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Triplet Lifetimes, Solvent, and Intramolecular Capture of Isoxazolones

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The first step in the photochemical decarboxylation of isoxazolones is the formation of the triplet state of the isoxazolone. We present evidence for the first time from flash laser photolysis of the lifetime of such species, and examples of their capture by solvent and by intramolecular cycloaddition.

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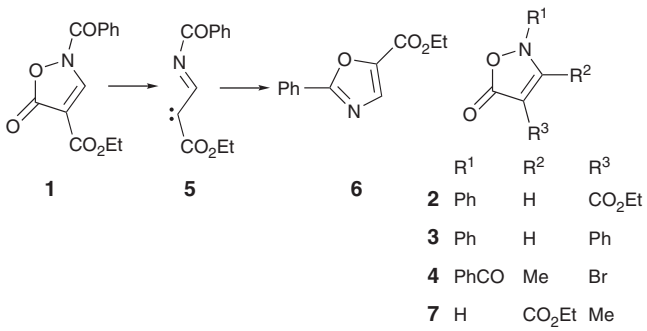
Introduction

For some years we have concentrated our attention on the synthetic possibilities built into isoxazolones. These are basically of two types: base-induced reactions,[1–7] which lead to the formation of a ketenimine that may be trapped intra- or intermolecularly by nucleophiles, or reaction of carbenes, generated from the isoxazolone by photochemical[8–13] or thermal means.[8,14,15] We have reported that there is a cascade of transformations that leads from the isoxazolone to the key singlet carbene intermediate in the latter reactions,[16] and have presented evidence that the triplet isoxazolone and carbene are important in this process.[17] However, we have not previously had evidence for the triplet state of the initial isoxazolone itself. In this paper we present kinetic evidence for such species, and report the isolation of several products derived directly from them.

Discussion

Since we had considerable evidence from product composition of isoxazolone photolyses that their reactivity and rate of reaction is highly substituent-dependent, we initially examined the representative group of isoxazolones **1**–**4**, Scheme 1, by laser flash photolysis (LFP), hoping to observe evidence for the intermediate carbene, for example **5**. LFP of **1** in acetonitrile (Fig. 1) led to the formation ($k = 4.6 \pm 0.6 \times 10^7$ s^{-1} at 25°C) and decomposition ($k = 2.73 \pm 0.06 \times 10^6$ s^{-1}) of the triplet state of the isoxazolone itself. The rise time matches that expected, given the pulse duration of the laser used and the response time of the detector. Support for the multiplicity of the species was obtained by addition of the triplet quencher, 9-methylanthracene, which resulted in immediate disappearance of the signal. While we were unable to detect the carbenoid species **5** under these conditions, we nonetheless isolated the derived oxazole product **6**[13] from the photolysis mixture. LFP of the isoxazolones **2** and **3** gave species with similar lifetimes to that of **1**; that of the bromo compound **4** showed a considerably longer lifetime, but clearly several species were now involved and it was not possible to find detection wavelengths which would allow deconvolution of the rise and fall of species involved. While these measurements are clearly of a preliminary nature, they are relevant as they support our interpretation of the formation and reaction of the isoxazolone in its triplet excited state.



Scheme 1.

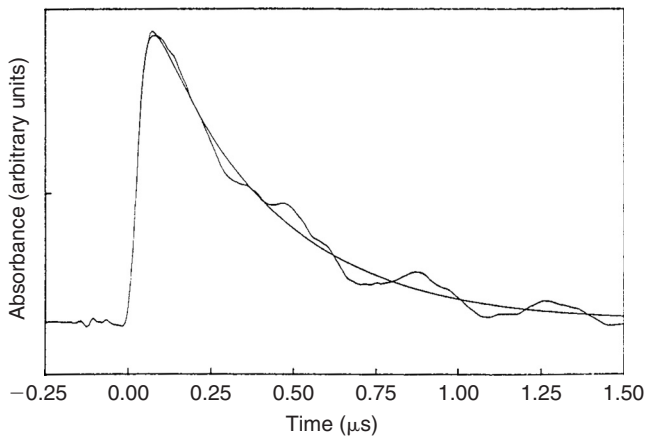


Fig. 1. Laser flash photolysis of **2**. The smooth curve is a fit to the experimental trace.

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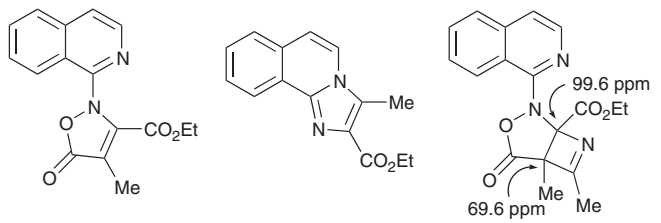
We had noticed that the product composition from isoxazolones derived from the 3-ester **7**, as from the corresponding 1,2,3-triazoles,[18] was routinely the most complex, which suggested that with this substitution pattern, intermediate lifetimes were longer and more comparable, so several derivatives have been studied in more detail. Treatment of 1-chloroisoquinoline with ethyl 4-methyl-2,5-dihydroisoxazole-3-carboxylate **7**, gave the isoxazolone **8**, Scheme 2, photolysis of which in acetonitrile at 300 nm gave in low yield the carbene cyclization product **9** (13%), together with the solvent capture product **10** (75%). While such [2 + 2]-cyclizations might be expected, we have not observed them with other substitution patterns. The regioselectivity was attested to by the ^{13}C NMR spectrum of **10**, in which C-3 of the isoxazolone resonated at 99.6 ppm and C-4 at 69.6 ppm. The methylene group of the ester resonated as two doublets of quartets, as expected for their diastereotopic nature.

In order to obtain a better source of the imidazoisoquinoline **9** for confirmation of structure, the isoxazolone **8** was subjected to pyrolysis under varying conditions. Attempted flash vacuum pyrolysis (FVP) was unsatisfactory, as **8** underwent considerable decomposition in the sublimation oven at only 130°C. While the small amount of material that did sublime through to the pyrolysis furnace provided us with the authentic sample of **9** for comparison, the partly decomposed material in the sublimation furnace contained the pyrimidine **11** and not the imidazole **9**. Pyrimidine **11** arises from an alternative thermal pathway involving isomerization of the isoxazolone to the imidoylketene, cyclization and deoxygenation of which (Scheme 3) gives **11**. Such pathways have been observed previously.[11]



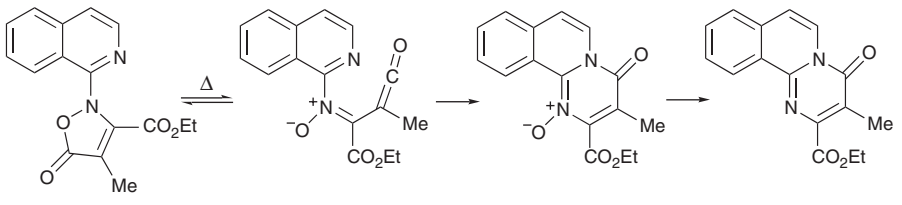
8 **9** **10**

Scheme 2.

We have previously reported[19] that the *N*-vinyl compound **12**, Scheme 4, when photolyzed in acetone or acetonitrile at 300 nm gave the carbene adducts **13** and **14**. We have re-examined these products, and find they are actually the [2 + 2]-cycloaddition products **15** and **16**. Their composition was confirmed by mass spectrometry and infrared spectroscopy (presence of the saturated lactone stretch at 1798 cm^{-1}). The regiochemistry of the addition in **15** was supported by the chemical shift of C-3 at 111.3 ppm; the relevant shifts in **16** were similar to those in **10**. The acetone acts as a sensitizer for the formation of triplet states in the photolysis of **12**, leading to higher yields of **15** than of **16**.

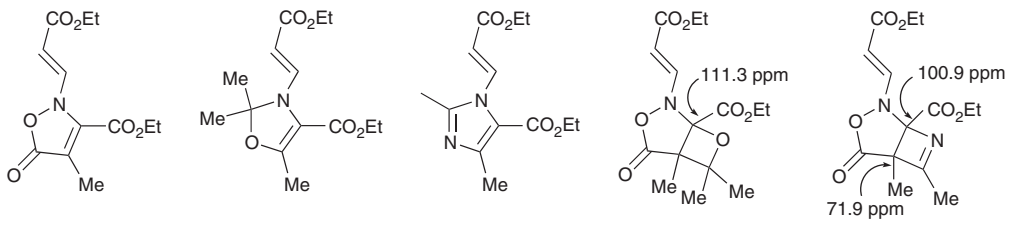
Since the lifetime of the isoxazolone triplet state in these systems appeared sufficient to allow reactions in competition with decarboxlation to the carbene, we sought an intramolecular example to test this hypothesis. The conjugated ester **17**, Scheme 5, appeared to be the ideal model,[20] and was synthesized in two steps by treating the isoxazolone **7** with acrolein, which yielded the *N*-alkylated product **18** (29%) and the *C*-alkylated product **19** (41%). The aldehyde **18** was treated with ethoxycarbonylmethylenetriphenylphosphorane at 25°C to yield **17**. While **17** decomposed under pyrolytic conditions, photolysis at 300 nm in acetone gave the intramolecular [2 + 2]-cyclization product **20** as the sole isolable material. NMR spectroscopy showed the presence of only a single diastereomer, the relative stereochemistry and connectivity of which was deduced by two-dimensional NMR studies (Table 1). In particular, the observation of nuclear Overhauser effect interactions between H_F and H_D and between H_E and H_C confirms the stereochemistry of the cyclobutane ring. It is interesting that the intramolecular cycloaddition occurs to the total exclusion of reaction with the solvent.

While [2 + 2]-cycloadditions are generally believed to proceed by a stepwise pathway involving triplet biradical



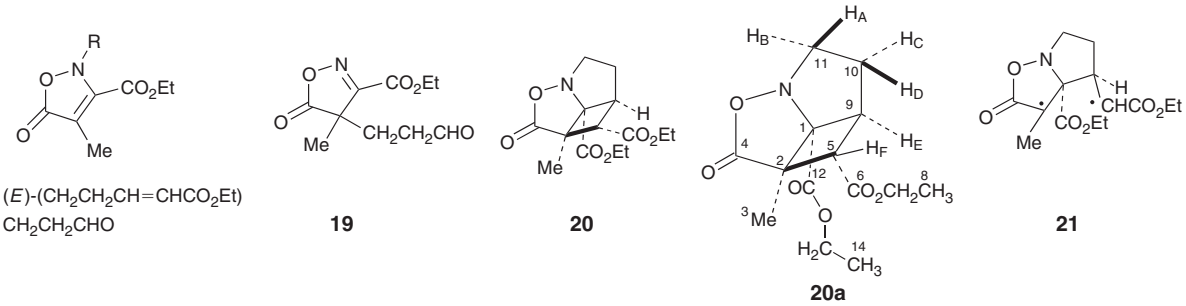
8 **11**

Scheme 3.



12 **13** **14** **15** **16**

Scheme 4.



Scheme 5.

Table 1. NMR correlations for compound 20a

Atom[A]	δ_C [ppm]	δ_H [ppm]	HMBC	COSY	ROESY
C-1	80.0		C-1 → H_A, H_E, H_F, H_D, H-3		
C-2	48.6		C-2 → H_E, H_F, H-3		
C-3	14.1	1.38	C-3 → H_F		
C-4	177.1		C-4 → H_F, H-3		
C-5	47.5	(H_F) 2.85	C-5 → H_E, H_C, H_F, H_D, H-3	H_F → H_E	H_F → H_D, H-8
C-6	170.0		C-6 → H_E, H_F, H_D, H-7		
C-7	61.5	4.26	C-7 → H-8	H-7 → H-8	H-7 → H-8
C-8	14.2	1.29	C-8 → H-7	H-8 → H-7	H-8 → H-7
C-9	39.2	(H_E) 3.60	C-9 → H_A, H_B, H_E, H_C, H_D, H-3	H_E → H_C, H_D, H_F	H_E → H_C
C-10	31.3	(H_C) 2.40	C-10 → H_E, H_B, H_F	H_C → H_A, H_B, H_E, H_D	H_C → H_B, H_E, H_D
C-10	31.3	(H_D) 2.04	C-10 → H_E, H_B, H_F	H_D → H_A, H_B, H_E, H_C	H_D → H_A, H_F, H_C
C-11	61.5	(H_A) 3.75	C-11 → H_E, H_D	H_A → H_B, H_C, H_D	H_A → H_B, H_D
C-11	61.5	(H_B) 3.30	C-11 → H_E, H_D	H_B → H_A, H_C, H_D	H_B → H_A, H_C
C-12	167.1		C-12 → H_E, H-13		
C-13	62.1	4.22	C-13 → H-14	H-13 → H-14	H-13 → H-14
C-14	14.2	1.30	C-14 → H-13	H-14 → H-13	H-14 → H-13

[A] Arbitrary numbering; see **20a**.

intermediates,[21] the stereospecificity in this case would appear to preclude such a pathway. Nonetheless, the regiochemistry of the addition leading to **20** is that expected from the observation that the major product in such reactions arises from initial addition of the biradical in a manner that leads to the formation of a five-membered ring, if possible,[22] as shown in **21**.

Conclusions

The presence of an ethoxycarbonyl group at C-3 of an isoxazolone ring increases the lifetime of its triplet state to allow [2 + 2]-cycloaddition reactions either intermolecularly with molecules containing polar multiple bonds, or intramolecularly with carbon–carbon double bonds. The presence of the easily reducible N—O bond suggests these products may have some synthetic interest.

Experimental

All solvents used were freshly distilled and dried according to the methods of Perrin and Amarego.[23] Melting points were determined on a Reichert hot stage microscope and are uncorrected. ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR measurements were recorded on a Gemini Varian 300 spectrometer in deuteriochloroform using tetramethylsilane for calibration, unless otherwise stated. 2D NMR spectra were determined on a Varian Unity 600 MHz spectrometer, using the pulse sequences gHMBC, gHMQC, gCOSY, ROESY, and TOCSY. Infrared spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrophotometer, using fused sodium chloride cells, measured as Nujol mulls or films. Mass spectra and high resolution mass spectra were recorded on a Kratos MS25RF spectrometer. Microanalyses were performed by Chemical & Micro Analytical Services, Melbourne. FVP studies were carried out by slowly subliming the substrate through a silica tube (400 mm × 25 mm), packed with silica chips, and heated to the quoted temperature under reduced pressure. The products were collected in a liquid nitrogen cold trap. Photolyses were performed under nitrogen using a Hanovia mercury medium pressure arc source filtered through pyrex, to give an irradiation source considered to be nominally 300 nm and above. Compounds **1**,[24] **2**,[25] **3**,[26] **4**,[13] and **7**[27] were available from previous work.

Laser Flash Photolysis

A solution of the isoxazolone in distilled acetonitrile was flowed continuously through a quartz cuvette which was irradiated with the output of a XeCl excimer laser (308 nm; pulse duration approx. 20 ns; pulse energy approx. 50 mJ). The excimer pulse initiates the photophysical or photochemical process of interest. A continuous-wave argon ion laser operating at 488 nm provided the probe beam. The probe beam was split into two beams before the sample cell to create a signal and reference beam. The signal beam entered the solution orthogonal to the XeCl pulse. The signal and reference beam intensities were monitored by photodiodes, and the signals subtracted in a differential amplifier to yield the transient absorption signal. This signal was observed on a digital oscilloscope (HP54510), averaged, and downloaded to a computer for analysis and curve fitting. The curves were fitted to a bi-exponential to determine rise and decay times. Oscillations in the experimental traces are an artifact of the differential amplifier, and do not affect the measured rate constants.

*Ethyl 2-(Isoquinolin-1-yl)-4-methyl-5-oxo-2,5-dihydroisoxazole-3-carboxylate **8***

A mixture of the ethyl 4-methyl-5-oxo-1,5-dihydroisoxazole-3-carboxylate **7** (960 mg, 5.6 mmol) and 1-chloroquinoline (1 g, 5.6 mmol)

was refluxed in dichloroethane (20 mL) for 7 h. The solvent was removed, and the product passed through a plug of silica with dichloromethane to give a cream solid which was recrystallized from methyl *t*-butyl ether to give **8** as fine colourless needles, mp 125–127°C (90%). (Found: C 64.5, H 4.8, N 9.4%. $C_{16}H_{14}N_2O_4$ requires C 64.4, H 4.7, N 9.4%). δ_H 8.53 (1H, dd, *J* 8, 1), 8.19 (1H, d, *J* 5.6), 7.84 (1H, dd, *J* 8, 1), 7.71 (2H, dt, *J* 10, 1), 7.63 (1H, d, *J* 5.6), 4.26 (2H, q, *J* 7), 2.26 (3H, s), 1.11 (3H, t, *J* 7). δ_C 170.8, 159.0, 151.6, 151.4, 140.1, 137.9, 131.1, 128.3, 126.5, 125.1, 123.5, 122.2, 113.3, 61.9, 13.6, 8.1. ν_{max}/cm^{-1} 1770, 1740, 1252, 1240, 1076, 846, 757, 738. *m/z* 298 (M^+, 43%), 254 (27), 209 (16), 180 (37), 128 (100), 44 (36).

Photolysis of ***8***

Isoxazolone **8** (200 mg, 0.67 mmol) was dissolved in acetonitrile (200 mL) and irradiated (300 nm) for 2 h. The solvent was removed and the crude product purified by radial chromatography (ethyl acetate/dichloromethane 3 : 97) to afford two products.

The first fraction was isolated as a gummy solid and identified as *ethyl 2-(isoquinolin-1-yl)-5,6-dimethyl-4-oxo-2,7-diaza-3-oxa[3.2.0]bicyclohept-6-ene-1-carboxylate* **10** (170 mg, 75%). (Found: M^+ 339.1211. $C_{18}H_{17}N_3O_4$ requires M^+ 339.1219). δ_H 8.45 (1H, d, *J* 7.5), 7.69 (1H, d, *J* 8), 7.56 (1H, t, *J* 7.5), 7.39 (1H, t, *J* 7.5), 7.31 (1H, d, *J* 7.5), 6.36 (1H, d, *J* 8), 4.30 (2H, m), 2.13 (3H, s), 1.53 (3H, s), 1.28 (3H, t, *J* 7). δ_C 167.7, 165.7, 165.7, 148.5, 133.4, 133.0, 128.2, 128.1, 126.3, 125.5, 121.7, 109.7, 99.5, 69.5, 62.5, 30.4, 14.5, 14.1. ν_{max}/cm^{-1} 1765, 1732, 1659, 1601, 1735, 1303, 1266. *m/z* 339 (M^+, 29%), 297 (8), 266 (100), 225 (11), 197 (23), 169 (22), 155 (28), 128 (80), 96 (69).

The second fraction was identified as *ethyl 3-methylimidazo[2,1-a]isoquinoline-2-carboxylate* **9** (22 mg, 13%) by direct comparison with the sample obtained below.

Pyrolysis of ***8***

The isoxazolone **8** (100 mg, 0.33 mmol) was pyrolyzed under FVP conditions (540°C, 130°C, 0.05 mmHg, 60 min). Only a small amount of the isoxazolone had sublimed when the pyrolysis was stopped, as the sample melted and appeared to decompose. The product was washed from the pyrolysis tube, and eluted through a short plug of silica (dichloromethane) to give **9** (17 mg, 20%), mp 154–155°C, identical to the sample obtained previously.[11] (Found: C 71.1, H 5.4, N 11.1%, M^+ 254.1060. $C_{15}H_{14}N_2O_2$ requires C 70.9, H 5.6, N 11.0%, M^+ 254.1055). δ_H 8.78 (1H, d, *J* 7.2), 7.75–7.58 (4H, m), 7.15 (1H, d, *J* 7.4), 4.50 (2H, q, *J* 7), 2.84 (3H, s), 1.48 (3H, t, *J* 7). δ_C 163.8, 141.8, 132.6, 129.6, 129.2, 128.7, 127.0, 124.4, 121.6, 120.1, 116.0, 114.9, 61.0, 14.5, 9.5. ν_{max}/cm^{-1} 1700, 1656, 1570, 1311, 1283, 1218, 1153, 1069, 786, 697. *m/z* 254 (M^+, 42%), 210 (26), 180 (89), 144 (33), 128 (100).

The material from the sublimation flask was passed through a short plug of silica (dichloromethane) to give a solid (13 mg, 15%), mp 87–89°C, identified as *ethyl 3-methyl-4-oxo-4*H*-pyrimido[2,1-a]isoquinoline-3-carboxylate* **11**. (Found: M^+ 282.1000. $C_{16}H_{14}N_2O_3$ requires M^+ 282.1004). δ_H 9.03 (1H, dd, *J* 8.2, 1.6), 8.72 (1H, d, *J* 7.7), 7.82–7.66 (3H, m), 7.28 (1H, d, *J* 7.7), 4.51 (2H, q, *J* 7), 2.39 (3H, s), 1.47 (3H, t, *J* 7). δ_C 160.4 (vwk), 160.0, 134.4 (vwk), 132.9, 132.6, 128.9, 127.3, 126.5, 121.6, 116.8, 116.0, 62.0, 14.2, 12.4, two resonances unsighted. ν_{max}/cm^{-1} 1732, 1682, 1519, 1248, 1215, 1062, 807, 763. *m/z* 282 (M^+, 49%), 253 (5), 236 (9), 208 (76), 182 (20), 128 (100), 101 (25), 77 (10).

Treatment of ***7*** *with Acrolein*

Isoxazolone **7** (500 mg, 2.9 mmol), acrolein (164 mg, 2.9 mmol), and triethylamine (30 mg, 0.3 mmol) were stirred in dichloromethane (10 mL) at room temperature for 30 min. The solvent was evaporated to give an orange oil (536 mg), which was purified by radial chromatography (50% ethyl acetate/light petroleum) to give two fractions.

The first fraction contained *ethyl 4-(2-formylethyl)-4-methyl-5-oxo-4,5-dihydroisoxazole-3-carboxylate* **19**, isolated as a pale orange oil (275 mg, 41%). (Found: $[M+H]^+$ 228.0873. $C_{10}H_{14}NO_5$ requires 228.0875). δ_H 9.66 (1H, s), 4.4 (2H, q, *J* 7.1), 2.48–2.30 (3H, m), 2.16–2.09 (1H, m), 1.54 (3H, s), 1.39 (3H, t, *J* 7.1). δ_C 198.8, 178.7, 162.6, 157.9, 62.9, 48.3, 38.5, 27.5, 20.9, 13.9. ν_{max}/cm^{-1} 1809, 1728, 1584, 1451, 1403, 1376. *m/z* 228 ($[M+H]^+$, 8%), 208 (10), 182 (48), 170 (100), 156 (54), 143 (27), 110 (56), 95 (29), 83 (53).

The second fraction contained *ethyl 2-(2-formylethyl)-4-methyl-5-oxo-2,5-dihydroisoxazole-3-carboxylate* **18** (191 mg, 29%), isolated as a pale yellow oil. (Found: M^+ 227.0798. $C_{10}H_{13}NO_5$ requires M^+ 227.0794). δ_H 9.74 (1H, t, *J* 0.96), 4.41 (2H, q, *J* 7.1), 4.08 (2H, t, *J* 6.4), 2.8 (2H, dt, *J* 0.96, 6.4), 2.03 (3H, s), 1.39 (3H, t, *J* 7.1). δ_C 198.9, 170.9, 158.6, 151.4, 111.2, 62.6, 47.1, 39.9, 13.9, 8.4. ν_{max}/cm^{-1} 1808, 1730, 1624, 1444, 1411. *m/z* 227 (M^+, 22%), 184 (100), 171 (98), 156 (83), 143 (98), 125 (81), 110 (34), 95 (31), 82 (30), 67 (52).

Ethyl 2-(4-Ethoxycarbonylbut-3-enyl)-4-methyl-5-oxo-2,5-dihydroisoxazole-3-carboxylate ***17***

Isoxazolone **18** (104 mg, 0.45 mmol) and ethoxycarbonylmethylenetriphenylphosphorane (159 mg, 0.45 mmol) were stirred at room temperature in anhydrous tetrahydrofuran (3 mL) under N_2 for 24 h. The solvent was evaporated to give a deep orange red oil (260 mg), which was purified by radial chromatography (20% ethyl acetate/light petroleum) to give the *title compound* as a colourless oil (71 mg, 52%). (Found: M^+ 297.1215. $C_{14}H_{19}NO_6$ requires 297.1212). δ_H 6.84 (1H, dt, *J* 7.0, 15.8), 5.85 (1H, dt, *J* 1.5, 15.7), 4.38 (2H, q, *J* 7.1), 4.15 (2H, q, *J* 7.1), 3.89 (2H, t, *J* 6.9), 2.53 (2H, dq, *J* 1.5, 6.9), 2.04 (3H, s), 1.38 (3H, t, *J* 7.1), 1.25 (3H, t, *J* 7.1). δ_C 171.0, 165.8, 158.6, 150.9, 143.4, 124.2, 110.7, 62.6, 60.3, 52.1, 29.2, 14.1, 13.9, 8.5. ν_{max}/cm^{-1} 1753, 1734, 1703, 1655, 1275, 1227, 1178. *m/z* 297 (M^+, 7%), 252 (23), 224 (21), 206 (8), 184 (100), 156 (28), 127 (4), 99 (3), 83 (12).

Photolysis of ***17***

Isoxazolone **17** (71 mg, 0.24 mmol) was photolyzed through pyrex at 300 nm in dry acetone (150 mL) under N_2 at room temperature for 3 h. The solvent was evaporated and the residue purified by radial chromatography (10% ethyl acetate/light petroleum) to give *diethyl 1-aza-8-oxa-7-oxo-6-methyltricyclo[4.2.1.$0^{4,9}$]nonan-5,9-dicarboxylate* **2** as a colourless oil (47 mg, 66%). (Found: M^+ 297.1213. $C_{14}H_{19}NO_6$ requires 297.1212). δ_H (600 MHz) 4.26 (2H, dq, *J* 1.8, 7.14), 4.22 (2H, dq, *J* 1.8, 7.4), 3.75 (1H, ddd, *J* 3.0, 6.6, 13.8), 3.60 (1H, ddd, *J* 4.2, 4.8, 9.0), 3.30 (1H, ddd, *J* 7.2, 9.6, 13.8), 2.85 (1H, d, *J* 4.0), 2.40 (1H, dddd, *J* 3.6, 7.8, 9.0, 13.8), 2.04 (1H, dddd, *J* 5.4, 6.6, 9.6, 13.8), 1.38 (3H, s), 1.30 (3H, t, *J* 7.14), 1.29 (3H, t, *J* 7.14). δ_C 177.1, 170.0, 167.1, 80.0, 62.1, 61.5, 61.5, 48.6, 47.5, 39.2, 31.3, 14.2, 14.2, 14.1. ν_{max}/cm^{-1} 1777, 1735, 1720, 1642, 1449, 1371, 1309, 1238. *m/z* 297 (M, 6%), 280 (3), 252 (5), 224, (18), 206 (4), 196 (7), 184 (28), 168 (5), 156 (14), 141 (100), 129 (7), 113 (73), 85 (20), 67 (5), 43 (29).

Acknowledgments

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