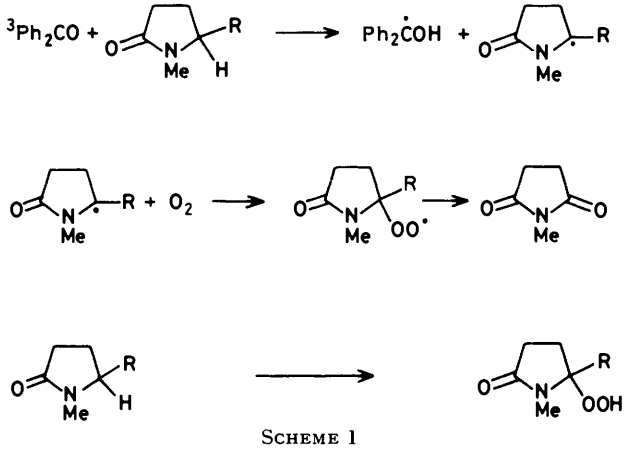
Photo-oxidation of Oxazolidones and Hydantoins in the Presence of Benzophenone

By **Jean-Claude Gramain** * and **Roland Remuson**, Laboratoire de Chimie et Biochimie des Substances Naturelles Equipe de Recherche Associée au CNRS 392, Université de Clermont II B.P. 45, 63170 Aubiere, France

Irradiation in the presence of benzophenone and oxygen of nitrogen-containing heterocycles having an NCO group yields products arising out of regioselective oxidation α to the nitrogen atom. Direct irradiation (in the absence of benzophenone and oxygen) of 5-methyl- and 5,5-dimethyl-hydantoins yields allophanates. The first step of this reaction involves the homolysis of the C(4)–C(5) bond of the hydantoin.

We recently described a new method for the photochemical oxidation of amides and lactams in the presence of benzophenone.[1,2] The first step of this reaction is the photoreduction of benzophenone by the lactam LH to give $Ph_2\dot{C}OH$ and L· radicals. The latter is formed by regioselective abstraction of a hydrogen atom α to the nitrogen. In the presence of oxygen, these radicals are oxidized to give Ph_2CO, which is thus regenerated, and the corresponding α-oxidized lactam, imide or hydroperoxide (Scheme 1).



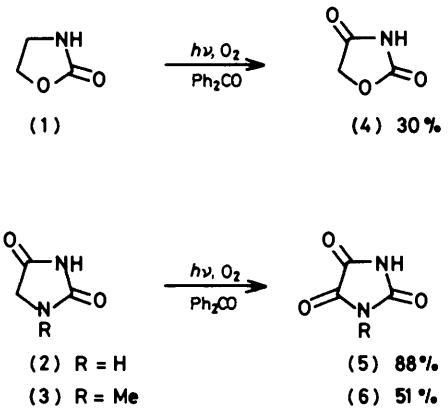
Scheme 1

Other nitrogen-containing heterocycles such as oxazolidones or hydantoins also possess abstractable hydrogen α to the nitrogen atom of an NCO group. They would, therefore, be expected to undergo similar reactions with the triplet of an aromatic ketone if these hydrogen atoms are ' activated ' as in case of lactams and amides. Here we report the results of photo-oxidation of these compounds in the presence of benzophenone.

RESULTS AND DISCUSSION

As expected, irradiation (high-pressure mercury lamp, Pyrex filter) of compounds (1), (2), and (3) in the presence of benzophenone (*C* 0.1M) in t-butyl alcohol saturated with oxygen gave oxazolidine-2,4-dione (4) and the parabanic acids (5) and (6) respectively.

The initial step, as with lactams,[2] is abstraction of the hydrogen α to the nitrogen atom to give a radical which is then trapped by oxygen. The peroxy-radical thus formed gives α-oxidation products in good yield by a mechanism analogous to that already described for amides.[2] The reaction is regioselective and the new carbonyl group is introduced α to the nitrogen and not α to the oxygen. The oxidation product (4) of 2-oxazolidone is easily distinguished from the isomeric



Scheme 2

oxazolidine-2,5-dione (prepared according to ref. 3) by its melting point and by the chemical shift of the singlet observed in the n.m.r. spectra: δ 4.85 for (4) and δ 4.15 for oxazolidine-2,5-dione.

By analogy with previous results obtained for the photo-oxidation of lactams bearing substituents α to the nitrogen atom, the 5-monosubstituted hydantoins (7a) and (7b) might have been expected to give the tertiary hydroperoxide (26). However, the only products isolated were the acylureas (12a) and (12b) (Scheme 3).

This unexpected result indicates that the mechanism of oxidation of these compounds is more complex than that of the corresponding lactams.

The acylureas (12a) and (12b) need not necessarily be derived from the hydroperoxide (26), assuming the formation of the latter, and the possibility of the involvement of an excited state of hydantoin cannot be ruled out. In order to test this hypothesis, the photochemical behaviour with direct irradiation of 5-substituted hydantoins in the absence of oxygen was studied. The results are summarized in the Table.

5,5-Dimethylhydantoin (13) and 5-methylhydantoin (7a) gave the methyl esters (allophanates) (14a) and (18) in methanol. The following mechanism (Scheme 4)

accounts for the formation of these products. Homolysis of the C(4)–C(5) bond followed by intramolecular transfer of the hydrogen on the N(3) nitrogen to the C(5) carbon gives the isocyanate (19). This is then trapped by the solvent giving the corresponding ester.

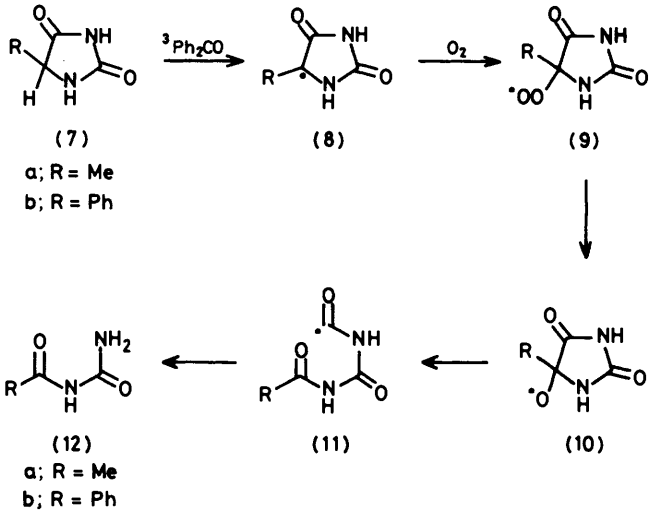
since the photochemistry of isocyanates is not well-known,[5] and the synthesis of the isocyanate (11) has not yet been possible.

Nonetheless, the model (20) (Scheme 4) was prepared: the reaction of methyl acrylate with 2-pyrrolidone

Photochemical behaviour of 5,5-dimethylhydantoin (13) and 5-methylhydantoin (7a) under direct irradiation in the absence of oxygen

Compound irradiated	Solvent	Photoproduct	Yield (%)
5,5-Dimethylhydantoin (13)	MeOH	$MeO_2CNHCONHPr^i$ (14a)	93
5,5-Dimethylhydantoin (13)	Bu^tOH	$Bu^tO_2CNHCONHPr^i$ (14b)	59
5,5-Dimethylhydantoin (13)	H_2O	$H_2NCONHPr^i$ (15)	35
5,5-Dimethylhydantoin (13)	CH_3CN–$NHEt_2$	$Et_2NCONHCONHPr^i$ (16)	17
5,5-Dimethylhydantoin (13)	CH_3CN–$H_2N(CH_2)_5CH_3$	n-HexylNHCONHCONHPr^i (17)	29
5-Methylhydantoin (7a)	MeOH	$MeO_2CNHCONHEt$ (18)	20

This hypothesis is supported by the following results. Irradiation of 5,5-dimethylhydantoin (13) in t-butyl alcohol gave the corresponding t-butyl ester (14b). In the presence of a secondary amine, the carbamoylureas (16) and (17) were isolated. Finally, when irradiation was performed in aqueous solution, reaction of the isocyanate with water gave the corresponding carbamic



Scheme 3

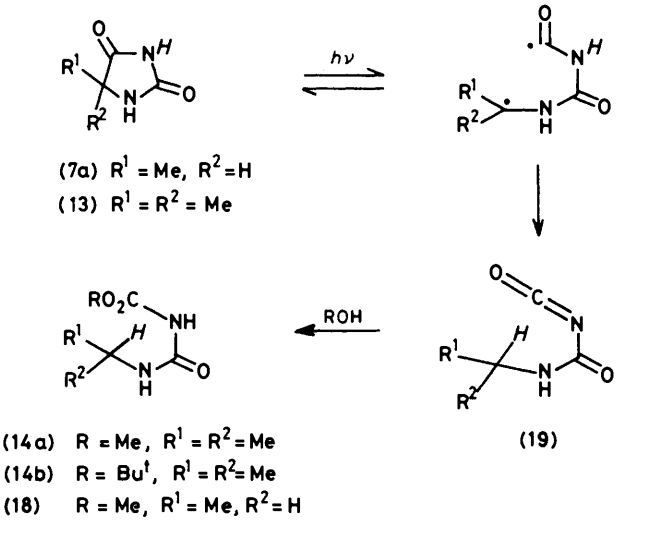
acid which undergoes spontaneous decarboxylation, to give the urea (15). 3,5,5-Trimethylhydantoin which has no transferable hydrogen in the 3-position was found to be photochemically inert.

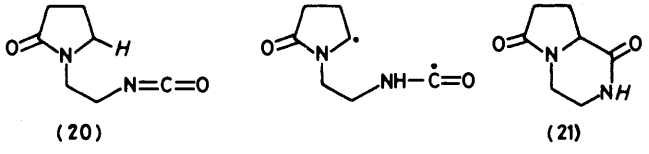
This mechanism is, moreover, similar to that postulated to account for the photochemical behaviour of dihydrothymidines.[4]

The same products (allophanates and carbamoylureas) were isolated after irradiation of the hydantoin (13) in acetonitrile containing a low concentration of an alcohol or an amine, but no reaction occurred in pure acetonitrile. This latter finding is somewhat surprising since the intermediate isocyanate (19) might have been expected to be obtained. Presumably, in the absence of an alcohol or an amine able to trap it, the formation of isocyanate is reversible.

It is difficult to obtain evidence to test this hypothesis

yields *N*-(2-methoxycarbonylethyl)-2-pyrrolidone which was transformed into compound (20) in two steps according to literature procedures.[6,7] The hydrogen α to the nitrogen of 2-pyrrolidone is known to be readily



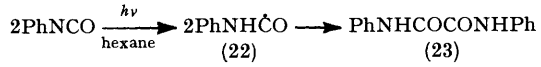


Scheme 4

abstracted and the structure of the isocyanate (20) is close to that of the more complex isocyanate (19). This compound was found to be photostable under the conditions of irradiation employed (250-W high-pressure mercury-vapour lamp. quartz reaction vessel) and did not yield the expected bicyclic compound (21) (Scheme 4). This disappointing result does not refute the hypothesis advanced above, given the structural differences between the α-alkyl isocyanate (20) and the isocyanate (19).

However, the following observation lends some support to this hypothesis; photolysis in hexane of phenyl iso-

cyanate gives the dimer (23) (Scheme 5) resulting from coupling of the radicals (22) formed by photoreduction of the substrate by the solvent, hydrogen attaching itself to the nitrogen atom as in the case of the hydantoins (13) and (7a).

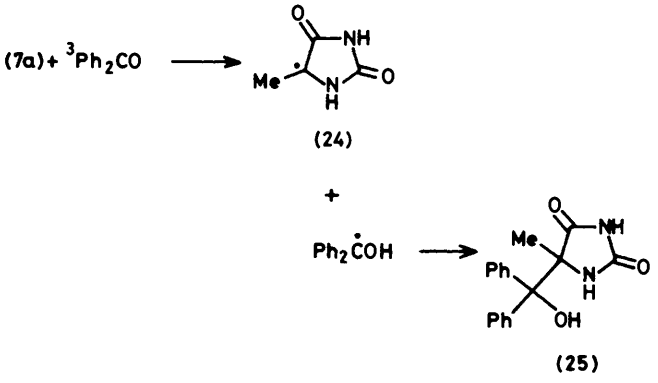


SCHEME 5

The compounds isolated after photo-oxidation of hydantoins in the presence of benzophenone have a quite different structure from those obtained above, and so the involvement of an excited state of hydantoin in this type of reaction can be safely discounted.

Since the photoreduction of benzophenone by 5-methylhydantoin (7a) in the absence of oxygen yields the adduct (25), resulting from the coupling of the hydroxybenzhydryl radical and the radical (24), as in the case of lactams [8] it may be that this radical is responsible for the formation of the products isolated, according to Scheme 3.

Thus the mechanism shown in Scheme 3 accounts for the formation of the acylureas (12a) and (12b) from the radical (8). This radical is trapped by oxygen to give the peroxy-radical (9) (Scheme 3), then the oxy-radical (10).

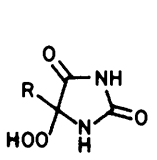


SCHEME 6

The postulated intermediates (8) and (9) may be generated independently by other methods. The radical (8) in the presence of oxygen and the radical (9) in the absence of oxygen yield the same products as the photochemical oxidation of 5-methylhydantoin (7a) and 5-phenylhydantoin (7b) in the presence of benzophenone.

Photolysis of 5-bromo-5-phenylhydantoin (27) prepared by bromination of 5-phenylhydantoin (7b) [9] gave, in the presence of oxygen, benzoylurea (12b). The first step is homolysis of the C–Br bond to give the radical (8) which is oxidized by oxygen to lead to the peroxy-radical (9). Decomposition of the latter gave the oxy-radical (10; R = Ph) then the radical (11; R = Ph). Benzoylurea (12b) and also 1-benzoyl-3-formylurea (28) came from the last product resulting from abstraction of a hydrogen atom at the solvent by the radical (11).

Photolysis, in the absence of oxygen, of 5-phenyl-5-t-butoxyhydantoin (29) prepared by the action of di-t-butylperoxide on 5-bromo-5-phenylhydantoin (27) according to Davies *et al.*,[10] also gave benzoylurea (12b). The first step is photochemical decomposition of the peroxide to give the oxy-radical (10). The allophanate (30) was also isolated, resulting from coupling of the radical (11) with the $Bu^tO^{\bullet}$ radical.



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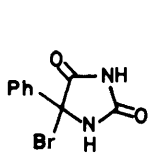

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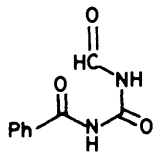

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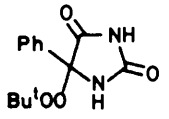

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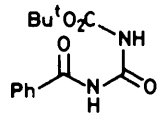

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EXPERIMENTAL

All melting points were determined using a Reichert hot-stage microscope. I.r. spectra were recorded on a Perkin-Elmer 377 spectrophotometer. ^1H N.m.r. spectra were measured with JEOL C 60 H or Perkin-Elmer R-24 instruments. ^{13}C N.m.r. spectra were measured with a JEOL FX 60 instrument. In both cases chemical shifts are quoted as δ values with $SiMe_4 = 0$.

Thin-layer chromatography and column chromatography were performed with Kieselgel 60 silica (Merck).

Photochemical reactions with benzophenone were performed in a Pyrex glass vessel using a high-pressure mercury lamp (Hanau 125 W). Photo-oxygenations were carried out in distilled Bu^tOH, the reaction mixture being thoroughly flushed with a stream of dry oxygen.

Direct irradiations of hydantoins were performed in a quartz glass vessel using a low-pressure mercury lamp (Hanau TNN 15/32). The reaction mixture was flushed with a stream of dry nitrogen to remove oxygen.

The following compounds were prepared according to literature procedures: 5-methylhydantoin (7a), m.p. 150—152 °C (lit.,[11] 149—151 °C); 3,5,5-trimethylhydantoin, m.p. 149—150 °C (lit.,[12] 148.5—149 °C); 5-bromo-5-phenylhydantoin (27), m.p. 212 °C (lit.,[9] 210 °C).

5-Phenylhydantoin (7b).—A solution of benzaldehyde cyanohydrin (30 g, 0.23 mol) and ammonium carbonate (43 g, 0.23 mol) in water (90 ml) was stirred for 1 h at 55 °C. It was then rapidly heated to boiling point after which it was chilled and filtered to afford the product (7b) (15 g, 40%), m.p. 179—180 °C (lit.,[13] 178 °C), $\nu_{max.}$ ($CHCl_3$) 3 440, 1 780, and 1 720 cm^{-1}; δ [$(CD_3)_2SO$] 5.1 (1 H, s), 7.3 (5 H, m, arom.), 8.4 (1 H, s, NH), and 10.5 (1 H, s, NH).

5-Phenyl-5-t-butylperoxyhydantoin (29).—Silver trifluoroacetate (2.65 g, 0.12 mol) was added in small portions to a stirred solution of t-butyl hydroperoxide [1.5 ml of a solution of t-butyl hydroperoxide (80%) in di-t-butyl peroxide] and 5-bromo-5-phenylhydantoin (27) (2.86 g, 0.12 mol) in tetrahydrofuran chilled in ice. The solution

was kept overnight at room temperature. Silver bromide was filtered off and washed with water and the filtrate was extracted with methylene dichloride. The extracts were combined and dried (Na_2SO_4) and the solvent removed to give compound (29) (2.4 g, 81%), m.p. 182—183 °C (Found: C, 59.15; H, 6.1; N, 10.7. $C_{13}H_{16}N_2O_4$ requires C, 59.08; H, 6.10; N, 10.60); $\nu_{max.}$ ($CHCl_3$) 3 430, 1 798, and 1 745 cm^{-1}; δ ($CDCl_3$) 1.3 (9 H, s, Bu^t), 7.5 (5 H, m, arom.), 9.2 (1 H, s, NH), and 11.2 (1 H, s, NH).

Photo-oxygenation of 2-Oxazolidone (1).—A solution of oxazolidone (1) (1 g) and benzophenone (1 g) in t-butyl alcohol (70 ml) flushed with a stream of dry oxygen was irradiated for 69 h at 330 nm. The reaction mixture was purified by column chromatography on silica gel. Elution with methylene dichloride afforded benzophenone (0.9 g) and oxazolidine-1,4 dione (4) (0.25 g, 30%); it was recrystallized from methylene dichloride–hexane, and had m.p. 85—86 °C (lit.,[14] 89—90 °C); $\nu_{max.}$ ($CHCl_3$) 3 430, 1 834, 1 796, and 1 766 cm^{-1}; δ [$(CD_3)_2SO$] 4.85 (2 H, s, CH_2O) and 7.45 (1 H, s, NH) (Found: C, 35.35; H, 2.55; N, 13.75. $C_3H_3NO_3$ requires C, 35.65; H, 2.99; N, 13.86).

Photo-oxygenation of Hydantoin (2).—A solution of hydantoin (2) (0.7 g) and benzophenone (1 g) in t-butyl alcohol (70 ml) was irradiated under oxygen for 73 h. The solvent was evaporated and the reaction mixture was purified by column chromatography on silica gel. Elution with methylene dichloride gave benzophenone (0.9 g) and elution with hexane–ethyl acetate (3 : 2) gave parabanic acid (5) (0.2 g, 88% based on starting material consumed); elution with ethyl acetate gave hydantoin (2) (0.5 g).

Photo-oxygenation of 1-Methylhydantoin (3).—A solution of 1-methylhydantoin (3) (1 g) and benzophenone (1 g) in t-butyl alcohol (70 ml) was irradiated under oxygen for 112 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel: elution with methylene dichloride gave benzophenone (0.85 g) and 1-methyl-5-oxohydantoin (6) (0.4 g, 51%), m.p. 131 °C (EtOH) (lit.,[15] 127—128 °C), δ [$(CD_3)_2SO$] 3.0 (3 H, s, CH_3) and 11.0 (1 H, s, NH); elution with ethyl acetate gave 1-methylhydantoin (3) (0.3 g).

Photo-oxygenation of 5-Methylhydantoin (7a).—A solution of 5-methylhydantoin (7a) (0.8 g) and benzophenone (1 g) in t-butyl alcohol (70 ml) was irradiated under oxygen for 69 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel: elution with methylene dichloride gave benzophenone (0.93 g) and elution with ethyl acetate gave acetylurea (12a) (0.15 g, 35%) identified by comparison with an authentic sample [16] and 5-methylhydantoin (7a) (0.3 g).

Photo-oxygenation of 5-phenylhydantoin (7b).—A solution of 5-phenylhydantoin (7b) (1 g) and benzophenone (3 g) in t-butyl alcohol (250 ml) was irradiated under oxygen for 70 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel; elution with methylene dichloride–hexane (1 : 1) gave benzopinacol (0.28 g) and benzophenone (2.23 g); elution with hexane–ethyl acetate (1 : 1) gave benzoylurea (12b) (0.42 g, 64%) identified by comparison with an authentic sample, m.p. 216 °C (lit.,[17] 215 °C).

Photo-oxygenation of 5-Bromo-5-phenylhydantoin (27).—A solution of 5-bromo-5-phenylhydantoin (27) (1 g) in t-butyl alcohol (70 ml) was irradiated under oxygen for 15 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel; elution with hexane–ethyl acetate (1 : 1) gave 1-benzoyl-3-formylurea (28) (0.25 g, 42%), m.p. 159 °C (EtOH), $\nu_{max.}$ (CCl_4) 3 600, 1 750, and 1 690 cm^{-1}; δ [$(CD_3)SO$] 7.8 (5 H, m), 9.15 (1 H, s, CHO), 10.6 (1 H, s, NH), and 11.0 (1 H, s, NH) (Found: C, 56.25; H, 4.25; N, 14.5. $C_9H_8N_2O_3$ requires C, 56.25; H, 4.17; N, 14.58) and benzoylurea (12b) identified by comparison with an authentic sample.

Irradiation of 5-Phenyl-5-t-butylperoxyhydantoin (29).—A solution of 5-phenyl-5-t-butylperoxyhydantoin (29) (1 g) in t-butyl alcohol (70 ml) was irradiated under oxygen for 2.5 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel; elution with hexane–ethyl acetate (1 : 1) gave t-butyl *N*-benzoylallophanate (30) (0.2 g, 40%), m.p. 153 °C (ether), $\nu_{max.}$ (CCl_4) 1 790, 1 765, 1 725, and 1 690 cm^{-1}; δ ($CDCl_3$) 1.5 (9 H, s, Bu^t), 7.8 (5 H, m), 10.0 (1 H, s, NH), and 10.2 (1 H, s, NH) (Found: C, 58.8; H, 5.95; N, 10.45. $C_{13}H_{16}N_2O_4$ requires C, 59.08; H, 6.10; N, 10.06) and benzoylurea (12b) identified by comparison with an authentic sample.

Photolysis of 5-Methylhydantoin (7a) *in Methanol.*—A solution of 5-methylhydantoin (7a) (0.6 g) in methanol (60 ml) flushed with a stream of dry nitrogen was irradiated (low-pressure mercury lamp) for 120 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel; elution with hexane–ethyl acetate (3 : 2) gave methyl *N*-ethylallophanate (18) (0.5 g, 20%), m.p. 90 °C (H_2O) [lit.,[18] 95 °C (H_2O)], $\nu_{max.}$ (CCl_4) 1 740 and 1 698 cm^{-1}; δ ($CDCl_3$) 1.2 (3 H, t, CH_3CH_2), 3.4 (2 H, q, CH_2CH_3), 3.8 (3 H, s, CO_2CH_3), 7.8 (1 H, s, NH), and 8.4 (1 H, s, $NHCO_2Me$).

Photolysis of 5,5-Dimethylhydantoin (13) *in Methanol.*—A solution of 5,5-dimethylhydantoin (13) (3 g) in methanol (250 ml) was irradiated (Philips 250 W) under nitrogen for 30 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel: elution with hexane–ethyl acetate (1 : 1) gave methyl *N*-isopropylallophanate (14a) (3.5 g, 93%), m.p. 70 °C (H_2O) (lit.,[18] 70 °C) $\nu_{max.}$ (CCl_4) 1 742 and 1 698 cm^{-1}; δ ($CDCl_3$) 1.25 (6 H, d), 3.4 [1 H, m, $CH(CH_3)_2$], 3.8 (3 H, s, CO_2CH_3), 7.8 (1 H, s, NH), and 8.4 (1 H, s, NH).

Photolysis of 5,5-Dimethylhydantoin (13) *in Water.*—A solution of 5,5-dimethylhydantoin (13) (1 g) in water (150 ml) was irradiated under nitrogen for 168 h. The solvent was evaporated and the reaction mixture purified by column chromatography: elution with hexane–ethyl acetate gave 1-isopropylurea (15) (0.250 g, 35%), m.p. 154—155 °C (AcOEt) (lit.,[18] 154 °C), $\nu_{max.}$ (CCl_4) 3 420 and 1 675 cm^{-1}; δ [$(CH_3)_2SO$] 1.05 (6 H, d), 3.55 [1 H, m, $CH(CH_3)_2$], 5.3 (1 H, s, NH_2), and 5.7 (1 H, s, NH).

Photolysis of 5,5-Dimethylhydantoin (13) *in t-Butyl Alcohol.*—A solution of 5,5-dimethylhydantoin (13) (1 g) in t-butyl alcohol (60 ml) was irradiated under nitrogen for 164 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel; elution with hexane–ethyl acetate (1 : 1) gave t-butyl *N*-isopropylallophanate (14b) (0.75 g, 59% based on starting material consumed), m.p. 120 °C (H_2O); $\nu_{max.}$ (CCl_4) 3 440, 1 730, and 1 690 cm^{-1}; δ ($CDCl_3$) 1.25 (6 H, d), 1.5 (9 H, s, Bu^t), 3.5 [1 H, m, $CH(CH_3)_2$], 7.8 (1 H, s, NH), and 8.1 (1 H, s, NH).

Photolysis of 5,5-Dimethylhydantoin (13) *in Acetonitrile–diethylamine.*—A solution of 5,5-dimethylhydantoin (13) (2 g) and diethylamine (1.14 g) in acetonitrile (250 ml) was irradiated (Philips 250 W) under nitrogen for 66 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel; elution with hexane–

ethyl acetate (1 : 1) gave 1-(*NN'*-diethylcarbamoyl)-3-isopropylurea (16) (0.5 g, 17%), m.p. 110 °C (H_2O), $\nu_{max.}$ (CCl_4) 1 680 and 1 650 cm^{-1}; δ ($CDCl_3$) 1.0 (12 H, m), 3.1 (4 H, q, CH_2CH_3), 3.7 [1 H, m, $CH(CH_3)_2$], and 8.1 (2 H, s, NH) (Found: C, 53.8; H, 9.35; N, 21.05. $C_9H_{19}N_3O_2$ requires C, 53.70; H, 9.52; N, 20.88).

Photolysis of 5,5-*Dimethylhydantoin* (13) *in Acetonitrile–n-Hexylamine*.—A solution of 5,5-dimethylhydantoin (13) (1 g) and n-hexylamine (0.8 g) in acetonitrile (150 ml) was irradiated (Philips 250 W) under nitrogen for 70 h. The solvent was evaporated and the reaction mixture purified by column chromatography on silica gel; elution with hexane–ethyl acetate (1 : 1) gave 1-n-hexylcarbamoyl-3-isopropylurea (17) (0.51 g, 29%), $\nu_{max.}$ (CCl_4) 1 680 cm^{-1}; δ ($CDCl_3$) 1.2 (17 H, m), 3.2 (2 H, m, CH_2NCO), 3.9 [1 H, m, $CH(CH_3)_2$], 7.1 (2 H, s, NH), and 9.2 (1 H, s, NH) (Found: C, 57.6; H, 10.05; N, 18.4. $C_{11}H_{23}N_3O_2$ requires C, 57.61; H, 10.11; N, 18.33).

N-(2-*Isocyanatoethyl*)-2-*pyrrolidone* (20).—(a) *N*-(2-*Methoxycarbonylethyl*)-2-*pyrrolidone*.[19] Methyl acrylate (15 g, 0.17 mol) was added dropwise to a solution of 2-pyrrolidone (15.5 g, 0.18 mol) and Triton B (1.05 ml) in dioxan (60 ml). The reaction mixture was stirred at room temperature for 72 h and then acidified. The solvent and unconsumed methyl acrylate were evaporated. The residue was distilled under reduced pressure to give the product (22 g, 72%), b.p. 90 °C at 0.5 mmHg, $\nu_{max.}$ (CCl_4) 1 740 and 1 702 cm^{-1}; δ ($CDCl_3$) 2.4 (6 H, m), 3.6 (4 H, m), and 3.75 (3 H, s, CO_2CH_3).

(b) *Hydrazide of* N-(2-*methoxycarbonylethyl*)-2-*pyrrolidone*.[16] An aqueous solution (98%) of hydrazine hydrate (10 ml, 0.02 mol) and absolute ethanol (2.5 ml) was gently refluxed. *N*-(Methoxycarbonylethyl)-2-pyrrolidone (1.71 g, 0.01 mol) was added dropwise (1—2 h) to the boiling stirred solution at such a rate that a separate liquid phase did not accumulate in the reaction mixture. The boiling was continued for 5 min after completion of the addition and the contents of the flask were then cooled to room temperature. The precipitate was filtered off and the crystals washed with absolute ethanol to give product (1.6 g, 94%), m.p. 100 °C, $\nu_{max.}$(CCl_4) 1 670 and 1 625 cm^{-1}; δ ($CDCl_3$) 2.4 (6 H, m) and 3.6 (7 H, m).

(c) *N-Chloropropionyl*-2-*pyrrolidone*.[7] A solution of the above hydrazide (3.2 g, 0.02 mol) dissolved in methylene dichloride (25 ml) was saturated with dry hydrogen chloride and then dry chlorine was passed into the mixture until the solid had been dissolved (1—2 h). After removal of the solvent, the product was distilled, $\nu_{max.}$ (CCl_4) 1 750 and 1 680 cm^{-1}.

(d) *N*-(2-*Isocyanatoethyl*)-2-*pyrrolidone* (20). Trimethyl silyl azide (0.854 g, 0.0076 mol) was added to a solution of acid chloride (1.2 g, 0.007 mol) in toluene (10 ml). The reaction mixture was refluxed for 20 h. The solvent was evaporated and the residue distilled under reduced pressure to give the product (0.6 g, 56%), b.p. 115 °C at 0.5 mmHg, $\nu_{max.}$ (CCl_4) 2 280 cm^{-1} (NCO).

Oxazolidin-2,5-*dione*.—This compound was prepared according to ref. 3, m.p. 100 °C (lit.,[3] 100 °C); δ [$(CD_3)_2SO$] 4.15 (2 H, s, CH_2N) and 8.65 (1 H, s, NH).

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