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# PHOTOCYCLIZATION OF *N*-ALKYL-*N*-(3-ARYL-3-BUTENYL) UREAS. HYDROGEN TRANSFER VIA CHARGE TRANSFER EXCIPLEXES IN ALKENE PHOTOCHEMISTRY

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## ABSTRACT

Photolysis of *N*-alkyl-*N*-(3-aryl-3-butenyl)ureas (**1**) in acetonitrile gave cyclization products, 3-aryl-3-methyl-pyrrolidines, in good yields, whereas irradiation of **1** in methanol afforded methanol adducts as well as the cyclization products. Both the reactions are singlet reactions, and the cyclization is presumed to proceed via 1,6-hydrogen transfer from exciplexes with charge transfer character.

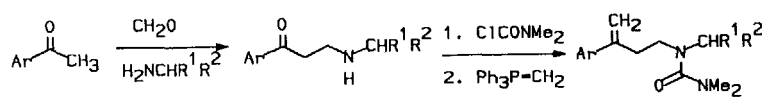
## INTRODUCTION

It is well-known that some cyclic olefins undergo inter- or intramolecular hydrogen abstraction on excitation to the triplet states[1,2] as with carbonyl compounds (Norrish type II reactions).[3,4] Photochemical hydrogen abstraction of acyclic olefins is quite rare except for 1,1-diphenylethylene derivatives,[5] because of the presence of competitve processes such as *cis–trans* isomerization. In relation to our previous studies on photochemical reactions of olefins having a nitrogen-containing functional group,[6,7] we report here efficient photocyclization of *N*-alkyl-*N*-alkenylureas which involves hydrogen abstraction by olefinic carbons from the singlet states via charge transfer exciplexes.

## RESULTS AND DISCUSSION

### Synthesis of *N*-Alkyl-*N*-Alkenylureas

The ureas (**1a–f**) were easily synthesized as shown in Scheme I from the aminoketones which were prepared by the Mannich reaction.

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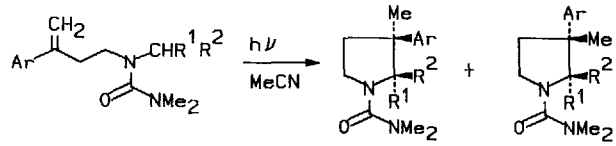
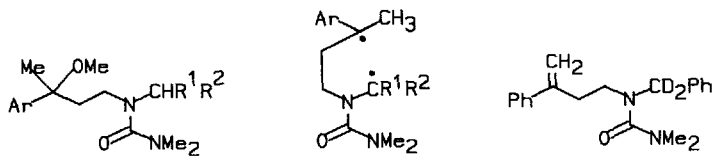
**Photolysis, and Identification of Photoproducts**

When *N*,*N*',*N*'-trimethyl-*N*-(3-phenyl-3-butenyl)urea (**1a**) in acetonitrile was irradiated under argon with a low pressure mecury lamp, 1-dimethylcarbamoyl-3-methyl-3-phenylpyrrolidine (**2a**) was obtained in 70% yield. Photolysis of other ureas (**1b–f**) also gave the corresponding cyclization products in good yields (Scheme II, Table 1).




1 2 3

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-$MeOC_6H_4$, $R^1$=H, $R^2$=Ph
f: Ar=4-$PhC_6H_4$, $R^1$=H, $R^2$=Ph




4 5 1d-D

Table 1. Photolysis of **1** in Acetonitrile

| Reactant | Quantum Yield | Product (%) | |
|---|---|---|---|
| | | **2** | **3** |
| **1a** | | 70 | |
| **1b** | | 49[a] | 22[a] |
| **1c** | | 56 | |
| **1d** | 0·055 | 49[a] | 14[a] |
| **1e** | 0·005 | 76[a] | trace[a] |
| **1f** | | 53[a] | 21[a] |

[a]Determined by the NMR spectra.

The structure of these products were determined on the basis of the spectral data and elemental analyses. The products from **1b** and **1d–f** were mixtures of two stereoisomers. The major isomers (**2d–f**) were isolated by recrystallization, but the minor isomers (**3d–f**) were not completely purified. The separation of the isomers (**2b** and **3b**) was not achieved. The stereochemistry of these isomers was assigned on the basis of the $^1$H-NMR spectra. The $^1$H-NMR spectrum of the major isomer (**2b**) showed the signal of the C-2 methyl group at an unusually high field (δ 0·80, d). This fact is reasonably explained by the anisotropic effects of the C-3 phenyl group which is *cis* to the methyl group. The NMR spectrum of **2d** showed

signals of aromatic protons at an unusually high field (δ 6·6–6·9, 2H). This indicates that the phenyl groups at C-2 and C-3 are *cis*. Analogous anisotropic effects have been observed for pyrrolidinones.[6] The stereochemistry of other major isomers (**2e–f**) was determined in a similar manner.

When the *N*-isopropyl derivative (**1c**) was irradiated in methanol, a methanol adduct (**4c**) was obtained (34%) and the cyclization product (**2c**) was not detected. In the cases of *N*-methyl and *N*-ethyl derivatives (**1a** and **1b**), the NMR spectra of the photolysates indicated the formation of both the methanol adducts and the cyclization products, but they could not be separated even by repeated chromatography. Meanwhile, photolysis of *N*-benzyl derivatives (**1d–f**) in methanol gave only the cyclization products as with that in acetonitrile (Table 2).

Table 2. Photolysis of **1** in Methanol

| Reactant | Product (%) | |
|---|---|---|
| | **2+3** | 4 |
| **1a** | 26[a] | 18[a] |
| **1b** | 23[a] | 20[a] |
| **1c** | 0 | 34 |
| **1d** | 61 | 0 |
| **1e** | 22 | 0 |
| **1f** | 63 | 0 |

[a]Determined by the NMR spectra.

## Mechanism

The formation of **2** and **3** can be resonably explained in terms of hydrogen abstraction by the terminal olefinic carbon followed by cyclization of the resulting 1,5-diradical (**5**). This mechanism was supported by the experiment using a deuterium-labeled urea (**1d**-D). Irradiation of **1d**-D gave **2d**-D in which one of benzylic deuterium atoms was completely incorporated into the $C_3$-methyl group. The photoreaction of **1d** was not sensitized by thioxanthone ($E_T$=66 kcal) or xanthone (74 kcal).[8,9] Moreover, the reaction was not quenched by 1,3-pentadiene (0.07 M, 59 kcal).[8] These findings clearly show that the photoreaction proceeds from the singlet state. This result is unusual because it is well-known that direct hydrogen abstraction of olefins takes place from the triplet states.[1,2,5b] The primary reactions of the $S_1$ ($\pi,\pi^*$) states of olefins are not diradicaloid but zwitterionic or polar in nature,[10] and direct hydrogen abstraction of styrenes from the singlet states is hitherto unknown to the best of our knowledge.[1]

The photochemical methanol addition of **1a–c** is also a singlet reaction since it is neither sensitizable nor quenchable.

## Intramolecular Charge Transfer Interaction

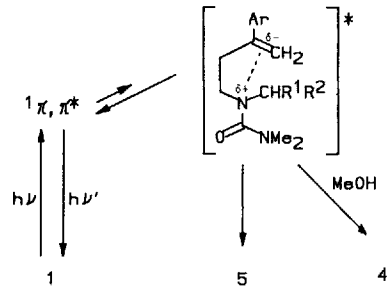
It is known that the $S_1$ states of olefins form charge transfer exciplexes with amines and proton transfer takes place from the exciplexes to give radical pairs.[11] We recently reported the photochemical intramolecular hydrogen abstraction of γ,δ- and δ,ε-unsaturated amines.[7] This reaction proceeds via intramolecular charge transfer exciplexes in which amino groups behave as donors. Charge transfer exciplexes are also presumed to play important roles in the

photochemistry of β,γ-unsaturated amides.[6] Both the reactions proceed from the singlet states. Ureas are weaker electron donors than amines, but stronger donors than amides.[12] Therefore it is highly probable that the singlet photoreactions of the alkenyl ureas (**1a–f**) also involve charge transfer exciplexes as intermediates. The low efficiency of the reaction of the 4-methoxy derivative (**1e**) (Table 1) is consistent with the charge transfer mechanism since introduction of an electron-donating methoxy group to a styrene should raise the energy of its highest occupied molecular orbital and lower its electron affinity in the excited states.[11]

The formation of the methanol adduct in the photolysis of **1c** in methanol also supports this mechanism. It is difficult to explain the addition in terms of simple polar addition from the π,π* singlet state of **1c**, since α-methyl styrene which has almost the same chromophore as that of **1c** did not give methanol adducts on irradiation in methanol. It is known that photolysis of styrenes in methanol in the presence of electron donors gives Markovnikov adducts as with the present reaction.[1,5b]

Odaira *et al.*[13] reported intermolecular photoaddition of tetramethylurea (TMU) to 1,1-diphenylethylene. This reaction has also been explained in terms of a charge transfer mechanism. Interestingly, this intermolecular reaction is different from the present intramolecular reaction of **1** with respect to the multiplicity and direction of the hydrogen transfer: the reaction is a triplet reaction, and the hydrogen of TMU is transfered to the disubstituted olefinic carbon rather than to the terminal methylene carbon (anti-Markovnikov addition). In contrast to the efficient photoreaction of 1,1-diphenylethylene with TMU, α-methylstyrene did not react with TMU on irradiation. Moreover, the fluorescence of α-methylstyrene was not quenched by TMU in distinction from the efficient quenching by amines.[11] These facts indicate that the interaction between the $S_1$ states of styrenes and ureas is considerably weak, and that the interaction is important only when the styrene and urea groups are involved in the same molecule as with **1** (proximity effects).

The alkenylurea (**1d**) showed the fluorescence similar to styrenes, and did not exhibit the exciplex emission. This finding indicates that rapid deactivation processes of the $S_1$ state of **1d** do not exist. Therefore, the formation of the exciplex from the $S_1$ state can not be exothermic and irreversible. The photocyclization of **1** is most reasonably explained by the mechanism shown in Scheme III in which the $S_1$ state is in equilibrium with the charge transfer exciplex and the formation of the exciplex is slightly endothermic. (The reduction potentials of α-alkylstyrenes could not be measured by the cyclic voltammetry because the potentials were too negative, and $\Delta G$ values for the electron transfer could not be estimated.)[11]




Recently, Wagner *et al.*[14] reported the photoreduction of ketones with alkylbenzenes via charge transfer exciplexes. In this reaction, hydrogen transfer proceeds via irreversible, rate-determing complexation when the formation of the exciplexes is exothermic, whereas the triplet ketones form exciplexes reversibly with alkylbenzenes when the exciplex formation is

endothermic. The photoreactions of the olefins having a nitrogen function are quite analogous to this photoreduction. When the nitrogen functions are strong electron donors as with amino groups, intramolecular charge transfer exciplexes are formed exothermically and irreversibly, and both hydrogen (or proton) transfer and emission take place from the exciplexes.[7] In the case of weak donors such as ureas or amides the complexation should be slightly endothermic and the exciplexes are presumed to be equilibrated with the $S_1$ states. Thus, emission from the $S_1$ states and reaction from the exciplexes are ovserved. The failure to observe the exciplex emission in this case may be attributed to the small population of the exciplexes or their non-emissive characters. In these exciplexes, the olefin moiety should have partial negative charge and the nitrogen should possess partial positive charge[15] (Scheme III). This positive charge makes the hydrogens on the adjacent carbon acidic. It is known that partial charge separation in the exciplexes significantly enhance the rate of hydrogen (or proton) transfer.[14]

Finally, the results of the photoreactions of **1a–c** in methanol are also consistent with the mechanism involving the charge transfer exciplexes. The chemoselectivity in these photoreactions can be explained in terms of kinetic acidity[14] of the hydrogen to be abstracted as follows. The isopropyl methine hydrogen of the exciplex from **1c** is least acidic and so least reactive toward abstraction, and the methanol adduct (**1c**) was obtained as a sole product. In the cases of the N-methyl and N-ethyl derivatives (**1a** and **1b**), the methyl and methylene hydrogens activated by the nitrogen with partial positive charge are more acidic and thus more reactive toward abstraction, and the hydrogen transfer can complete with the methanol addition. Wagner *et al.*[14] reported that in the above-mentioned photoreduction of ketones the metyl hydrogens of cymene were more reactive toward abstraction than the isopropyl methine hydrogen when exciplex formation involved a sufficient charge transfer. The fact that no methanol adducts were obtained in the case of the N-benzyl derivatives (**1d–f**) is also compatible with the above explanation. The benzylic hydrogens should be acidic in comparison with methyl hydrogens because phenyl groups are electron-withdrawing and also stabilize adjacent anionic centers.

## CONCLUSION

Photolysis of *N*-alkyl-*N*-(3-aryl-3-butenyl)ureas (**1**) gives the corresponding pyrrolidines (**2** and **3**). This cyclization is useful for synthesis of some pyrrolidines, since (a) the yields are good or moderate, (b) synthesis of the reactants is easy, and (c) the photoreaction proceeds regardless of the nature of the alkyl and aryl groups. This photoreaction is presumed to proceed via, 1,6-hydrogen transfer from the intermediary exciplexes. The results of the present reaction together with those of photoreactions of unsaturated amines and unsaturated amides[6,7] indicate that charge transfer interactions play important roles in the photochemical hydrogen transfer of olefins as with that of carbonyl compounds.

## EXPERIMENTAL

IR spectra were measured on a JASCO IRA-1 Infrared spectrophototometer. $^1$H- and $^{13}$C-NMR spectra were recorded on a JEOL FX-90Q or FX-100 spectrometer. UV spectra were obtained on a Shimadzu UV-365 spectrometer. Fluorescence spectra were obtained on a JASCO FP-550 spectrofluorometer. Mass spectra were recorded on a Hitachi RMU-6MG spectrometer. Elemental analyses were performed by a Perkin Modle 240 elemental analyzer. A Rayonet photochemical reactor (RPR 2537 A) was used as an irradiation source.

**General Procedure for Preparation of *N*-Alkenylureas (1a–f)**

To 3-(*N*-alkylamino)-1-arylpropan-1-one (13 mmol) which is prepared by the Mannich reaction[16] and triethylamine (15 mmol) in benzene (30 ml) was added *N*,*N*-dimethylcarbamoylchloride (15 mmol) in benzene (20 ml), and the resulting mixture was heated to 50 °C for 2 h. After cooling, the mixture was washed with 2M hydrochloric acid, aqueous sodium bicarbonate, water and brine. The organic phase was dried and evaporated, and the residue was chromatographed on silica gel. The resulting product (13 mmol) was dissolved in THF (20 ml), and added under argon to a THF solution (300 ml) of the phosphorus ylide prepared from tri-phenylmethylphosphonium bromide (13 mmol) and butyllithium.[17] After the solution had been stirred for 10 min, water was added and the aqueous layer was extracted with benzene. The combined organic layer was dried and evaporated, and the residue was chromatographed on silica gel.

*N*′,*N*′,*N*-Trimethyl-N-(3-phenyl-3-butenyl)urea (**1a**): b.p. 110–120 °C/0·1 torr (bath temperature); IR ($CHCl_3$) 1620 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 2·5–2·9 (m, 2H, $CH_2$), 2·70 (s, 6H, $NMe_2$), 2·77 (s, 3H, NMe), 3·1–3·4 (m, 2H, $NCH_2$), 5·09 and 5·33 (each br. s, 2H, olefinic), 7·0–7.6 (m, 5H, Ph); $^{13}$C-NMR ($CDCl_3$) δ 33·4 (t), 36·9 (q), 38·6 (q), 49·7 (t), 113·7 (t), 125·9 (d), 127·5 (d), 128·3 (d), 140·5 (s), 145·8 (s), 165·2 (s); UV (MeOH) $\lambda_{max}$ 238 nm (ε 9250); mass spectrum, *m*/*z* 232 ($M^+$). Analyses calculated for $C_{14}H_{20}N_2O$: C, 72·37; H, 8·67; N, 12·05. Found: C, 72·08; H, 8·75; N, 11.92.

*N*′,*N*′-Dimethyl-*N*-ethyl-*N*-(3-phenyl-3-butenyl)urea (**1b**): b.p.110–120 °C/0·1 torr (bath temperature); IR ($CHCl_3$) 1620 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1·03 (t, 3H, J=7 Hz, $CH_2Me$), 2·5–2.9 (m, 2H, $CH_2$), 2·71 (s, 6H, $NMe_2$), 2·9–3·3 (m, 4H, $NCH_2$), 5·08 and 5·31 (each br. s, 2H, olefinic), 7·1–7·5 (m, 5H, Ph); $^{13}$C-NMR ($CDCl_3$) δ 13·3 (q), 33·8 (t), 38·5 (q), 43·4 (t), 46·7 (t), 113·5 (t), 125·9 (d), 127·3 (d), 128·2 (d). 140·4 (s), 146·0 (s), 164·9 (s); UV (MeOH) $\lambda_{max}$ 237 nm (ε 9790); mass spectrum *m*/*z* 246 ($M^+$). Analyses calculated for $C_{15}H_{22}N_2O$: C, 73·13; H, 9·00; N, 11·37. Found: C, 72·95; H, 9·10; N, 11·20.

*N*′,*N*′-Dimethyl-*N*-isopropyl-*N*-(3-phenyl-3-butenyl)urea (**1c**): b.p. 110–120 °C/0·1 torr (bath temperature); IR ($CHCl_3$) 1620 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 0·99 (d, 6H, J=7 Hz, $CHMe_2$), 2·5–2·8 (m, 2H, $CH_2$), 2·75 (s, 6H, $NMe_2$), 2·9–3·2 (m, 2H, $NCH_2$), 3·66 (sep, 1H, J=7 Hz, CH), 5·06 and 5·33 (each d, 2H, J=1·5 Hz, olefinic), 7·1–7·6 (m, 5H, Ph); $^{13}$ C-NMR ($CDCl_3$) δ 20·3 (q), 34·9 (t), 38·3 (q), 40·9 (t), 50·4 (d), 113·4 (t), 126·0 (d), 127·3 (d), 128·2 (d), 140·5 (s), 146·4 (s), 165·2 (s); UV (MeOH) $\lambda_{max}$ 239 nm (ε10200); mass spectrum *m*/*z* 260 ($M^+$). Analyses calculated for $C_{16}H_{24}N_2O$: C, 73·80; H, 9·29; N, 10·75. Found: C, 73·88; H, 9·28; N, 10·74.

*N*-Benzyl-*N*′,*N*-dimethyl-*N*-(3-phenyl-3-butenyl)urea (**1d**): m.p. 66–67 °C; IR ($CHCl_3$) 1625 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 2·6–2·9 (m, 2H, $CH_2$), 2·76 (s, 6H, $NMe_2$), 3·0–3·3 (m, 2H, $NCH_2$), 4·35 (s, 2H, benzylic), 5·04 and 5·31 (each d, 2H, J=1·5 Hz, olefinic), 6·9–7·6 (m, 10H, Ph); $^{13}$C-NMR ($CDCl_3$) δ 33·4 (t), 38·6 (q), 47·0 (t), 52·2 (t), 113·8 (t), 125·9–128·5, 138·1 (s), 140·2 (s), 145·6 (s), 165·1 (s); UV (MeOH) $\lambda_{max}$ 235 nm (ε 10500); fluorescence spectrum $\lambda_{max}$ 306 nm ($\lambda_{excitation}$ 250 nm); mass spectrum *m*/*z* 308 ($M^+$). Analyses calculated for $C_{20}H_{24}N_2O$: 77·88; H, 7·84; N, 9·08. Found: C, 77·79; H, 7·78; N, 9·04.

*N*-Benzyl-*N*′,*N*′-dimethyl-*N*-[3-(4′methoxyphenly)-3-butenyl]-urea (**1e**); b.p. 130–140/$10^{-3}$ torr (bath temperature); IR ($CHCl_3$) 1620 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 2·5–2·9 (m, 2H, $CH_2$), 2·78 (s, 6H, $NMe_2$), 3·0–3·3 (m, 2H, $NCH_2$), 3·77 (s, 3H, OMe), 4·36 (s, 2H, benzylic), 4·95 (br. s, 1H, olefinic), 5·23 (d, 1H, J=1·5 Hz, olefinic), 6·7–7·4 (m, 9H, aromatic); $^{13}$C-NMR ($CDCl_3$) δ 33·5 (t), 38·7 (q), 47·2 (t), 52·2 (t), 55·2 (q), 112·1 (t), 113·7 (d), 127·0–128·5, 132·7 (s), 138·2 (s), 145·0 (s), 159·2 (s), 165·2 (s); UV (MeOH) $\lambda_{max}$ 254 nm (ε 12700); mass spectrum (CI) *m*/*z* 339 (M+1). Analyses calculated for $C_{21}H_{26}N_2O_2$: C, 74·15; H, 7·75; N, 8·15. Found: C, 74·52; H, 7·74; N, 8·27.

*N*-Benzyl-*N'*,*N'*-dimethyl-N-[3-(4'-biphenyl)-3-butenyl]urea (**1f**): b.p. 150–160 °C/$10^{-3}$ torr (bath temperature); IR ($CHCl_3$) 1625 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 2·5–2·9 (m, 2H, $CH_2$), 2·78 (s, 6H, $NMe_2$), 3·0–3·3 (m, 2H, $NCH_2$), 4·37 (s, 2H benzylic), 5·07 and 5·38 (each d, 2H, J=1·5 Hz, olefinic), 7·0–7·7 (m, 14 H, aromatic); $^{13}$C-NMR ($CDCl_3$) δ 33·4 (t), 38·6 (q), 47·1, (t), 52·3 (t), 113·8 (t), 126·3–128·7, 138·1 (s), 139·2 (s), 140·3 (s), 140·6 (s), 145·2 (s), 165·2 (s); UV (MeOH) $\lambda_{max}$ 272 nm (ε 22200); mass spectrum (CI) *m/z* 339 (M+1). Analyses calculated for $C_{26}H_{28}N_2O$:C, 80·80; H, 7·36; N, 7·15. Found: C, 81·21; H, 7·34; N, 7·28.

**General Procedure for Preparative Photolyses**

An acetonitrile (or methanol) solution (70 ml) of an *N*-alkenylurea (300 mg) in a quartz tube was deaerated by argon bubbling and irradiated with a low pressure mercury lamp for 10–20 h. After removal of the solvent, the residue was chromatographed on silica gel.

1-Dimethylcarbamoyl-3-methyl-3-phenylpyrrolidine (**1a**): b.p. 110–120 °C/0·1 torr (bath temperature); IR ($CHCl_3$) 1610 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1·34 (s, 3H, Me), 1·9–2·2 (m, 2H, $CH_2$), 2·84 (s, 6H, $NMe_2$), 3·2–3·8 (m, 4H, $NCH_2$), 7·0–7·4 (m, 5H, Ph); $^{13}$C-NMR ($CDCl_3$) δ 27·3 (q), 37·6 (t), 38·3 (q), 45·2 (s), 47·0 (t), 59·6 (t), 125·6 (d), 126·2 (d), 128·4 (d), 147·0 (s), 163·5 (5); mass spectrum (CI) *m/z* 233 (M+1). Analyses calculated for $C_{14}H_{20}N_2O$: C, 72·37; H, 8·67; N, 12·05. Found (the analyses are relatively poor because these pyrrolidines are slightly hygroscopic): 71·79; H, 8·77; N, 11·90.

*Z*- and *E*-2,3-dimethyl-1-dimethylcarbamoyl-3-phenylpyrrolidines (**2b** and **3b**) could not be separated. The mixture had b.p. 110–120 °C/0·1 torr (bath temperature): IR ($CHCl_3$ for the mixture 1610 $cm^{-1}$. The isomer (**2b**) showed $^1$H-NMR ($CDCl_3$) δ 0·80 (d, 3H, J=7 Hz, 2-Me), 1·32 (s, 3H, 3-Me), 1·8–2·6 (m, 2H, $CH_2$), 2·86 (s, 6H, $NMe_2$), 3·2–3·8 (m, 2H, $NCH_2$), 4·38 (q, 1H, J=7 HZ, methine), 7·1–7·5 (m, 5H, Ph). The isomer (**3b**) showed $^1$H-NMR ($CDCl_3$ δ 1·16 (d, 3H, J=7 Hz, 2-Me), 1·32 (s, 3H, 3-Me), 1·8–2·6 (m, 2H, $CH_2$), 2·85 (s, 6H, $NMe_2$), 3·2–3·8 (m, 2H, $NCH_2$), 4·22 (q, 1H, J=7 Hz, methine), 7·1–7·5 (m, 5H, Ph). Analyses calculated for $C_{15}H_{22}N_2O$: C, 73·13; H, 9·00; N, 11·37. Found (for mixture) (the analyses are relatively poor because these pyrrolidines are slightly hygroscopic): C, 72·64; H, 9·09; N, 11·26.

1-Dimethylcarbamoyl-2,2,3-trimethyl-3-phenylpyrrolidine (**2c**): m.p. 104–105 °C; IR ($CHCl_3$) 1620 $cm^{-1}$; $^1$H-NMR ($CDCl_3$ δ 1·04 (s, 3H, Me), 1·38 (s, 3H, Me), 1·54 (s, 3H, Me), 1·6–1·9 and 2·6–2·9 (each m, 2H, $CH_2$), 2·80 (s, 6H, $NMe_2$), 3·3–3·8 (m, 2H, $NCH_2$), 7·1–7·5 (m, 5H, Ph); $^{13}$C-NMR ($CDCl_3$) δ 21·1 (q), 23·0 (q), 23·7 (q), 33·4 (t), 38·6 (q), 46·1 (t), 50·8 (s), 66·2 (s), 126·2 (d), 126·7 (d), 127·9 (d), 144·2 (s), 163·1 (s); mass spectrum (CI) *m/z* 261 (M+1). Analyses calculated for $C_{16}H_{24}N_2O$: C, 73·80; H, 9·29; N, 10·75. Found: C, 73·71; H, 9·35, N, 10·73.

*Z*-1-Dimethylcarbamoyl-2,3-diphenyl-3-methylpyrrolidine (**2d**) was separated from the minor *E*-isomer (**3d**) by recrystallization from hexane-chloroform: m.p. 158–159 °C; IR ($CHCl_3$) 1620 $cm^{-1}$; $^1$H-NMR ($CDCl_3$ δ 1·53 (s, 3H, Me), 1·8–2·1 and 2·5–2·9 (each m, 2H, $CH_2$), 2·77 (s, 6H, $NMe_2$), 3·7–4·0 (m, 2H, $NCH_2$), 5·00 (s, 1H, 2–H), 6·6–6·9 (m, 2H, Ph), 6·9–7·2 (m, 8H, Ph); $^{13}$C-NMR ($CDCl_3$) δ 28·0 (q), 33·6 (t), 38·6 (q), 47·5 (t), 50·1 (s), 73·5 (d), 126·0–127·5, 141·2 (s), 143·4 (s), 163·8 (s); mass spectrum *m/z* 308 (M+). Analyses calculated for $C_{20}H_{24}N_2O$: C, 77·88; H, 7·84; N, 9·08. Found: C, 77·83; H, 7·88; N, 8·98. The minor *E*-isomer (**3d**) was not completely purified: characteristic signals, $^1$H-NMR ($CDCl_3$) δ 1·08 (s, 3H, Me), 2·89 (s, 6H, $NMe_2$), 5·25 (s, 1H, 2-H).

*Z*-1-Dimethylcarbamoyl-3-(4'-methoxyphenyl)-3-methyl-2-phenylpyrrolidine (**2e**) was separated from the minor *E*-isomer (**3e**) by recrystallization from hexane-chloroform: m.p.

111–112 °C; IR ($CHCl_3$) 1615 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1·50 (s, 3H, Me), 1·8–2·1 and 2·4–2·7 (each m, 2H, $CH_2$), 2·76 (s, 6H, $NMe_2$), 3·70 (S, 3H, OMe), 3·7–4·1 (m, 2H, $NCH_2$), 4·94 (s, 1H, 2-H), 6·5–6·7 (m, 2H, aromatic), 6·7–7·0 (m, 5H, aromatic), 7·0–7·1 (m, 3H, aromatic); $^{13}$C-NMR ($CDCl_3$) δ 28·0 (q), 33·9 (t), 38·6 (q), 47·5 (t), 49·4 (s), 55·0 (q), 73·6 (d), 112·8 (d), 126·3–128·0, 135·4 (s), 141·3 (s), 157·6 (s), 163·7 (s); mass spectrum *m/z* 338 (M). Analyses calculated for $C_{21}H_{26}N_2O_2$: C, 74·52; H, 7·74; N, 8·27. Found: C, 74·52; H, 7·74; N, 8·24. The minor isomer (**3e**) was not completely purified: characteristic signals $^1$H-NMR ($CDCl_3$) δ 1·07 (s, 3H, Me), 2·86 (s, 6H, $NMe_2$), 5·20 (s, 1H, 2-h).

*Z*-3-(4′-Biphenyl)-1-dimethylcarbamoyl-3-methyl-2-phenyl pyrrolidine (**2f**) was separated from the minor *E*-isomer (**3f**) by recrystallization from hexane–chloroform: m.p. 165–167 °; IR ($CHCl_3$) 1620 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1·56 (s, 3H, Me), 1·9–2·1 and 2·5–2·9 (each m, 2H, $CH_2$), 2·78 (s, 6H, $NMe_2$), 3·7–4·1 (m, 2H, $NCH_2$), 5·02 (s, 1H, 2-H), 6·7–6·9 (m, 2H, Ph), 6·9–7·2 (m, 5H, aromatic) 7·2–7·6 (m, 7H, aromatic); $^{13}$C-NMR ($CDCl_3$) δ 27·9 (q), 33·8 (t), 38·5 (q), 47·6 (t), 49·9 (s), 73·5 (d), 126·1–128·6, 138·6 (s), 140·6 (s), 141·1 (s), 142·4 (s), 163·7 (s); mass spectrum (CI) *m/z* 385 (M+1). Analyses calculated for $C_{26}H_{28}N_2O$: C, 81·21; H, 7·34; N, 7·28. Found: C, 80·90; H, 7·28; N, 7·16. The minor *E*-isomer (**3f**) was not completely purified: Characteristic signals $^1$H-NMR ($CDCl_3$) δ 1·09 (s, 3H, M2), 2·82 (s, 6H, $NMe_2$), 5·29 (s, 1H, 3-H).

*N′,N′*-Dimethyl-*N*-isopropyl-*N*-(3-methoxy-3-phenylbutyl)urea (**4c**): b.p. 100–110/$10^{-3}$ torr (bath temperature); IR ($CHCl_3$) 1620 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1·04 (d, 6H, J=7 Hz, $CHMe_2$), 1·54 (s, 3H, 3-Me), 1·8–2·1 (m, 2H, $CH_2$), 2·73 (s, 6H, $NMe_2$), 2·8–3·1 (m, 2H, $NCH_2$), 3·13 (s, 3H, OMe), 3·73 (sep, 1H, J=7 Hz, $CHMe_2$), 7·1–7·5 (m, 5H, Ph); $^{13}$C-NMR ($CDCl_3$) δ 20·4 (q), 24·0 (q), 37·1 (t), 38·5 (q), 40·9 (t), 50·1 (d and q), 78·1 (s), 125·9 (d), 126·7 (d), 128·0 (d), 145·2 (s), 165·2 (s); mass spectrum (CI) *m/z* 293 (M+1). Analyses calculated for $C_{17}H_{28}N_2O_2$: C, 69·82; H, 9·65; N, 9·57. Found: C, 69·55; H, 9·61; N, 9·47.

*N,N′,N′*-Trimethyl-*N*-(3-methoxy-3-phenylbutyl)urea (**4a**) could not be separated from **2a**: characteristic signals $^1$H-NMR ($CDCl_3$) δ 1·55 (s, 3H, 3-Me), 2·68 (s, 6H, $NMe_2$), 2·70 (s, 3H, NMe), 3·11 (s, 3H, OMe); $^{13}$C-NMR ($CDCl_3$) δ 23·2 (q), 36·3 (q), 38·3 (q), 39·4 (t), 46·0 (t), 50·0 (q), 77·8 (s), 165·1 (s).

*N′,N′*-Dimethyl-*N*-ethyl-*N*-(3-methoxy-3-phenylbutyl)urea (**4b**) could not be separated from **2b** and **3b**: characteristic signals $^1$H-NMR ($CDCl_3$) δ 1·01 (t, 3H, J=7 Hz, $CH_2CH_3$), 1.54 (s, 3H, 3-Me), 2·68 (s, 6H, $NM3_2$), 3·12 (s, 3H, OMe); $^{13}$C-NMR ($CDCl_3$)δ 13·3 (q), 23·5 (q), 38·5 (q), 39·9 (t), 43·0 (t), 43·1 (t), 50·1 (q), 78·0 (s), 165·1 (s).

Synthesis and Photolysis of the Deuterium-labeled Compound (**1d**-D). Synthesis and photolysis of **1d**-D was done as in the case of **1d**. The $^1$H-NMR spectrum of **2d**-D clearly showed the presence of a $CH_2D$ group [δ 1·51 (br.s, 2H)].

Quantum Yield Determination. Hexanone actinometry[8] was used. Irradiation was performed in a merry-go-round apparatus (Rayonet Photochemical Reactor RPR 2537A). The samples in quartz tubes were degassed to ca. $10^{-3}$ torr by three freeze-thaw cycles. The degree of reaction (consumption of **1**) was determined by gas chromatography.

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