Tetrahedron. Vol. 32, pp. 251 to 256. Pergamon Press 1976. Printed in Great Britain

PHOTOCHEMISTRY OF HETEROCYCLIC COMPOUNDS

AZETIDIN-2,4-DIONES[1a]

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(*Received in the UK* 10 *June* 1974; *Accepted for publication* 10 *July* 1975)

Abstract—Irradiation of several substituted azetidin-2,4-diones in methanol at 253·7 nm revealed three primary competing modes of decomposition:

(a) cycloreversion to yield ketene and isocyanate which react with methanol to respectively a methylester and a methylurethane;

(b) decarbonylation to an aziridinone, which undergoes ring opening in methanol;

(c) ring expansion to an oxacarbene, which in methanol forms a 5-methoxy-isoxazolid-3-one.

These results are interpreted in terms of initial cleavage of the N–C bond to form a 1,4-biradical which undergoes a second cleavage or rearrangement to oxacarbene. The influence of the nature of the nitrogen substituent on the different pathways was studied. Evidence is presented which support the proposition that decomposition occurs from the first excited singlet state or from a very short lived triplet. Comparison is made with the photochemical behavior of cyclobutanones in methanol.

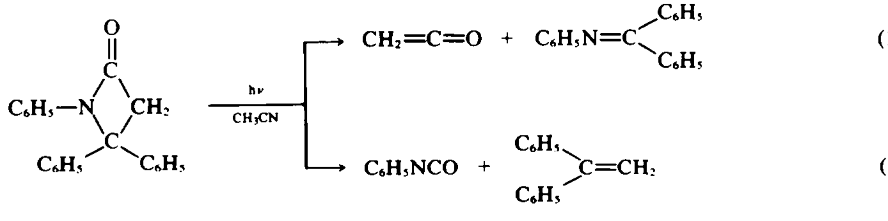
Considerable interest has been and is still shown in the liquid phase photolysis of 4-membered rings containing one[2] or two[3] CO groups. On irradiation of cyclobutanone in solution, three reaction paths were observed: cycloreversion, decarbonylation and cycloexpansion to yield a 5-membered oxygen containing ring. Photolysis of tetrasubstituted 1,3-cyclobutanediones in solution can be accounted for by the following three primary processes: cycloreversion, decarbonylation to cyclopropanone and decarbonylation to ethylene.

The heterocyclic analogs of these alicyclic compounds have been less studied.[1,4,5] N-Aryl-azetidin-2-ones,[4] on irradiation in solution, undergo cycloreversion along pathway a (eqn 1a) or b (eqn 1b), the latter gaining in importance if C_4 is substituted with an electron withdrawing group.

RESULTS AND DISCUSSION

The products derived from the photolyses at 253·7 nm of substituted azetidin-2,4-diones in methanol are illustrated in Scheme 1, while their respective yields are assembled in Table 1.

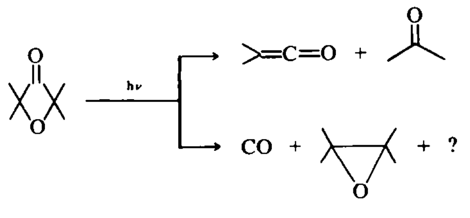
Thus, in a typical experiment, irradiation of azetidin-2,4-dione (**1a**) in methanol afforded a 20% yield of methylurethane (**3a**) and an 80% yield of 5-methoxy-4,4′-diisopropylisoxazolid-3-one (**2a**), which was characterized by its spectral properties (NMR, IR and mass spectrum) and elemental analysis. The NMR spectrum of **2a** revealed a one proton singlet at τ 4·28 corresponding to the acetal proton and a three-proton singlet at τ 6·6 for the OMe protons. The Me protons of the isopropyl groups were observed as two doublets at τ 9·05 while the methine protons of these groups were found as a septet at τ 7·92.



(1a)

(1b)

Photolysis of tetramethyloxetanone[5] leads to cycloreversion (eqn 2a) and decarbonylation (eqn 2b). The importance of the second reaction path decreases in polar solvents.



(2a)

(2b)

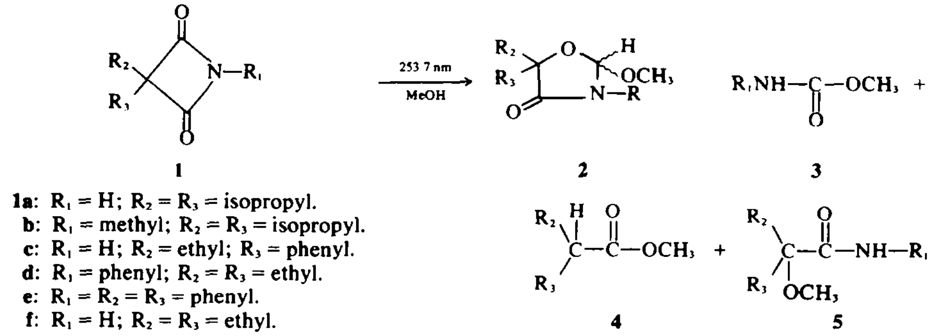
The aim of this paper is to study the influence of the substituent of the ring nitrogen on the photochemical properties of azetidin-2,4-diones.

Table 1. Percent yields of products derived from photolysis of azetidin-2,4-diones in CH_3OH[a]

Compd. 1	Photo ring expansion (%) 2	Photodecarbonylation 5 (%)	Photocycloreversion 3 (%)	4 (%)
a	a (80)	—	a (20)	—
b	b (80)	—	b (20)	—
c	c (80)	—	c (20)	c (20)
d	d (5)	d (5)	d (90)	d (90)
e[b]	e (44)	—	e (27)	e (27)
f	f (60)	—	f (40)	f (40)

[a] The yields were determined by NMR spectroscopy.

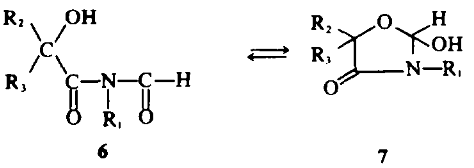
[b] 39% of the products were unidentified photodegradation products of 2*e* after 4 h irradiation (see Experimental).



1a: R$_1$ = H; R$_2$ = R$_3$ = isopropyl.
b: R$_1$ = methyl; R$_2$ = R$_3$ = isopropyl.
c: R$_1$ = H; R$_2$ = ethyl; R$_3$ = phenyl.
d: R$_1$ = phenyl; R$_2$ = R$_3$ = ethyl.
e: R$_1$ = R$_2$ = R$_3$ = phenyl.
f: R$_1$ = H; R$_2$ = R$_3$ = ethyl.

Scheme 1.

A broad peak observed at τ 1·8 was due to the NH-proton. The IR spectrum of **2a** revealed a strong band at 1710 cm^{-1} and the mass spectrum displayed a molecular ion at *m*/*e* 201 (relative intensity 4). Additional support for the structure of compound **2a** was obtained by its hydrolysis to 2-formyl-2,2′-diisopropyl-acethydroxamic acid (**6a**). In dimethyl sulphoxide at room temperature compound **6a** was found to be in equilibrium with the ring-closed form **7a**. The contribution of compound **6a** and **7a** amounts to 60% and 40% respectively.



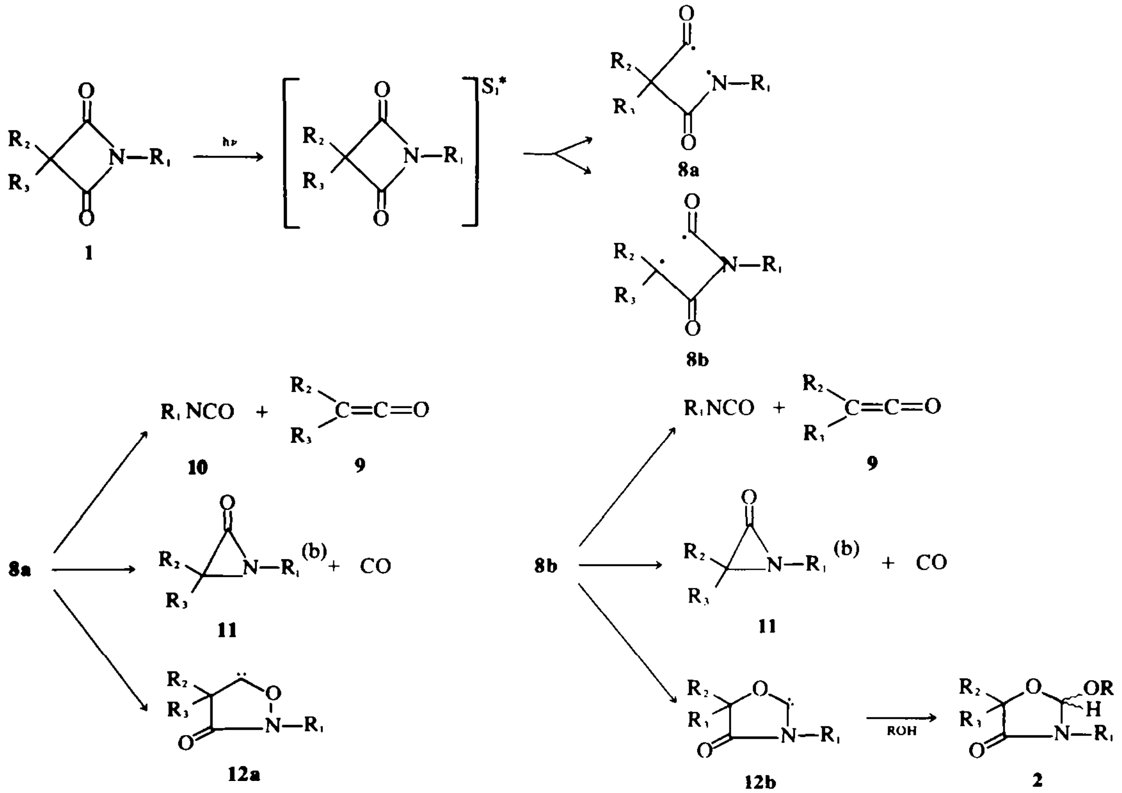
6a: R$_1$ = H; R$_2$ = R$_3$ = isopropyl.
b: R$_1$ = methyl; R$_2$ = R$_3$ = isopropyl.

The isoxazolid-3-ones **2b,c,d,e,f** also displayed similar absorptions in their NMR spectra between τ 3·38 and 4·4 and also between τ 6·89 and 6·54. The IR spectra of **2b,c,e** revealed a strong band between 1710 and 1725 cm^{-1}. In addition all isoxazolid-3-ones have in their mass spectra a molecular ion with a weak intensity. Hydrolysis of **2b** to 5-hydroxy-4,4′-diisopropyl-2-methyl-isoxazolid-3-one (**7b**) gave an analogous additional support for **2b**.

Irradiation of azetidin-2,4-dione **1b** in MeOD afforded again the expected isoxazolid-3-one **2b** but with incorporation of one deuterium instead of hydrogen at the 5-position of the isoxazolid-3-one, as shown by the absence of the one proton absorption at 4·4 τ in NMR.

These results can be interpreted according to the reaction pathways presented in Scheme 2.

In the liquid phase, the vibrationally hot azetidin-2,4-dione (S$_0^*$) will be effectively quenched by the solvent molecules. Therefore all of the observed products are likely to arise from either an azetidin-2,4-dione (S$_1^*$) or a



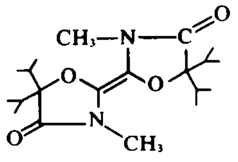
Scheme 2(a).

triplet azetidin-2,4-dione (T_1^*). No quenching of the reaction was observed in the presence of 10^{-2}M *cis*-1,3-pentadiene or in air-saturated methanol solution. One can thus rule out the triplet unless its lifetime is so short that scavenging is improbable. On sensitization of **1d** with acetophenone or acetone no reaction occured, but, since no emission has been detected for the azetidin-2,4-diones **1a–f** the adequacy of the sensitization used cannot be ascertained. Photolysis of **1b** in isopropanol resulted in a primary photochemical behaviour, identical to that in methanol; no reduction was observed. Thus, indirect evidence indicates the absence of a triplet species as a contributor to the reaction in pathway a and c.[†] Although concerted reactions from the azetidin-2,4-dione (S_1^*) cannot be excluded, the intermediacy of the biradical **8**[‡] is more attractive to explain the experimental results.

Further fragmentation of **8** (path a) gives ketene (**9**) and isocyanate (**10**), which was identified as respectively ester (**4**) and urethane (**3**).

Photodecarbonylation (path b) affords aziridinone (**11**) which reacts with methanol in analogy with the reactions described by Sheehan.[7] Pathway b was only observed in the photolysis of **1d**.

Photocycloexpansion (path c) involves the intermediacy of an oxacarbene (**12**), which is trapped by methanol to form isoxazolid-3-one (**2**). When the photolysis is conducted in methanol-0-d deuterium incorporation occurs exclusively at the 5-position of the isoxazolid-3-one. Other evidence supporting its intermediacy was obtained by irradiating **1b** in n-hexane. This product afforded product **13**, a dimer of the oxacarbene in almost quantitative yield.



13

An analogous behaviour has been reported[2][§] in the photolysis of cyclobutanones in methanol. For example 2,2',4,4'-tetramethylcyclobutanone (**14**) gives on irradiation in methanol methylisobutyrate (**15**) for 13%, 1,1',2,2'-tetramethylcyclopropanone (**16**) for 11% and 2-methoxy-3,3',5,5'-tetramethylhydrofuran (**17**) for 68%. These products are respectively formed by following three primary processes: photocycloreversion, photodecarbonylation and photocycloexpansion of **14**.

The remarkable difference in behaviour of the azetidin-2,4-diones **1a**, **1b** and **1c** as compared with **1d** leads us to suggest that the intermediacy of biradical **8** is more attractive to explain the ratio of the products formed in this photolysis. A phenyl substituent on the nitrogen should stabilize the radical, diminish the nucleophility and thus favour a second rupture in the biradical and disfavour the ringexpansion to oxacarbene **12**.

To check the relative importance of these factors the photolysis of **1g**[¶] ($R_1 = 2,2,2$-trifluoro-ethyl, $R_2 = R_3 =$ isopropyl) in methanol at 253·7 nm was studied. The corresponding isoxazolid-3-one **2g** was obtained in a yield identical to this for **1a**, **1b** and **1c**. Therefore the possibility to delocalize the radical seems to be the more important factor.

The influence of electronic factors on the choice of the reaction pathway has been observed in the photolysis of cyclobutanones. It was found that trifluoromethyl groups in the α-position of the CO group of the cyclobutanone strongly diminish the photocycloexpansion.[2f]

It should also be pointed out that neither cyclobutane-1,3-dione[3] nor oxetanone[5] show photocycloexpansion.

Contribution of steric factors in the biradical derived from **1e** could be responsible for the more extensive formation of the photocycloexpansion product **2e** relative to photocycloreversion products **3e** and **4e**. The two bulky phenyl groups[||] on the C atom could bring the biradical in a suitable conformation to form the oxacarbene.

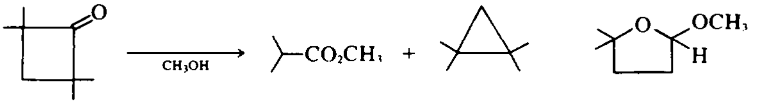
An analogous steric influence can be seen on comparison of **1a** and **1f**. The less bulky ethyl substituents in **1f** lead to a diminishing of the cycloexpansion.

The ratio of the products formed in the photolysis of **1a**, **1b** and **1c** are practical the same, indicating that there is no influence on the choice of the reaction pathways on changing one alkyl by one phenyl group on C-3 even if intramolecular sensitization should occur. Indeed, photolysis of **1a** in a benzene–methanol mixture in which benzene absorbed all the light at 253·7 nm gave the same results as in a direct photolysis of **1**. Photosensitized decomposition of cyclobutanone by singlet benzene was also mentioned by Klemm.[2c]

The disappearance of **1b** and the product formation in CD_3OD on irradiation in a NMR-quartz tube was followed to 80% reaction and was found to be linear with irradiation time. The ratio of the products yields remained constant. These data imply that the products are formed directly from **1b** and are proportional to the light absorbed by **1b** and the quantum yield of the reaction from **1b** (Fig. 1).

The quantum yields for the disappearance of **1a**, **1b**, **1c**, **1d** and **1f** in methanol and of **1b** in n-hexane at 253·7 nm have been determined and are listed in Table 2.

The influence of the nitrogen substituent is found back in the quantum yield of the reaction. Compound **1d**



14 **15** **16** **17**

[†] Although there is no experimental evidence we feel that the biradical hypothesis for path b is also more attractive since it allows rationalization of the three kinds of reactions observed from 1 on the basis of one intermediate.

[‡] A diradical, formed by cleavage of the C–C bond, cannot adequately explain the observed substituent effect.

[§] In the liquid phase on irradiation of cyclobutanones products which are likely to arise from a cyclobutanone [S_1^*], a diradical intermediate [$\dot{C}H_2CH_2CH_2\dot{C}O$] and a cyclic oxacarbene intermediate are formed. Indirect evidence supports the absence of a triplet cyclobutanone (see Ref. 2).

[¶] Since the pK_b value for 1-amino-2,2,2-trifluoro-ethane and 1-amino-ethane are respectively 8·30 and 3·3 it is clear that a withdrawing group as 2,2,2-trifluoroethyl will diminish the nucleophility at the N atom.[8]

[||] It was also suggested that a steric factor can be responsible for the unusual photocycloexpansion of α-spirocyclopropyl cyclopentanon (see Ref. 2*f*). The formation of azetidin-2,4-diones substituted with bulky groups was also found to be more favourable.[9]

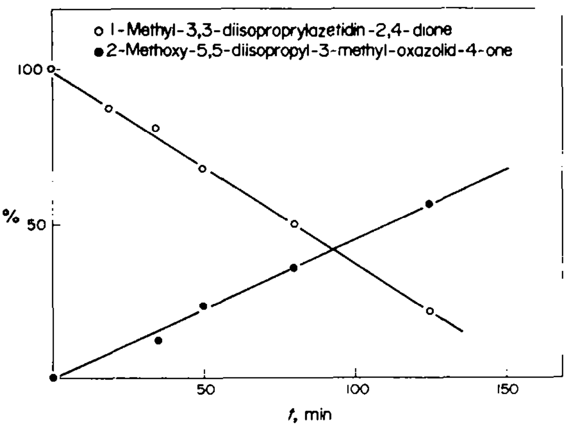


Fig. 1.

Table 2. Quantum yields for the disappearance of the azetidin-2,4-diones[a]

Azetidin-2,4-dione	Φ methanol	Φ n-hexane
1a	0·65[b]	
1b	0·48[b]	0·075[c]
1c	0·44[c]	
1d	0·12[c]	
1f	0·41[b]	

[a] Irradiation at 253·7 nm.

[b] Potassium ferrioxalate actinometry: C. A. Parker, *Proc. Roy. Soc.* **A220**, 104 (1953); C. G. Hatchard and C. A. Parker, *Ibid.* **A235**, 518 (1956).

[c] Azetidin-2,4-dione **1d** was used for actinometry (see Experimental).

bearing a phenyl substituent on the nitrogen has the lowest quantum yield suggesting that ringclosure of the biradical **8** to starting material might be a desactivation pathway, explaining a quantum yield lower than one in the absence of emissive desactivation processes. The fact that the quantum yield for the disappearance of **1b** is lower in n-hexane than in methanol could indicate that, in absence of a suitable captor, the oxacarbene can convert back to 1.

EXPERIMENTAL

All commercial chemicals employed were of reagent or spectrophotometric quality, and unless specified, were used without further purification. Irradiations were carried out in a Rayonet preparative reactor, R.P.R.-208 with R.U.L.-2537 Å lamps manufactured by the Southern New England Ultraviolet Company at 35° (air-cooled), and photolysis tubes were constructed of quartz. IR spectra were taken on a Perkin-Elmer 257 grating spectrophotometer. NMR spectra were taken on a Varian A-60 (60 MHz) or a Varian XL 100 (100 MHz), analytical high-resolution NMR spectrometer. Chemical shifts are reported in τ units from internal TMS (τ 10·00). Mass spectra were taken on a AEI MS 920 S mass spectrometer (ionization energy 70 eV). Product yields were determined by NMR. The apparatus used for preparative GLC was a Perkin Elmer F21 and for analytical GLC a Perkin Elmer F11 gas chromatograph. All m.ps are uncorrected.

3,3'-Diisopropyl-azetidin-2,4-dione (**1a**) was prepared by ringclosure of 2,2'-diisopropylmalonic acid amide in the presence of thionylchloride and pyridine by the method mentioned by Testa and Fontanella.[10]

Irradiation of 3,3'-*diisopropyl-azetidin*-2,4-*dione* (**1a**) *in* MeOH

In a 150-ml soln degassed with argon 3,3'-diisopropyl-azetidin-2,4-dione (3·384 g; 20 mmol) in MeOH was irradiated in a quartz tube for 9 h. The MeOH was evaporated under reduced pressure at room temp. NMR study of the residue in $CDCl_3$ revealed the photolysis was carried to 100% conversion and the product percentages gave **2a**, 80%, and **3a**, 20%. The **3a** formed had the same NMR as commercially available material. The structure of **3a**, purified by crystallization (m.p. 54–55°), was deduced from spectral data:† NMR ($CDCl_3$) τ 9·05 (2 d, 12), 7·92 (septet, 2), 6·6 (s, 3), 4·28 (s, 1), 1·8 (broad s, 1); IR $_{max}^{KBr}$ cm^{-1} 3420, 3200, 3100, 2970, 2940, 2900, 2880, 2845, 1710 (vs), 1470, 1450, 1430, 1400, 1350, 1286, 1200, 1120, 1080, 1040. 1030, 990; MS (70 eV) *m/e* (relative intensity) 201 (M^+, 4), 170 (8·8), 169 (3·5), 158 (85·8), 127 (8·8), 125 (15·9), 115 (5·3), 97 (5·3), 83 (26·4), 71 (26·4), 60 (100·0), 55 (15·9), 43 (49·5). High resolution mass determination of M^+ (Found: 201·1364813. Calcd. for $C_{10}H_{19}NO_3$: 201·136485). (Found: C, 59·60; N, 7·00; O, 23·95; H, 9·65. Calcd. for $C_{10}H_{19}NO_3$: C, 59·70; N, 6·96; O, 23·82; H, 9·45%).

Hydrolysis of 5-*methoxy*-4,4'-*diisopropyl*-*isoxazolid*-3-*one* (**2a**)

A soln of **2a** in $CHCl_3$ afforded—in the presence of air—humidity-quantitatively **6a** after standing some days. **6a** was purified by crystallization from a chloroform–n-hexane, m.p.: 134–135°. This structure was deduced from spectral data: NMR ($CDCl_3$) τ 9·02 (2 doublets, 12), 7·9 (septet, 2), 7·5 (1 singlet, 1), 1·0 (s, 1), 0·82 (s, 1); IR $_{max}^{KBr}$ cm^{-1}: 3430, 3270, 2970, 2940, 2900, 2880, 1720 (vs), 1680 (vs), 1460 (vs), 1405, 1370, 1360, 1290, 1210 (vs), 1175, 1150, 1030, 810; MS (70 eV) *m/e* (relative intensity) 187 (M^+, 0·07), 144 (2·3), 115 (75·7), 97 (5·1), 83 (13·8), 73 (17·2), 71 (79·4), 55 (34·4), 43 (100·0), 41 (38), 39 (17·2). (Found: C, 57·55; N, 7·55; O, 25·65; H, 9·40. Calcd. for $C_9NO_3H_{17}$: C, 57·5; N, 7·4; O, 25·6; H, 9·3%).

In DMSO at room temp **6a** has been found to be in equilibrium with 5 **7a** by an NMR study. The contribution of compound **6a** and **7a** amounts to 60% and 40% respectively; NMR (TMS, internal standard, DMSO-d_6) τ 9·12 (1 d, 12, open form **6a**), 9·05 (m, 12, closed form **7a**), 8·02 (septet, 2, for each form), 6·78 (s, 1, –OH of **7a**), 3·92 (s, 1, hemiacetal proton of **7a**), 1·00 (s, 1, aldehyde proton of **6a**), NH-peaks of **6a** and **7a** and OH-peak of **6a** were not clearly observed from the noice of the apparatus, but their presence was affirmed by integration.

1-*Methyl*-3,3'-*diisopropyl*-*azetidin*-2,4-*dione* (**1b**) was prepared by methylation of **1a** with MeI in accord with the method of Testa and Fontanella.[10]

Irradiation of 1-*methyl*-3,3'-*diisopropyl azetidin*-2,4-*dione* (**1b**) *in* MeOH

To **1b** (1·83 g; 10 mmol) in a quartz tube was added 100 ml of MeOH. The sample, degassed with argon, was photolyzed for 5 h. After removal of the MeOH under reduced pressure and at room temp, NMR study of the residue in $CDCl_3$ revealed the photolysis was carried to 100% conversion and the product percentages gave **2b**, 80%, and **3b**, 20%. The **3b** formed had the same NMR as an authentical sample formed by reaction of an excess of MeOH with methylisocyanate. The structure of **2b**, isolated and purified by column chromatography (silicagel as adsorbens and chloroform as eluens) was determined by spectral data: NMR ($CDCl_3$) τ 9·05 (2 d, 12), 7·89 (septet, 2), 7·21 (s, 3), 6·54 (s, 3), 4·4 (s, 1); IR $_{max}^{liquid\ film}$ cm^{-1} 2970, 2940, 2880, 2840, 1710 (vs), 1470, 1450, 1405, 1390, 1350, 1325, 1280, 1200, 1090 (s), 1050 (vs), 995, 970, 960; MS (70 eV) *m/e* (relative intensity) 215 (M^+, 4·8), 184 (6·4), 173 (27·0), 172 (6·4), 125 (16·0), 97 (3·2), 83 (3·2), 74 (100·0), 71 (10·0), 55 (7·2), 43 (20·0).

Hydrolysis of 5-*methoxy*-4,4'-*diisopropyl*-2-*methyl*-*isoxazolid*-3-*one* (**2b**)

A soln of **2b** in $CHCl_3$ gave in the presence of air humidity quantitatively **7b** after standing some days. From a chloroform, n-hexane mixture **7b** was purified by crystallization, m.p. 89–91°.

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†Abbreviations: s, singlet; d, doublet; m, multiplet; t, triplet; q, quartet.

Identification: NMR ($CDCl_3$) τ 9·05 (m, 12), 7·82 (septet, 2), 7·15 (s, 3), 6·25 (d, 1, J = 8 c/s), 3·98 (d, 1, J = 8 c/s); IR $_{\max}^{\mathrm{KBr}}$ cm^{-1} 3470 (s), 2980, 2950, 2925, 2890, 1690 (vs), 1500, 1460, 1410, 1390, 1370, 1350, 1290 (s), 1105 (s), 1050 (s), 975, 960, 950, 780; MS (70 eV) *m/e* (relative intensity) 201 (M^+, 2·1), 184 (1·3), 159 (36·8), 158 (39·3), 114 (2·1), 83 (4·7), 71 (73·5), 60 (100·0), 55 (8·7), 43 (58·0), 41 (13·1), 39 (4·4). (Found: C, 59·66; N, 6·88; H, 9·57. Calcd. for $C_{10}H_{19}O_3N$: C, 59·70; N, 6·96; H, 9·45%).

3-*Ethyl,3-phenyl-azetidin-2,4-dione* (**2c**) was obtained by ring-closure of 2-ethyl, 2-phenyl-malonic acid amide in the presence of thionylchloride and pyridine in accord with the method of Testa *et al.*[11]

Irradiation of 2-ethyl, 2-phenyl-azetidin-2,4-dione (2c) *in* MeOH

In a 100 ml soln, degassed with argon, **2c** (1·89 g; 10 mmol) in MeOH was irradiated in a quartz tube for 24 h. Under reduced pressure the MeOH was evaporated at room temp. NMR study of the residue in $CHCl_3$ revealed the photolysis was carried to 100% conversion and the product percentages gave **2c** (a mixture of isomers), 80%, **4c**, 20%, and **3c**, 20%. The **3c** formed had the same NMR as commercially available material, **2c** and **4c** were isolated by column chromatography (silicagel as adsorbens and chloroform as eluens). Compound **4c** was identified by spectral analysis: NMR (CCl_4) τ 9·15 (t, 3), 8·20 (m, 2), 6·69 (t, 1), 6·45 (s, 3), 2·80 (s, 5H); IR $_{\max}^{\text{liquid film}}$ cm^{-1} 3060, 3030, 2965, 2940, 2880, 1745 (vs), 1600, 1490, 1450, 1205, 1165, 695; MS (70 eV) *m/e* (relative intensity) 178 (M^+, 24·2), 150 (12·1), 145 (7·9), 121 (33·3), 119 (79·0), 117 (36·3), 105 (39·3), 91 (100·0), 77 (24·1).

Identification of **2c**. NMR ($CDCl_3$) τ 9·15 (t, 3), 8·09 (q, 2), 6·89, 6·63 (two s, 3, ratio 5:3, $-OCH_3$ from *cis* and *trans* isomers), 4·11, 4·08 (two s, 1, ratio 5:3, acetal proton from *cis* and *trans* isomers), 2·8, 2·55 (two m, 5, ratio 5:3, phenyl protons from *cis* and *trans* isomers), 0·9 (broad, 1); IR $_{\max}^{\text{liquid film}}$ cm^{-1} 3250 (broad), 3060, 3025, 2980, 2940, 2880, 2845, 1720 (C=O), 1450, 1400, 1200, 1100, 1070, 1025, 790, 765, 700; MS (70 eV) *m/e* (relative intensity) 221 (M^+, 1·8), 189 (60·5), 149 (19·7), 135 (15·8), 118 (42·0), 117 (100·0), 105 (21·0), 91 (18·4), 77 (13·1). High resolution mass determination of M^+ (Found: 221, 105467. Calcd. for $C_{12}H_{15}O_3N$: 221, 105186).

1-*Phenyl-3,3'-diethyl-azetidin-2,4-dione* (**1d**) was prepared from diethyl-malonic acid dichloride and aniline in the presence of pyridine by the method mentioned by Ebnöther *et al.*[12] It was purified by preparative GLC [(column 1·8 m × 9·5 m) type 8P, 5% SE 30 on gaschrom Q; column temp 220°].

Irradiation of 1-phenyl-3,3'-diethyl-azetidin-2,4-dione (1d) *in* MeOH

To **1d** (3·26 g; 15 mmol) in a quartz tube was added 30 ml of MeOH. The soln was degassed with argon and irradiated for 24 h. Under reduced pressure the MeOH was evaporated at room temp. NMR study of the residue in $CDCl_3$ revealed the photolysis was carried to 88% conversion and extrapolation of the product percentages to 100% reaction gave **3d**, 90%, **4d**, 90%, **5d**, 5%, and **2d**, 5%. The molecular ion of the different products were observed in a mass spectral analysis of the mixture. The **3d** formed had the same NMR, IR, m.p. and GLC retention time (4 m × 3 mm column, 5% SE 30 on varaport 30), as an authentical sample formed by reaction of phenylisocyanate with an excess MeOH. **5d** and **4d** were isolated and purified by GLC (same column as for purification of **1d**, column temp 220°). The structure of **4d** was deduced from spectral data: NMR ($CDCl_3$) τ 9·10 (t, 6), 8·50 (octet, 4), 7·80 (quintet, 1), 6·33 (s, 3); IR $_{\max}^{\text{liquid film}}$ cm^{-1} 2980, 2945, 2890, 1745 (C=O, vs), 1465, 1390, 1270, 1230, 1195, 1170, 1150, 1090, 990; MS (70 eV) *m/e* 130 (M^+). In the case of **5d** the structure was proved by: NMR (CCl_4) τ 9·22 (t, 6), 8·20 (q, 4), 6·75 (s, 3H), 2·72 (m, 6, –NH and phenyl protons); IR $_{\max}^{CCl_4}$ cm^{-1} 3440 (w), 3400, 3060, 3030, 2975, 2940, 2880, 2840, 1690 (C=O, s), 1460, 1445, 1310, 1185, 1160, 1080, 945; MS (70 eV) *m/e* (relative intensity) 221 (M^+, 27·9), 190 (2·5), 160 (4·9), 120 (13·1), 101 (100·0), 93 (27·9), 77 (31·0), 59 (44·3), 29 (49·2).

Compound **2d** was isolated by preparative TLC (silicagel, benzene) and identified by NMR ($CDCl_3$) τ 9·05 (t, 6), 8·15 (q, 4), 6·54 (s, 3), 3·81 (s, 1), 2·65 (m, 5) and MS *m/e* 249 (M^+), 218 (M^+ $-OCH_3$).

1,3,3'-*Triphenyl-azetidin-2,4-dione* (**1e**) was obtained by reaction of diphenyl-malonic acid dichloride with aniline in the presence of pyridine in accord with the method of Ebnöther *et al.*[15]

Irradiation of 1,3,3'-triphenyl-azetidin-2,4-dione (1e) *in* MeOH

A 250 ml soln, degassed with argon, **1e** (0·5 g; 1·6 mmol) in MeOH was irradiated in a quartz tube for 4 h. After the MeOH has been removed at room temp under reduced pressure, NMR study of the residue in $CDCl_3$ revealed the photolysis was carried to about 90% conversion and extrapolation of product percentages to 100% reaction gave **3e**, 27%, **4e**, 27%, **2e**, 44%, and 39% unidentified photodegradation products of **2e**. Prolonged irradiation of the soln resulted in a more extensive photodegradation of **2e**, the residue of a soln, irradiated for 20 h after evaporation of MeOH, was polymeric.

Products **3e**, **2e** and **4e** were isolated by preparative TLC (silicagel, benzene). **3e** formed had the same NMR, IR, m.p. as an authentical sample of **3e**.

Compound **4e** showed the same NMR and IR as an authentic sample formed by reaction of diphenyl-ketene with an excess of MeOH.

Identification of **2e** m.p. 93–94° is based on the following spectral data: NMR ($CDCl_3$) τ 6·55 (s, 3), 3·38 (s, 1), 2·5 (m, 15); IR$_{\max}^{\mathrm{KBr}}$ cm^{-1} 3070, 3030, 2980, 2945, 2840, 1725, (C=O, s), 1600, 1505, 1495, 1450, 1405 (s), 1195, 1140, 1120, 1060, 1040, 870, 800, 765, 750, 722, 692, 600; MS (70 eV) *m/e* (relative intensity) 345 (M^+, 0·7), 314 (2·0), 285 (22·0), 226 (22·0), 194 (5·4), 182 (42·0), 167 (100·0), 166 (40·0), 165 (94·0), 149 (32·0), 105 (72·0), 77 (52·0), 51 (18·0). (Found: C, 76·65; H, 5·60; N, 4·05. Calcd. for $C_{22}H_{19}O_3N$: C, 76·52; H, 5·55; N, 4·05%).

3,3'-*Diethyl-azetidin-2,4-dione* (**1f**) was synthesised as described by Testa *et al.*[14]

Irradiation of 3,3'-diethyl-azetidin-2,4-dione (1f) *in* MeOH

A 1 ml soln of **1f** (0·140 g; 1 mmole) in MeOH, degassed with argon, was irradiated in a quartz NMR tube until completion of the reaction. The yield of **2f** formed was determined by NMR. On evaporation **2f** showed the following NMR absorptions in $CDCl_3$: τ 9·14 and 9·04 (2 t, 6), 8·32 and 8·29 (2 q, 4), 6·58 (s, 3), 4·13 (s, 1), 2·03 (broad s, 1). The products found in the photolysis were not isolated.

Irradiation of 1-methyl-3,3'-diisopropyl-azetidin-2,4-dione (1b) *in isopropanol*

A 10 ml soln, degassed with argon, **1b** (0·183 g; 1 mmol) in isopropanol was irradiated in a quartz tube at 253·7 nm for 5 h. Analysis on an analytical GLC (4 m × 3 mm column, 5% SE 30 on varaport 30, column temp 25°) of the photolysate by comparison with an authentic sample of aceton in isopropanol revealed the absence of acetone in the photolysate. After evaporation of the solvent at room temp under reduced pressure, the conversion was determined by a NMR study of the residue in $CDCl_3$ to be 100%. Addition of D_2O to the soln did not change the NMR spectrum. Apart from the absorptions due to the protons of the isopropyl groups and the Me groups, a singlet at τ 4·20 typical for the acetal proton of the isoxazolid-3-one, which was formed for 80% was observed.

Irradiation of 1b *in n-hexane*

A 20 ml soln of **1b** (0·4 g; 2·1 mmol) in dry n-hexane was irradiated in a quartz tube for 4 h. By NMR the conversion was determined to be 30%, essentially one product, the dimer **13** was formed. The dimer was isolated by TLC (silicagel, chloroform) and crystallized from n-hexane m.p. 151–153°, spectral data: NMR ($CDCl_3$) τ 9·00 (m, 24), 7·80 (septet, 4), 6·73 (s, 6); IR $_{\max}^{\mathrm{KBr}}$ cm^{-1} 2980, 2950, 2910, 2890, 1705 (C=O, s), 1470, 1430, 1390, 1370, 1180, 1140, 1110, 1095, 1045, 1035, 975, 955; MS (70 eV) *m/e* (relative intensity) 366 (M^+, 32·0), 323 (7·0), 241 (28·0), 157 (15·0), 141 (26·0), 125 (100·0), 111 (9·0), 97 (9·0), 83 (20·0), 71 (34·0), 60 (36·0), 55 (48·0), 43 (68·0). High resolution mass determination of M^+ (Found: 366·2518. Calcd. for $C_{20}H_{34}N_2O_4$: 366·252109).

1 - (2,2,2 - *Trifluoro - ethyl*) - 3,3′ - *diisopropyl - azetidin* - 2,4 - *dione* (**1g**)

To **1a** (1 g) and K_2CO_3 (1 g) in 50 ml dry acetone was added 2 ml 2,2,2-trifluoro-ethyliodide. The soln was refluxed for 20 h. After adding a second amount of 2 ml of 2,2,2-trifluoro-ethyliodide the soln was again refluxed for 20 h. After evaporation of acetone, the residue was purified with water and ether. The ether layer was separated from the water layer and was dried over $CaCl_2$. The ether was evaporated and the residue was solved in a little chloroform. Compound **1f** was purified with column chromatography (silicagel as adsorbens and benzene as eluent). After crystallization from n-hexane colourless needles of **1g** were obtained, m.p. 52–53°, yield 21%. NMR ($CDCl_3$) τ 8·92 (d, 12), 7·8 (septet, 2), 6·05 (q, 2, J = 9·1 c/s); IR $^{\text{KBr}}_{\text{max}}$ cm^{-1} 3000, 2980, 2940, 2880, 1730 (s), 1470, 1390, 1340, 1260, 1170, 1030, 915, 840; MS (70 eV) *m/e* (relative intensity) 251 (M^+, 0·66), 126 (88·8), 111 (100·0), 83 (37·7), 55 (33·0), 41 (22·2). (Found: C, 52·33; N, 5·31; H, 6·46. Calcd. for $C_{11}H_{16}N_1O_2F_3$: C, 52·59; N, 5·57; H, 6·37%).

Irradiation of 1-(2,2,2-*trifluoroethyl*)-3,3′-*diisopropyl - azetidin*-2,4-*dione* (**1g**) *in* MeOH

A 2 ml soln of **1g** (0·1 g; 0·4 mmol) in MeOH was irradiated in a quartz tube for 5 h. After the MeOH has been removed at room temp under reduced pressure, NMR study of the residue in $CDCl_3$ revealed the photolysis was carried to 100% conversion and **2g** was formed for 80%. An ^{19}F-NMR study of the residue in CCl_3F revealed the same yield for **2g**. The structure of **2g** purified by crystallization from n-hexane, m.p. 49–51°, was deduced from spectral data: NMR ($CDCl_3$, 100 MHz) τ 9·03 (m, 12), 7·84 (m, 2), 6·48 (s, 3), 4·16 (s, 1), an AB pattern combined with the coupling of the fluoratoms was observed between τ 5·40 and 6·7 for the two methylene protons, $\tau_A = 5{\cdot}72$, $\tau_B = 6{\cdot}44$, $J_{AB} = -15$ Hz and $J_{H-C-C-F} = 9{\cdot}1$ Hz; ^{19}F-NMR ($CDCl_3 \div 10\%$ CCl_3F, 100 MHz), $\Phi = -70{\cdot}53$ (t); IR $^{\text{KBr}}_{\text{max}}$ cm^{-1} 2985, 2970, 2940, 2910, 2880, 2840, 1730 (s), 1470, 1435, 1420, 1400, 1380, 1357, 1290, 1270, 1155, 1126, 1090, 1040, 995; MS (70 eV) *m/e* (relative intensity) 283 (M^+, 4·6), 241 (13·0), 240 (26·9), 142 (100·0), 125 (11·5), 83 (2·69), 71 (30·7), 55 (3·45), 43 (26·9). High resolution mass determination of M^+ (Found: 283·13382. Calcd. for $C_{12}H_{20}N_1O_3F_3$: 283·139523).

Quantum yields were determined for degassed solns of **1a**, **1b** and **1f** ($2{\cdot}5 \times 10^{-2}$ M) in MeOH at 253·7 nm (Bausch and Lomb monochromator). The disappearance (about 10%) of **1a**, **1b** and **1f** was followed by the change in optical density on a Hitachi-Perkin Elmer Spectrophotometer 139. The absorptivity at 253·7 nm was taken as a measure of the concentration of the soln. The actinometer used was potassium ferrioxalate.

Another method was used for the determination of quantum yields for **1c** and **1d** in MeOH and for **1b** in n-hexane. The actinometer used was azetidin-2,4-dion **1b** in MeOH. NMR-quartz tubes with 0·5 ml of a 10% non-degassed soln of respectively **1b**, **1c** and **1d** in a merry-go-round was irradiated in a Rayonet reactor with RUL 2537 Å lamps. The disappearance of the diones (about 30%) was determined by NMR spectroscopy.

Acknowledgements—The generous financial support of the Nationaal Fonds voor Wetenschappelijk Onderzoek and the I.W.O.N.L. (fellowship to J.S.) is gratefully acknowledged. The authors are indebted to Drs. S. Toppet and F. Compernolle for their assistance in the interpretation of NMR and mass spectra and to Dr. R. Merenyi for the ^{19}F-NMR data.

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