Photocyclization of *NN*-Dialkyl β,γ-Unsaturated Amides. 1,6-Hydrogen Transfer *via* Charge-transfer States

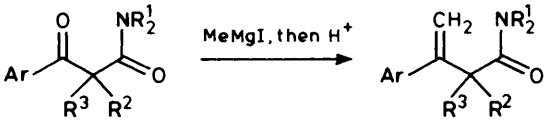
Hiromu Aoyama,* Yoshiaki Arata, and Yoshimori Omote
Department of Chemistry, The University of Tsukuba, Sakura-mura Ibaraki, 305 Japan

NN-Dibenzyl and *NN*-diallyl β,γ-unsaturated amides undergo cyclization on irradiation to give the corresponding pyrrolidin-2-ones *via* 1,6-hydrogen transfer from the singlet states. The reaction is presumed to involve charge transfer from the amide group to the excited styrene moiety.

Photochemical hydrogen abstraction of carbonyl compounds (*e.g.* Norrish type-II reaction) has been one of the most intensively investigated photoreactions.[1] Although examples of hydrogen abstraction in the photolysis of olefins are less common, there are now a number of reports in the literature which show that some cyclic olefins can undergo such reactions from the π,π* triplet states.[2] In the case of acyclic olefins, these reactions are usually quite inefficient because of the presence of competitive processes such as *cis–trans* isomerization.[3] It is well known that intramolecular hydrogen abstraction through seven-membered cyclic transition states (1,6-hydrogen transfer) is less favourable than that through six-membered ones (1,5-hydrogen transfer) in acyclic systems.[4] We report here the full details of our study on the photochemical reaction of *NN*-dialkyl β,γ-unsaturated amides.[5] These compounds undergo quite rare intramolecular hydrogen abstraction by the olefinic carbon atom through seven-membered cyclic transition states.

Results and Discussion

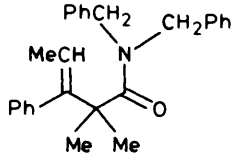
Synthesis of NN-*Dialkyl* β,γ-*Unsaturated Amides.*—The β,γ-unsaturated amides (**11**)—(**18**) having two methyl groups at the α position were synthesized by reaction of the corresponding β-oxo amides with methyl- (or ethyl-) magnesium iodide followed by dehydration [equation (1)]. α-Monoalkyl amides (**19**) and (**20**) were also prepared in a similar way.



(1)

(1)	Ar = Ph, R^1 = Et, R^2 = R^3 = Me	(11)
(2)	Ar = Ph, R^1 = Pr^i, R^2 = R^3 = Me	(12)
(3)	Ar = Ph, R^1 = CH_2=$CHCH_2$, R^2 = R^3 = Me	(13)
(4)	Ar = Ph, R^1 = $PhCH_2$, R^2 = R^3 = Me	(14)
(5)	Ar = 4-ClC_6H_4, R^1 = $PhCH_2$, R^2 = R^3 = Me	(15)
(6)	Ar = biphenyl-4-yl, R^1 = $PhCH_2$, R^2 = R^3 = Me	(16)
(7)	Ar = 4-$MeOC_6H_4$, R^1 = $PhCH_2$, R^2 = R^3 = Me	(17)
(8)	Ar = 3,4,5-$(MeO)_3C_6H_2$, R^1 = $PhCH_2$, R^2 = R^3 = Me	(18)
(9)	Ar = Ph, R^1 = $PhCH_2$, R^2 = H, R^3 = Me	(19)
(10)	Ar = Ph, R^1 = $PhCH_2$, R^2 = H, R^3 = $PhCH_2CH_2$	(20)

Photolysis, and Identification of Photoproducts.—*NN*-Diethyl and *NN*-di-isopropyl-2,2-dimethyl-3-phenylbut-3-enamides (**11**) and (**12**) were inert toward photolysis. However, when the *NN*-dibenzyl amide (**14**) in methanol was irradiated with a low-pressure mercury lamp, pyrrolidin-2-ones (**22**) and (**23**) were obtained. Photoreaction of other *NN*-dibenzyl amides (**15**)—(**17**), (**19**), and (**20**) gave similar results [equation (2)], though complete purification of the minor products (**25**), (**27**), and



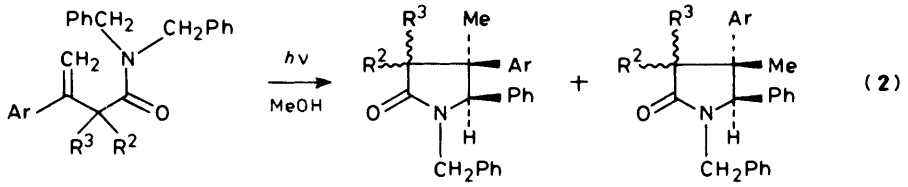
(**21**)

(**29**) was not achieved. Their structures were assigned by comparison of their n.m.r. and i.r. spectra with those of compound (**23**). The stereochemistry of the products from anides (**19**) and (**20**) was not determined. A product from an *NN*-diallyl amide (**13**) was presumed to be a cyclization product from the spectral data, but it was not completely purified. A trimethoxyphenyl derivative (**18**) was unreactive and was recovered unchanged even after prolonged irradiation. The photoreaction of *NN*-dibenzyl-2,2-dimethyl-3-phenylpent-3-enamide (**21**) having a trisubstituted carbon–carbon double bond was sluggish, and prolonged irradiation resulted in the formation of an intractable mixture.

The structures of the photoproducts were determined on the basis of elemental analyses and spectral data. The i.r. spectrum of compound (**22**) showed a carbonyl absorption at 1 670 cm^{-1} characteristic of five-membered lactams.[6] The ^1H and ^{13}C n.m.r. spectra of compound (**22**) clearly showed the presence of three methyl groups and the absence of a terminal methylene group. Stereochemistry of the major product and the minor product was assigned as shown in equation (2) on the basis of the n.m.r. spectra. The spectrum of compound (**22**) showed a signal for aromatic protons at an unusually high field (δ_H 6.5—6.65, 2 H). This indicates that the phenyl groups at C-4 and C-5 are *cis*. The signal of the C-5 methine proton of compound (**23**) (δ_H 5.01) appeared at a field considerably lower than that for its isomer (**22**) (δ_H 4.21). This fact is reasonably explained in terms of the anisotropic effects of the C-4 phenyl group which is *cis* to the methine hydrogen in compound (**23**). This assignment was further supported by the similarity of the n.m.r. spectra of the two products (**22**) and (**23**) to those of closely related pyrrolidin-2-ones.[7]

Mechanisms.—The formation of the photoproducts is quite reasonably explained in terms of 1,6-hydrogen transfer followed by cyclization of the resulting 1,5-diradical (**31**) (Scheme 1, path a). The possibility that some radicals formed during irradiation initiate the cyclization (path b) was excluded because (i) addition of ethanethiol (a radical scavenger)[8] did not change the efficiency of the reaction of compound (**14**) and (ii) isomerization of the radicals (**32**) ⟶ (**33**) is energetically unfavourable and should be quite inefficient.

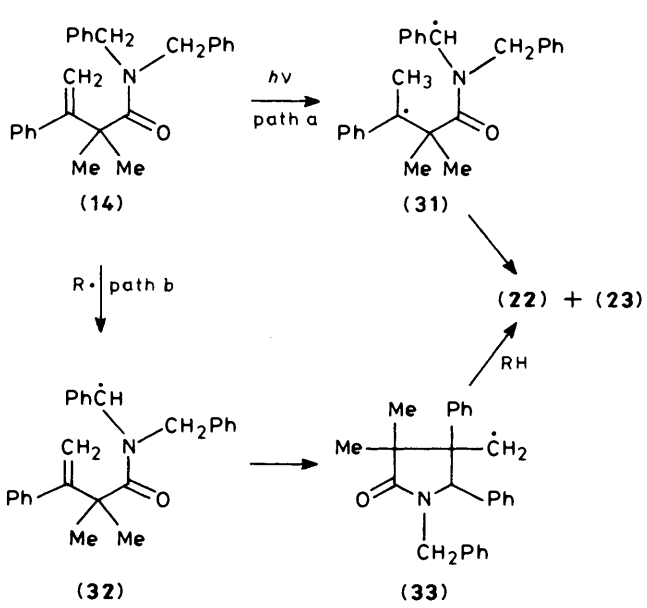
Path a was further supported by the experiment using a deuterium-labelled amide [$^2H_4$](**14**). Irradiation of [$^2H_4$](**14**)



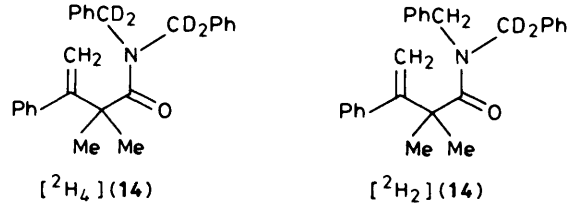
(2)

(14)	(Φ = 0.049)	(22) 51%	(23) 7%
(15)		(24) 66%	(25) 12%[a]
(16)	(Φ = 0.017)	(26) 60%	(27) 13%[a]
(17)	(Φ = 0.006)	(28) 41%	(29) 7%[a]
(19)		(30) 66%	

[a] Estimated by n.m.r. spectroscopy.

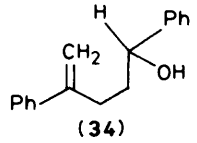


Scheme 1.



gave cyclization products, [$^2H_4$](22) and [$^2H_4$](23), in which one of the benzylic deuterium atoms was completely incorporated into the C-4 methyl group. On the basis of these results, we can conclude that the cyclization proceeds *via* the 1,5-diradical (31) formed by 1,6-hydrogen shift.

Photoreaction of the unsaturated amides took place by direct irradiation as described above, and was not sensitized by 4-methoxyacetophenone (E_T 72 kcal mol^{-1}),* xanthone (74 kcal mol^{-1}), or acetone (79—82 kcal mol^{-1}).[9]†* Furthermore, the reaction was not quenched by penta-1,3-diene (0.1M) (59 kcal mol^{-1}). These facts clearly show that the photoreaction proceeds from the singlet state. The quantum yield of reaction of compound (14) was 0.049 [based on consumption of (14)]. The deuterium isotope effect obtained from the experiments using [$^2H_2$](14) was relatively small (Φ_H/Φ_D 2.0).



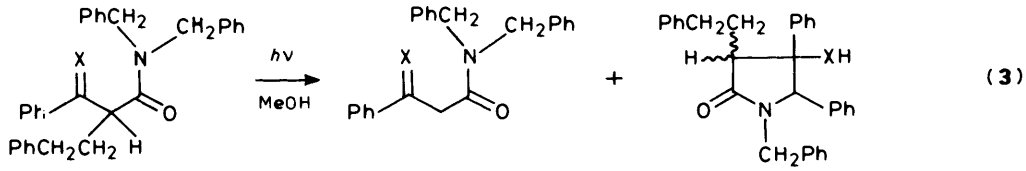
(34)

Hornback and Proehl recently reported intramolecular hydrogen abstraction (1,5-hydrogen shift) of a styrene (34).[3] The photoreaction of compound (34) is quite different from that of (14) in spite of the fact that the both compounds possess almost the same chromophore. The reaction of compound (34) takes place only from the triplet state and the efficiency is quite low (Φ 0.0005). The isotope effect of this reaction is much larger (Φ_H/Φ_D5) than that in the reaction of [$^2H_2$](14). These differences cannot be explained by the strength of the C–H bonds to be broken as detailed below. The methine hydrogen of the styrene (34) which is abstracted by the olefinic carbon is activated by both a phenyl group and an oxygen atom, whereas the methylene hydrogens of compound (14) are activated by both a phenyl group and an amide nitrogen. Padwa and Chou reported photochemical intramolecular hydrogen abstraction of olefins bearing heteroatoms,[10] in which the reactivity of benzylic hydrogens activated by an adjacent oxygen atom is higher than that of benzylic hydrogens activated by an amide nitrogen. It is also known that tertiary hydrogens (methines) are more reactive than secondary hydrogens (methylenes) toward abstraction. Furthermore, 1,5-hydrogen shift [as with the styrene (34)] is sterically much more favourable than 1,6-hydrogen shift [as with compound (14)] as described above. Therefore, it is difficult to explain the efficient 1,6-hydrogen shift of the unsaturated amides in terms of direct hydrogen abstraction from the singlet states. It is also known that the primary reactions of the S_1 state of olefins are not diradicaloid but zwitterionic or polar in nature,[11] and direct hydrogen abstraction of olefins from the singlet states has not been reported to our knowledge. These facts suggest that the photoreaction of the amides involves charge (or electron) transfer followed by proton transfer rather than one-step hydrogen transfer. The relatively small isotope effect in the reaction of [$^2H_2$](14) is consistent with the charge-transfer mechanism since isotope effects in hydrogen shift *via* charge (or electron) transfer are usually small.[12] The effects of substituents on the phenyl group also support this mechanism. Introduction of electron-donating methoxy groups to a styrene should raise the energy of its highest occupied orbital and lower its electron affinity in the excited states.[13] Therefore, the low reactivity of compound (17) and the non-reactivity of compound (18) are compatible with the mechanism *via* charge transfer.

Further evidence in support of the charge-transfer mechanism was obtained by the following experiments. Recently, Hasegawa *et al.* reported the competitive 1,5- and 1,6-hydrogen transfer of *NN*-dialkyl β-oxo amides having an alkyl substituent at the α position.[14] This reaction involves direct hydrogen abstraction from the n,π^* triplet states. We examined the photoreaction of a

* 1 kcal = 4.185 kJ.

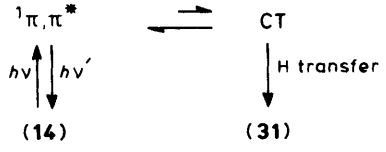
† Concentrations of the sensitizers were adjusted so that 95% or more of the incident light was absorbed by the sensitizers.



(10) X = O (35) 71% (36) < 11%
(20) X = CH_2 0% (37) 57%

(3)

β-oxo amide (**10**) and that of a β,γ-unsaturated amide (**20**) whose structure is closely related to that of compound (**10**). Photolysis of (**10**) in methanol gave a dealkylation product [(**35**), 71%] formed *via* 1,5-hydrogen transfer (type-II cleavage) as the main product, accompanied by a small amount of a 1,6-hydrogen-transfer product [(**36**), <11%] which could not be purified. This finding indicates that the 1,5-hydrogen transfer is much more favourable than the 1,6-hydrogen transfer. In contrast, irradiation of compound (**20**) afforded only a 1,6-hydrogen-transfer product [(**37**), 57%] [equation (3)]. The remarkably enhanced 1,6-hydrogen transfer of compound (**20**) strongly indicates the presence of the interaction between the amide group and the excited styrene moiety.



Scheme 2.

In spite of the results described above, the fluorescence of α-methylstyrene was *not* quenched by *NN*-disubstituted primary *amides* such as *NN*-dimethylacetamide, in contrast to the fact that the fluorescence *is* effectively quenched by tertiary *amines*.[13] This finding indicates that the interaction between an amide group and an excited styrene group is important only when the two groups are involved in the same molecule (proximity effects). The formation of the intramolecular exciplex from the S_1 state of compound (**14**) may be slightly endothermic. In view of the fact that the unsaturated amide (**14**) shows fluorescence similar to that of α-methylstyrene, the S_1 state of (**14**) is presumed to be in equilibrium with the intramolecular exciplex (Scheme 2), though it is also conceivable that the exciplex formation and the emission take place competitively.

Experimental

M.ps were measured on a Yanagimoto Micro Melting Point apparatus and are uncorrected. Yields are isolated yields unless otherwise indicated. I.r. spectra were recorded for $CHCl_3$ solutions on a JASCO IRA-1 infrared spectrophotometer, and ^1H and ^{13}C n.m.r. spectra were measured for $CDCl_3$ solutions on a JEOL-100 spectrometer (100 MHz) with internal $SiMe_4$ as standard.

General Procedure for Preparation of β-*Oxo Amides* (**1**)—(**10**).—An *NN*-dialkyl aroylacetamide (5 g)[7] solution in chloroform (30 ml) was placed in a thick glass tube with a stopper at the top, and cooled to −10 °C. An excess of methyl bromide (*ca.* 5 g) which had been cooled to −10 °C was then added. After addition of cold aqueous sodium hydroxide (10%; 30 ml) and tetrabutylammonium chloride (1 g; a phase-transfer catalyst), the tube was stoppered and the two-phase solution was stirred overnight at room temperature. After separation of the organic layer, the aqueous layer was extracted with chloroform and the combined organic layers were dried ($MgSO_4$) and evaporated at a reduced pressure. The α-monomethyl derivative thus obtained was almost pure in most cases, and was used for further methylation without purification.

The crude monomethyl derivative (2 g) was dissolved in dry dimethylformamide (DMF) (30 ml) and sodium hydride (0.5 g) was added. The mixture was kept for 1 h and an excess of methyl iodide (1 g) was then added. The resulting mixture was set aside for 2 h at room temperature. After the solution had been diluted with benzene (150 ml), ice–water (50 ml) was added with cooling. The organic layer was washed with water ten times in order to remove the DMF. The resulting solution was worked up as usual and the product was isolated by chromatography on silica gel. The following β-keto amides were prepared.

2-*Benzoyl*-NN-*diethyl*-2-*methylpropanamide* (**1**): 29%; m.p. 54—56 °C; $\nu_{max.}$ 1 665 and 1 615 cm^{-1}; δ_H 0.75 (3 H, t, *J* 7 Hz, CH_2Me), 1.01 (3 H, t, *J* 7 Hz, CH_2Me), 1.51 (6 H, s, CMe_2), 2.98 (2 H, q, *J* 7 Hz, NCH_2), 3.34 (2 H, q, *J* 7 Hz, NCH_2), 7.1—7.7 (3 H, m, ArH), and 7.9—8.2 (2 H, m, ArH) (Found: C, 72.65; H, 8.55; N, 5.55. $C_{15}H_{21}NO_2$ requires C, 72.85; H, 8.55; N, 5.65%).

2-*Benzoyl*-NN-*di-isopropyl*-2-*methylpropanamide* (**2**): 48%; m.p. 78—79 °C; $\nu_{max.}$ 1 670 and 1 620 cm^{-1}; δ_H 0.73 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.41 (6 H, d, *J* 7 Hz, $CHMe_2$), 1.51 (6 H, s, CMe_2), 3.0—3.9 (2 H, m, $CHMe_2$), 7.2—7.7 (3 H, m, ArH), and 7.9—8.3 (2 H, m, ArH) (Found: C, 74.3; H, 9.1; N, 5.1. $C_{17}H_{25}NO_2$ requires C, 74.15; H, 9.15; N, 5.1%).

NN-*Diallyl*-2-*benzoyl*-2-*methylpropanamide* (**3**): 22%; b.p. 160—170 °C/0.1 Torr (bath temp.); $\nu_{max.}$ 1 665 and 1 620 cm^{-1}; δ_H 1.54 (6 H, s, CMe_2), 3.56 and 3.92 (each 2 H, each m, 2 × NCH_2), 4.9—5.1 (6 H, m, olefinic), 7.2—7.6 (3 H, m, ArH), and 7.8—8.1 (2 H, m, ArH) (Found: C, 75.05; H, 7.8; N, 5.1. $C_{17}H_{21}NO_2$ requires C, 75.25; H, 7.8; N, 5.15%).

2-*Benzoyl*-NN-*dibenzyl*-2-*methylpropanamide* (**4**): 22%; the spectral data of this compound have been reported.[15]

NN-*Dibenzyl*-2-(4-*chlorobenzoyl*)-2-*methylpropanamide* (**5**): 23%; m.p. 123—124 °C; $\nu_{max.}$ 1 670 and 1 630 cm^{-1}; δ_H 1.63 (6 H, s, CMe_2), 4.14 and 4.45 (each 2 H, each s, 2 × NCH_2), 6.7—7.4 (12 H, m, ArH), and 7.8 (2 H, s, ArH) (Found: C, 74.15; H, 5.95; N, 3.4. $C_{25}H_{24}ClNO_2$ requires C, 73.95; H, 5.95; N, 3.45%).

NN-*Dibenzyl*-2-(4-*phenylbenzoyl*)-2-*methylpropanamide* (**6**): 33%; m.p. 142—143 °C; $\nu_{max.}$ 1 665 and 1 625 cm^{-1}; δ_H 1.68 (6 H, s, CMe_2), 4.21 and 4.50 (each 2 H, each s, 2 × NCH_2), 6.7—7.7 (17 H, m, ArH), and 8.03 (2 H, d, ArH) (Found: C, 83.25; H, 6.55; N, 3.1. $C_{31}H_{29}NO_2$ requires C, 83.2; H, 6.55; N, 3.1%).

NN-*Dibenzyl*-2-(4-*methoxybenzoyl*)-2-*methylpropanamide* (**7**): 68%; m.p. 136—137 °C; $\nu_{max.}$($CHCl_3$) 1 665, 1 620, and 1 595 cm^{-1}; δ_H 1.62 (6 H, s, CMe_2), 3.84 (3 H, s, OMe), 4.15 and 4.50 (each 2 H, each s, 2 × NCH_2), 6.7—7.35 (12 H, m, ArH), and 7.9 (2 H, d, ArH) (Found: C, 77.7; H, 6.75; N, 3.45. $C_{26}H_{27}NO_3$ requires C, 77.75; H, 6.75; N, 3.5%).

NN-Dibenzyl-2-(3,4,5-trimethoxybenzoyl)-2-methylpropanamide (**8**) was not completely purified, and the crude product was used for the synthesis of compound (**18**).

* Triplet energies of styrenes are 60—66 kcal mol^{-1}: P. M. Crosby, J. M. Dyke, J. Metcalfe, A. J. Rest, K. Salisbury, and J. R. Sodeau, *J. Chem. Soc., Perkin Trans. 2*, 1977, 182.

2-*Benzoyl*-NN-*dibenzyl*-4-*phenylbutanamide* (**10**) was prepared as in the case of the α-monomethyl derivatives (*vide supra*) with 2-phenylethyl bromide in place of methyl bromide: b.p. 150—170 °C/10^{-3} Torr (bath temp.); $\nu_{max.}$ 1 680 and 1 640 cm^{-1}; δ_H 2.2—2.9 (4 H, m, CH_2CH_2), 4.08 and 4.32 (2 H, ABq, *J* 17 Hz, NCH_2), 4.20 and 4.96 (2 H, ABq, *J* 15 Hz, NCH_2), 4.39 (1 H, t, *J* 6 Hz, 2-H), and 6.8—7.7 (20 H, m, 4 × Ph) (Found: C, 83.1; H, 6.5; N 3.15. $C_{31}H_{29}N_2$ requires C, 83.2; H, 6.55; N, 3.1%).

General Procedure for the Synthesis of β,γ-*Unsaturated Amides* (**11**)—(**20**).—To an ether solution (50 ml) of methylmagnesium iodide, prepared from methyl iodide (1 g) and magnesium (250 mg), was added a solution of the appropriate β-oxo amide (300 mg) in dry ether (20 ml) dropwise at 0 °C. After being stirred for 2 h at room temperature, the solution was treated as usual. The resulting crude alcohol was dissolved in dry benzene (30 ml) and toluene-*p*-sulphonic acid (300 mg) was added. The solution was refluxed for 3—12 h using a Dean–Stark trap, and worked up as usual. The β,γ-unsaturated amide was isolated by chromatography on silica gel, eluant benzene–ethyl acetate. The yields described below are those from the corresponding β-oxo amide.

NN-*Diethyl*-2,2-*dimethyl*-3-*phenylbut*-3-*enamide* (**11**): 18%; b.p. 100—110 °C/10^{-3} Torr (bath temp.); $\nu_{max.}$ 1 610 cm^{-1}; δ_H 0.85 (3 H, br t, CH_2Me), 0.95 (3 H, br t, CH_2Me), 1.47 (6 H, s, 2-Me_2), 3.25 (4 H, br q, 2 × NCH_2), 5.24 (2 H, s, $=CH_2$), and 7.25 (5 H, br s, Ph) (Found: C, 78.3; H, 9.55; N, 5.8. $C_{16}H_{23}NO$ requires C, 78.3; H, 9.45; N, 5.7%).

NN-*Di-isopropyl*-2,2-*dimethyl*-3-*phenylbut*-3-*enamide* (**12**): 72%; b.p. 110—120 °C/10^{-3} Torr (bath temp.); $\nu_{max.}$ 1 620 cm^{-1}; δ_H 0.92 (6 H, d, *J* 6 Hz, $CHMe_2$), 1.36 (6 H, d, *J* 6 Hz, $CHMe_2$), 1.42 (6 H, s, 2-Me_2), 3.20 (1 H, sep, *J* 6 Hz, NCH), 4.16 (1 H, sep, *J* 6 Hz, NCH), 5.19 and 5.33 (each 1 H, each s, $=CH_2$), and 7.0—7.6 (5 H, m, Ph) (Found: C, 79.0; H, 10.0; N, 5.15. $C_{18}H_{27}NO$ requires C, 79.1; H, 9.95; N, 5.1%).

NN-*Diallyl*-2,2-*dimethyl*-3-*phenylbut*-3-*enamide* (**13**): 15%; b.p. 150—160 °C/0.1 Torr (bath temp.); $\nu_{max.}$ 1 610 cm^{-1}; δ_H 1.49 (6 H, s, 2-Me_2), 3.81 and 3.99 (4 H, each br s, 2 × NCH_2), 4.7—5.7 (6 H, m, olefinic), 5.2 (2 H, s, olefinic), and 7.24 (5 H, s, Ph) (Found: 79.75; H, 8.5; N, 5.15. $C_{18}H_{23}NO$ requires C, 80.25; H, 8.6; N, 5.2%).

NN-*Dibenzyl*-2,2-*dimethyl*-3-*phenylbut*-3-*enamide* (**14**): 34%; m.p. 147.5—148.5 °C; $\nu_{max.}$ 1 610 cm^{-1}; δ_H 1.56 (6 H, s, 2-Me_2), 4.5 (4 H, br s, 2 × NCH_2), 5.19 and 5.21 (2 H, each s, $=CH_2$), and 6.6—7.4 (15 H, m, 3 × Ph) (Found: C, 84.4; H, 7.35; N, 3.85. $C_{26}H_{27}NO$ requires C, 84.5; H, 7.35; N, 3.8%).

NN-*Dibenzyl*-3-(4-*chlorophenyl*)-2,2-*dimethylbut*-3-*enamide* (**15**): 46%; m.p. 84—86 °C; $\nu_{max.}$ 1 625 cm^{-1}; δ_H 1.56 (6 H, s, 2-Me_2), 4.48 (4 H, br s, 2 × NCH_2), 5.23 and 5.29 (each 1 H, each s, $=CH_2$), and 6.7—7.7 (14 H, m, ArH) (Found: C, 74.15; H, 5.95; N, 3.4. $C_{26}H_{26}ClNO$ requires C, 74.0; H, 5.95; N, 3.45%).

NN-*Dibenzyl*-3-(4-*biphenylyl*)-2,2-*dimethylbut*-3-*enamide* (**16**): 65%; m.p. 101—103 °C; $\nu_{max.}$ 1 620 cm^{-1}; δ_H 1.62 (6 H, s, 2-Me_2), 4.49 and 4.50 (4 H, each br s, 2 × NCH_2), 5.29 (2 H, s, $=CH_2$), and 6.7—7.8 (19 H, m, ArH) (Found: C, 86.15; H, 7.05; N, 3.0. $C_{32}H_{31}NO$ requires C, 86.25; H, 7.0; N, 3.15%).

NN-*Dibenzyl*-3-(4-*methoxyphenyl*)-2,2-*dimethylbut*-3-*enamide* (**17**): 68%; m.p. 106—107 °C; $\nu_{max.}$ 1 625, 1 605, and 1 505 cm^{-1}; δ_H 1.60 (6 H, s, 2-Me_2), 3.82 (3 H, s, OMe), 4.48 and 4.53 (4 H, each br s, 2 × NCH_2), 5.20 (2 H, s, $=CH_2$), and 6.6—7.4 (14 H, m, ArH) (Found: C, 81.2; H, 7.3; N, 3.45. $C_{27}H_{29}NO_2$ requires C, 81.15; H, 7.3; H, 3.5%).

NN-*Dibenzyl*-2,2-*dimethyl*-3-(3,4,5-*trimethoxyphenyl*)*but*-3-*enamide* (**18**): 35%; m.p. 97—98 °C; $\nu_{max.}$ 1 620 and 1 570 cm^{-1}; δ_H 1.65 (6 H, s, 2-Me_2), 3.72 (6 H, s, 2 × OMe), 3.89 (3 H, s, OMe), 4.43 and 4.51 (each 2 H, each br s, 2 × NCH_2), 5.26 and 5.28 (2 H, each s, $=CH_2$), and 6.4—7.45 (12 H, m, ArH) (Found: C, 75.6; H, 7.2; N, 3.05. $C_{29}H_{33}NO_5$ requires C, 75.8; H, 7.25; N, 3.05%).

NN-*Dibenzyl*-2-*methyl*-3-*phenylbut*-3-*enamide* (**19**) was prepared from 2-benzoyl-*NN*-dibenzylpropanamide (**9**):[14] 56%; m.p. 59—60 °C; $\nu_{max.}$ 1 630 cm^{-1}; δ_H 1.41 (3 H, d, *J* 7 Hz, Me), 3.81 (1 H, q, *J* 7 Hz, 2-H), 4.01 and 5.22 and (2 H, ABq, *J* 15 Hz, NCH_2), 4.16 and 4.56 (2 H, ABq, *J* 16 Hz, NCH_2), 5.28 and 5.37 (2 H, each s, $=CH_2$), and 6.8—7.5 (15 H, m, 3 × Ph) (Found: C, 84.3; H, 7.15; N, 3.9. $C_{25}H_{25}NO$ requires C, 84.45; H, 7.1; N, 3.95%).

NN-*Dibenzyl*-3-*phenyl*-2-*phenethylbut*-3-*enamide* (**20**) was prepared from compound (**10**): b.p. 160—170 °C/10^{-3} Torr (bath temp.); $\nu_{max.}$ 1 630 cm^{-1}; δ_H 1.7—3.0 (4 H, m, CH_2CH_2), 3.65 (1 H, dd, *J* 4 and 9 Hz, 2-H), 4.08 and 4.46 (2 H, ABq, *J* 15 Hz, NCH_2), 4.08 and 5.25 (2 H, ABq, *J*, 15 Hz, NCH_2), 5.31 and 5.41 (2 H, each s, $=CH_2$), and 6.9—7.4 (15 H, m, 3 × Ph) (Found: C, 85.75; H, 7.15; N, 3.0. $C_{32}H_{31}NO$ requires C, 86.25; H, 7.0; N, 3.15%).

NN-*Dibenzyl*-2,2-*dimethyl*-3-*phenylpent*-3-*enamide* (**21**) was prepared as described for the preparation of compound (**11**), but with ethylmagnesium bromide in place of methylmagnesium iodide: 8%; m.p. 102—104 °C; $\nu_{max.}$ 1 620 cm^{-1}; δ_H 1.34 (3 H, d, *J* 7 Hz, $=CHMe$), 1.39 (6 H, s, 2-Me_2), 4.6 (4 H, m, 2 × NCH_2), 5.68 (1 H, q, *J* 7 Hz, =CH), and 6.7—7.6 (15 H, m, 3 × Ph) (Found: C, 84.7; H, 7.65; N, 3.6. $C_{27}H_{29}NO$ requires C, 84.55; H, 7.6; N, 3.65%).

General Procedure for Preparative Photolyses.—A methanol solution (40 ml) of a β,γ-unsaturated amide (300 mg) in a quartz tube was deaerated by argon bubbling, and irradiated with a low-pressure mercury lamp (Rayonet Photochemical Reactor RPR 2537 A) for 4—40 h. After removal of the solvent, the residue was chromatographed on silica gel, eluant benzene–ethyl acetate.

1-*Benzyl*-3,3,4-*trimethyl*-r-4,c-5-*diphenylpyrrolidin*-2-*one* (**22**): m.p. 138.5—139.5 °C; $\nu_{max.}$ 1 670 cm^{-1}; δ_H 1.06 (3 H, s, Me), 1.12 (3 H, s, Me), 1.35 (3 H, s, Me), 3.63 and 5.29 (2 H, ABq, *J* 15 Hz, NCH_2), 4.21 (1 H, s, 5-H), 6.5—6.65 (2 H, m, ArH), and 6.85—7.35 (13 H, m, ArH); δ_C 17.03 (q, Me), 19.43 (q, Me), 22.96 (q, Me), 44.80 (dd, NCH_2), 47.32 (s, C-3), 51.61 (s, C-4), 69.28 (d, C-5), 126.46—128.93 (Ph), 134.03 (s, Ph), 135.97 (s, Ph), 140.14 (s, Ph), and 182.35 (s, C=O) (Found: C, 84.35; H, 7.35; N, 3.85. $C_{26}H_{27}NO$ requires C, 84.5; H, 7.35; N, 3.8%).

1-*Benzyl*-3,3,4-*trimethyl*-r-4,t-5-*diphenylpyrrolidin*-2-*one* (**23**): m.p. 163—165 °C; $\nu_{max.}$ 1 670 cm^{-1}; δ_H 0.60 (3 H, s, Me), 1.12 (3 H, s, Me), 1.21 (3 H, s, Me), 3.74 and 5.40 (2 H, ABq, *J* 15 Hz, NCH_2), 5.01 (1 H, s, 5-H), and 6.9—7.5 (15 H, m, 3 × Ph); δ_C 20.20 (q, Me), 20.96 (q, Me), 22.90 (q, Me), 45.21 (dd, NCH_2), 48.50 (s, C-3), 49.96 (s, C-4), 66.11 (d, C-5), 126.46—129.28 (Ph), 135.80 (s, Ph), 143.14 (s, Ph), 151.30 (s, Ph), and 179.82 (s, C=O) (Found: C, 84.7; H, 7.4; N, 3.85%).

1-*Benzyl*-r-4-(4-*chlorophenyl*)-3,3,4-*trimethyl*-c-5-*phenylpyrrolidin*-2-*one* (**24**): m.p. 162—164 °C; $\nu_{max.}$ 1 670 cm^{-1}; δ_H 1.03 (3 H, s, Me), 1.11 (3 H, s, Me), 1.33 (3 H, s, Me), 3.64 and 5.29 (2 H, ABq, *J* 14 Hz, NCH_2), 4.21 (1 H, s, 5-H), 6.5—6.7 (2 H, m, ArH), and 6.7—7.3 (12 H, m, ArH); δ_C 17.12 (q, Me), 19.39 (q, Me), 22.92 (q, Me), 44.91 (dd, NCH_2), 47.34 (s, C-3), 51.47 (s, C-4), 69.07 (d, C-5), 127.31—130.02 (Ph), 132.46 (s, Ph), 133.81 (s, Ph), 135.87 (s, Ph), 138.90 (s, Ph), and 182.19 (s, C=O) (Found: C, 77.55; H, 6.5; N, 3.5. $C_{26}H_{26}ClNO$ requires C, 77.3; H, 6.5; N, 3.5%).

1-Benzyl-*r*-4-(4-chlorophenyl)-3,3,4-trimethyl-*t*-5-phenylpyrrolidin-2-one (**25**) was not completely purified; $\nu_{max.}$($CHCl_3$) 1 670 cm^{-1}; δ_H 0.60 (3 H, s, Me), 1.07 (3 H, s, Me), 1.19 (3 H, s, Me), 3.72 and 5.36 (2 H, ABq, *J* 14 Hz, NCH_2), 4.92 (1 H, s, 5-H), and 6.9—7.5 (14 H, m, ArH).

1-*Benzyl*-r-4-*biphenyl*-4-*yl*-3,3,4-*trimethyl*-c-5-*phenylpyrrolidin*-2-*one* (**26**): m.p. 166—167 °C; $\nu_{max.}$ 1 670 cm^{-1}; δ_H 1.12

(3 H, s, Me), 1.14 (3 H, s, Me), 1.39 (3 H, s, Me), 3.66 and 5.31 (2 H, ABq, J 14 Hz, NCH_2), 4.24 (1 H, s, 5-H), 6.5—6.75 (2 H, m, ArH), and 6.75—7.6 (17 H, m, ArH); δ_C 17.08 (q, Me), 19.55 (q, Me), 23.01 (q, Me), 44.91 (dd, NCH_2), 47.38 (s, C-3), 51.67 (s, C-4), 69.40 (d, C-5), 125.70—129.10 (Ph), 134.10 (s, Ph), 136.03 (s, Ph), 139.03 (s, Ph), 139.38 (s, Ph), 140.44 (s, Ph), and 182.35 (s, C=O) (Found: C, 86.25; H, 7.1; N, 3.1. $C_{32}H_{31}NO$ requires C, 86.25; H, 7.0; N, 3.15%).

1-Benzyl-*r*-4-biphenyl-4-yl-3,3,4-trimethyl-*t*-5-phenylpyrrolidin-2-one (**27**) was not completely purified; $\nu_{max.}$ 1 670 cm^{-1}; δ_H 0.66 (3 H, s, Me), 1.15 (3 H, s, Me), 1.23 (3 H, s, Me), 3.74 and 5.39 (2 H, ABq, J 14 Hz, NCH_2), 5.06 (1 H, s, 5-H), and 6.9—7.7 (19 H, m, ArH).

1-Benzyl-*r*-4-(4-methoxyphenyl)-3,3,4-trimethyl-*c*-5-phenylpyrrolidin-2-one (**28**): m.p. 150—151 °C; $\nu_{max.}$ 1 670 cm^{-1}; δ_H 1.05 (3 H, s, Me), 1.10 (3 H, s, Me), 1.31 (3 H, s, Me), 3.63 and 5.28 (2 H, ABq, J 14 Hz, NCH_2), 3.72 (3 H, s, OMe), 4.19 (1 H, s, 5-H), 6.4—6.7 (4 H, m, ArH), and 6.7—7.7 (10 H, m, ArH); δ_C 17.23 (q, Me), 19.45 (q, Me), 22.86 (q, Me), 44.80 (dd, NCH_2), 47.40 (s, C-3), 51.14 (s, C-4), 55.04 (q, OMe), 69.40 (d, C-5), 112.47 and 127.36—129.69 (Ph), 132. 35 (s, Ph), 134.30 (s, Ph), 136.09 (s, Ph), 157.97 (s, Ph), and 182.51 (s, C=O) (Found: C, 81.15; H, 7.3; N, 3.5. $C_{27}H_{29}NO_2$ requires C, 81.2; H, 7.3; N, 3.5%).

1-Benzyl-*r*-4-(4-methoxyphenyl)-3,3,4-trimethyl-*t*-5-phenylpyrrolidin-2-one (**29**) was not completely purified; $\nu_{max.}$ 1 670 cm^{-1}; δ_H 0.62 (3 H, s, Me), 1.08 (3 H, s, Me), 1.17 (3 H, s, Me), 3.73 (3 H, s, OMe), 3.70 and 5.33 (2 H, ABq, J 14 Hz, NCH_2), 4.97 (1 H, s, 5-H), 6.5—6.8 (2 H, m, ArH), and 6.8—7.5 (12 H, m, ArH).

The photoproduct from compound (**13**) was presumed to be 1-allyl-3,3,4-trimethyl-4-phenyl-5-vinylpyrrolidin-2-one, but it did not crystallize and was not completely purified; $\nu_{max.}$ 1 675 and 1 620 cm^{-1}; δ_H 0.76 (3 H, s, Me), 1.20 (3 H, s, Me), 1.40 (3 H, s, Me), 3.50 (1 H, dd, J 15 and 7 Hz, $CHHCH{=}CH_2$), 4.36 (1 H, d, J 15 and 5 Hz, $CHHCH{=}CH_2$), 4.10 (1 H, d, J 7 Hz, 5-H), 4.8—6.0 (6 H, m, olefinic), and 7.0—7.4 (5 H, m, Ph).

1-*Benzyl*-3,4-*dimethyl*-r-4-c-5-*diphenylpyrrolidin*-2-*one* (**30**): m.p. 135—136.5 °C; $\nu_{max.}$ 1 670 cm^{-1}; δ_H 1.24 (3 H, d, J 7 Hz, Me), 1.38 (3 H, s, Me), 3.43 (1 H, q, J 7 Hz, 3-H), 3.50 and 5.31 (2 H, ABq, J 15 Hz, NCH_2), 4.15 (1 H, s, 5-H), 6.6—6.8 (2 H, m, ArH), and 6.8—7.4 (13 H, m, ArH); δ_C 9.04 (q, Me), 24.01 (q, Me), 41.45 (d, C-3), 44.1 (dd, NCH_2), 49.14 (s, C-4), 71.57 (d, C-5), 126.17—128.69 (Ph), 136.24 (s, Ph), 136.44 (s, Ph), 141.38 (s, Ph), and 175.95 (s, C=O) (Found: C, 84.5; H, 7.1; 3.95. $C_{25}H_{25}NO$ requires C, 84.45; H, 7.1; N, 3.95%).

1-*Benzyl*-4-*methyl*-3-*phenethyl*-r-4,c-5-*diphenylpyrrolidin*-2-*one* (**37**): m.p. 129.5—130 °C; $\nu_{max.}$ 1 665 cm^{-1}; δ_H 1.40 (3 H, s, Me), 1.48—3.36 (5 H, m, CH_2CH_2CH), 3.47 and 5.33 (2 H, ABq, J 15 Hz, NCH_2), 4.08 (1 H, s, 5-H), 6.5—6.8 (2 H, m, ArH), and 6.8—7.4 (18 H, m, ArH); δ_C 23.60 (q, Me), 27.42 (t, CH_2), 34.29 (t, CH_2), 44.91 (dd and d, NCH_2 and C-3), 49.32 (s, C-4), 71.57 (d, C-5), 125.81—128.75 (Ph), 136.33 (s, Ph), 140.91 (s, Ph), 142.02 (s, Ph), and 175.90 (s, C=O) (Found: C, 86.05; H, 7.05; N, 3.1. $C_{32}H_{31}NO$ requires C, 86.25; H, 7.0; N, 3.15%).

Synthesis of Deuteriated Compounds [$^2H_2$](**14**) *and* [$^2H_4$](**14**).—These compounds were prepared from [$^2H_2$] and [$^2H_4$](benzoyl-*NN*-dibenzylacetamide), respectively as in the case of the unlabelled compound (**14**). The labelled amides were synthesized by the reaction[7] of ethyl benzoylacetate with [$^2H_2$]dibenzylamine ($PhCH_2NHCD_2Ph$)[16] and [$^2H_4$]-dibenzylamine [$(PhCD_2)_2NH$], respectively. [$^2H_4$]Dibenzylamine was obtained by reaction of lithium aluminium deuteride with $PhCONHCD_2Ph$, which was prepared from benzoic anhydride and $PhCD_2NH_2$.[16]

Measurement of Isotope Effects.—Photolysis of ($^2H_2$)(**14**) and isolation of the major product, [$^2H_2$](**22**), was carried out as in the case of photolysis of (**14**). The value of Φ_H/Φ_D was calculated from the ratio of integration of signals δ_H 4.21 (s, 5-H) and 3.63 (d, NCH_2).

Quantum Yield Determination.—Hexanone actinometry[9] was used. Irradiations were performed in a merry-go-round apparatus (Rayonet Photochemical Reactor RPR-2537A). The samples in quartz tubes were deaerated by argon bubbling (20 min). The actinometer solutions were treated in the same way. After the irradiation, the degree of reaction was determined by gas chromatography.

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