Reactions of Ketenes XVII. Intermediates in the Reactions Between Ketene Acetals and Ethyl Azidoformate (1).

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The reaction of the ketene acetals with ethyl azidoformate proceeds *via* 1-ethoxycarbonyl-5,5-dialkoxy-Δ^2-1,2,3-triazolines. The latter decomposes easily at room temperature, the reaction pathway depending on the presence of the substituents at the 4-position. Thermolysis and photolysis of the 4-alkyl-substituted triazolines proceed *via* 1,3-diradicals. The photodecomposition of the 4-unsubstituted triazolines proceeds similarly. The thermal decomposition of the latter is considered either to involve homolytic cleavage of the N_1-N_2 bond to give a 1,5-diradical, or to proceed by a concerted mechanism.

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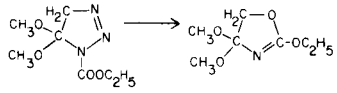
The reactions of ethyl azidoformate with several ketene acetals have been previously investigated. Ketene dialkylacetals at 35° gave almost exclusively 2,4,4-trialkoxy-Δ^2-oxazolines with traces of *N*-alkoxycarbonyl-α-alkoxyiminoethers (2). From mono- and dialkylketene dialkylacetals the *N*-alkoxycarbonyl-α-alkoxyiminoethers were obtained in very high yields, while in the reaction mixtures the absence of Δ^2-oxazolines was established (3).

The pathway of the above mentioned reactions was also studied and indirect evidence was obtained that the reaction products derive from the initially formed unstable 1-alkoxycarbonyl-Δ^2-1,2,3-triazolines. This result needs further investigation, as thermal decomposition of 1-alkoxycarbonyl-Δ^2-1.2.3-triazolines into Δ^2-oxazolines had never been observed before (4). Moreover, the difference between the reaction products obtained from unsubstituted and alkyl-substituted ketene acetals might be explained on the basis of reaction pathways involving different intermediates.

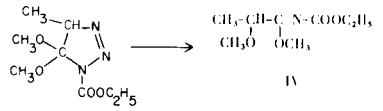
In order to ascertain the formation of the Δ^2-triazolines intermediates, a reinvestigation of the above reactions was undertaken.

When ketene dimethylacetal and ethyl azidoformate were allowed to stand at -15° for 1 month, after removal of the starting materials *in vacuo* at room temperature, pure 1-ethoxycarbonyl-5,5-dimethoxy-Δ^2-1,2,3-triazoline (I) was isolated and characterized by its ir and ^{1}H nmr spectra. Likewise 1-ethoxycarbonyl-4-methyl-5,5-dimethoxy-Δ^2-1,2,3-triazoline (II) was obtained from methylketene dimethylacetal.

Triazolines I and II can be isolated, but at room temperature they decompose by evolution of nitrogen. At 35° after 5 days I gave 2-ethoxy-4,4-dimethoxy-Δ^2-oxazoline (III) in 85% yield, and II gave *N*-ethoxycarbonyl-α-methoxypropionimino methyl ether (IV) in 94% yield after 1 day.



I III



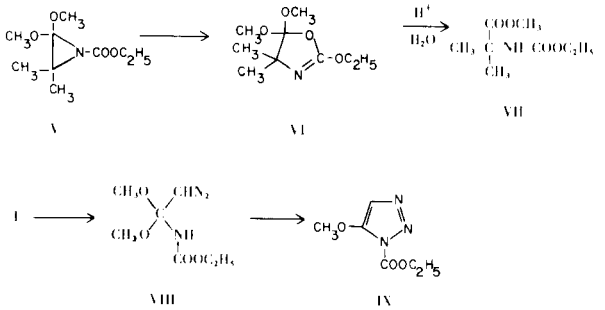
II IV

The above results confirm the previous proposed (2,3) according to which the reactions of ketene acetals with ethyl azidoformate proceed *via* 1-ethoxycarbonyl-Δ^2-1,2,3-triazolines. These decompose at room temperature, the reaction pathway depending on the presence or absence of substituents at the 4-position.

In order to gain information concerning the successive stages of the reactions, other experiments, planned on the basis of what is known about the behaviour of the Δ^2-triazolines were carried out.

The thermal conversion of triazolines to imines and/or aziridines is a well known reaction (5). Therefore the possibility that triazoline I first decomposes to 1-ethoxycarbonyl-2,2-dimethoxyaziridine which subsequently rearranges to the observed product III was taken into

consideration. This possibility could have been verified by studying the thermolysis of the 1-ethoxycarbonyl-2,2-dimethoxyaziridine. Unfortunately all of the attempts to synthetize this compound failed. However, useful information could be drawn by investigating the thermal behaviour of its 3,3-dimethyl derivative. When 1-ethoxycarbonyl-2,2-dimethoxy-3,3-dimethylaziridine (V) (6) was heated at 90° for 4 days the ir and ^{1}H nmr spectra of the reaction mixture showed that aziridine was entirely changed into the 2-ethoxy-4,4-dimethyl-5,5-dimethoxy-Δ^2-oxazoline (VI), so that only the cleavage of the bond between nitrogen and acetal carbon occurs. The selective rearrangement of V to VI does not give a clear-cut answer to the problem, however on the basis of steric factors as well as electronic effects, V would undergo C_3-N cleavage more easily than the 3-unsubstituted aziridine. It is apparent that the amide acetal portion of the aziridine molecule is the most reactive and therefore the intermediacy of an aziridine in the conversion of I to III can be very likely excluded. Structure VI was assigned on the basis of elemental and spectral analyses and chemical data [hydrolysis into methyl *N*-ethoxycarbonyl-α-aminoisobutyrate (VII)].



In certain instances triazolines isomerize to diazo derivatives (7,8) and in particular it has been pointed out a 1-ethoxycarbonyl-4-phenyl-5,5-dimethoxy-Δ^2-1,2,3-triazoline/1-phenyl-2,2-dimethoxy-2(*N*-ethoxycarbonylamino)-diazoethane mutual interconversion (9). The latter by thermolysis at 90° gave rise to the corresponding triazole, but, by photolysis or thermolysis at 160° gave oxazole derivatives (10). Therefore, the possibility that triazoline I, carrying two hydrogen atoms in the 4-position, isomerizes to 2,2-dimethoxy-2(*N*-ethoxycarbonylamino)diazoethane (VIII) which subsequently decomposes to oxazoline III, was examined. When triazoline I was heated at 60°, a part isomerized within a few hours to diazoamide acetal VIII whose presence was deduced from the appearence of the yellow colour and from the ir and ^{1}H nmr spectra of the reaction mixture. When the above mixture was allowed to stand 2 days at room temperature, VIII transformed quantitatively into triazole IX. It is to be noted that the latter compound is present only in traces when triazoline I was allowed to stand at room temperature for 5 days.

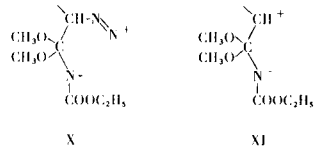
Table I

Rate Constants for the Decomposition of the Triazolines I and II at 36.0° in Various Solvents

Solvent	Triazoline I 10^{-2} K_1 (h^{-1})	Triazoline II 10^{-2} K_1 (h^{-1})
Perdeuteriocycloexane	0.44	6.24
Carbon tetrachloride	0.48	12.62
Perdeuteriobenzene	1.17	16.26
Perdeuterioacetone	3.32	19.91
Perdeuterionitrobenzene	3.78	22.66
Perdeuterioacetonitrile	7.35	32.89
DMF-d_7	8.73	26.83
Perdeuterionitromethane	8.98	58.57

These results indicate that the conversion of triazoline I to oxazoline III does not occur *via* the diazoamide acetal VIII.

Over a wide range of polarities the rates of decomposition of the triazolines I and II showed a remarkably small solvent dependence (Table I) which argues against a heterolytic cleavage *via* the zwitterionic intermediates X and/or XI in the conversion both of I to III and of II to IV. This is in agreement with the former results of the thermal decomposition of the Δ^2-triazolines carrying an electron-withdrawing substituent in the 4-position (11,8) though in contrast with the mechanism suggested, even recently (12), for the thermal decomposition of Δ^2-triazolines.



It is known that the photodecomposition of Δ^2-1,2,3-triazolines proceeds *via* 1,3-diradicals (13,14). Therefore I and II were subjected to direct photolysis in order to ascertain what happens to the 1,3-diradicals in our cases.

The irradiation of a solution of I was carried with a high pressure mercury lamp (Hanovia 450 W) with a corex filter sleeve. Inspection of the ^{1}H nmr spectrum of the irradiation mixture showed the presence of *N*-ethoxycarbonyl-α-methoxyacetimino methyl ether (XIII), trimethyl *N*-ethoxycarbonyl-α-aminoorthoacetate (XVIa) and dimethyl ethoxycarbonylimidocarbonate (XV) (Scheme I). No spectral evidence was obtained to support the presence of the 1-ethoxycarbonyl-2,2-dimethoxyaziridine (XIVa) whose formation was to be expected on the basis of the previous results in this area (13,14). However alumina chromatography allowed the isolation of methyl *N*-ethoxycarbonyl-α-aminoacetate (XVIIa) which was evidently formed by hydrolysis of XIVa during the separation procedure, as it has been observed in similar cases (3a,9). Also XIII and XV undergo hydrolysis during the separation procedure

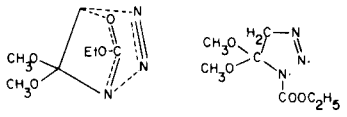
(2,3,9). Furthermore the alumina column afforded the ortho ester XVIa; its structure was assigned on the basis of elemental and spectral analysis and confirmed by hydrolysis to XVIIa.

Ortho ester XVIa was evidently formed during the irradiation from aziridine XIVa and methanol. Loss of methanol from triazoline I led to triazole IX. However the ^{1}H nmr spectrum excluded the presence of IX. This result is explained by the instability of triazoles to photolysis (15).

The composition of the irradiation mixture was confirmed by the results obtained from mild acid hydrolysis of the crude reaction mixture. It should be noted that oxazoline III after photolysis under the above conditions was quantitatively recovered partly as III and partly as 2-ethoxy-2,4-dimethoxy-Δ^3-oxazoline (16).

Triazoline II photolysis gave analogous products. The results are summarized in Scheme I.

The results obtained by photodecomposition of triazoline I indicate that, because of the energy supplied to the system, I mainly decomposes by loss of nitrogen to give the 1,3-diradical XIIa. This intermediate then undergoes rearrangement to the iminoether XIII or ring closure to aziridine XIVa, confirmed by observation in similar cases (13,14). At 35° the decomposition of the 4-unsubstituted triazoline I proceeds *via* a different reaction pathway to oxazoline III because the supply of energy is not sufficient to give rise to the 1,3-diradical XIIa. Oxazoline formation might be considered a concerted process with removal of nitrogen through a five-center transition state XX.



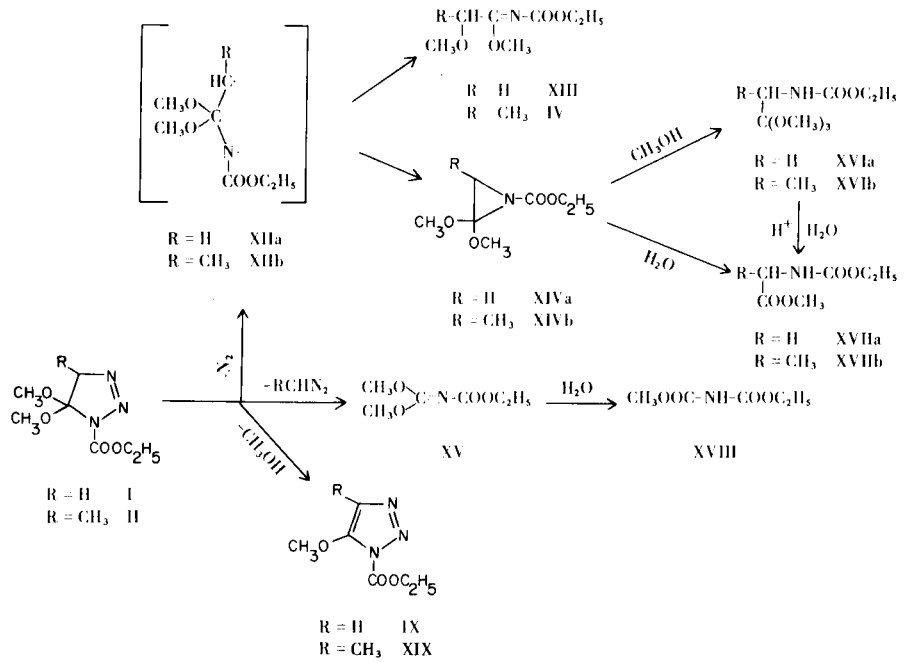
XX XXI

A path involving the 1,5-diradical XXI is an alternative formulation for the reaction. At present, however, an unambiguous mechanistic interpretation of the results does not seem possible.

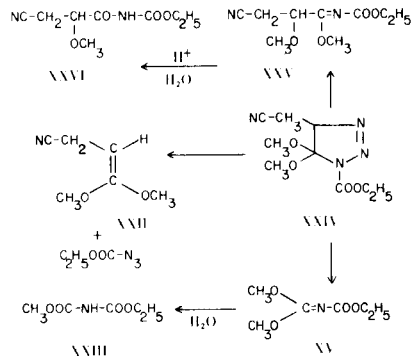
The 4-alkyl substituted triazoline II either by thermolysis or by photolysis decomposes to the 1,3-diradical XIIb. This is interpreted in terms of the capacity of the substituents to stabilize the odd-electron on the 3-carbon. The intermediate XIIb, obtained by thermolysis, rearranges to the iminoether IV almost exclusively; when it is obtained by photolysis it afforded a mixture of iminoether and aziridine. These higher yields of aziridine by photolysis has been observed in similar cases (13,14).

The 1-ethoxycarbonyl-4-cyanomethyl-5,5-dimethoxy-Δ^2-1,2,3-triazoline (XXIV) by thermolysis behaves like the 4-alkyl substituted triazoline II (Scheme II). Triazoline XXIV was obtained from the reaction between cyanomethylketene dimethylacetal (XXII) and ethyl azidoformate (XXIII) at -15°. It is not stable enough to be isolated either by distillation or by chromatographic methods, therefore, after removal of the azidoformate *in vacuo* at room temperature the remaining solution of triazoline XXIV in ketene acetal XXII was characterized by ^{1}H nmr.

Scheme I



Scheme II



After heating at 35° for 15 days the ^{1}H nmr spectrum of the crude reaction mixture showed, in addition to the ketene acetal XXII and small quantities of dimethyl ethoxycarbonylimidocarbonate (XV), the presence of *N*-ethoxycarbonyl-α-methoxy-β-cyanopropionimino methyl ether (XXV) which was isolated by distillation, in 78% yield, as a colorless oil with b. p. 120-122°/0.5 mm. The structure XXV was assigned on the basis of elemental analysis and by comparison (ir and ^{1}H nmr spectra) with very similar products (2,3,9). Mild acid hydrolysis of XXV yielded quantitatively *N*-ethoxycarbonyl-α-methoxy-β-cyanopropionamide (XXVI). The structure of the latter was determined on the basis of elemental and spectral analysis.

The composition of the reaction mixture, deduced on the basis of the ^{1}H nmr spectrum was confirmed by the results obtained from mild acid hydrolysis of the crude reaction mixture followed by chromatography on silica gel.

EXPERIMENTAL

Ir spectra were recorded on a Perkin-Elmer 157 spectrophotometer; ^{1}H nmr were determined in carbon tetrachloride, unless otherwise specified, on a Perkin-Elmer R12A spectrometer with TMS as the internal standard. Silica gel 0.05-0.20 mm (Merck) or neutral alumina (Woelm) was used for column chromatography. Light petroleum refers to the fraction b. p. 30-50°.

Preparation of Triazoline I.

A mixture of ketene dimethylacetal (17) (3.48 mmoles) and ethyl azidoformate (18) (3.48 mmoles), under rigorously anhydrous conditions, was kept at -15° for 1 month. After removal of the unreacted reagents under reduced pressure (0.5 mm) at room temperature the remaining colorless liquid (60%) was analyzed by ^{1}H nmr: τ 5.72 (q, J = 7 Hz, CH_2-O), 5.78 (s, CH_2-N), 6.70 (s, 6H, 2 OCH_3), 8.64 (t, J = 7 Hz, 3H, CH_3); the signals at 5.72 and 5.78 integrate complessively for 4 protons; ir ν max (carbon tetrachloride): 1735 ($COOC_2H_5$) cm^{-1}.

Thermal Decomposition of Triazoline I.

A sample of I was kept at 35° under anhydrous conditions. During 5 days evolution of nitrogen was observed in *ca.* 90% of the theoretical amount. An inspection of the ^{1}H nmr spectrum of the decomposition mixture showed the presence of oxazoline III as the main product. Only traces of iminoether XIII, imidocarbonate XV and triazole IX were present. All the compounds were identified by comparison with authentic samples (2). A portion of the decomposition mixture (360 mg.) was chromatographed on alumina B III (18 g.). Elution with light petroleum/benzene (9:1) afforded oxazoline III (300 mg., 85%).

A sample of I was heated at 60° under anhydrous conditions. After *ca.* 2 hours the mixture became yellow. The ir spectrum showed a diazo absorption at 2100 cm^{-1} and a NH at 3320 cm^{-1}. An inspection of ^{1}H nmr spectrum showed, in addition to oxazoline III and small quantities of XIII and XV, the presence of triazole IX and a broad signal at τ 3.96 assigned to NH of diazoamide acetal VIII. A small drop of DMF was added to the mixture and the ^{1}H nmr spectrum was recorded again. Molar ratio DMF:IX:VIII was *ca.* 3:2:1 on the basis of the relative areas of the signal at τ 2.16 (CH of DMF), at 2.72 (CH of IX) and at 3.96 (NH of VIII). The above mixture was kept at room temperature. After 2 days its ir spectrum showed the disappearance of the diazo absorption. The ^{1}H nmr spectrum showed a molar ratio DMF:IX *ca.* 1:1.

Photolysis of Triazoline I.

A 2% solution of I (1.5 g.) in anhydrous benzene was irradiated with a high-pressure mercury lamp (Hanovia 450 W) placed in a water-cooled quartz immersion well with a corex filter sleeve. The reaction was complete in 2.5 hours, when nitrogen ceased to evolve. After removal of the solvent under reduced pressure (0.5 mm.) at room temperature the oily residue was analyzed by ^{1}H, nmr and ir. Compounds XIII, XV and XVIa were detected.

A portion of the irradiation mixture (720 mg.) was chromatographed on alumina B III (60 g.). Elution with light petroleum/ether (19:1) gave methyl α-methoxyacetate (from XIII). Elution with light petroleum/ether (4:1) yielded *ortho* ester XVIa (82 mg., 10%). Elution with light petroleum/ether (7:3) yielded XVIIa (57 mg., 9%). Elution with light petroleum/ether (1:4) gave a mixture of urethane (from XIII) and XVIII (from XV). Compounds other than XVIa were identified by comparison (ir and ^{1}H nmr spectra) with authentic samples (2).

Ortho ester XVIa is a colourless liquid: ir ν max (carbon tetrachloride): 3330 (NH), 1720 ($COOC_2H_5$), 1100-1050 (C-O-C) cm^{-1}; ^{1}H nmr: τ 5.97 (q, J = 7 Hz, 2H, CH_2-O), 6.67 (d, J = 5 Hz, CH_2-N), 6.77 (s, 3 O-CH_3), 8.76 (t, J = 7 Hz, 3H, CH_3) and a broad hump at 5.23-5.51 (NH); the signals at 6.67 and 6.77 integrate complessively for 11 protons.

Anal. Calcd. for $C_8H_{17}NO_5$: C, 46.37; H, 8.27; N, 6.76. Found: C, 46.18; H, 8.32; N, 6.95.

A solution of the irradiation mixture (590 mg.) in dioxane (2 ml.) and 2*N* hydrochloric acid (0.12 ml.) 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 mg.). Elution with light petroleum/ether (4:1) gave ester XVIIa (103 mg., 19%, from XIVa and XVIa). Elution with light petroleum/ether (1:4) gave a mixture of XVIII (57 mg., 12% from XV) and *N*-ethoxycarbonyl-2-methoxyacetamide (110 mg., 20%, from XIII). All the compounds were identified by comparison (ir and ^{1}H nmr spectra) with authentic samples (2).

Photolysis of Oxazoline III.

Photolysis was performed as above described for triazoline I. The irradiation mixture was submitted to the ^{1}H nmr analysis. Molar ratio Δ^2-oxazoline III: 2-ethoxy-2,4-methoxy-Δ^3-oxazoline (16) was *ca.* 5:1 on the basis of the relative areas of the signals at τ 6.80 (OCH_3 of III) + 6.78 (OCH_3 of the Δ^3-oxazoline) and 6.10 (=C-OCH_3 of the Δ^3-oxazoline). No evidence was obtained to

support the presence of the other compounds.

Preparation and Thermal Decomposition of Triazoline II.

Triazoline II was obtained as above described for triazoline I, using methylketene dimethylacetal (19). Pure II was obtained as a colorless liquid in 60% yield; ^{1}H nmr: τ 5.72 (q, J = 7 Hz, CH_2), 5.83 (q, J = 7 Hz, CH), 6.58 (s, 3H, OCH_3), 6.72 (s, 3H, OCH_3), 8.61 (t, J = 7 Hz, CH_3-C(H_2)), 8.67 (d, J = 7 Hz, CH_3-C(H)); the signals at 5.72 and 5.83 integrate complessively for 3 protons; at 8.61 and 8.67 for 6 protons; ir ν max (carbon tetrachloride): 1735 ($COOC_2H_5$) cm^{-1}.

During 1 day at 35° evolution of nitrogen was observed in *ca.* 90% of the theoretical amount. Inspection of the ^{1}H nmr spectrum of the decomposition mixture showed only the presence of the iminoether IV (3b). Distillation gave IV in 94% yield, b. p. 109°/14 mm (3b).

Mild acid hydrolysis of the decomposition mixture under the same conditions as previously described (3b) gave *N*-ethoxycarbonyl-α-methoxypropionamide m. p. 56-57° (3b) in 94% yield. No spectral evidence was obtained to support the presence of oxazoline hydrolysis products.

Photolysis of Triazoline II.

Photolysis on 1.61 g. of II was performed as above described for triazoline I. A portion of the irradiation mixture (720 mg.) was chromatographed on alumina B III (60 g.). Elution with light petroleum/ether (19:1) gave methyl α-methoxypropionate (27 mg., from IV). Elution with light petroleum/ether (9:1) yielded *ortho* ester XVIb (160 mg., 20%). Elution with light petroleum/ether (4:1) yielded XVIIb (104 mg., 16%, from XIVb). Elution with light petroleum/ether (1:1) gave a mixture of urethane (30 mg., from IV) and XVIII (16 mg., 3%, from XV). Compounds other than XVIb were identified by comparison (ir and ^{1}H nmr spectra) with authentic samples (3b).

Ortho ester XVIb is a colourless liquid: ir ν max (carbon tetrachloride): 3330 (NH), 1720 ($COOC_2H_5$), 1100-1050 (C-O-C) cm^{-1}; ^{1}H nmr τ 6.01 (q, J = 7 Hz, CH_2), 6.02-6.08 (m, CH), 6.72 (s, 9H, 3 OCH_3), 8.80 (t, J = 7 Hz, CH_3-C(H_2)), 8.93 (d, J = 7 Hz, CH_3-C(H)) and a broad hump at 5.35-5.70 (NH); the signals at 6.01 and 6.02-6.08 integrate complessively for 3 protons, at 8.80 and 8.93 for 6 protons.

Anal. Calcd. for $C_9H_{19}NO_5$: C, 48.85; H, 8.66; N, 6.33. Found: C, 49.01; H, 8.46; N, 6.48.

Hydrolysis with hydrochloric acid of the irradiation mixture of II (716 mg.) was performed as above described for irradiation mixture of I. The hydrolysis mixture was chromatographed on silica gel (60 g.). Elution with light petroleum/ether (4:1) gave ester XVIIb (225 mg., 35%, from XIVb and XVIb). Elution with light petroleum/ether (7:3) yielded XVIII (15 mg., 3%, from XV). Elution with light petroleum/ether (1:1) yielded *N*-ethoxycarbonyl-α-methoxypropionamide (275 mg., 42%, from IV). All the compounds were identified by comparison (ir, ^{1}H nmr spectra) with authentic samples.

Kinetic Determinations of the Thermal Decomposition of Triazolines I and II.

Triazolines I or II (0.2 mmoles) were dissolved in deuterated anhydrous solvents (1 ml.) in an nmr tube at constant temperature (36 ± 0.1°) and the tube was placed in a thermostat at 36 ± 0.1°. From time to time ^{1}H nmr spectrum was recorded (nmr probe termostatted at 36 ± 0.1°). Decomposition rates were followed by integration of the methoxyl singlets of I and III and respectively, II and IV.

First-order rate constants were calculated and reported in Table I.

Isomerization of Aziridine V.

The fraction at b. p. 47-50°/0.2 mm obtained from the reaction mixture between dimethylketene dimethylacetal and ethyl azidoformate at 35° is composed of V and *N*-ethoxycarbonyl-α-methoxyisobutyrimino methyl ether (3a,6). The ir spectrum showed three carbonyl bands at 1736 ($COOC_2H_5$ of V), 1724 and 1696 cm^{-1} (N=C-C=O of the iminoether). The mixture was heated under anhydrous conditions for 4 days at 90°. Inspection of the ir spectrum of the reaction mixture showed the disappearance of the at 1736 band and, in addition of the bands at 1724 and 1696, a band at 1680 cm^{-1}. The ^{1}H nmr spectrum showed, in addition to the signals of the iminoether, only the presence of the oxazoline VI. Distillation *in vacuo* gave oxazoline VI as colourless liquid b. p. 94°/14 mm; ir ν max (carbon tetrachloride): 1680 (C = N) cm^{-1}; ^{1}H nmr τ 5.82 (q, J = 7 Hz, 2H, CH_2), 6.60 (s, 6H, OCH_3), 8.66 (t, J = 7 Hz, CH_3-C(H_2)), 8.81 (s, CH_3); the signals at 8.66 and 8.81 integrate complessively for 9 protons.

Anal. Calcd. for $C_9H_{17}NO_4$: C, 53.19; H, 8.43. Found: C, 53.40; H, 8.43.

Oxazoline VI by mild acid hydrolysis (VI, 50 mg.; dioxane, 0.5 ml.; 2*N* hydrochloric acid, 0.01 ml.; for 30 minutes at room temperature) gave VII quantitatively (4).

A portion of the crude reaction mixture was submitted to mild acid hydrolysis (200 mg.; dioxane, 2 ml.; 2*N* hydrochloric acid, 0.04 ml.; for 30 minutes at room temperature). The usual workup gave an oil which was chromatographed on silica gel (20 g.). Elution with light petroleum/ether (4:1) gave VII (102 mg., 54%, from VI); Elution with light petroleum/ether (7:3) gave *N*-ethoxycarbonyl-α-methoxyisobutyramide (3a) (79 mg., 42%, from *N*-ethoxycarbonyl-α-methoxyisobutyrimino methyl ether).

Preparation and Thermal Decomposition of Triazoline XXIV.

Triazoline XXIV was obtained as above described for triazoline I, using cyanomethylketene dimethylacetal (XXII) (20). The unreacted azidoformate XXIII was distilled under reduced pressure (0.5 mm) at room temperature. Inspection of the ^{1}H nmr spectrum of the reaction mixture showed, in addition to the ketene acetal XXII, only the presence of triazoline XXIV: τ 5.47 (t, J = 7 Hz, CH), 5.65 (q, J = 7 Hz, CH_2O), 6.46 (s, 3H, CH_3O), 6.67 (s, 3H, CH_3O), 7.22 (d, J = 7 Hz, 2H, CH_2CN), 8.60 (t, J = 7 Hz, 3H, CH_3); the signals at 5.47 and 5.65 integrate complessively for 3 protons. On the basis of the relative areas of the methoxyl signals of XXIV and XXII the yield of XXIV was shown to be close to 40%. Attempts to purify XXIV were unsuccessful. It decomposes at 35° and during 15 days evolution of nitrogen was observed in *ca.* 80% (21) of the theoretical amount. Inspection of the ^{1}H nmr spectrum of the decomposition mixture showed, in addition to the ketene acetal XXII, the presence of the iminoether XXV and traces of imidocarbonate XV. Distillation gave the iminoether XXV as colourless liquid b. p. 120-121°/0.5 mm, yield 78% (21); ir ν max (carbon tetrachloride): 2250 (C≡N), 1725 and 1696 (C=N-C=O) cm^{-1}; ^{1}H nmr τ 5.85 (q, J = 7 Hz, CH_2O), 5.90 (t, J = 7 Hz, CH), 6.22 (s, 3H, CH_3O), 6.62 (s, 3H, CH_3O), 7.19 (d, J = 7 Hz, 2H, CH_2-CN), 8.70 (t, J = 7 Hz, 3H, CH_3); the signals at 5.85 and 5.90 integrate for 3 protons.

Anal. Calcd. for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.65; H, 6.66; N, 13.06.

Mild acid hydrolysis (XXV 735 mg., dioxane 2 ml., 2*N* hydrochloric acid 0.12 ml., for 30 minutes at room temperature) gave amide XXVI (97% yield), m. p. 69-70° from carbon tetrachloride;

ir ν max (carbon tetrachloride): 3300 (NH), 2250 (C≡N), 1800 and 1740 (O=C-NH-C=O) cm^{-1}; ^1H nmr (deuteriochloroform): τ 1.31 (bs, 1H, NH), 5.72 (q, J = 7 Hz, CH_2O), 5.82-5.94 (X part of an ABX system, CH), 6.43 (s, 3H, CH_3O), 6.74-7.45 (AB part of an ABX system. 2H, CH_2-CN), 8.68 (t, J = 7 Hz, 3H, CH_3); the signals at 5.72 and 5.82-5.94 integrate for 3 protons.

Anal. Calcd. for $C_8H_{12}N_2O_4$: C, 47.99; H, 6.04; N, 13.99. Found: C, 48.20; H, 6.29; N, 14.22.

A portion of the crude reaction mixture (1.49 g.) was submitted to mild acid hydrolysis (dioxane 6 ml., 2*N* hydrochloric acid 0.36 ml., for 30 minutes at room temperature). The usual workup gave an oil which was chromatographed on silica gel (100 g.). Elution with light petroleum/ether (7:3) gave methyl β-cyanopropionate (from XXII). Elution with light petroleum/ether (1:1) yielded XVIII [40 mg., 10% (21), from XV]. Elution with ether gave XXVI [460 mg., 75% (21), from XXV]. The residue of every fraction was submitted to ^1H nmr analysis. None of them showed signals attributable to Δ^2-oxazoline hydrolysis products.

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