Route of Triacylamine Formation in the Thermal Conversion of 2,3,7-Trioxa-5-azabicyclo[2.2.1]hept-5-enes Investigated by Nuclear Magnetic Resonance Experiments

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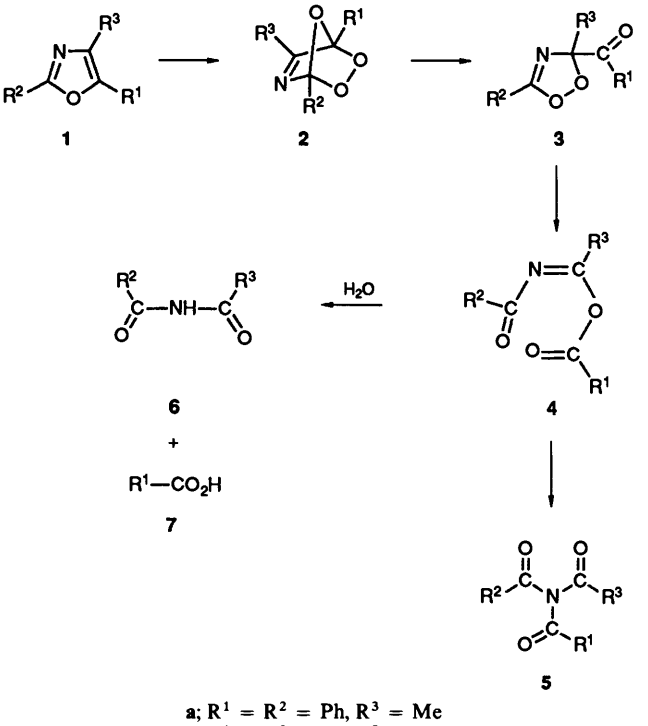
Thermal conversion of the typical aryl-, alkyl- and/or hydrogen-substituted oxazole *endo*-peroxides **2a–c** into the triacylamines **5a–c** proceeds by three subsequent rearrangements. The first leads to the dioxazoles **3a–c**, which in the second stage rearrange into the imino anhydrides **4a–c**. The latter collapse into the triacylamines **5a–c**.

The mechanism by which 2,3,7-trioxa-5-azabicyclo[2.2.1]hept-5-enes substituted with aryl groups, alkyl groups and/or hydrogen are converted into triacylamines† has not, until now, been conclusively established[1,2] although this problem was tackled for the first time in 1966.[3] At the time it was suggested that, *via* a Baeyer–Villiger rearrangement, the *endo*-peroxides gave the imino anhydrides, which then rearranged into the triacylamines. Recently this hypothesis seemed to be supported by experimental evidence.[2] However, in the course of a study of the thermal conversion of the *endo*-peroxides of α-alkoxy oxazoles the intermediate formation of 3*H*-1,2,4-dioxazoles was shown to occur independently of the position of the alkoxy group.‡ The dioxazoles yield diacylcarbamates *via* the imino anhydrides.[4] In order to verify the lack of influence of the alkoxy group on the thermal rearrangement of the oxazole *endo*-peroxides, we have carried out tetraphenylporphyrin-sensitized photooxygenation of the oxazoles **1a–c** in $CDCl_3$–$CFCl_3$ at −70 °C. When the reactions were complete, samples were transferred from the reaction apparatus into the spectrometer. ^1H and ^{13}C NMR spectra, recorded at −70 °C, showed the presence of only the 2,3,7-trioxa-5-azabicyclo[2.2.1]hept-5-enes **2a–c** (Table 1). The subsequent rearrangements starting from the latter (Scheme 1) were evidenced by NMR spectroscopic analysis at various times and temperatures. Periodically the product distribution was determined by ^1H NMR analysis on the basis of the relative areas of the singlets of the hydrogens and/or of the methyl groups. Table 2 shows the product percentages so deduced. The *endo*-peroxide **2a** started to rearrange at −25 °C, leading to the dioxazole **3a** and 2 h later a trace amount of the imino anhydride **4a** was also present. After 7 h the *endo*-peroxide **2a** had completely disappeared and compounds **3a** and **4a** were present in the reaction mixture, in addition to a trace of the triacylamine **5a**. By carrying out the thermal conversion at −10 °C, and starting from the solution kept for 2 h at −25 °C, we obtained the imino anhydride **4a** almost quantitatively after 2 h. The latter was quantitatively converted, within a few minutes at 25 °C, into the triacylamine



a; $R^1 = R^2 = Ph$, $R^3 = Me$
b; $R^1 = R^2 = Ph$, $R^3 = H$
c; $R^1 = H$, $R^2 = Ph$, $R^3 = Me$

Scheme 1

5a, which was the only product obtained on performing the thermal conversion of the *endo*-peroxide **2a** at 25 °C. The triacylamine **5a** was isolated by silica gel chromatography and was identified by comparison with an authentic sample.[3] Table 1 shows its ^1H and ^{13}C NMR data, previously unreported. The structure of the dioxazole **3a** was assigned by ^1H and ^{13}C NMR spectral data which were deduced from those of the reaction mixture obtained in Run 2 (Table 2), the *endo*-peroxide **2a** signals being subtracted. The structure of the imino anhydride **4a** was assigned by ^1H and ^{13}C NMR spectral data which were deduced from those of the reaction mixture obtained in Run 4 (Table 2), signals for the triacylamine **5a** being subtracted. The data so obtained are reported in Table 1. As mentioned above, Table 2 shows the results obtained when using $CDCl_3$–$CFCl_3$ as solvent. However, control experiments showed that reactions carried out in [$^2H_6$]acetone or in [$^2H_3$]acetonitrile gave the same sequence of products over a range of temperatures. In

† This transformation is remarkable in that the relatively stable oxazole ring undergoes rearrangement of the carbon–nitrogen skeleton in high yield to give a triacylamine which may then serve as an excellent acylating agent.[1]

‡ The 3*H*-1,2,4-dioxazoles were quantitatively obtained from the *endo*-peroxides of the 5-alkoxy oxazoles and were the main products from the *endo*-peroxides of the 2-alkoxy oxazoles, the minor products being the dioxetanes deriving from scission of the bond between C-4, bearing the alkoxy group, and the peroxy oxygen.[4] It should be noted that in the series of *endo*-peroxides of the α-alkoxy furans the scission of the bond between the carbon bearing the alkoxy group and the peroxy oxygen only is involved.[5–7]

Table 1 Physical, spectral and analytical data for the products derived from dye-sensitized photooxygenation of the oxazoles **1a–c**

Product	M.p./°C	$\nu_{max}(CHCl_3)/cm^{-1}$	$\delta_H[CDCl_3–CFCl_3\ (3:1)]$	$\delta_C[CDCl_3–CFCl_3\ (3:1)]$[a]
2a			2.27 (3 H, s, Me), 7.40–8.10 (10 H, m, 2 × Ph)	15.2 (q, Me), 110.7 (s, C-1), 120.2 (s, C-4), 125.3 and 125.4 (2 s, C-1 of the two Ph), 126.0, 128.5, 128.8, 128.9, 130.9 and 131.8 (6 d, CH of the two Ph), 176.9 (s, C-6)
2b			7.40–8.10 (10 H, m, 2 × Ph), 8.51 (1 H, s, CH)	110.1 (s, C-1), 121.5 (s, C-4), 124.4 and 125.5 (2 s, C-1 of the two Ph), 127.4, 128.8, 129.1, 131.8 and 131.9 (5 d, CH of the two Ph), 164.7 (d, C-6)
2c			2.49 (3 H, s, Me), 6.53 (1 H, s, CH), 7.40–8.00 (5 H, m, Ph)	15.9 (q, Me), 101.5 (d, C-1), 120.7 (s, C-4), 125.0 (s, C-1 of Ph), 128.5, 128.8 and 131.8 (3 d, CH of Ph), 174.9 (s, C-6)
3a			1.97 (3 H, s, Me), 7.40–8.40 (10 H, m, 2 × Ph)	23.7 (q, Me), 110.4 (s, C-3), 121.6 (s, C-1 of Ph at C-5), 159.4 (s, C-5), 194.2 (s, CO)[b]
3b			7.05 (1 H, s, CH), 7.40–8.30 (10 H, m, Ph)	102.3 (d, C-3), 122.0 (s, C-1 of Ph at C-5), 159.6 (s, C-5), 194.4 (s, CO)[b]
3c[c]			1.79 (3 H, s, Me), 7.40–7.90 (5 H, m, Ph), 9.64 (1 H, s, CHO)	18.6 (q, Me), 108.7 (s, C-3), 121.2 (s, C-1 of Ph), 128.8, 129.1 and 133.6 (3 d, CH of Ph), 161.0 (s, C-5), 192.9 (d, CHO)
4a			2.38 (3 H, s, Me), 7.40–8.10 (10 H, m, 2 × Ph)	20.3 (q, Me), 128.6, 129.6, 130.2, 133.7 and 134.3 (5 d, CH of the two Ph), 127.5 and 131.3 (2 s, C-1 of the two Ph), 156.2 (br s, C=N), 162.9 (s, CO_2), 176.0 (s, CO)
4b[d]	95 (decomp.)	1793, 1753, 1693br	7.40–8.20 (10 H, m, 2 × Ph), 9.09 (1 H, br s, CH)[e]	126.8 and 132.5 (2 s, C-1 of the two Ph), 128.7, 129.0, 130.2, 130.8, 133.9 and 135.2 (6 d, CH of the two Ph), 149.6 (d, CH), 162.5 (s, CO_2), 177.0 (s, CO)
5a[f]	84–86 (lit.,[3] 85–86)		2.50 (3 H, s, Me), 7.40–7.90 (10 H, m, 2 × Ph)[g]	25.5 (q, Me), 128.9, 129.2 and 133.6 (3 d, CH of the two Ph), 133.3 (s, C-1 of the two Ph), 172.2 (s, CO of the two Bz), 174.3 (s, CO of Ac)[g]
5b[f]	77–80 (lit.,[9] 78–80)	1727, 1697	7.30–7.85 (10 H, m, 2 × Ph), 9.36 (1 H, s, CHO)[g]	129.0, 129.5 and 134.1 (3 d, CH of the two Ph), 132.6 (s, C-1 of the two Ph), 162.5 (d, CHO), 170.6 (s, 2 × CO)[g]
5c[h,i]	74–76[j]	1740, 1720, 1707		24.2 (q, Me), 129.1, 130.0 and 135.0 (3 d, CH of Ph), 131.9 (s, C-1 of Ph), 161.9 (d, CHO), 170.6 and 171.2 (2 s, 2 × CO)[g]

[a] The ^{13}C chemical-shift assignment of quaternary carbons was obtained by long-range C–H heteronuclear selective decoupling experiments. [b] The phenyl carbons were not assigned since their signals and those of the products present in the mixture overlap. [c] See footnote ‡. [d] Isolated by suitable treatment (see Experimental). (Found: C, 70.8; H, 4.4; N, 5.4. Calc. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.37; N, 5.53%). [e] When the spectrum was recorded at room temperature the broad signal became a sharp singlet (δ 9.00). [f] Known product, but spectral data are new. [g] Recorded in $CDCl_3$. [h] Known product,[2] whose ^1H NMR data only have been reported. [i] (Found: C, 62.7; H, 4.7; N, 7.3. Calc. for $C_{10}H_9NO_3$: C, 62.82; H, 4.75; N, 7.33%). [j] Recrystallization solvent was hexane.

particular, the rate of the rearrangement of peroxide **2a** into the dioxazole **3a** did not increase upon increasing the solvent polarity.

The same sequence of products was seen (Table 2) in the thermal conversion of the *endo*-peroxide **2b**. The latter started to decompose at −15 °C and led to the dioxazole **3b**, which in turn rearranged into the imino anhydride **4b**. The latter was the only product of rearrangement present in the reaction mixture after 9 h. The imino anhydride **4b** is more thermally stable than **4a**; however, upon being heated at 60 °C it yielded the triacylamine **5b**. It is to be noted that under the above conditions* compound **4b** partly underwent hydrolysis into *N*-formylbenzamide **6b**[8] and benzoic acid **7a**,† therefore the percentage yields reported in Table 2 (Runs 9–11) include some amounts of the latter two products. In order to isolate compound **4b** we have carried out sensitized photooxygenation of the oxazole **1b** at room temperature under strictly anhydrous conditions. In this way the imino anhydride **4b** was obtained almost quantitatively and was isolated by precipitation from dry diethyl ether. On being heated at 60 °C, the imino anhydride **4b** quantitatively rearranged into the triacylamine **5b**, which was isolated by chromatography on polyamide resin and identified by comparison with an authentic sample.[9] Table 1 shows its ^1H and ^{13}C NMR data, previously unreported. The structure of the dioxazole **3b** was assigned by ^1H and ^{13}C NMR spectral data which were deduced from those of the reaction mixture obtained in Run 7, the signals of **2b** being subtracted. The spectral data of the dioxazole **3b** so obtained are reported in Table 1. This Table also reports physical, spectral, and analytical data for the anhydride **4b**.

Thermal conversion of the *endo*-peroxide **2c** at −30 °C after 1 h quantitatively led to the dioxazole **3c**‡ (Table 2). All

* The transfer of the NMR sample at −70 °C from the reaction apparatus into the spectrometer is responsible for the presence of adventitious moisture in the sample.

† Control experiments showed that compound **4b**, upon mild hydrolysis, yields compounds **6b** and **7a** almost quantitatively.

‡ In the aforementioned study of the thermal conversion of the oxazole *endo*-peroxides[2] the structure of the imino anhydride **4c** was assigned on the basis of the ^1H NMR spectrum to the product obtained at −30 °C from the dye-sensitized photooxygenation of the oxazole **1c**.

Table 2 Product percentages in the sequence of the rearrangements from the *endo*-peroxides **2a–c** to the triacylamines **5a–c** as a function of temperature and/or time

Series	Run[a]	T/°C	Time	Products (%)[b] 2	3	4	5
a	1	−25	0	100			
	2	−25	2 h	70[c]	30	trace	
	3	−25	7 h		60[d]	40	trace
	4[e]	−10	2 h			90	10
	5	25	4–5 min				100
b	6	−15	0	100			
	7	−15	1 h	60	40		
	8	−15	2 h	45	50	5	
	9	−15	9 h			100[f]	
	10	25	9 h			95[f]	5
	11	60	6 h				100[f]
c	12	−30	0	100			
	13	−30	1 h		100		
	14	−10	4 h		40		60[g]
	15	−10	8 h				100[g]

[a] Starting from 0.1 mol dm^{-3} solutions of the *endo*-peroxides **2** obtained at −70 °C in $CDCl_3$–$CFCl_3$. [b] Deduced on the basis of the ^1H NMR spectrum. [c] Percentage includes trace amount of **4a**. [d] Percentage includes trace amount of **5a**. [e] Starting from Run 2. [f] Percentage includes small amounts of *N*-formylbenzamide **6b** and benzoic acid **7a** owing to the experimental conditions not being strictly anhydrous. [g] Percentage includes some amounts of **6a** and **7c**.

attempts to detect the anhydride **4c** by carrying out the thermal conversion of the dioxazole **3c** in the range −25 to 0 °C failed; only starting material **3c** and/or the triacylamine **5c** were present (the latter as rearrangement product) in solution.* However, the formation of the imino anhydride **4c** during the thermal conversion of compound **3c** was indicated by mild hydrolysis, at −10 °C, of the photooxygenation mixture. In this way, in addition to the triacylamine **5c**, *N*-acetylbenzamide **6a**[10] and formic acid **7c** were recovered.† By carrying out the sensitized photooxygenation of compound **1c** at room temperature under strictly anhydrous conditions the triacylamine **5c**[2] was formed quantitatively and was isolated by chromatography on polyamide resin. The structure of the dioxazole **3c** was deduced from the NMR spectral data reported in Table 1, which also shows physical, spectral and analytical data for compound **5c**, previously unreported.

The results are indicative of three subsequent rearrangements in the conversion of the *endo*-peroxides **2** into the triacylamines **5**, as summarized in Scheme 2. Indeed the imino anhydrides **4** are precursors of the triacylamines **5** as previously suggested,[2,3] but they form from *endo*-peroxides **2** *via* dioxazoles **3**. The lack of solvent effect on the rate of the conversion of peroxide **2a** into the dioxazole **3a** may support a concerted rearrangement as shown in pathway A. The rearrangement of the dioxazoles **3** into the imino anhydrides **4** can be considered as a Baeyer–Villiger rearrangement in which an acyl group migrates without competition with alkyl or hydrogen transfer (pathway B).[11] However, it is also conceivable that the rearrangement proceeds *via* an 'epoxy ion' mechanism (pathway C). A mechanism similar to this one was recently demonstrated in the oxidation of benzil by peracid to the corresponding acid anhydrides.[12] Support for this alternative hypothesis is given from the behaviour of the fully substituted 3*H*-1,2,4-dioxazoles. The 3-alkoxycarbonyl derivatives such as **3d** are stable at room temperature,[13] while the 3-benzoyl derivatives **3a**, **b** and **3e**[4] and the 3-formyl derivative **3c**, in which the carbonyl group is strongly polarized, are thermally more unstable and can be detected only below −15 °C.

Finally the 1,3-O-to-N transfer of an acyl group in an acyl imidate, sometimes called the Mumm rearrangement and proposed to occur in several cases,[14,15] is responsible for the rearrangement of the imino anhydrides **4** into the triacylamines **5**. Although the *Z* isomers of **4** would form initially, the *Z*–*E* interconversion would be fast compared with the subsequent rearrangement which should take place through the *E*-isomers.[15]

Experimental

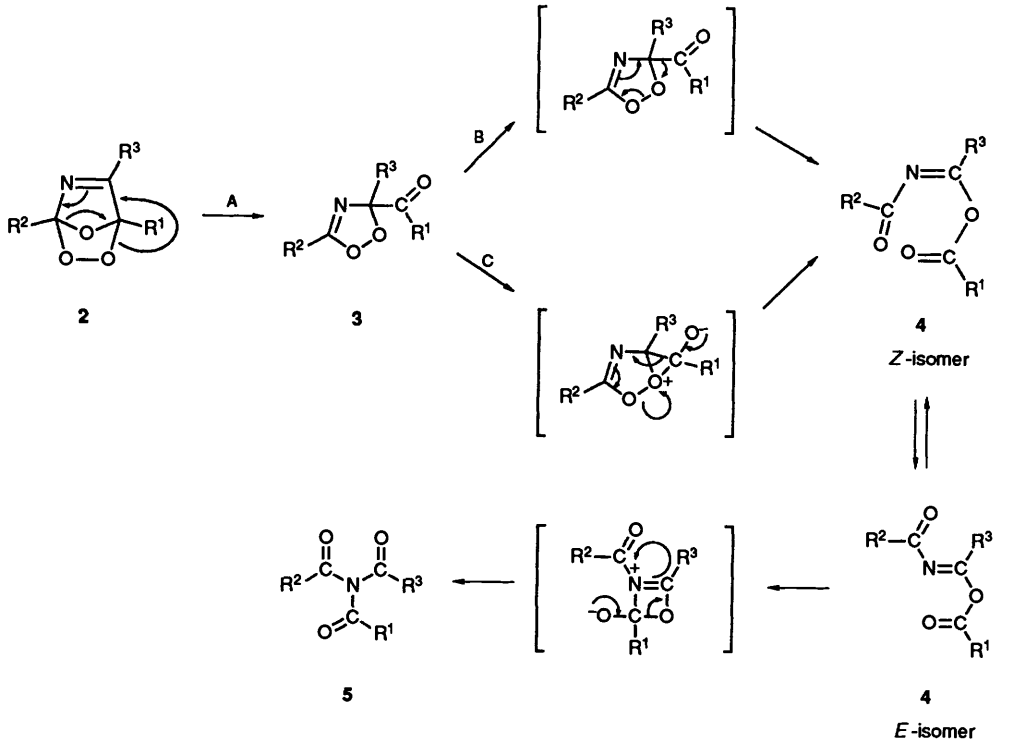
IR spectra were recorded on a Perkin-Elmer 1760X-FT spectrophotometer with chloroform as solvent. ^1H and ^{13}C NMR spectra were recorded with Bruker AC-270 or AM-400 spectrometers with deuteriochloroform–trichlorofluoromethane (3:1) as solvents, unless otherwise stated, and tetramethylsilane as internal standard. The solvents used in the photooxygenation reactions were anhydrous. Silica gel 0.05–0.20 mm (Merck), neutral alumina (Fluka) or MN-polyamide-AC (Macherey, Nagel), and light petroleum (b.p. 40–70 °C) were used for column chromatography. Tetraphenylporphyrin (TPP), Rose Bengal (RB) and Methylene Blue (MB) (Fluka) were used without purification.

2,5-Diphenyloxazole **1b** was purchased (Fluka). 4-Methyl-2-phenyloxazole **1c**[16] was prepared according to a procedure previously reported for different oxazoles,[17] starting from bromoacetone and benzamide. Alumina B-III chromatography of the reaction mixture with light petroleum–diethyl ether (4:1) as eluent gave compound **1c** (50%) as an oil.

Dye-sensitized Photooxygenation of the Oxazole **1a** *and Thermal Conversion of the* endo-*Peroxide* **2a**.—A 0.1 mol dm^{-3}

* As reported in Table 2, *N*-acetylbenzamide **6a** and formic acid **7c** derived from hydrolysis of the undetected **4c** intermediate (see below) were also present to a certain extent in the reaction mixture. See footnote * (previous page).

† Control experiments showed that the triacylamine **5c**, upon mild hydrolysis under the same conditions, was quantitatively recovered, as well as the dioxazole **3c** under mild hydrolysis at −30 °C. Therefore compounds **6a** and **7c** were evidently formed by hydrolysis of the intermediate imino anhydride **4c** (*cf.* similar results obtained by hydrolysis of compound **4b**).



a; $R^1 = R^2 = Ph$, $R^3 = Me$
b; $R^1 = R^2 = Ph$, $R^3 = H$
c; $R^1 = H$, $R^2 = Ph$, $R^3 = Me$
d; $R^1 = OMe$, $R^2 = Ph$, $R^3 = Me$
e; $R^1 = Ph$, $R^2 = OMe$, $R^3 = Me$

Scheme 2

solution of the oxazole **1a**[18] (1 mmol) in $CDCl_3$–$CFCl_3$ (3:1) was irradiated with a halogen-superhot lamp (Osram, 650 W) in the presence of TPP (3.6×10^{-4} mmol). During the irradiation, dry oxygen was bubbled through the solution which was kept at −70 °C. Periodically the solution was monitored (^{1}H NMR spectoscopy) for the disappearance of the oxazole **1a**. When the reaction was complete (2 h), a sample was transferred from the reaction apparatus to the spectrometer (probe temperature −70 °C). The analysis of the ^{1}H and ^{13}C spectra of the reaction mixture showed only the presence of the *endo*-peroxide **2a**, whose spectral data are reported in Table 1. When the probe temperature was raised to −25 °C the *endo*-peroxide **2a** started to decompose into the dioxazole **3a**. Table 2 reports the product distribution in the rearrangement sequence from the *endo*-peroxide **2a** to the triacylamine **5a** as a function of temperature and/or time. Quantification was made on the basis of the ^{1}H NMR spectra. The spectral data of the dioxazole **3a** and of the imino anhydride **4a** listed in Table 1 were deduced, after computer subtraction of the signals for other components, from the NMR spectra of the reaction mixtures obtained in Run 2 and Run 4, respectively. The remainder of the photooxygenation mixture was kept at room temperature. After 10 min the ^{1}H NMR spectrum showed the presence of only the triacylamine **5a**. The solvents were removed under reduced pressure and the residue was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (7:3) gave the triacylamine **5a** (95%), which was identified by comparison with an authentic sample.[3]

Solutions (0.1 mol dm^{-3}) of the *endo*-peroxide **2a**, obtained by dye-sensitized photooxygenation at −40 °C* of **1a** in [$^2H_6$]acetone (sensitizer RB) and [$^2H_3$]acetonitrile (sensitizer MB), were kept at −25 °C. After 2 h, the ^{1}H NMR spectra of the solutions recorded at −25 °C, showed the presence of compounds **2a** and **3a** in *ca.* 9:1 molar ratio.† By raising the probe temperature to −10 °C, compound **3a** rearranged into the imino anhydride **4a** and the latter into triacylamine **5a**.

TPP-sensitized Photooxygenation of the Oxazole **1b** *and Thermal Conversion of the* endo-*Peroxide* **2b**.—The reactions were carried out as described above for compounds **1a** and **2a**, respectively. The results obtained by the thermal conversion of the *endo*-peroxide **2b** are summarized in Table 2. Table 1 reports the spectral data of compound **2b** (obtained by recording the spectra at −70 °C) and those of compound **3b**. The latter were deduced by ^{1}H and ^{13}C NMR spectra of the sample of the photooxygenation kept at −15 °C for 1 h (Run 7) after computer subtraction of the signals for peroxide **2b**. The solutions deriving from Runs 9–11 in addition to the main products showed (^{1}H NMR spectroscopy) the presence of some *N*-formylbenzamide[8] **6b** and benzoic acid **7a**. The latter two products, which were identified by comparison with authentic samples, were derived from hydrolysis of compound **4b** (see below), caused during the transfer of the sample at −70 °C from the reaction apparatus to the spectrometer when adventitious inclusion of moisture occurred. Imino anhydride **4b** was obtained in the pure state by carrying out the sensitized photooxygenation in $CHCl_3$ at room temperature under strictly anhydrous conditions. When the reaction was complete, the solution was concentrated and compound **4b** was isolated by precipitation with dry diethyl ether. A chloroform solution of compound **4b** was heated at 60 °C. After 6 h, removal of the solvent yielded crude triacylamine **5b**, which was chromatographed on polyamide resin (10 g). Elution with light petroleum

* Temperature compatible with the freezing point of acetonitrile.
† It is to be noted that in $CDCl_3$–$CFCl_3$ the rearrangement rate is higher. At present this experimental evidence is unexplained.

gave more triacylamine **5b** in 95% yield, which was identified by comparison with an authentic sample.[9] Table 1 reports physical, spectral and analytical data for compound **4b** and some previously unreported spectral data for compound **5b**.

Hydrolysis of the Imino Anhydride **4b**.—To a 0.1 mol dm^{-3} solution of imino anhydride **4b** in $CHCl_3$ (5 cm^3) was added acetone–water (9:1) (5 cm^3) and the resulting solution was kept at 4 °C for 1 h. After removal of the solvents the residue was treated with saturated aq. sodium hydrogencarbonate and extracted with chloroform. The organic layer gave *N*-formylbenzamide **6b**[8] (80%). The aqueous layer was acidified and extracted with chloroform to give benzoic acid **7a** (75%). Both the products were identified by comparison with authentic samples.

TPP-sensitized Photo-oxygenation of the Oxazole **1c** *and Thermal Conversion of the* endo-*Peroxide* **2c**.—The reactions were carried out as described for compounds **1a** and **2a**, respectively. The results obtained in the thermal conversion of the *endo*-peroxide **2c** are summarized in Table 2. Table 1 reports spectral data for compounds **2c** and **3c** obtained by recording the ^1H and ^{13}C NMR spectra of their solutions at −70 and −30 °C, respectively. All attempts to detect the anhydride **4c** by carrying out the thermal conversion of the dioxazole **3c** in the range −25 to 0 °C failed. The solutions deriving from Runs 14 and 15 in addition to the triacylamine **5c** showed (^1H NMR spectroscopy) the presence of some diacylamine **6a**[10] and formic acid **7c**. The latter two products, deriving from hydrolysis of the undetected anhydride **4c** (see below), were identified by comparison (^1H NMR spectroscopy) with authentic samples. When the photooxygenation of compound **1c** in $CHCl_3$ was carried out at room temperature under strictly anhydrous conditions and, after removal of the solvents, the residue was chromatographed on polyamide resin (10 g), elution with light petroleum gave quantitatively the triacylamine **5c**. The latter was identified by comparison with an authentic sample.* Previously unreported physical, spectral and analytical data for compound **5c** are reported in Table 1.

Hydrolysis of the Imino Anhydride **4c**.—A 0.1 mol dm^{-3} solution (1 cm^3) of the *endo*-peroxide **2c** in $CDCl_3$–$CFCl_3$ (3:1) was kept at −30 °C. After 1 h the solvents were removed at −30 °C under reduced pressure and the dioxazole **3c** was dissolved in deuterioacetone–deuterium oxide (9:1) (1 cm^3) pre-cooled at this temperature. An aliquot was kept at −30 °C; after 8 h, the ^1H NMR spectrum recorded at this temperature showed the presence of the unchanged dioxazole **3c** in addition to only trace amounts of other compounds. A second aliquot was kept at −10 °C; after 8 h, the ^1H NMR spectrum showed the presence of the triacylamine **5c**, *N*-acetylbenz[$^2H_1$]amide, and formic [$^2H_1$]acid in *ca.* 1:1:1 molar proportions. The latter two products were identified by comparison of the ^1H NMR spectrum of the reaction mixture with those of authentic samples of compounds **6a** and **7c** recorded in deuterioacetone–deuterium oxide (9:1). When a 0.1 mol dm^{-3} solution of the triacylamine **5c** in acetone–water (9:1) was kept at −10 °C for 8 h the triacylamine **5c** was recovered quantitatively.

* Only ^1H NMR data of triacylamine **5c** have previously been reported.[2]

Acknowledgements

This work was financially supported by Progetto Finalizzato del CNR (Rome) Chimica Fine 2. The NMR spectra were taken at the Centro di Metodologie Chimico Fisiche, Università di Napoli (I. Giudicianni).

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Paper 0/04108D
Received 10*th September* 1990
Accepted 5*th March* 1991