Photolysis and Thermolysis of *N*-Alkoxycarbonyl-α-diazoamide Acetals (1)

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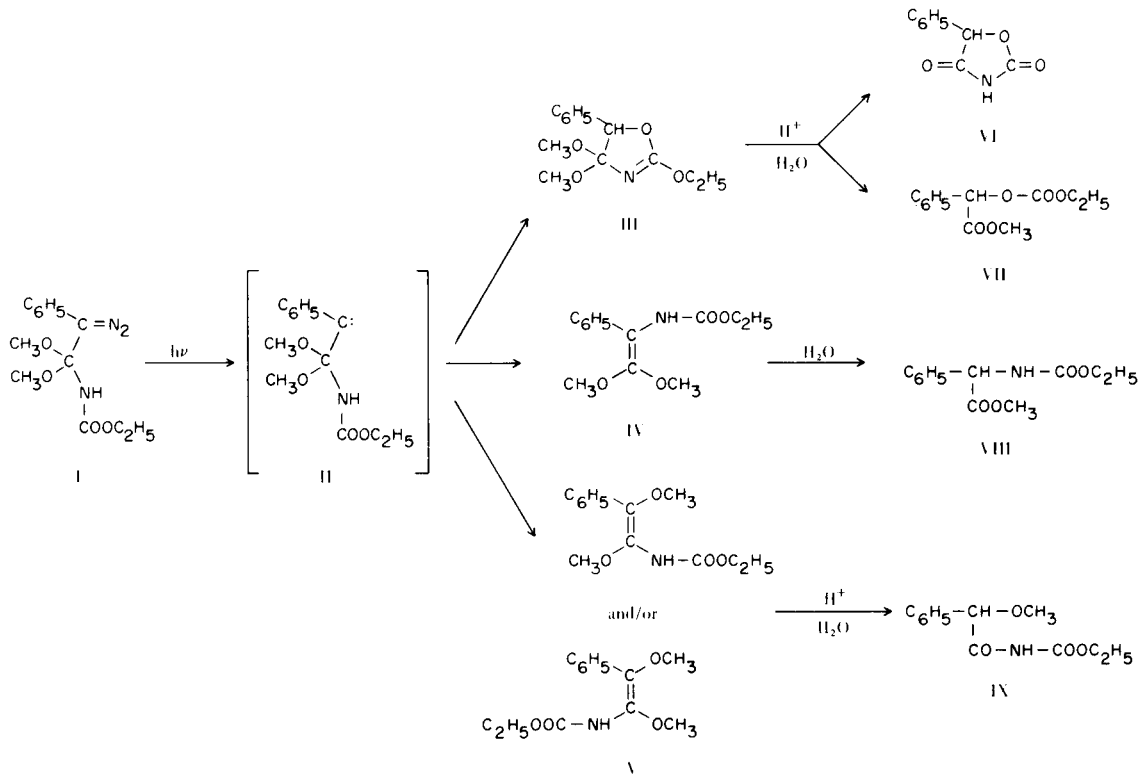
In the photoysis and thermolysis of 1-phenyl-2,2-dimethoxy-2-(*N*-alkoxycarbonylamino)-diazoethanes the presence of the *N*-alkoxycarbonylamino substituent is of fundamental importance. In both cases the carbene intermediate, through intramolecular addition to carbonyl oxygen, gives, as main products, oxazole derivatives. In the thermolysis, especially at relatively low temperature (160°), the diazoamide acetals in part cyclize to form triazole derivatives.

Photolysis and thermolysis of 2,2-diethoxydiazoethane was subjected to investigations in recent years; this compound decomposes to diethoxymethylcarbene which rearranges to *cis*- and *trans*-1,2-diethoxyethylene and keten diethylacetal (2).

Recently we reported the synthesis of 1-phenyl-2,2-dimethoxy-2-(*N*-ethoxycarbonylamino)diazoethane (I), the first example of diazoamide acetals (3,4). In order to examine the effect of the *N*-ethoxycarbonylamino substituent at position 2 on the carbene rearrangement we have

SCHEME I



now investigated the thermal- and photo-decomposition of this compound.

Irradiation of a solution of I with a high-pressure mercury lamp (Hanovia 450 W) with a pyrex filter sleeve, gave a quite simple mixture. 2-Ethoxy-4,4-dimethoxy-5-phenyl-Δ^2-oxazoline (III) (4) as the major product and 1,1-dimethoxy-2-phenyl-2-(*N*-ethoxycarbonylamino)ethene (IV) and *cis*- and/or *trans*-1,2-dimethoxy-1-(*N*-ethoxycarbonylamino)-2-phenylethene (V) as the minor products were obtained (Scheme I). The composition of the reaction mixture was presumed on the basis of spectral data; ir (carbon tetrachloride) revealed the presence of >NH (3885 cm^{-1}), $-COOC_2H_5$ (1750-1720 cm^{-1}), >C=N- (1661 cm^{-1}), >C=C< (1637 cm^{-1}) functions; nmr showed the presence of oxazoline III, identified by comparison with the nmr spectrum of the pure compound (4); moreover a slightly broadened signal centered at τ 4.04 (NH of IV and V) and three singlets at τ 6.18, 6.36, 6.47 (OCH_3 of IV and V) are also present; the area of the singlet at τ 6.36 equals about (5) the sum of the areas of the ones at τ 6.18 and 6.47, while the relative areas of the signals at τ 4.04 and 6.36 are about 1:3 (5). The composition of the reaction mixture was chromatographically and chemically confirmed: alumina chromatography allowed the isolation of oxazoline III (38%) and methyl α-(*N*-ethoxycarbonylamino)-α-phenylacetate (VIII) (4) (*ca.* 16%), the latter compound being evidently formed by hydrolysis of IV during the separation procedure, as observed in similar cases (4). No unequivocal evidence was obtained, by alumina chromatography, to support the presence in the reaction mixture of V: however its presence was confirmed by the results obtained from mild acid hydrolysis of the crude reaction mixture followed by chromatography on silica gel. In this way it was possible to isolate *ca.* 6% of *N*-ethoxycarbonyl-α-methoxy-α-phenylacetamide (IX) (4, 6), evidently formed by hydrolysis of V. Additional products isolated were 5-phenyloxazolidine-2,4-dione (VI) and methyl α-ethoxycarbonyl-oxy-α-phenylacetate (VII) [from oxazoline III (4)] and ester VIII [*ca.* 16%, from ketene acetal IV].

These results provide useful information for the attribution of the methyl singlets (τ 6.18, 6.36 and 6.47) in the nmr spectrum of the irradiation mixture. Because ester VIII and amide IX were obtained in a *ca.* 3:1 molar ratio, it seems very probable that in the original mixture IV and V were present in a similar ratio (7). On the other hand, since in the nmr spectrum of the irradiation mixture the relative areas of the singlets at τ 6.18, 6.36 and 6.47 were *ca.* 1:4:3, it can be deduced that the methoxyl groups of IV resonate at τ 6.47 and 6.36, while the methoxyl groups of V resonate at τ 6.36 and 6.18.

No spectral evidence was obtained to support the presence in the irradiation mixture of appreciable amounts of 1-ethoxycarbonyl-2,3-dimethoxy-3-phenylaziridine (X),

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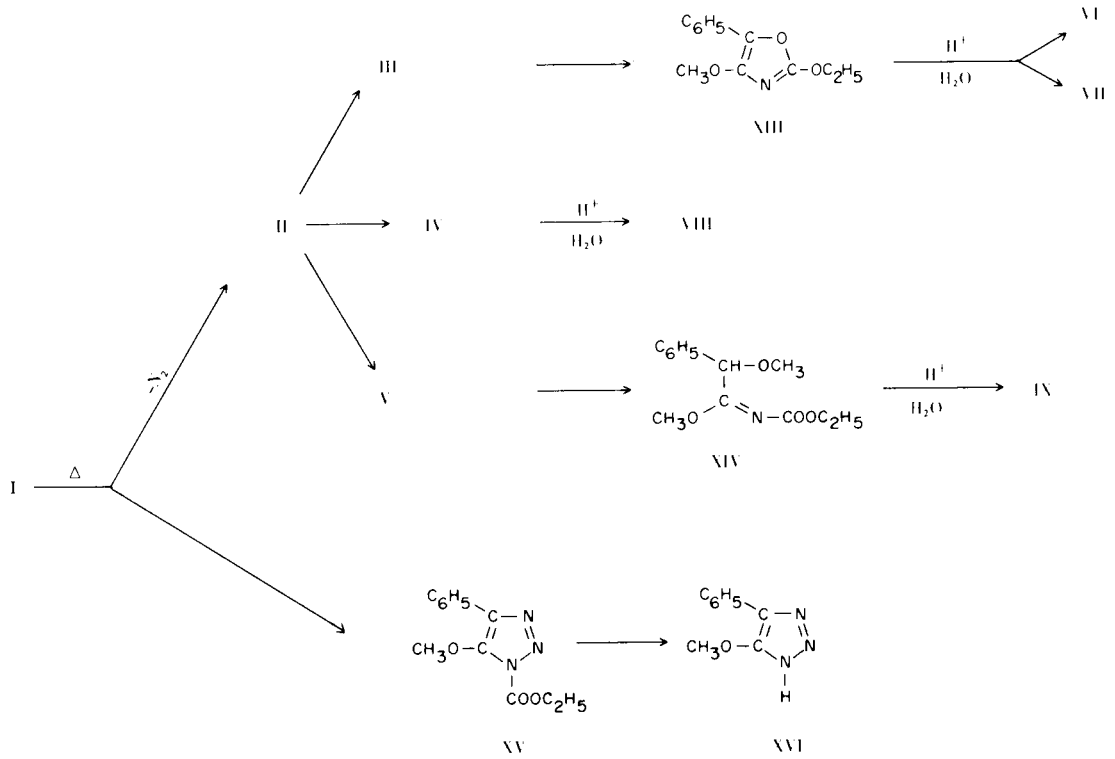
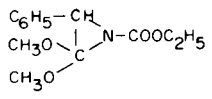
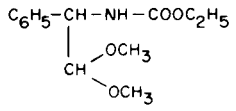


whose formation was to be expected on the basis of mechanistic considerations. It was also impossible to detect X by vapor phase chromatography of the reaction mixture owing to the unavailability of an authentic sample (8) and the instability of the mixture components (9). An attempt to identify aziridine X by means of its hydrogenolysis derivative, after catalytic hydrogenation of the crude irradiation mixture, was also performed. This experiment was made difficult because the same compound XII should form by catalytic hydrogenation of X and III, both present in the irradiation mixture. It should be remarked, however, that although it is generally assumed that *O*-debenzylation takes place with greater ease than *N*-debenzylation, there are examples of selective *N*-benzyl group hydrogenolysis in substrates containing both hydrogenolyzable groups over palladium on carbon under a few atmospheres of hydrogen (10). Therefore, on the basis of the data published in the literature and considering that hydrogenolysis of X might take place without affecting oxazoline III because of the favourable release of strain energy involved, the hydrogenation of the irradiation mixture was tested.

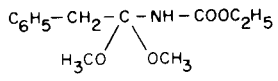
The reaction was carried out over Pd/C at room temperature and 1.2 atmospheres for a short reaction time. In addition to oxazoline III, α-ethoxycarbonyl-amino-α-phenylacetaldehyde dimethylacetal (XI) (from ketene acetal IV) as the major product and *N*-ethoxycarbonyl-α-phenylacetamide dimethylacetal (XII) as the minor product were obtained in this way. Acetals XI and XII were



X



XI



XII

isolated from the hydrogenation mixture by chromatography on alumina and their structures were assigned on the basis of elemental analysis and spectral data. The structure of amide acetal XII was confirmed by hydrolysis to *N*-ethoxycarbonyl-α-phenylacetamide (11).

Although amide acetal XII might be formed by aziridine X hydrogenolysis, its presence does not represent unequivocal evidence for the presence of aziridine X in the irradiation mixture. Indeed, though only in very small quantities, in the same experimental conditions oxazoline III gave the same products.

By photolysis under the above conditions, 1-phenyl-2, 2-dimethoxy-2-(*N*-isopropoxycarbonylamino)diazoethane behaved similarly yielding 2-isopropoxy-4,4-dimethoxy-5-phenyl-Δ^2-oxazoline as the main product.

Thermal decomposition of diazoamide acetal I at 160° gave a mixture which, on the basis of its nmr spectrum, was quite different from the photodecomposition mixture. Inspection of the nmr spectrum of the mixture showed the presence of 1-ethoxycarbonyl-4-phenyl-5-methoxy-1,2,3-triazole (XV) as the major product, 2-ethoxy-4-methoxy-5-phenyloxazole (XIII), ketene acetal IV, *N*-ethoxycarbonyl-α-methoxy-α-phenylacetimino methyl ether (XIV) as the minor products and very small quantities of oxazoline III and 4-phenyl-5-methoxy-1,2,3-triazole (XVI) (12). Oxazole XIII was identified by comparing it with the compound obtained by thermal decomposition at 160° of oxazoline III. The identities of iminoether XIV, triazoles XV and XVI, oxazoline III were proved by comparison with authentic samples. Finally indentification of ketene acetal IV was performed by comparing the nmr spectrum of the pyrolysis mixture with that of the photolysis mixture.

The composition of the pyrolysis mixture was confirmed by the results obtained from mild acid hydrolysis of the crude reaction mixture followed by chromatography on silica gel. In this way it was possible to isolate oxazolidine-2,4-dione VI and ester VII (both formed by hydrolysis of oxazole XIII as it can be deduced from the results obtained by hydrolysis of a pure sample of XIII), ester VIII (from ketene acetal IV), amide IX (from imino-ether XIV), triazoles XV and XVI.

Thermal decomposition of I at 220° gave the same products obtained at 160°; however in this case the amounts of triazoles XV and XVI are very small, while the main product of the reaction is oxazole XIII.

The results obtained by thermal decomposition of I at 160° can be discussed on the basis of those obtained by decomposition of I at 90° (4). At 160° diazoamide acetal I gave, in addition to triazoles XV and XVI, remarkable quantities of oxazole XIII, iminoether XIV and ketene acetal IV, while at 90° we essentially obtained XV and XVI.

This indicates that in both experiences a cyclization of I to triazole XV (12) occurs. However at 90° it can be supposed that this is approximately the only transformation of I; on the contrary at 160°, because of the greater thermal energy supplied to the system, I can also decompose to a large extent, through a breakdown of the C-N linkage, to carbene II, which successively can transform to III, IV and V. By aromatization III gives oxazole XIII, while V in the experimental conditions used, by tautomerization, is transformed into iminoether XIV (13) (Scheme II). The rearrangement V → XIV, to be expected

on the basis of the data reported in the literature (14), was confirmed by heating the irradiation mixture at 160°; from the nmr spectrum of the resultant mixture (singlets at τ 5.28, 6.43 and 6.75, characteristic for the iminoether XIV) the formation of XIV was definitively proved.

When I is heated at 220° the formation of carbene II predominates over the reaction of cyclization to triazole; successively, at this temperature, II yields preferentially oxazoline III and oxazole XIII.

Conclusion

The above results point out that the *N*-alkoxycarbonylamino substituent at position 2 of diazoethanes is of fundamental importance in the photolysis and thermolysis *via* carbene; the carbene intermediate, in fact, through intramolecular addition to the carbonyl oxygen, gives oxazole derivatives in both cases.

These results can be related to those obtained from photolysis of diazoketones and diazoester (15,16) which indicated in the photochemical Wolff rearrangement the transient existence of oxirene structures arising from the carbene intermediate by addition to the carbonyl oxygen. Of interest in this regard is that in the thermal decomposition, also in our experiments, cyclization of the carbene intermediate occurs to a large extent only when the reaction is performed at high temperature (16).

EXPERIMENTAL

Melting points are uncorrected. Uv and ir spectra were recorded on Perkin-Elmer 402 and 137 Infracord spectrophotometers; nmr were determined in carbon tetrachloride on a Perkin-Elmer R12A spectrometer with TMS as the internal standard. Silica Gel 0.05-0.20 mm (Merck), alumina neutral (Woelm), polyamid-SC 6 (Macherey-Nagel) were used for column chromatographies. Tlc's were carried out on pre-coated plates on silica gel F 254 (Merck). For the column chromatographies light petroleum, b.p. 30-50°, was used.

Irradiation of Diazoamide Acetal I.

In a 2% solution of I (1,2 g.) in anhydrous cyclohexane nitrogen was bubbled; the solution was then irradiated with a high-pressure mercury lamp (Hanovia 450 w) placed in a water-cooled quartz immersion well with a pyrex filter sleeve. The reaction was complete in 2.3 hours, when nitrogen ceased to evolve and the orange solution became colorless. After removal of the solvent under reduced pressure (0.5 mm) at room temperature the oily residue was analyzed by nmr and ir.

A portion of the irradiation mixture (570 mg.) was immediately (9) chromatographed on alumina B III (30 g.). Elution with 210 ml. of light petroleum/ether (9:1) yielded methyl α-methoxy-α-phenylacetate (18 mg., from V); elution with 240 ml. of the same eluent yielded oxazoline III (4) (220 mg., 38%) elution with light petroleum/ether (1:1) yielded aminoester VIII (4) (110 mg., 16%); finally elution with ether gave ethyl carbamate (28 mg. from V). All of the compounds were identified by comparison (ir and nmr spectra) with authentic samples. A portion of the irradiation mixture (536 mg.) was immediately (9) dissoved in a mixture of dioxane (2 ml.) and 2*N* hydrochloric acid (0.05 ml.) and was kept at room temperature. After 30 minutes the solvent was removed *in vacuo*. The residue was dissolved in chloroform and the solution washed with water and dried. After removal of the solvent the residue was chromatographed on silica gel (60 g.). Elution with light petroleum/ether (9:1) gave ester VII (4,17) (26 mg. 5%); elution with light petroleum/ether (4:1) gave amino ester VIII (82 mg., 18%); elution with light petroleum/ether (7:3) gave oxazolidine-2,4-dione VI (18) (30 mg.); finally elution with light petroleum/ether (1:1) afforded 70 mg. of a mixture which on the basis of its nmr spectrum was shown to contain 30 mg. (6%) of amide IX (4) and 40 mg. of oxazolidione VI [11.5%; total yield 20% (17)]. All of the compounds were identified by comparison (ir and nmr spectra) with authentic samples.

Hydrogenation of the Above Irradiation Mixture.

A solution of I (800 mg.) was irradiated as described above and immediately hydrogenated at room temperature and 1.2 atmospheres pressure in the presence of 10% Pd-C catalyst (80 mg.) for 1.30 hours. The catalyst was removed and the filtrate was evaporated under reduced pressure to give a colorless oil which, after ir and nmr analysis, was chromatographed on alumina B III (80 g.). Elution wtih light petroleum/ether (9:1) yielded oxazoline III (240 mg., 36%), elution with light petroleum/ether (4:1) yielded amide acetal XII (27 mg., 4%), elution with light petroleum/ether (1:1) yielded acetal XI (90 mg., 12%).

Amide acetal XII was recrystallized from light petroleum (b.p. 40-70°) to give white crystals, m.p. 59-61°; ir ν max (carbon tetrachloride): 3455 (NH), 1724 ($COOC_2H_5$) cm^{-1}; nmr: τ 2.90 (1, 5H, aromatic), 5.23 (bs, 1H, NH), 6.01(q, J = 7 Hz, 2H, CH_2), 6.74 (s, 2H, PH-CH_2), 6.83 (s, 6H, OCH_3), 8.82 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.93; H, 7.41; N, 5.83.

Amide acetal XII undergoes hydrolysis in the presence of atmospheric moisture to *N*-ethoxycarbonyl-α-phenylacetamide m.p. 106° (11).

Acetal XI was recrystallized from light petroleum (b.p. 40-70°) to give white crystals, m.p. 60-62°; ir ν max (carbon tetrachloride): 3475 (NH), 1727 ($COOC_2H_5$) cm^{-1}; nmr: τ 2.80 (s, 5H, aromatic), 4.72 (bd, J = 7 Hz, 1H, NH), 5.32 (dd, J = 7 and 3 Hz, 1H, Ph-CH-), 5.72 (d, J = 3 Hz, 1H, O-CH-O, 6.02 (q, J = 7 Hz, 2H, CH_2), 6.71 (s, 3H, OCH_3), 6.75 (s, 3H, OCH_3), 8.82 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.97; H, 7.50; N, 5,58.

Hydrogenolysis of Oxazoline III.

A solution of III in anhydrous cyclohexane was hydrogenated at room temperature and 1.2 atmospheres pressure in the presence of 10% Pd-C catalyst for 1.3 hours. After removal of the catalyst and evaporation of the solvent the residue was analyzed by nmr. Traces of amide acetal XII were identified by comparison with authentic samples (nmr spectra).

Preparation of 1-Phenyl-2,2-dimethoxy-2-(*N*-isopropoxycarbonylamino)diazoethane.

A mixture of phenylketene dimethylacetal (19) (26.55 mmoles) and isopropyl azidoformate (20) (26.55 mmoles) was kept at 35° for 8 days. An aliquot of the reaction mixture (6.56 g.) was chromatographed on alumina (120 g., B IV) (21). Elution with 400 ml. of light petroleum/benzene (4:1) afforded a mixture which was discarded; elution with increasing concentration of benzene in light petroleum (from 1:4 up to 7:3), 400 ml.,

afforded a mixture (1.14 g.) which was rechromatographed in light petroleum on polyamide (140 g., ϕ column 16 mm); 50 ml. fractions were collected; fractions 12-20 gave diazoamide acetal (1 g.) as red crystals, m.p. 55-58°; uv λ max (chloroform): 288 (log ϵ 4.31) and 488 mμ (log ϵ 1.78); ir ν max (carbon tetrachoride): 3390 (NH), 2074 (C=N_2), 1736 and 1715 (NH-C=O), 1125-1076 cm^{-1} (C-O-C-O-C); nmr: τ 2.6-3.2 (m, 5H, aromatic), 3.78 (bs, 1H, NH), 5.27 (h, J = 7 Hz, 1H, CH-O), 6.81 (s, 6H, 2 OCH_3), 8.94 (d, J = 7 Hz, 6H, 2 CH_3).

Anal. Calcd. for $C_{14}H_{19}N_3O_4$: C, 57.32; H, 6.53; N, 14.33. Found: C, 57.23; H, 6.75; N, 14.34.

Preparation of 2-Isopropoxy-4,4=dimethoxy-5-phenyl-Δ^2-oxazoline.

A 2% solution of 1-phenyl-2,2-dimethoxy-2-(*N*-isopropoxycarbonylamino)diazoethane (1.2 g.) in anhydrous nitromethane was photoylzed for 1.3 hours as described above for diazoamide acetal I. After removal of the solvent under reduced pressure at room temperature the irradiation mixture was chromatographed on alumina B III (60 g.). Elution with light petroleum/ether (9:1) yielded 2-isopropoxy-4,4-dimethoxy-5-phenyl-Δ^2-oxazoline (490 mg., 46%), as a colorless oil ir ν max (carbon tetrachloride): 1661 (C=N) cm^{-1}; nmr τ 2.73 (s, 5H, aromatic), 4.79 (s, 1H, Ph-CH-O), 5.02 (h, J = 6.5 Hz, 1H), 6.70 (s, 3H, O CH_3), 7.16 (s, 3H, O CH_3), 8.59 (d, J = 6.5 Hz, 6H, 2 CH_3); m/e 265 (M^+), 233 (M^+-CH_3OH), 223 (M^+-C_3H_6), 206 (M^+-C_3H_7O), 191 (233-C_3H_6).

Thermal Decomposition of Diazoamide Acetal at 160°.

A sample of diazoamide acetal I was placed in an nmr test tube and pyrolized under nitrogen in a silicone oil bath previously heated at 160°. After 10 minutes an inspection of the nmr spectrum of the reaction mixture showed the presence of triazole XV (main product), oxazole XIII, iminoether XIV (molar ratio XIII:XIV *ca.* 1:1), ketene acetal IV and very small quantities of oxazoline III and triazole XVI. The compounds XIII, XIV, XV, XVI and III were identified by comparison with authentic samples; ketene acetal IV by comparison with nmr spectrum of the irradiation mixture.

An aliquot of I (280 mg.) was pyrolized as described above and the resultant mixture, dissolved in dioxane, hydrolyzed under a stream of nitrogen in the same experimental conditions used for the hydrolysis of the irradiation mixture of I.

The hydrolyzate was chromatographed on a silica gel column (30 g.). Elution with 480 ml. of light petroleum/ether (9:1) yielded ester VII [5 mg., 2% (17)]; elution with 700 ml. of the same eluent gave a mixture (104 mg.) of triazoles XV and XVI [87 mg. of XV (35%) and 17 mg. of XVI (10%) (22)]. Elution with light petroleum/ether (4:1) gave aminoester VIII (25 mg., 10%). Elution with light petroleum/ether (1:4) yielded a mixture (62 mg.) of oxazolinedione VI and amide IX [22 mg. of VI 12% (17) and 40 mg. of IX 16% (22)].

Thermal Decomposition of Diazoamide Acetal I at 220°.

A sample of I was pyrolyzed as described above at 220° for 3 minutes. Inspection of the nmr spectrum of the reaction mixture, showed the presence of oxazole XIII as the main product. Compounds XIV, IV, XV, XVI, III were also present. Molar ratio XIII:XIV *ca.* 2:1.

Thermal Decomposition of Oxazoline III: Oxazole XIII.

Oxazoline III was pyrolyzed as above described for diazoamide acetal I, thus obtaining pure XIII as a colorless oil; nmr: τ 2.4-3.1 (m, 5H, aromatic), 5.62 (q, J = 7 Hz, 2H, CH_2), 6.08 (s, 3H, OCH_3), 8.55 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 66.00; H, 6.22; N, 6.58.

Although XIII is reasonably stable under nitrogen, it decomposes rapidly at room temperature in the presence of atmospheric oxygen to give a mixture which is under investigation.

Oxazole XIII (100 mg.) by mild acid hydrolysis as described for the pyrolysis mixture gave oxazolidine-2,4-dione VI (42 mg.) and ester VII (10 mg.) which were separated on tlc (chloroform-ethyl acetate 97:3, uv light) and identified by comparison with authentic material (4).

Acknowledgements.

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REFERENCES

(1) Part of this work was reported in preliminary form: M. L. Graziano, R. Scarpati and D. Tafuri, *Tetrahedron Letters*, 2469 (1972).

(2) W. Kirmse and M. Buschhoff, *Chem. Ber.*, **100**, 1491 (1967).

(3) R. Scarpati and M. L. Graziano, *Tetrahedron Letters*, 2085 (1971).

(4) R. Scarpati and M. L. Graziano, *J. Heterocyclic Chem.*, **9**, 1087 (1972).

(5) The determination of the areas cannot be rigorous owing to the presence of the methylenes quartets of the esters IV and V in the same region of the spectrum.

(6) Amide IX could not be isolated by alumina chromatography, because in its turn it undergoes hydrolysis in contact with alumina.

(7) This deduction is true provided that the transformation of IV and V into VIII and IX is almost quantitative; this seems to be very probable when considering the chemical behaviour of ketene acetals and the experimental conditions used.

(8) All attempts to synthesize aziridine X, according to P. Scheiner [*Tetrahedron*, **24**, 2757 (1968)] by thermal or photo decomposition of 1-ethoxycarbonyl-4-phenyl-5,5-dimethoxy-Δ^2-1,2,3-triazoline failed.

(9) The components of the reaction mixture are very unstable; at room temperature the nmr spectrum gradually changed, developing new peaks whereas the signals assigned to the compounds III, IV and V decreased in intensity and after 12 hours disappeared. Pure oxazoline III is considerably more stable.

(10) M. Freifelder, "Practical Catalytic Hydrogenation," Wiley-Interscience, New York, 1971 p. 430.

(11) T. Berger, F. Gagin, G. Pollak and C. Schonberger, *Chem. Abstr.*, 53, 6213d (1959).

(12) Because decarbalkoxylation of heterocyclic *N*-carboxylic esters easily occurs, [cfr. H. A. Staab, *Ann. Chem.*, **609**, 83 (1957); *Angew. Chem. Internat. Edit. Engl.*, **1**, 351 (1962)], it seems very probable that XVI derives from XV.

(13) In a previous paper (4) we demonstrated that at 35° iminoether XIV originates from 1-ethoxycarbonyl-4-phenyl-5,5-dimethoxy-Δ^2-1,2,3-triazoline XVII which is in equilibrium with I. At higher temperature (160-220°) I is so rapidly transformed that equilibrium cannot be reached and therefore XIV must originate from carbene *via* V. The interconversion I $\rightleftharpoons$ XVII is now confirmed from the XV:XIV molar ratios at different temperatures (at 35° 1:1; at 90° 10:1; at 160° 3:1; at 220° 1:3) and from the absence of dimethyl ethoxycarbonylimidocarbonate in the decom-

position mixtures at 160° and 220°.

(14) H. Ahlbercht, *Tetrahedron Letters*, 4421 (1968).

(15) G. Frater and O. P. Strausz, *J. Am. Chem. Soc.*, **92**, 6654 (1970); J. Fenwick, G. Frater, K. Ogi and O. P. Strausz, *ibid.*, **95**, 124 (1973); I. G. Csizmadia, H. E. Gunning, R. K. Gosavi and O. P. Strausz, *ibid.* **95**, 133 (1973).

(16) S. A. Matline and P. G. Sammes, *Chem. Commun.*, 11 (1972).

(17) It should be noted that hydrolysis of III and XIII is not quantitative.

(18) W. Traube and R. Ascher, *Ber.*, **46**, 2077 (1913).

(19) J. E. Baldwin and L. E. Walker, *J. Org. Chem.*, **31**, 3985 (1964).

(20) R. Kreher and G. Jager, *Z. Naturforschg.*, **20b**, 276 (1965).

(21) Because of diazoamide acetal sensitivity to hydrolysis, chromatography was practiced at a higher rate than normally used.

(22) The yields were calculated on the basis of the nmr spectrum of the reaction mixture.