

Oxidation of Fully Substituted Alkoxyoxazoles with Singlet Molecular Oxygen

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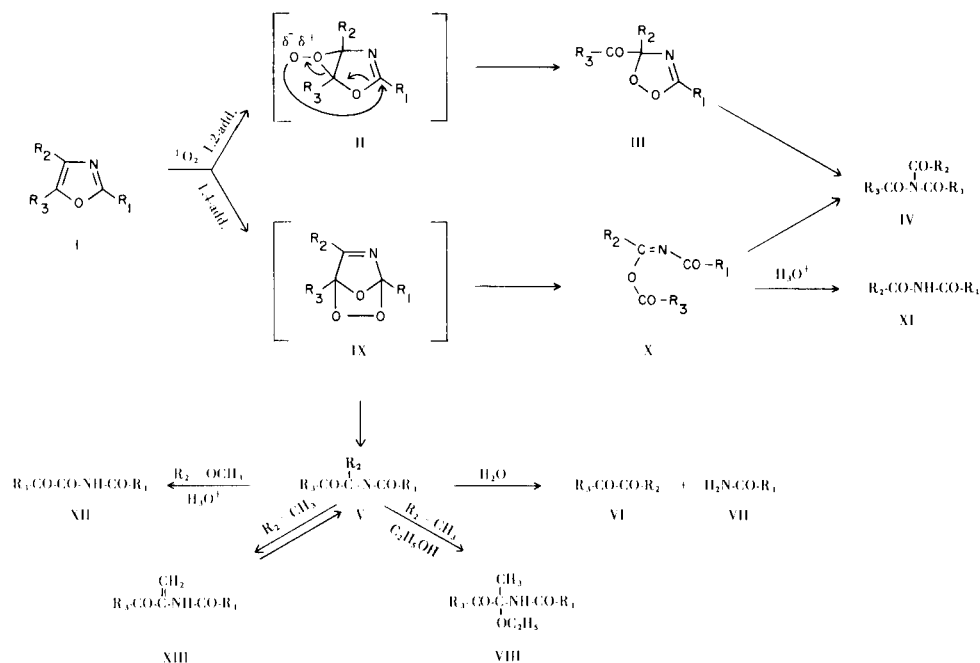
Diacylcarbamates IV can be prepared from alkoxyoxazoles I by $^1\text{O}_2$ oxidation. When the reaction is opportunely carried out a new heterocyclic system, namely the 3H-1,2,4-dioxazole III, is formed. A mechanistic interpretation of the results is suggested.

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The researches on the oxidation of oxazoles with $^1\text{O}_2$ by Wasserman, *et al.*, (1) have shown a route for the preparation of triamides. In order to provide a useful method for the preparation of diacylcarbamates we have extended this synthetic process to alkoxyoxazoles. The study of the alkoxyoxazole oxidation with $^1\text{O}_2$ appeared of some interest also in order to examine the effect of the alkoxy substituents on the heterocyclic system.

In this paper we report the results obtained using 2-phenyl-4-methyl-5-methoxyoxazole (Ia), 2-phenyl-4-methyl-5-ethoxyoxazole (Ib) and 2-ethoxy-4-methoxy-5-phenyloxazole (Ic). From each of these compounds, diacylcarbamates IV were obtained in good yield. Furthermore, when the oxidation was opportunely carried out, a new heterocyclic system, namely the 3H-1,2,4-dioxazole (III), was formed.

Scheme



- a. $\text{R}_1 = \text{C}_6\text{H}_5$; $\text{R}_2 = \text{CH}_3$; $\text{R}_3 = \text{OCH}_3$
 b. $\text{R}_1 = \text{C}_6\text{H}_5$; $\text{R}_2 = \text{CH}_3$; $\text{R}_3 = \text{OC}_2\text{H}_5$
 c. $\text{R}_1 = \text{OC}_2\text{H}_5$; $\text{R}_2 = \text{OCH}_3$; $\text{R}_3 = \text{C}_6\text{H}_5$

The dye-sensitized photooxygenation of the alkoxyoxazoles (I) was accomplished in anhydrous chloroform at room temperature with methylene blue as the sensitizer using a halogen-superphot lamp (Osram 650 W). The reaction was periodically sampled and the samples analyzed by ^1H nmr. Inspection of ^1H nmr spectrum of the Ia oxidation mixture, after the signals of the starting material had disappeared (1 hour), showed the presence of 3-methoxycarbonyl-3-methyl-5-phenyl-1,2,4-dioxazole (IIIa), methyl *N*-acetyl-*N*-benzoylcarbamate (IVa) and methyl 2-benzoyliminopropionate (Va) (Scheme). The composition of the reaction mixture, which had been presumed on the basis of the ^1H nmr spectrum, was chromatographically and chemically confirmed as follows. Silica

gel chromatography allowed the isolation of dioxazole IIIa (47%), carbamate IVa (10%) and benzamide (VIIa). The last compound was evidently formed by hydrolysis of Va which hydrolyzes into VIIa and methyl pyruvate (VIa) even by atmospheric moisture. The presence of Va in the oxidation mixture and its quantitation were confirmed by the results obtained by the addition of dry ethanol to the crude reaction mixture; under these conditions the ketimine Va gave methyl 2-ethoxy-2-benzoylaminopropionate (VIIIa) which was isolated by silica gel chromatography (yield 40% of the starting material Ia). The IIIa, IVa and VIIIa structures were assigned on the basis of elemental analysis and spectral data reported in the Table.

The mechanistic origin of the dioxazole IIIa, that is the

Table

Physical, Spectral and Analytical Data of Products Derived from Oxazoles Ia-c Oxidation

| Compound | M.p., °C (b.p., °C/mm) | Ir Spectrum (chloroform), cm^{-1} | ^1H Nmr Spectrum (deuteriochloroform) τ (J, Hz) | Empirical formula | Anal., % | | |
|----------|---------------------------|--|---|---|----------------|--------------|------------------|
| | | | | | Calcd. C, | H, | N |
| IIIa | Oil | 1750, 1660 | 2.00-2.64 (5H, m, C_6H_5), 6.20 (3H, s, OCH_3), 8.16 (3H, s, CH_3) | $\text{C}_{11}\text{H}_{11}\text{NO}_4$ | 59.72 60.12 | 5.01 5.33 | 6.33 (a) 6.16 |
| IIIb | Oil | 1750, 1660 | 1.95-2.65 (5H, m, C_6H_5), 5.72 (2H, q, $J = 7$, OCH_2), 8.16 (3H, s, CH_3), 8.70 (3H, t, $J = 7$, CH_3) | $\text{C}_{12}\text{H}_{13}\text{NO}_4$ | 61.27 61.66 | 5.57 5.90 | 5.96 (b) 5.90 |
| IVa | 95-96 (c) | 1765, 1745, 1710 | 2.00-2.60 (5H, m, C_6H_5), 6.28 (3H, s, OCH_3), 7.42 (3H, s, CH_3) | $\text{C}_{11}\text{H}_{11}\text{NO}_4$ | 59.72 59.78 | 5.01 5.30 | 6.33 6.26 |
| IVb | 81-83 (c) | 1765, 1745, 1710 | 2.00-2.60 (5H, m, C_6H_5), 5.82 (2H, q, $J = 7$, OCH_2), 7.42 (3H, s, CH_3), 8.88 (3H, t, $J = 7$, CH_3) | $\text{C}_{12}\text{H}_{13}\text{NO}_4$ | 61.27 61.25 | 5.57 5.61 | 5.96 6.03 |
| IVc | Oil | 1805, 1765, 1750, 1730 | 2.00-2.60 (5H, m, C_6H_5), 5.78 (2H, q, $J = 7$, OCH_2), 6.22 (3H, s, OCH_3), 8.86 (3H, t, $J = 7$, CH_3) | $\text{C}_{12}\text{H}_{13}\text{NO}_5$ | 57.37 57.37 | 5.22 5.36 | 5.58 5.59 |
| Vc | (140-143/3) | 1728, 1715, 1695, 1680, 1645 | 1.95-2.70 (5H, m, C_6H_5), 5.92 (2H, q, $J = 7$, OCH_2), 6.01 (3H, s, OCH_3), 8.84 (3H, t, $J = 7$, CH_3) | $\text{C}_{12}\text{H}_{13}\text{NO}_4$ | 61.27 60.99 | 5.57 5.81 | 5.96 5.71 |
| VIIIa | 124-126 (c) | 3365, 1730, 1670 | 2.00-2.60 (5H, m, C_6H_5), 6.14 (3H, s, OCH_3), 6.50 and 6.54 (2H, two q, $J = 7$, OCH_2), 8.11 (3H, s, CH_3), 8.80 (3H, t, $J = 7$, CH_3) | $\text{C}_{13}\text{H}_{17}\text{NO}_4$ | 62.14 62.02 | 6.82 6.88 | 5.57 5.62 |
| VIIIb | 93-95 (c) | 3365, 1730, 1675 | 2.03-2.65 (5H, m, C_6H_5), 5.69 (2H, q, $J = 7$, COOCH_2), 6.50 and 6.54 (2H, two q, $J = 7$, OCH_2), 8.10 (3H, s, CH_3), 8.68 and 8.79 (6H, two t, $J = 7$, 2CH_3) | $\text{C}_{14}\text{H}_{19}\text{NO}_4$ | 63.38 63.48 | 7.22 7.40 | 5.28 5.47 |
| XIIc | 78-80 (c) | 3330, 1798, 1763, 1738, 1710, 1695, 1687 | 1.15 (1H, bs, NH), 1.70-2.63 (5H, m, C_6H_5), 5.74 (2H, q, $J = 7$, OCH_2), 8.73 (3H, t, $J = 7$, CH_3) | $\text{C}_{11}\text{H}_{11}\text{NO}_4$ | 59.72 59.99 | 5.01 5.02 | 6.33 6.32 |
| XIIIa | Oil | 3365, 1720, 1675, 1640 | 1.45 (1H, bs, NH), 2.00-2.65 (5H, m, C_6H_5), 3.18 and 4.00 (each 1H, s and d, $J = 1.3$), 6.13 (3H, s, OCH_3) | $\text{C}_{11}\text{H}_{11}\text{NO}_3$ | 64.38 64.62 | 5.40 5.61 | 6.83 6.63 |

(a) Active oxygen Calcd: 7.2%. Found: 6.9%. (b) Active oxygen Calcd: 6.8%. Found: 6.3%. (c) Recrystallization solvent: light petroleum (b.p. 40-70°).

major product of the Ia sensitized photooxidation, can be explained by 1,2-addition of the $^1\text{O}_2$ on the electron-rich heterocyclic system to give the unstable peroxirane intermediate IIa as it has been suggested for alkenes or dienes (2). The intermediate IIa because of its peculiar structure could rearrange into dioxazole IIIa as depicted in the Scheme.

In order to gain information concerning the origin of the carbamate IVa, dioxazole IIIa was irradiated under the same conditions as adopted for the oxidation reaction. In this way trace amounts of IVa were obtained, which shows the conversion of Ia to IVa proceeding through dioxazole IIIa as possible. However, the low yield of IVa obtained in this reaction, compared with the yield of IVa in the oxidation mixture, indicates that the conversion of Ia into IVa does not occur only *via* dioxazole IIIa. In support of this, it should be noted that, when the dye-sensitized photooxidation of Ia was carried out in deuteriochloroform at 0° , the ^1H nmr spectrum of the reaction mixture recorded before Ia had completely changed (30 minutes) showed singlets at τ 7.84 and 6.15 attributable respectively to $\text{CH}_3\text{-C=}$ and $\text{CH}_3\text{O-C=O}$ of the imino-anhydride Xa (3), in addition to the signals of Ia, IIIa, Va and IVa (only trace amounts of the last one were present). When this reaction mixture was kept at 35° the ^1H nmr spectrum gradually changed, the signals of IVa increased whereas the signals assigned to Xa disappeared. If 2*N* hydrochloric acid was added to the mixture immediately after the oxidation was stopped, diamide XIa, evidently formed by hydrolysis of Xa, was obtained in addition to Ia, IIIa, IVa, VIa and VIIa (4). Therefore we suggest that IVa is also formed through a 1,4-addition of the $^1\text{O}_2$ to the oxazole-diene system *via* endoperoxide IXa by a step-wise sequence involving first endoperoxide IXa formation, then Baeyer-Villiger-like rearrangement to the imino anhydride Xa and finally *O*-acyl to *N*-acyl transfer, as previously suggested for the $^1\text{O}_2$ oxidation of phenyl- and alkyl-substituted oxazoles (1).

The formation of the ketimine Va during the oxidation is more difficult to explain; a possible precursor might be the endoperoxide IXa, which could lose in some way one oxygen atom, perhaps to give it to another molecule of Ia. The well known decomposition of the furan endoperoxides into diacylethylenes is in support of this hypothesis (5).

Alkoxyoxazole Ib by dye-sensitized photooxidation behaved just like Ia (Table). Under the above conditions dialkoxyoxazole Ic gave a mixture which, on the basis of its ^1H nmr spectrum, was composed of carbamate IVc and imino-ether Vc in *ca.*, 6:4 molar ratio. Imino-ether Vc undergoes hydrolysis by atmospheric moisture into methyl phenylglyoxylate (VIc) and urethane (VIIc), nevertheless, its stability to hydrolysis is higher than that of Va and it was isolated from the oxidation mixture by distillation;

its structure was assigned on the basis of elemental and spectral analyses and confirmed by quantitative mild acid hydrolysis to (*N*-ethoxycarbonyl)phenylglyoxylamide (XIIc). Carbamate IVc was isolated by silica gel chromatography and its structure was assigned on the basis of elemental analysis and spectral data. Mild acid hydrolysis under the conditions adopted for Vc left IVc unchanged; therefore the quantitation of IVc and Vc in the reaction mixture was confirmed by mild acid hydrolysis of the crude reaction mixture followed by silica gel chromatography, which allowed the isolation of carbamate IVc (58%) and amide XIIc (36%) (Table). In order to ascertain also in this case the formation of the dioxazole IIIc and the imino-anhydride Xc as intermediates, the Ic dye-sensitized photooxidation was carried out at 0° in deuteriochloroform. The ^1H nmr spectrum of the reaction mixture, recorded before Ic had completely changed, showed two singlets at τ 6.52 and 6.30 attributable to OCH_3 of IIIc and Xc (6) respectively, in addition to the signals of Ic, Vc and IVc. When the oxidation mixture was kept at 35° , the ^1H nmr spectrum gradually changed; the signals of IVc increased whereas the signals assigned to IIIc and Xc disappeared after 30 minutes. These results point out that the reaction pathway of Ic is very similar to that of Ia; the absence of IIIc in the reaction mixture at 35° can be due to its thermal stability, which is much lower than that of IIIa. In fact control experiments demonstrated that dioxazole IIIa undergoes thermal rearrangement into carbamate IVa much more slowly than IIIc [a solution of IIIa in chloroform heated at 35° for 7 days gave a solution which on the basis of its ^1H nmr spectrum was composed of IIIa (60%) and IVa (40%)].

The oxidation of Ia-c was also carried out using 9,10-diphenylanthracene peroxide (DPAP) as an $^1\text{O}_2$ donor (7). The reactions were accomplished in refluxing anhydrous benzene in a slow current of nitrogen until ^1H nmr spectrum of the oxidation mixtures showed the complete consumption of the starting materials. The reaction of Ia was complete after 96 hours and the oxidation mixture showed the presence of the carbamate IVa, ketimine Va and methyl 2-benzoylaminoacrylate (XIIIa) in *ca.*, 6:3:1 molar ratio. The composition of the reaction mixture was chromatographically and chemically confirmed. The structure (XIIIa) was assigned on the basis of elemental and spectral analyses (*cf.* Table). In control experiments we have found that Va, by heating in benzene solution, partly isomerizes into XIIIa. This imide Va \rightleftharpoons enamide XIIIa equilibrium was expected on the basis of the data reported in the literature (8).

Alkoxyoxazole Ib, in the reaction with thermally generated $^1\text{O}_2$, behaved like Ia. The reaction of the dialkoxyoxazole Ic was complete after 28 hours; the oxidation mixture was composed of carbamate IVc (80%) and imino-

ether Vc (13%).

We can provide no direct evidence for the presence of dioxazole III intermediate. However, control experiments showed that IIIa, by heating in refluxing benzene, was completely transformed into IVa after 7 hours also in the presence of DPAP. Therefore, the transient formation of III during the reaction of I with the thermally generated $^1\text{O}_2$ cannot be excluded. Further experiments in this regard are in progress.

Conclusion.

The above results point out that diacylcarbamates IV can be prepared from alkoxyoxazoles I in one-step reaction by DPAP decomposition in refluxing benzene or in two-step reaction by dye-sensitized oxidation and successive heating of the dioxazoles III intermediates which are the first examples of 3H-1,2,4-dioxazoles. Their formation by the oxidation of the alkoxyoxazoles I is due to the presence of alkoxy groups on the heterocyclic system.

EXPERIMENTAL

Melting and boiling points are uncorrected. Ir spectra were recorded on a Perkin Elmer 157 spectrophotometer; ^1H nmr on a Perkin Elmer R 12 A spectrometer with TMS as an internal standard. Chloroform used in the oxidation reactions was anhydrous and ethanol free. Silica gel 0.05-0.20 mm (Merck) and light petroleum b.p. 30-50° were used for column chromatography.

General Procedure for Photosensitized Oxidation.

A 2% solution of Ia-c in chloroform, after the addition of 2% of methylene blue, was irradiated with a halogen-superphot lamp (Osram 650 W). During the irradiation, dry oxygen was bubbled through the solution which was cooled with a water sleeve. The reaction was periodically sampled and the samples analyzed by ^1H nmr. The reaction time and the composition of the reaction mixture were established by ^1H nmr analysis. The composition of the reaction mixture was chromatographically confirmed.

Photosensitized Oxidation of Ia.

Oxidation was accomplished on 640 mg. of Ia (9). The reaction was complete within 1 hour. Inspection of the ^1H nmr spectrum of the reaction mixture showed, in addition to the signals of IIIa and IVa, two singlets at τ 6.20 (3H, OCH₃) and 7.77 (3H, CH₃) assigned to Va (10). On the basis of the relative areas of the methyl signals, molar ratio IIIa:IVa:Va was ca. 5:1:4. Ketimine Va is very sensitive to hydrolysis: if the ^1H nmr is recorded again after a few minutes, it shows the presence of the pyruvate VIa. The compounds IIIa, IVa and VIa were identified by comparison (^1H nmr spectra) with authentic samples.

Evaporation *in vacuo* of an aliquot of the irradiation solution (16 ml.) afforded 320 mg. of the crude oxidation mixture which was chromatographed on silica gel (30 g.). Elution with light petroleum/ether (9:1) and (4:1) and with ethyl acetate gave IIIa (47%), IVa (10%), VIIa (40%) successively.

A second aliquot of the solution (16 ml.) was treated with 0.2 ml. of dry ethanol. After 24 hours the solvent was removed *in vacuo*. The residue (360 mg.) was chromatographed on silica gel (30 g.). Elution with light petroleum/ether (9:1), (4:1) and (3:2) and with ethyl acetate gave IIIa (47%), IVa (10%), VIIIa (40%),

VIIa (trace amounts) successively.

When during the irradiation (Ia 500 mg.) the solution (solvent deuteriochloroform) was cooled with ice-water the ^1H nmr spectrum of the reaction mixture, recorded after 30 minutes, showed the presence of Ia, IIIa, Va, Xa [singlets at τ 6.15 (3H, OCH₃) and 7.84 (3H, CH₃)] and trace amounts of IVa.

An aliquot of the solution (12.5 ml.) was immediately treated with 2N hydrochloric acid in acetone solution; after 30 minutes, usual work gave a mixture (215 mg.) which was chromatographed on silica gel (20 g.). Elution with light petroleum/ether (9:1) afforded 156 mg. of a mixture which, on the basis of its ^1H nmr spectrum, was shown to contain 107 mg. of Ia and 58 mg. (35%) of IIIa. Elution with light petroleum/ether (4:1), (1:1) and ethyl acetate gave IVa (2%), XIa [11%; identified by comparison of the ir and ^1H nmr spectra with those of an authentic sample (11)] and VIIa (40%). The yields are based on unrecovered starting Ia. A second aliquot (12.5 ml.) was kept at 35°; after 30 minutes an inspection of the ^1H nmr spectrum showed Xa was completely changed. The solution was treated with 2N hydrochloric acid in acetone solution and worked up as above described: in addition to Ia, IIIa and VIIa, IVa was isolated in 12% yield.

Photosensitized Oxidation of Ib.

Oxidation was accomplished on 460 mg. of Ib (9). The reaction was complete after 1 hour. ^1H nmr spectrum of the reaction mixture showed, in addition to the signals of IIIb and IVb, signals at τ 5.75 (2H, q, J = 7 Hz, OCH₂), 7.76 (3H, s, CH₃), 8.78 (3H, t, J = 7 Hz, CH₃) assigned to Vb (12). On the basis of the relative areas of the methyl signals, molar ratio IIIb:IVb:Vb was ca. 5:1:4. A portion of the oxidation mixture was partitioned, as above described for the oxidation mixture of Ia, in IIIb (45%), IVb (10%), VIIb (40%). A second portion was treated with dry ethanol, worked up as above described for the oxidation mixture of Ia and partitioned in IIIb (45%), IVb (10%) and VIIIb (40%).

Photosensitized Oxidation of Ic.

Oxidation was accomplished on 230 mg. of Ic (13). The reaction was complete within 1 hour. ^1H nmr spectrum of the reaction mixture showed the presence of carbamate IVc and imino-ether Vc in ca. 6:4 molar ratio (on the basis of the relative areas of the methoxyl signals). Evaporation *in vacuo* of the solvent yielded 245 mg. of colorless liquid, which by repeated distillations afforded pure Vc. Imino-ether Vc is sensitive to hydrolysis: it is hydrolyzed also by atmospheric moisture into VIc and VIIc (identified by comparison with authentic samples); mild acid hydrolysis (Vc 100 mg., dioxane 2 ml., 2N hydrochloric acid 0.02 ml., for 30 minutes at room temperature) gives quantitatively XIIc.

The oxidation mixture, obtained starting from 210 mg. of Ic, was chromatographed on silica gel (20 g.). Elution with light petroleum/ether (9:1) yielded a mixture of Vc and VIc. Elution with light petroleum/ether (7:3) gave IVc (140 mg.). Elution with ether gave VIIc. Carbamate IVc was rechromatographed on silica gel; it was quantitatively recovered after treatment with hydrochloric acid under the conditions employed for Vc.

The oxidation mixture, obtained starting from 210 mg. of Ic, was treated with 2N hydrochloric acid as above described for imino-ether Vc. Usual work up gave 220 mg. of a mixture which was chromatographed on silica gel (20 g.). Elution with light petroleum/ether (7:3) and (3:2) gave IVc (58%) and XIIc (36%) successively.

When during the irradiation the solution (solvent deuteriochloroform) was cooled with ice-water, the ^1H nmr spectrum of the reaction mixture, recorded after 10 minutes, showed the presence of Ic, IIIc, IVc, Vc and Xc. The solution was kept at

35°, after 30 minutes the ¹H nmr spectrum showed the presence of Ic, IVc and Vc.

General Procedure for Oxidation by DPAP.

A 2% solution of Ia-c in dry benzene, after addition of DPAP (14) (1:2 molar ratio), was refluxed in the dark under nitrogen.

The reaction was periodically sampled and the samples analyzed by ¹H nmr. The reaction time and the composition of the reaction mixture were based on ¹H nmr analysis. The composition of the reaction mixture was chromatographically confirmed.

Oxidation of Ia by DPAP.

Oxidation was accomplished on 400 mg. of Ia. The reaction was complete within 96 hours. Inspection of the ¹H nmr spectrum of the reaction mixture showed, in addition to DPAP and 9,10-diphenylanthracene, the presence of carbamate IVa, ketimine Va, enamide XIIIa in ca. 6:3:1 molar ratio (on the basis of the relative areas of the methyl and methoxyl signals). The compounds IVa and XIIIa were identified by comparison (¹H nmr spectra) with authentic samples, ketimine Va by comparison (¹H nmr spectrum) with the photosensitized oxidation mixture. After removal of the solvent *in vacuo* the residue was chromatographed on silica gel (90 g.). Elution with light petroleum/ether (9:1) and (4:1) and ethyl acetate gave a mixture of DPAP and 9,10-diphenylanthracene, XIIIa (10%), IVa (55%) and VIIa (30%) successively.

Oxidation of Ib by DPAP.

Oxidation was accomplished on 406 mg. of Ib. The reaction was complete within 96 hours. ¹H nmr spectrum of the reaction mixture showed the presence of carbamate IVb, ketimine Vb, enamide XIIIb in ca. 6:3.5:0.5 molar ratio (on the basis of relative areas of methyl and ethoxyl signals). The mixture was partitioned, as above described for Ia, in XIIIb (5%), IVb (55%), and VII (32%). The structure XIIIb was assigned by comparison (ir and ¹H nmr spectra) with XIIIa; ir ν max (chloroform): 3365, 1720, 1675, 1640 cm⁻¹; ¹H nmr (deuteriochloroform): τ 1.42 (1H, bs, NH), 2.00-2.65 (5H, m, C₆H₅), 3.21 and 4.02 (each 1H, s and d, J = 1.3 Hz), 5.68 (2H, q, J = 7 Hz, OCH₂), 8.64 (3H, t, J = 7 Hz, CH₃).

Oxidation of Ic by DPAP.

Oxidation was accomplished on 182 mg. of Ic. The reaction was complete within 28 hours. Inspection of the ¹H nmr spectrum of the reaction mixture showed the presence of IVc and Vc in ca. 8:1 molar ratio (on the basis of the relative areas of the methoxyl signals).

After removal of the solvent *in vacuo* the crude oxidation mixture was hydrolyzed by 2N hydrochloric acid as above described for imino-ether Vc. Usual work up gave 750 mg. of a mixture which was chromatographed on silica gel (40 g.). Elution with light petroleum/ether (9:1) and (7:3) gave a mixture of DPAP and 9,10-diphenylanthracene, IVc (80%) and XIIc (13%) successively.

Irradiation of IIIa.

Irradiation was accomplished on 80 mg. of IIIa as above described for photosensitized oxidation. After 1 hour inspection of the ¹H nmr of the mixture showed only trace amounts of IVa. After 15 hours, ¹H nmr analysis showed dioxazole IIIa and carbamate IVa in ca. 2:1 molar ratio (on the basis of the relative

areas of the methyl signals).

Heating of IIIa.

A 2% solution of IIIa in dry chloroform was heated at 35°. After 7 days the ¹H nmr spectrum showed dioxazole IIIa and carbamate IVa in ca. 3:2 molar ratio.

A 2% solution of IIIa in dry benzene was refluxed and periodically sampled. The samples were analyzed by ¹H nmr. After 7 hours only IVa was present. When, to the 2% solution of IIIa in dry benzene, DPAP (1:2 molar ratio) was added and the solution was refluxed, the same result was obtained.

Heating of the Sensitized Photooxidation Mixture of Ia.

The 2% benzene solution of the sensitized photooxidation mixture of Ia (500 mg.), after addition of DPAP (1.875 g.) was refluxed in the dark under nitrogen. After 4 days the ¹H nmr spectrum of the reaction mixture showed, in addition to DPAP, 9,10-diphenylanthracene and trace amounts of Va, only the presence of IVa and XIIIa in ca. 6:4 molar ratio. After removal of the solvent *in vacuo*, the mixture was chromatographed on silica gel (100 g.). Elution with light petroleum/ether (9:1), (4:1) and ethyl acetate gave a mixture of DPAP and 9,10-diphenylanthracene, XIIIa (38%), IVa (53%) and VIIa (trace amounts).

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