 675 cm^{-1}; n.m.r. ($CDCl_3$) δ 2.50 (s, 1 H, OH, D_2O-exchangeable), 3.03 (s, 2 H, 3-CH_2), 3.59 (d, 1 H, J = 14.0 Hz, N–CH_2Ph), 4.70 (s, 1 H, 5-H), 5.27 (d, 1 H, J = 14.0 Hz, N–CH_2Ph), and 6.8—7.8 (m, 17 H, aromatic)

(Found: C, 82.35; H, 5.95; N, 3.45. Calc. for $C_{27}H_{23}NO_2$: C, 82.4; H, 5.9; N, 3.55%).

Irradiation of N,N-*Dibenzyl*-2-(2-*naphthoyl*)*propionamide* (1f).—A solution of (1f) (200 mg) in benzene (70 cm³) was irradiated for 148 h. The reaction mixture was concentrated under reduced pressure and subject to silica-gel column chromatography with 20% ethyl acetate–benzene elution. In this way 45 mg of starting material was recovered and 77 mg (50% based on unrecovered starting material) of white solid was obtained. The n.m.r. spectrum of the solid showed the presence of isomers like in the case of (1c).[6b] Separation of the isomers by column chromatography and fractional recrystallization was attempted, but they could not be isolated. The i.r. spectrum of the isomer mixture showed the characteristic hydroxy (3 375 cm^{-1}) and five-membered lactam carbonyl absorption (1 665 cm^{-1}). The n.m.r. spectrum of the mixture exhibited two doublets at δ 1.20 and 1.23 which can be assigned to the C-3 methyl in the two isomers *trans* to the C-4 naphthyl group. The signals, which can be attributable to the C-5 methine hydrogens in the isomers, were observed at δ 4.75 and 4.52, which can be assigned to the hydrogen *cis* and *trans* to the C-4 naphthyl group respectively. The isomers, accordingly, were identified as 1-benzyl-4-hydroxy-*r*,3-methyl-*t*,4-naphthyl-*c*,5-phenylpyrrolidin-2-one (2f) (30%) and 1-benzyl-4-hydroxy-*r*,3-methyl-*t*,4-naphthyl-*t*,5-phenylpyrrolidin-2-one (2f') (20%). The yields were determined on the basis of the n.m.r. spectrum of the isomer mixture. The 3 : 2 mixture had m.p. 195—208 °C, n.m.r. ($CDCl_3$) (2f): δ 1.20 (d, 3 H, J = 7.0 Hz, C-3H_3), 2.0br (s, 1 H, OH), 2.99 (q, 1 H, J = 7.0 Hz, 3-H), 3.65 (d, 1 H, J = 14.5 Hz, N-CH_2Ph), 4.75 (s, 1 H, 5-H), 5.28 (d, 1 H, J = 14.5 Hz, N-CH_2Ph), and 6.5—7.8 (m, 17 H, aromatic); (2f'): δ 1.23 (d, 3 H, J = 7.0 Hz, 3-CH_3), 2.0br (s, 1 H, OH), 2.99 (q, 1 H, J = 7.0 Hz, 3-H), 3.62 (d, 1 H, J = 14.5 Hz, N-CH_2Ph), 4.75 (s, 1 H, 5-H), 5.28 (d, 1 H, J = 14.5 Hz, N-CH_2Ph), and 6.5—7.8 (m, 17 H, aromatic) {Found [for a mixture of (2f) and (2f')]: C, 82.45; H, 6.15; N, 3.25. Calc. for $C_{28}H_{25}NO_2$: C, 82.5; H, 6.2; N, 3.45%}.

Irradiation of N-*Benzyl*-N-*methylacetoacetamide* (1g).—A solution of (1g) (400 mg) in methanol (80 cm³) was irradiated for 133 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Starting amide (140 mg) was recovered and elution with 50% ethyl acetate–benzene afforded 204 mg (78% based on unrecovered starting material) of white solid which was recrystallized from benzene and identified as 1-benzyl-4-hydroxy-4-methylpyrrolidin-2-one (2g), m.p. 134—134.5 °C; i.r. (KBr) $\nu_{max.}$ 3 350 and 1 670 cm^{-1}; n.m.r. ($CDCl_3$) δ 1.36 (s, 3 H, 4-CH_3), 2.53 (s, 2 H, 3-CH_2), 2.85br (s, 1 H, OH), 3.22 (s, 2 H, 5-H), 4.46 (s, 2 H, N-CH_2Ph), and 6.29 (s, 5 H, aromatic) (Found: C, 70.45; H, 7.4; N, 6.7. Calc. for $C_{12}H_{15}NO_2$: C, 70.2; H, 7.35; N, 6.8%).

In this case the isomeric pyrrolidinone, 4-hydroxy-1,4-dimethyl-5-phenylpyrrolidin-2-one, could not be detected.

Irradiation of N-*Benzyl*-N-*methylbenzoylacetamide* (1h).—A solution of (1h) (300 mg) in methanol (70 cm³) was irradiated for 16 h. The reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel with 33% ethyl acetate–benzene. A white solid, 200 mg (67%), was recrystallized from benzene–n-hexane and identified as 1-benzyl-4-hydroxy-4-phenylpyrrolidin-2-one (2h), m.p. 118—119 °C, i.r. (KBr) $\nu_{max.}$ 3 300 and 1 665 cm^{-1}; n.m.r. ($CDCl_3$) δ 2.85 (ABq, 2 H, J = 16.2 Hz, 3-CH_2), 3.50 (s, 2 H, 5-CH_2), 3.7br (s, 1 H, OH, D_2O-exchangeable), 4.47 (s, 2 H, N-CH_2Ph), and 7.1—7.4 (m, 10 H, aromatic) (Found: C, 76.2; H, 6.4; N, 5.1. Calc. for $C_{17}H_{17}NO_2$: C, 76.4; H, 6.4; N, 5.25%).

Also isolated was 67 mg (22%) of white solid which was recrystallized from benzene–n-hexane and identified as 4-hydroxy-1-methyl-4,5-diphenylpyrrolidin-2-one (2h'), m.p. 213.5—214 °C; i.r. (KBr) $\nu_{max.}$ 3 325 and 1 665 cm^{-1}; n.m.r. ($CDCl_3$) δ 2.84 (s, 3 H, N-CH_3), 2.95 (ABq, 2 H, J = 16.0 Hz, 3-CH_3), 3.5br (s, 1 H, OH, D_2O-exchangeable), 4.64 (s, 1 H, 5-H), and 6.4—7.35 (m, 10 H, aromatic) (Found: C, 76.5; H, 6.3; N, 5.05. Calc. for $C_{17}H_{17}NO_2$: C, 76.4; H, 6.4; N, 5.25%).

Irradiation of N-*Benzyl*-N-*methyl*-2-*naphthoylacetamide* (1i).—A solution of 100 mg of (1i) in methanol (60 cm³) was irradiated for 146 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with 20% ethyl acetate–benzene afforded a white solid. The n.m.r. spectrum of the solid showed the presence of isomers, the isolation of which by column chromatography fractional recrystallization was unsuccessful. The i.r. spectrum of the isomers mixture showed the characteristic hydroxy (3 350 cm^{-1}) and five-membered lactam carbonyl absorption (1 685 cm^{-1}). The n.m.r. spectrum of the mixture showed the peaks at δ 4.48 and 2.75, which are attributable to benzylic and methyl hydrogen respectively. The isomers were identified as 1-benzyl-4-hydroxy-4-(2-naphthyl)pyrrolidin-2-one (2i) (31%) and 4-hydroxy-1-methyl-4-(2-naphthyl)pyrrolidin-2-one (2i') (13%). The yields were determined on the basis of the n.m.r. spectrum of the mixture. The mixture had m.p. 150—160 °C; n.m.r. ($CDCl_3$) (2i): δ 2.8—3.1 (m, 3 H, 3-CH_2 and OH), 3.57 (s, 2 H, 5-CH_2), 4.48 (s, 2 H, N-CH_2Ph), and 6.7—7.9 (m, 12 H, aromatic); (2i'): δ 2.75 (s, 3 H, N-CH_3), 2.8—3.1 (m, 3 H, 3-CH_2 and OH), 4.98 (s, 1 H, 5-H), and 6.7—7.9 (m, 12 H, aromatic) {Found [for a mixture of (2i) and (2i')]: C, 79.85; H, 6.05; N, 4.5. Calc. for $C_{21}H_{19}NO_2$: C, 79.45; H, 6.05; N, 4.4%}.

Irradiation of N-*Benzyl*-N,2-*dimethylbenzoylacetamide* (1j).—A solution of (1j) (700 mg) in methanol (400 cm³) was irradiated for 7 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel with 33% ethyl acetate–benzene. In this way 60 mg of starting material was recovered and two solid products were obtained. The n.m.r. spectrum of one product showed the characteristic *N*-methyl peak at δ 2.81 and that of the other at δ 2.92. The products, therefore, are formed involving benzylic hydrogen abstraction by ketone carbonyl. No 1-benzylpyrrolidinones were obtained. The structure of one product is assigned to 4-hydroxy-1,*r*,3-dimethyl-*t*,4,*t*,5-diphenylpyrrolidin-2-one (2j'-a): yield 157 mg (25%, based on unrecovered starting material); m.p. 187—188 °C (recrystallized from benzene); i.r. (KBr) $\nu_{max.}$ 3 400 and 1 690 cm^{-1}; n.m.r. ($CDCl_3$) δ 1.18 (d, 3 H, J = 7.0 Hz, 3-CH_3), 1.72 (s, 1 H, OH, D_2O-exchangeable), 2.81 (s, 3 H, N-CH_3), 3.00 (q, 1 H, J = 7.0 Hz, 3-H), 4.95 (s, 1 H, 5-H), and 6.9—7.4 (m, 10 H, aromatic) (Found: C, 76.7; H, 6.6; N, 4.75. Calc. for $C_{18}H_{19}NO_2$: C, 76.85; H, 6.8; N, 5.0%).

The structure of the other product is identified as 4-hydroxy-1,*r*,3-dimethyl-*t*,4,*c*,5-diphenylpyrrolidin-2-one (2j'-b): yield 315 mg (49% based on unrecovered starting material); m.p. 202—203 °C (from benzene–n-hexane); i.r. (KBr) $\nu_{max.}$ 3 350 and 1 690 cm^{-1}; n.m.r. (*$CDCl_3$*) δ 1.20 (d, 3 H, J = 6.8 Hz, 3-CH_3), 2.49 (s, 1 H, OH, D_2O-exchangeable), 2.92 (s, 3 H, N-CH_3), 3.32 (q, 1 H, J = 6.8 Hz, 3-H), 4.52 (s, 1 H, 5-H), and 6.7—7.4 (m, 10 H, aromatic) (Found:

C, 76.95; H, 6.85; N, 4.85. Calc. for $C_{18}H_{19}NO_2$: C, 76.85; H, 6.8; N, 5.0%).

Stern Volmer Plot of (1b).—Irradiations were performed in a merry-go-round apparatus (Rayonet Photochemical Reactor—RPR 3000 A). The samples in Pyrex tubes were degassed to *ca.* 10^{-3} mmHg in three freeze–thaw cycles. After the irradiation the degree of reaction was determined by n.m.r. spectroscopy.

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