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The Chemistry of 5-Oxodihydroisoxazoles V[1]

The Photolysis Of 2-Phenylisoxazol-5(2H)-one In Alcohols

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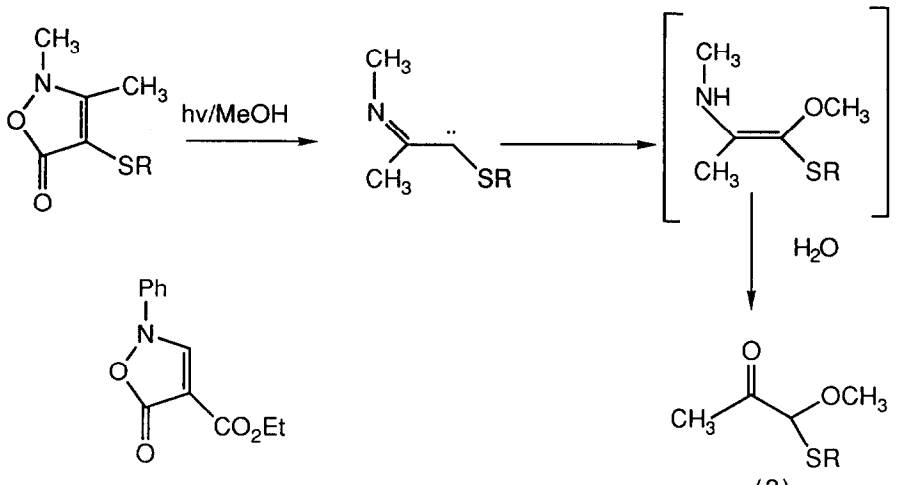
Abstract - Ethyl 5-oxo-2-phenyl-2,5-dihydroisoxazole-4-carboxylate(1) has been photolysed in methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, t-butyl alcohol, allyl alcohol and propargyl alcohol, and the products characterised. Two types of photo products are formed: methanetricarboxylic acid derivatives resulting from alcohol capture of the first formed ketene, and 2-alkoxy-3-phenylaminoacrylates, formed by capture, by the alcohol, of the imino-carbene arising from (1) by loss of carbon dioxide.

INTRODUCTION

In connection with our interest in the synthesis of possible muscle relaxants, we have reported the synthesis of a number of 2-arylisoxazol-5(2H)-ones,[2] and have noted that the compounds, both in the solid state and in solution, undergo facile light-induced transformations. We have begun a comprehensive study of such transformations,[3] which has delineated the two major photochemical pathways occurring, and has opened up some novel synthetic transformations. In this paper we report the photolysis of ethyl 5-oxo-2-phenyl-2,5-dihydroisoxazole-4-carboxylate(1) in a number of alcoholic solvents. This has allowed us to considerably extend the understanding of the photolysis of these systems, about which only a brief report by Sasaki and coworkers has appeared.[4] These workers photolysed methanolic solutions of a number of 2-methyl-4-substituted isoxazol-5-ones, substituted at C-4 with an alkylthio group, and found that carbon dioxide was lost. The formation of an intermediate imino-carbene was proposed, which was trapped by methanol to give the observed products (2).

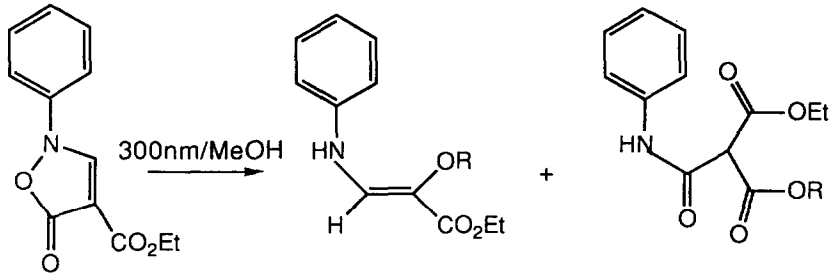


(1) (2)

The photolysis of isoxazolones bears an obvious similarity to that of triazoles,[5] and although no detailed study of these photolyses has been made, both diradical and carbene intermediates have been postulated.[6] In choosing, initially, to carry out the photolysis of (1) in alcoholic solvents, we hoped to establish whether carbene or diradical intermediates were involved, although our studies with isoxazolones substituted with heterocyclic groups on nitrogen showed no evidence for radical like intermediates.[7]

DISCUSSION

The photolysis of (1) in methanol occurs rapidly at both 254 and 300 nm, or in sunlight, but is very slow at 350 nm. Three products were isolated by chromatography, accounting essentially for all the material. The minor products were the (E) and (Z) isomers of the carbene-derived acrylate (3), involving loss of carbon dioxide and reaction with methanol, and the major product was the methanetricarboxylic acid derivative (4), in which all carbons of the isoxazolone were retained. In none of the examples reported below was there any 2- or 3-ethoxycarbonylindole formed, as has been found in the photolysis of triazoles.[8]

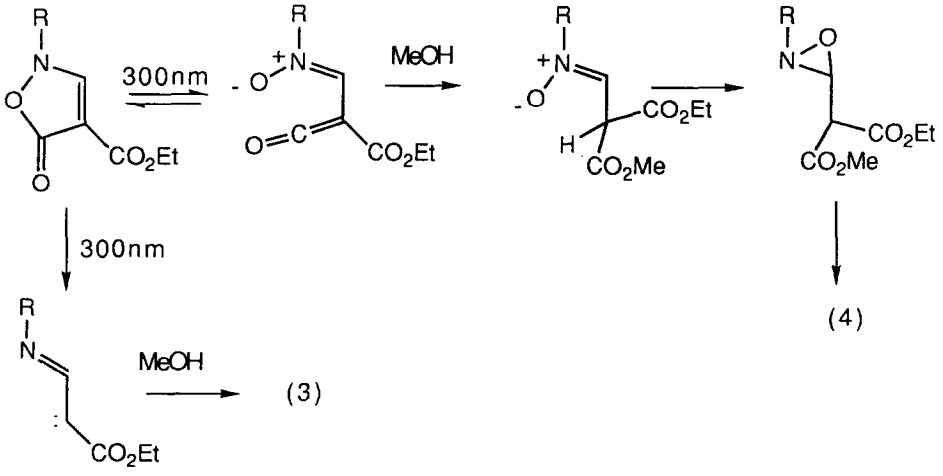


(1)

3a, R=Me; (E)+(Z) 34%
3b, R=Et
3c, R=1-Pr
3d, R=1-Bu
3e, R=2-Pr
3f, R=t-Bu
3g, R=$CH_2CH{=}CH_2$
3h, R=$CH_2C{\equiv}CH$

4a, R=Me; 61%
4b, R=Et
4c, R=1-Pr
4d, R=1-Bu
4e, R=2-Pr

Although the compound (4a) is that expected from the reaction of (1) with methoxide,[9,10] no such reaction occurred between (1) and methanol in the dark,[11,12] and there is no doubt that the formation of (4) is photochemically induced. We therefore propose that, as we have previously reported,[3] two competing photochemical pathways are in operation, and we have shown this to be quite general (Scheme 1).



Scheme 1

We suggest that the isomerisation of the isoxazolone(1) to the ketene is extremely rapid, and reversible. Capture of the ketene by a nucleophile, and subsequent photochemical[13-15] isomerisation of the nitrone to the amide, then gives (4). In the absence of efficient capture of the ketene, the slower but irreversible decomposition of the isoxazolone(1) to the carbene is established, leading ultimately to (3) This suggestion is based firstly on the observation that in the absence of nucelophiles, as in acetonitrile, the half life of the photolysis rose to 72 hours, contrasting with 15 minutes in methanol. Secondly, photolysis in other alcohols supported the hypothesis as shown in Table 1.

Table 1. Yields (%) of photolysis products from (1) in alcohols at 300nm

Alcohol	Carbene derived(3)[a]		Ketene derived(4)[a]	
(a) MeOH	34	(37[b])	61	(53[b])
(b) EtOH	0	(41[b])	100	(59[b])
(c) 1-PrOH	36	(46[b])	61	(39[b])
(d) 1-BuOH	24	(36[b])	71	(38[b])
(e) 2-PrOH	25		68	
(f) t-BuOH	66		0	
(g) CH_2=CH-CH_2OH	90[c]		0	
(h) CH C-CH_2OH	38		0	

[a] Yields refer to pure isolated compounds

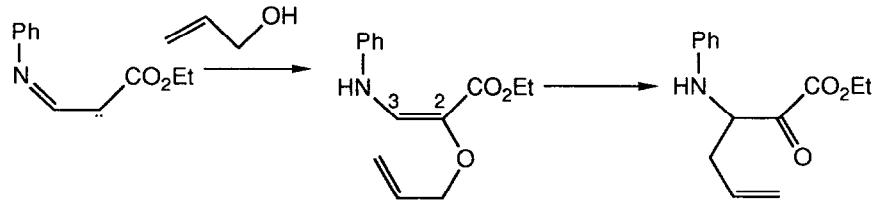
[b] Solvent contains trace of acid.

[c] Product rearranges to (5)

It became apparent that the product distribution was very sensitive to traces of acid: unless solvents were freshly distilled from sodium carbonate prior to use, traces of acid present caused an increase in the carbene derived products. Addition of 5% acetic acid to ethanol resulted in the formation of 41% of carbene products (3b), as well as the ketene product (4b) (HPLC analysis). Since the presence of small amount of pyridine led to exclusive formation of (4b), the nucleophilicity of the medium is clearly defining the product distribution. The choice of allyl alcohol and 2-propanol was suggested because they would readily act as hydrogen atom donors in the presence of any radical intermediates, such as a triplet carbene. The products from 2-propanol were entirely consistent with its reduced nucleophilicity towards the first formed ketene: no hydrogen abstraction could be detected. When the photolysis was carried out in acetone containing 2-propanol, the carbene products (3e) were increased from 25% to 39%. Photolysis of (1) in t-butyl alcohol neat, or in t-butyl alcohol in acetone, gave no ketene product (4f), but only the carbene product

(3f). Clearly, the reduced nucleophilicity of this alcohol prevents it from reacting rapidly with the ketene, thereby allowing carbene formation and capture. t-Butyl vinyl ethers are relatively uncommon, and their chemistry merits investigation.

Allyl alcohol is not only a weaker nucleophile than 1-propanol, but the carbene intermediate could react with the double bond to form a cyclopropane, with the hydroxyl group to form the vinyl ether, or insert into the allylic carbon-hydrogen bond. The only product isolated from the photolysis was ethyl 2-oxo-3-phenylaminohex-5-eneoate(5), which is derived from nucleophilic attack of the carbene by the hydroxyl group, followed by Claisen rearrangement (Scheme 2). No evidence for the ketene derived products or hydrogen abstraction could be found, nor could the presumed intermediate (6) for (5) be found.



(6) (5)

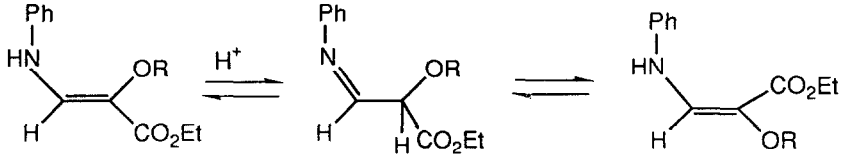
Scheme 2

Since Claisen rearrangements are usually induced by heat rather than light, the present extremely facile rearrangement presumably is facilitated by the electron withdrawing group at C-2, and the electron donating at C-3, as predicted by Carpenter[16] and Dewar[17]. Photolysis in propargyl alcohol led only to the formation of (3h), and no Claisen rearrangement of this product was observed.

The total absence of any cyclopropane (derived) products from the use of allyl and propargyl alcohols indicates that the iminocarbene is more reactive towards hydroxyl groups than double bonds. This is analogous to the observations of Ando[18,19] with diethoxycarbonyl carbene, derived from photolysis or pyrolysis of diazomalonate which reacts with sulphides more readily than with a double bond, and also of Ganem[20], who showed that this carbene reacts preferentially with an alcohol group in the presence of double bonds.

A number of structural features of the enamino esters (3) should be noted. The (E) and (Z) isomers in each series could be separated by chromatography, but the equilibrium was re-established over a few days at ambient temperature, or more rapidly in the presence of acid. Both isomers were fluorescent yellow oils (λ_{max} 316nm) except for (3f) the isomers of which were white (λ_{max} 250nm), in which case the t-butoxy group prevented adequate overlap of the enamine and ester groups in both isomers. The isomerisation of (3) presumably occurs via the imine (Scheme

3), but no spectroscopic evidence, by either ^1H or ^{13}C n.m.r. spectroscopy, for any significant concentration of this intermediate could be found.



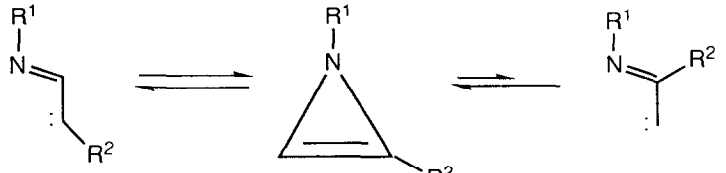
(Z) (E)

Scheme 3

Both the (E) and (Z) isomers showed strong coupling between the vinyl proton and the vicinal NH of 12-14Hz, characteristic of enamides[21]. Individual (E) and (Z) isomers were clearly recognisable by their ^{13}C and ^1H chemical shifts, but the assignment of the more stable isomer, characterised by the NH resonance at δ6.60 as the (Z) isomer was confirmed by 2D n.m.r. experiments, particularly NOESY, which showed through space interaction of the alkoxy group and the aromatic hydrogens of the N-phenyl group. In addition, molecular modelling ("PC Model")[22] predicts the (Z) isomer to be 0.81 kcal/mol more stable than the (E). Presumably the better conjugation of the (Z) isomer more than compensates for the better hydrogen bonding expected in the (E) isomer, characterised by the NH resonance at δ9.15.

The diester amides (4) appear to be largely in the non enolised form in chloroform, as guaged by the proton signal at δ4.55, and the carbon doublet at δ59.22. In addition, compound (4b) showed only two carbonyl resonances, δ159.99 (amide) and 165.78 (ester), which is inconsistent with an enolised system.

Finally, photolysis of some isoxazolones[7], and triazoles has in some instances[8] given rise to rearranged products, presumed to arise from the azirine (8) or the alternative carbene (9) derived from it. In the present studies no such products have been observed, presumably because the ethoxycarbonyl group stabilizes the carbene (7), possibly by about 11 kcal/mol.[8]



(7) (8) (9)

EXPERIMENTAL

Photolysis were carried out in 5 mM solutions under nitrogen at 300 nm in pyrex flasks or in an Oliphant carousel photochemical reactor (16 x 8 watt) at 25° in silica test tubes. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer as nujol mulls for solids, and liquid films for liquids. N.m.r. spectra were recorded on a Varian Gemini spectrometer at 300 MHz for ^1H, and 75.46 MHz for ^{13}C. Mass spectra

were recorded on a Kratos MS 25 spectrometer at 70 e.v. Ultraviolet spectra were recorded on a Hewlett Packard 8452A diode assay spectrophotometer. Chromatography employed a Chromatatron and Merck Kieselgel $60F_{254}$, and R_F values refer to the solvent system ether/light petroleum, 3:2. Analytical HPLC used a Waters instrument with a Spherisorb cyano column and U.V. detector. Melting points were obtained on a Reichert hot plate apparatus. Microanalyses were determined by the Australian Microanalytical Service, Melbourne.

Ethyl 5-oxo-2-phenyl-2,5-dihydroisoxazole-4-carboxylate(1). The literature procedure[23] was not entirely satisfactory, hence a modified procedure was used. Freshly prepared phenyl hydroxylamine[24](10.9g, 0.1mol) and diethyl ethoxymethylenemalonate(21.6g, 0.1mol) were refluxed in benzene(20ml) for 8h. Ether(10ml) was added and the resultant solution was allowed to cool for 10h. The crystals were collected and recrystallised from ethanol to afford colourless fine crystals(21.6g, 93%), m.p. 134-136°, (lit[23]; 133-134°).

Typical photolysis in methanol. The isoxazolone (1) (580mg, 0.25mmol) was dissolved in 500ml freshly distilled methanol, and photolysed at 300 nm. The progress of the reaction was monitored by silica t.l.c., and on consumption of starting material the solvent was removed and the product separated by radial chromatography on silica, using ether/light petroleum (3:2). The first fraction, R_F 0.94, was eluted as a yellow fluorescent oil which was identified as (E) ethyl 3-phenylamino-2-methoxypropenoate (3a)(13%). The analytical sample decomposed on transportation to Melbourne. (Found: C, 60.9; H, 6.8; N, 6.3; M^+ 221.1065. $C_{12}H_{15}NO_3$ requires C, 65.1; H, 6.3; N, 6.3%; 221.1052); ν_{max} 3312, 1739, 1631, 1600, 1520, 1026 cm^{-1}; δ_H 1.39 (3H, t, J 7Hz, $OCH_2\underline{CH_3}$), 3.65 (3H, s, OCH_3), 4.31 (2H, q, J 7Hz, $O\underline{CH_2}CH_3$), 6.80-7.90 (5H, m, ArH), 7.31 (1H, d, J 14Hz, C=CH), 9.07 (1H, d, J 14Hz, NH); δ_C 14.42 (CH_3), 60.03 (OCH_3), 62.14 (OCH_2), 114.79 (C-2'), 121.63 (C-4'), 125.85 (C-3), 129.53 (C-3'), 133.16 (C-2), 140.75 (C-1'), 166.92 (CO).

The second fraction, R_F 0.84, a yellow oil which decomposed on distillation at 95°/.05mm, was identified as (Z) ethyl 3-phenylamino-2-methoxypropenoate (21%). (Found: M^+ 221.1062. $C_{12}H_{15}NO_3$ requires 221.1052); ν_{max} 3323, 1692, 1600, 1551 cm^{-1}; δ_H 1.39 (3H, t, J 7Hz, $OCH_2\underline{CH_3}$), 3.65 (3H, s, OCH_3), 4.31 (2H, q, J 7Hz, $O\underline{CH_2}$-CH_3), 6.50 (1H, d, J 12Hz, NH), 6.80-7.90 (5H, m, ArH), 7.31 (1H, d, J 12Hz, C=CH); δ_C 14.52 (CH_3), 59.98 (OCH_3), 59.98 ($O\underline{CH_2}CH_3$), 114.54 (C-2'), 121.73 (C-4') 127.09 (C-2), 127.80 (C-3), 129.64 (C-3'), 140.53 (C-1'), 164.64 (CO).

The third fraction, R_F 0.60, was ethyl methyl phenylcarbamoylmalonate(4a) Crystallisation from benzene afforded white needles(61%), m.p. 144-146°. (Found: C, 58.9; H, 5.7; N, 4.6; M^+ 265.0939. $C_{13}H_{15}NO_5$ requires C, 58.8; H, 5.7; N, 5.2%; 265.0950;

ν_{max} 3302, 1753, 1661, 1451, 1138 cm^{-1}; δ_H 1.30 (3H, t, J 7Hz, $OCH_2\underline{C}H_3$), 3.79 (3H, s, OCH_3), 4.28 (2H, q, J 7Hz, $O\underline{C}H_2CH_3$), 4.55 (1H, s, CH), 6.80-7.70 (5H, m, ArH), 9.07 (1H, s, NH); δ_C 13.44 (CH_3), 52.93 (OCH_3), 59.22 ($\underline{C}HCO$), 62.36 ($O\underline{C}H_2CH_3$), 119.95 (C-2'), 124.49 (C-4'), 128.56 (C-3'), 137.01 (C-1'), 160.52 ($\underline{C}ONH$); 165.07 ($\underline{C}OCH_3$), 165.56 ($\underline{C}O_2Et$).

Photolysis in ethanol. Photolysis in ethanol, and chromatography as above, afforded colourless needles, m.p. 192-194°, R_F 0.57, of diethyl phenylcarbamoylmalonate (4b)(100%). (Found: C, 60.0; H, 5.7; N, 5.4; M^+ 279.1125. $C_{14}H_{17}NO_5$ requires C, 60.2; H, 6.1; N, 5.0%, 279.1107); ν_{max} 3302, 1753, 1661, 1451, 1153cm^{-1}; δ_H 1.32 (6H, t, J 7Hz, $OCH_2\underline{C}H_3$), 4.29 (4H, q, J 7Hz, OCH_2), 4.46 (1H, s, COCH), 7.14-7.59 (5H, m, ArH), 9.25 (1H, b s, NH); δ_C 13.96 (CH_3), 59.68 ($CO\underline{C}H$), 62.94 (OCH_2), 120.21 (C-2'), 124.88 (C-4'), 128.04 (C-3'), 137.25 (C-1'), 159.99 (CONH), 165.78 ($\underline{C}O_2CH_3$), 165.78 ($\underline{C}O_2CH_2CH_3$).

Photolysis in 1-propanol. Photolysis and isolation as above gave three compounds. The first, R_F 0.79, was (E) ethyl 3-phenylamino-2-propyloxypropenoate (3c)(13%), isolated as a yellow oil. (Found: M^+ 249.1352; $C_{14}H_{19}NO_3$ requires 249.1365); ν_{max} 3313, 1702, 1692, 1649, 1601 cm^{-1}; δ_H 0.97 (3H, t, J 6Hz, $(CH_2)_3\underline{C}H_3$), 1.32 (3H, t, J 7Hz, $OCH_2\underline{C}H_3$), 1.72 (2H, sextet, J 6Hz, $OCH_2\underline{C}H_2$), 3.70 (2H, t, J 6Hz, $O\underline{C}H_2CH_2$), 4.30 (2H, q, J 7Hz, $O\underline{C}H_2CH_3$), 6.90-7.40 (6H, m, ArH, C=CH), 9.05 (1H, d, J 13Hz, NH); δ_C 10.21 ($(CH_2)_2\underline{C}H_3$), 13.94 (CH_3), 22.94 ($OCH_2\underline{C}H_2$), 60.05 ($O\underline{C}H_2CH_3$), 76.85 (OCH_2), 121.71 (C-4'), 126.18 (C-3), 129.26 (C-3'), 134.46 (C-2), 140.76 (C-1'), 144.99 (C-2'), 166.96 (CO)

Fraction 2, R_F 0.69, was (Z) ethyl 3-phenylamino-2-propyloxypropenoate (3c)(23%), isolated as a yellow fluorescent oil which decomposed on distillation. (Found: M^+ 249.1379. $C_{14}H_{19}NO_3$ requires 249.1365); ν_{max} 3319, 1700, 1689, 1645 cm^{-1}; δ_H 1.05 (3H, t, J 6Hz, $O(CH_2)_2\underline{C}H_3$), 1.32 (3H, t, J 7Hz, $OCH_2\underline{C}H_3$), 1.72 (2H, sextet, J 6Hz,$OCH_2\underline{C}H_2$), 3.80 (2H, t, J 6Hz, $O\underline{C}H_2CH_2$), 4.20 (2H, q, J 7Hz, $O\underline{C}H_2CH_3$), 6.71 (1H, d, J 13Hz, NH), 6.90-7.40 (5H, m, ArH), 7.60 (1H, d, J 13Hz, C=CH); δ_C 10.59 ($(CH_2)_2\underline{C}H_3$), 14.74 (CH_3), 23.31 ($OCH_2\underline{C}H_2$), 59.94 ($O\underline{C}H_2CH_3$), 74.21 ($O\underline{C}H_2CH_2$), 114.79 (C-2'), 121.64 (C-4'), 128.05 (C-3), 128.61 (C-2), 129.67 (C-3'), 140.76 (C-1'), 164.84 (CO).

Fraction 3, m.p. 132-134°, R_F 0.60, was ethyl propyl phenylcarbamoylmalonate (4c) (61%). (Found: C, 61.6; H, 6.5; N, 5.1; M^+ 293.1231. $C_{15}H_{19}NO_5$ requires C, 61.4; H, 6.5; N, 4.7%; 293.1263); ν_{max} 3302, 1753, 1661, 1451, cm^{-1}; δ_H 0.95 (3H, t, J 6Hz, $(CH_2)_3CH_3$), 1.30 (3H, t, J 7Hz, $OCH_2\underline{C}H_3$), 1.70 (2H, sextet, J 6Hz, $OCH_2\underline{C}H_2$), 4.22 (4H, m), 4.50 (1H, s, COCH), 7.10-7.60 (5H, m, ArH), 9.37 (1H, s, NH); δ_C 10.22 ($(CH_2)_2\underline{C}H_3$), 13.96 ($OCH_2\underline{C}H_3$), 21.79 ($OCH_2\underline{C}H_2$), 59.68 ($CO\underline{C}H$), 62.94 ($O\underline{C}H_2CH_3$), 68.39 (OCH_2), 120.22 (C-2'), 124.84 (C-4'), 129.03 (C-3'), 137.27 (C-1'), 160.04 ($\underline{C}ONH$), 165.81 ($\underline{C}O_2CH_2$), 168.85 ($\underline{C}O_2CH_2CH_3$).

Photolysis 1-butanol. Photolysis in freshly distilled butanol gave three products. The first, R_F 0.75, was (E) ethyl 2-butoxy-3-phenylaminopropenoate(3d)(8%), isolated as a yellow oil which decomposed on distillation. (Found: M^+ 263.1520. $C_{15}H_{21}NO_3$ requires 263.1521); ν_{max} 3313, 1702, 1692, 1649, 1601 cm^{-1}; δ_H 0.97 (3H, t, J 6Hz,$(CH_2)_3\underline{CH_3}$), 1.32 (3H t, J 7Hz, $OCH_2\underline{CH_3}$), 1.49 (2H, sext, J 6Hz, $(CH_2)_2\underline{CH_2}$), 1.72 (2H, quint, J 6Hz, $OCH_2\underline{CH_2}$), 3.72 (2H, t, J 6Hz, $O\underline{CH_2}CH_2$), 4.35 (2H, q, J 7Hz, $O\underline{CH_2}CH_3$), 6.90-7.40 (6 H, m, ArH, C=CH), 9.23 (1H, d, J 13Hz, NH); δ_C 13.66 ($(CH_2)_3\underline{CH_3}$), 14.45 ($CH_2\underline{CH_3}$), 18.97 ($(CH_2)_2\underline{CH_2}$), 31.76 ($OCH_2\underline{CH_2}$), 60.06 ($O\underline{CH_2}CH_3$), 75.06 ($O\underline{CH_2}CH_2$), 115.01 (C-2'), 121.64 (C-4'), 126.27 (C-3), 129.69 (C-3'), 134.47 (C-2), 140.71 (C-1'), 166.39 (CO).

The second, R_F 0.68, was (Z) ethyl 2-butoxy-3-phenylaminopropenoate(3d)(16%), isolated as a yellow oil. (Found: C, 68.0; H, 7.6; N, 5.5; M^+ 263.1525. $C_{15}H_{21}NO_3$ requires C, 68.4; H, 8.0; N, 5.3; 263.1521). ν_{max} 3313, 1702, 1692, 1649, 1601 cm^{-1}; δ_H 0.97 (3H, t, J 6Hz, $(CH_2)_3\underline{CH_3}$), 1.32 (3H, t, J 7Hz, $OCH_2\underline{CH_3}$), 1.49 (2H, sextet, J 6Hz, $(CH_2)_2\underline{CH_2}$), 1.72 (2H, quint, J 6Hz, $OCH_2\underline{CH_2}$), 3.89 (2H, t, J 6Hz, $O\underline{CH_2}CH_2$), 4.22 (2H, q, J 7Hz, $O\underline{CH_2}CH_3$), 6.61 (1H, d, J 13 Hz, NH), 6.90-7.40 (5H, m, ArH), 7.60 (1H, d, J 13Hz, C=CH); δ_c 13.89 ($(CH_2)_3\underline{CH_3}$), 14.55 ($CH_2\underline{CH_3}$, 19.33 ($(CH_2)_2\underline{CH_2}$), 32.14 ($OCH_2\underline{CH_2}$), 59.96 ($O\underline{CH_2}CH_3$), 72.27 ($O\underline{CH_2}CH_2$), 114.77 (C-2'), 121.68 (C-4'), 124.06 (C-2), 127.99 (C-3), 129.69 (C-3'), 140.71 (C-1'), 164.83 (CO).

The third fraction, R_F 0.60, butyl ethyl phenylcarbamoylmalonate(4d), (71%), was isolated as a colourless gum which decomposed on purification.(Found: M^+ 307.1412. $C_{16}H_{21}NO_5$ requires 307.1419); ν_{max} 3302, 1753, 1661, 1451, 1153 cm^{-1}; δ_H 0.91 (3H, t, J 6Hz,$(CH_2)_3\underline{CH_3}$), 1.30 (3H, t, J 7Hz, $OCH_2\underline{CH_3}$), 1.49 (2H, sextet, J 6Hz, $(CH_2)_2\underline{CH_2}$), 1.65 (2H, quint , J 6Hz, $OCH_2\underline{CH_2}$), 4.28 (4 H, m, $O\underline{CH_2}CH_3$,OCH_2), 4.48 (1H, s, COCH), 7.10-9.9 (5H, m, ArH), 9.37 (1H, s, NH); δ_c13.59 ($(CH_2)_3\underline{CH_3}$), 13.95 ($OCH_2\underline{CH_3}$), 18.94 ($O(CH_2)_2\underline{CH_2}$), 30.35 ($OCH_2\underline{CH_2}$), 59.68 (CO<u>C</u>H), 62.94 ($O\underline{CH_2}CH_3$) 66.73($O\underline{CH_2}CH_2$), 120.21 (C-2'), 124.87 (C-4'), 129.02 (C-3'), 137.24 (C-1'), 159.98 ($\underline{C}O_2CH_3$), 165.81 (CONH), 165.86 ($\underline{C}O_2CH_2CH_3$).

Photolysis in 2-propanol. Photolysis as above, gave three compounds.
Fraction 1, R_F 0.91, was isolated as a yellow gum, and was identified as (E) ethyl 3-phenylamino-2-(2-propyloxy)propenoate(3e) (10%). (Found: M^+ 249.1338. $C_{14}H_{19}NO_3$ requires 249.1365); ν_{max} 3351, 1732, 1678, 1628, 1599, 1506 cm^{-1}; δ_H 1.12 (3H, t, J 7Hz,$OCH_2\underline{CH_3}$), 1.20 (6H, d, J 6Hz, CH_3), 3.80 (1H, sept, J 6Hz, OCH), 4.12 (2H, q, J 7Hz, OCH_2), 7.28 (1H, d, J 14Hz, C=CH), 6.50-7.40 (5H, m, ArH), 9.07 (1H, d, J 14Hz, NH); δ_C 14.42 ($CH_2\underline{CH_3}$), 21.89 (CH_3), 60.03 (OCH_2), 75.52 (OCH), 115.07 (C-2'), 121.73 (C-4'), 122.54 (C-3), 129.64 (C-3'), 135.04 (C-1), 140.82 (C-1'), 166.92 (CO).

The second fraction, R_F 0.84, was isolated as a yellow oil, and identified as (Z) ethyl 3-phenylamino-2-(2-propyloxy)propenoate(3e)(15%). (Found: M^+ 249.1373. $C_{14}H_{19}NO_3$ requires 249.1365); ν_{max} 3351, 1732, 1678, 1599, 1506 cm^{-1}; δ_H 1.10 (3H, t, J 7Hz, $OCH_2\underline{CH_3}$), 1.12 (6H, d, J 4Hz, CH_3), 4.10 (1H, sept, J 4Hz, OCH), 4.10 (2H, q, J 7Hz, OCH_2), 6.20 (1H, d, J 14Hz, NH), 7.45 (1H, d, J 14Hz, C=CH), 6.40-7.40 (5H, m).

The third fraction, R_F 0.44, was isolated as colourless needles, and identified as ethyl 2-propyl phenylcarbamoylmalonate(4e)(68%), m.p. 88-92°. (Found: C, 61.5; H, 6.2; N, 5.9; M^+ 293.1245. $C_{15}H_{19}NO_5$ requires C, 61.4; H, 6.5; N, 4.7%; 293.1263); ν_{max} 3351, 1732, 1678, 1628, 1599, 1506 cm^{-1}; δ_H 1.10 (3H, t, J 7Hz, $OCH_2\underline{CH_3}$), 1.12 (6H, d, J 4Hz, CH_3), 4.10 (1H, sept, J 4Hz, CH), 4.10 (2H, q, J 7Hz, OCH_2), 6.40-7.40 (5H, m, ArH), 9.01 (1H, b s, NH); δ_C 13.82 ($CH_2\underline{CH_3}$), 21.40 (CH_3), 62.68 (OCH_2), 62.68 ($CO\underline{C}H$), 70.86 (OCH), 120.00 (C-2'), 124.71 (C-4'), 128.88 (C-3'), 137.67 (C-1'), 160.83 (CONH), 165.18 ($\underline{C}O_2iPr$), 165.56 ($\underline{C}O_2Et$).

Photolysis in t-butyl alcohol. Two products were isolated by chromatography. Fraction 1, R_F 0.94, (20%), was isolated as colourless crystals, m.p. 47-51°, and identified as (E) ethyl 2-t-butoxy-3-phenylaminopropenoate(3f), (Found: M^+ 263.1567. $C_{15}H_{21}NO_3$ requires 263.1521); ν_{max} 3321, 1668, 1653, 1599, 1225, 1776 cm^{-1}; δ_H 1.12 (3H, t, J 7Hz, $CH_2\underline{CH_3}$), 1.20 (9H, s, CH_3), 4.12 (2H, q, J 7Hz, OCH_2), 6.61-7.72 (6H, m, ArH, C=CH), 9.25 (1H, d, J 12Hz, NH); δ_C14.31 ($CH_2\underline{CH_3}$), 27.96 (CH_3), 59.87 (OCH_2), 79.04(C-O), 114.96 (C-2'), 121.68 (C-4'), 122.00 (C-3), 129.64 (C-3'), 136.79 (C-2), 140.80 (C-1'), 168.87 (CO).

Fraction 2, R_F 0.84, (46%), was (Z) ethyl 2-t-butoxy-3-phenylaminopropenoate (3f) and was recrystallised from t-butyl methyl ether to give colourless crystals, m.p. 68-70°. (Found: C, 68.5; H, 7.7; N, 5.3; M^+ 263.1504. $C_{15}H_{21}NO_3$ requires C, 68.4; H, 8.0; N, 5.3%; 263.1521); ν_{max} 3331, 1702, 1643, 1599 cm^{-1}; δ_H 1.10 (3H, t, J 7Hz, $CH_2\underline{CH_3}$), 1.12 (9H, s, CH_3), 4.10 (2H, q, J 7Hz, OCH_2), 7.25 (1H, d, J 12Hz, C=CH), 6.61-7.72 (6H, m, ArH, NH); δ_C 12.63 ($CH_2\underline{CH_3}$), 28.71 (CH_3), 59.81 (OCH_2), 80.78 (C-O), 114.53 (C-2'), 121.46 (C-4'), 122.44 (C-2), 129.54 (C-3'), 130.35 (C-3), 140.42 (C-1'), 166.48 ($C\underline{O}$).

Photolysis in allyl alcohol. Only one pure product could be isolated after photolysis in a mixture of dioxan/allyl alcohol (10:1). The product was isolated as a yellow oil(90%) and identified as ethyl 2-oxo-3-phenylamino hex-5-eneoate(5) (Found: M^+, 246.1083. $C_{14}H_{17}NO_3$ requires 246.1085); ν_{max} 3361, 1722, 1643, 1599, 1496 cm^{-1}; δ_H 1.29 (3H, t J 7Hz, $OCH_2\underline{CH_3}$), 2.69 (2H, m, CH_2CH), 4.20 (1H, m), 4.25 (2H, q, J 7Hz, OCH_2), 4.60-6.45 (3H, m, $CH=CH_2$), 6.50-7.40 (6H, m, ArH, NH); δ_C 13.82 ($CH_2\underline{CH_3}$), 35.54 ($\underline{C}H_2CH$), 58.95 (CH-N), 62.51 (OCH_2), 113.72 (C-2'), 118.70 (C-4'), 119.46 ($\underline{C}H_2=C$), 129.32 (C-3'), 132.03 ($CH_2=\underline{C}H$), 145.95 (C-1'), 161.50 ($\underline{C}O_2$), 194.76 (CO).

Photolysis in propargyl alcohol. Only one pure product could be isolated, after photolysis in a mixture of dioxan/propargyl alcohol (10:1), R_F 0.94, (E) ethyl 3-phenylamino-2-(prop-2-ynoxy)propenoate(3h), 38%, a pale yellow viscous fluorescent oil which decomposed on standing.
(Found: M^+ 245.1050. $C_{14}H_{15}NO_3$ requires 245.1052). ν_{max}3320, 1721, 1681, 1630, 1600, 1500, cm^{-1}. δ_H 1.39 (3H, t, J 7Hz, $OCH_2\underline{C}H_3$), 2.50 (1H, t,J 3Hz,CH), 4.30 (2H, q, J 7Hz, $O\underline{C}H_2CH_3$), 4.82 (2H, d,J 3Hz, OCH_2C), 6.40-7.40 (m,5H,ArH,NH), 7.65 (1H, d, J 14Hz,C=CH); δ_C 14.72 ($OCH_2\underline{C}H_3$), 59.38 ($O\underline{C}H_2C$), 60.84 ($O\underline{C}H_2CH_3$), 75.09 ($\underline{C}$=CH), 79.75 (C=$\underline{C}$H), 114.91 (C-2'), 121.90 (C-4'), 124.50 (C-3), 129.64 (C-3'), 134.56 (C-2), 140.48 (C-1'), 164.37 ($\underline{C}$O).

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