Reactions of Ketenes XVI. 5,5-Dimethoxy-Δ^2-1,2,3-triazoline/2,2-Dimethoxy-2-aminodiazoethane Mutual Conversion (1)

R. Scarpati and M. L. Graziano

Institute of Organic Chemistry, University of Naples, Naples, Italy

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Phenylketene dimethylacetal reacts with ethyl azidoformate to give 1-ethoxycarbonyl-4-phenyl-5,5-dimethoxy-Δ^2-1,2,3-triazoline (III). The behaviour of the latter and of its isomerization product, 1-phenyl-2,2-dimethoxy-2(*N*-ethoxycarbonylamino)diazoethane (IV), have been investigated in detail. The results point out a triazoline III/diazoethane IV mutual conversion.

Introduction.

In the course of research performed for the purpose of studying the unusual behaviour of 1-alkoxycarbonyl-5,5-dialkoxy-Δ^2-1,2,3-triazolines (2) and their 4-substituted derivatives (3,4), obtainable from the reaction between ketene dialkylacetals and azidoformates, the reaction between phenylketene dimethylacetal (I) and ethyl azidoformate (II) was examined.

Under conditions previously used for the reaction, an initial rate-determining 1,3-dipolar addition followed by a rapid evolution of nitrogen in approximately quantitative amount gave only indirect evidence that the pathway involved an initially formed unstable Δ^2-triazoline. In this case being examined, the 1-ethoxycarbonyl-4-phenyl-5,5-dimethoxy-Δ^2-1,2,3-triazoline (III) was identified by nmr spectroscopy although it was not isolated.

Moreover the study of the behaviour of triazoline III and of its isomerization product (5), 1-phenyl-2,2-dimethoxy-2(*N*-ethoxycarbonylamino)diazoethane (IV), points out the III $\rightleftharpoons$ IV mutual conversion.

Compound IV is the first example of a diazoamide acetal.

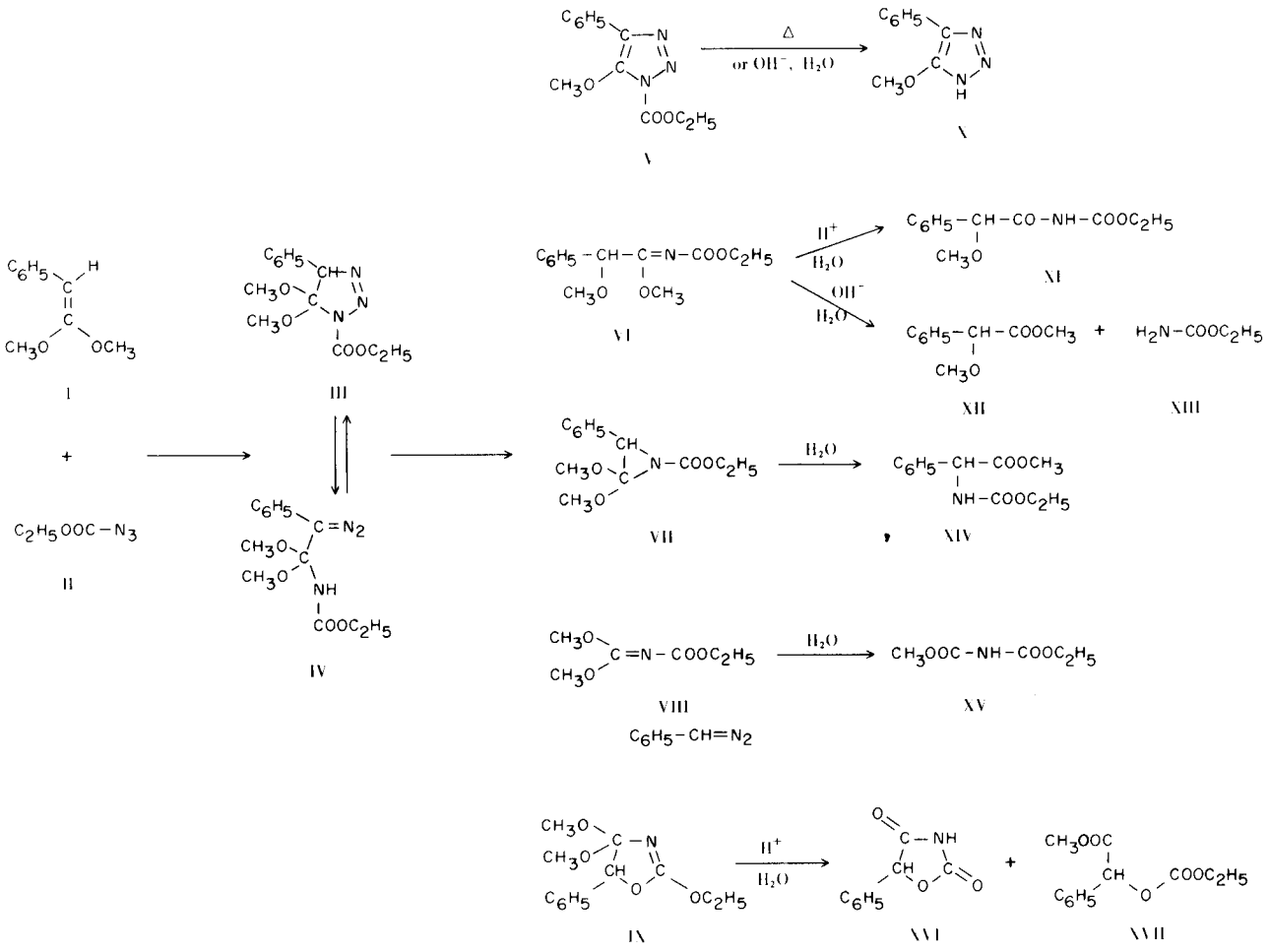
Results.

(a) Triazoline III.

When ketene acetal I and azidoformate II were allowed to stand at -15° for 2 months, the nmr spectrum of the mixture showed, in addition to the signals of the starting materials, signals consistent with the structure of the triazoline III. Azidoformate II was removed *in vacuo* at room temperature and the remaining solution (A) of triazoline III in ketene acetal I was analyzed by nmr; on the basis of the signals at τ 4.84 (Ph-CH-N of III) and τ 5.53 (Ph-CH= of I) with relative areas of 1:2, the yield in triazoline III was shown to be close to 33%.

Triazoline III is not stable enough to be isolated either by distillation or by chromatographic methods.

When solution (A) of triazoline III in ketene acetal I was heated at 35°, the nmr spectrum of the solution gradually changed developing new peaks whereas the signals assigned to triazoline III decreased in intensity. In order to obtain the complete transformation of the triazoline III, it was necessary to heat the solution for 60 hours. After heating, the nmr spectrum of the crude reaction mixture showed, in addition to ketene acetal I, the presence of diazoamide acetal IV as the main product, of 1-ethoxycarbonyl-4-phenyl-5-methoxy-1,2,3-triazole (V) and *N*-ethoxycarbonyl-α-methoxy-α-phenylacetimino methyl ether (VI) in *ca.* 1:1 molar ratio; smaller quantities of dimethyl ethoxycarbonylimidocarbonate (VIII) and of 2-ethoxy-4,4-dimethoxy-5-phenyl-Δ^2-oxazoline (IX), and traces of benzalazine presumably formed from phenyldiazomethane (6), were also present. No spectral evidence has been obtained to support the presence in the reaction mixture of 1-ethoxycarbonyl-2,2-dimethoxy-3-phenylaziridine (VII); however, alumina chromatography allowed the isolation of methyl *N*-ethoxycarbonyl-α-amino-α-phenylacetate (XIV) which is evidently formed by hydrolysis of VII during the separation procedure, as has been observed in similar cases (3). Also I, V, VI and VIII undergo hydrolysis during the separation procedure; therefore methyl phenylacetate (from unreacted ketene acetal I), 4-phenyl-5-methoxy-1,2,3-triazole (X) [from triazole V (7)], methyl α-methoxy-α-phenylacetate (XII) and urethane (XIII) [from imino-ether VI (7)], *N*-methoxycarbonylurethane (XV) (2,3) (from imidocarbonate VIII) were isolated. Furthermore the alumina column afforded the diazoamide acetal IV which was further purified on polyamide; its structure was assigned on the basis of elemental and spectral analyses.



When the triazoline-ketene acetal solution (A) was heated at 90° for 2 hours, conspicuous evolution of nitrogen was observed. Inspection of the nmr spectrum of the reaction mixture showed the presence of imino-ether VI and imidocarbonate VIII as the main products and very small quantities of triazole V (molar ratio of V:VI *ca.* 1:10), oxazoline IX and benzalazine. Moreover, the presence of aziridine VII in the crude reaction mixture was deduced through the isolation of its hydrolysis product XIV, after alumina chromatography. The composition of the reaction mixture, deduced on the basis of nmr spectrum and alumina chromatography, was confirmed by the results obtained from mild acid hydrolysis of the crude reaction mixture followed by chromatography on silica gel which allowed the isolation of *N*-ethoxycarbonyl-α-methoxy-α-phenylacetamide (XI) [from imino-ether VI (7)], urethane XV (from imidocarbonate VIII), ester XIV (from aziridine VII) and triazole V; molar ratio of XI to V was *ca.* 10:1.

In order to obtain the imino-ether VI in a shorter time than in the above two-step reaction, ketene acetal I and azide II were heated at 90° for 4 hours. Imino-ether VI was isolated, in 45% yield by distillation, as a colorless oil with b.p. 104-106°/0.2 mm; the structure VI was assigned on the basis of elemental analysis and by comparison (ir and nmr spectra) with very similar products (2,3,4). Alumina chromatography hydrolyzed VI to give the ester XII and urethane XIII as the main products. Mild acid hydrolysis of VI yielded the amide XI quantitatively. The structure of the latter compound was determined on the basis of elemental analysis and by comparison (ir and nmr spectra) with very similar products (2,3,4).

(b) Diazoamide Acetal IV.

In order to obtain IV in a shorter time than in the above two-step reaction, ketene acetal I and azidoformate II were allowed to stand at 35° for 8 days. The reaction was shown to contain (nmr spectrum and alumina chroma-

tography) the same compounds obtained by heating triazoline III at 35°. From the reaction mixture, after chromatography on alumina and polyamide, IV was isolated in 14% yield. Chromatography on polyamide also gave oxazoline IX, the structure of which was assigned on the basis of elemental and spectral analyses and chemical data [hydrolysis into 5-phenyloxazolidine-2,4-dione (XVI) (8) and methyl *O*-ethoxycarbonyl-α-hydroxy-α-phenylacetate (XVII)].

Diazoamide acetal IV decomposes in acids and in bases (9) and it is very heat-sensitive but can be stored several days at room temperature; however, after 80 days without solvent at 35°, 70% of IV remained unchanged (nmr analysis). There was 30% of IV converted into decomposition products.

A solution (B) of the compound IV in ketene acetal I (10), heated at 35° for 20 days, gave a solution which, on the basis of its nmr spectrum was composed of, in addition to ketene acetal I, the starting material IV (*ca.* 50%), triazole V and imino-ether VI in *ca.* 1:1 molar ratio, imidocarbonate VIII, oxazoline IX and traces of benzalazine. Alumina chromatography results are consistent with the ones obtained from thermal decomposition (35°) of triazoline III.

When solution (B) of diazoamide acetal IV in ketene acetal I was heated at 90° for 72 hours, examination of the crude reaction mixture, carried out by nmr analysis, showed the presence of triazole V as the main product, of triazole X and of very small quantities of the imino-ether VI [molar ratio (V+X):VI *ca.* 10:1], imidocarbonate VIII, oxazoline IX and benzalazine, in addition to ketene acetal I. The presence of aziridine VII, in the crude reaction mixture, was deduced through the isolation of its hydrolysis product XIV by alumina chromatography. The composition of the reaction mixture, deduced on the basis of nmr spectrum and alumina chromatography, was confirmed by the results obtained from mild acid hydrolysis of the crude reaction mixture followed by chromatography on silica gel which allowed the isolation of triazole V (yield 65%), triazole X, amide XI, urethane XV, ester XIV; molar ratio of V to XI was *ca.* 8:1. It seems reasonable to assume that IV, in this case, gave triazole X *via* triazole V.

The structures V and X were assigned on the basis of elemental and spectral analyses. Triazole V by alumina chromatography was partially hydrolised to triazole X; treatment with hydrochloric acid, under the same conditions adopted for hydrolysis of the above mixture, left it unchanged; its thermal decomposition at 90° yields triazole X.

Conclusions.

The above results point out a mutual conversion between triazoline III and diazoamide acetal IV; in fact, by heating III and IV at 90°, V and VI are obtained in a molar ratio of 1:10 and 10:1 respectively, whereas at 35°, the molar ratio is about 1:1. This indicates that imino-ether VI is formed through the triazoline III, whereas triazole V derives from diazoamide acetal IV, at least in part, without preliminary conversion into triazoline III. As to the origin of VII and VIII, they are likely formed through triazoline III in agreement with the behaviour of 1-phenyl-4,4-dialkyl-5,5-dimethoxy-Δ^2-1,2,3-triazolines (3) which at 120° decompose to give α-substituted *N*-phenyl-α-methoxyacetimino methyl ethers, dimethyl phenylimidocarbonate and 1-phenyl-2,2-dialkyl-3,3-dimethoxyaziridines.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Ultraviolet and infrared 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).

Preparation of Triazoline III.

A mixture of phenylketene dimethylacetal (I) (11) (3.48 mmoles) and ethyl azidoformate (II) (12) (3.48 mmoles), under rigorously anhydrous conditions, was kept at -15° for 2 months. The unreacted azidoformate was distilled under reduced pressure (0.5 mm) at room temperature and the oily residue (A) was analyzed by nmr: τ 2.60-3.20 (m, aromatic H), 4.84 (s, Ph-CH-N of III), 5.53 (s, Ph-CH= of I), 5.73 (q, J = 7 Hz, CH_2 of III), 6.35 and 6.43 (2s, 2 OCH_3 of I), 6.62 and 7.16 (2s, 2 OCH_3 of III), 8.63 (t, J = 7 Hz, CH_3 of III).

Attempts to purify triazoline III by chromatography were unsuccessful: in fact, alumina BIV chromatography (eluant ether) or chromatography on silica gel (eluant ether) gave only the triazoles V and X. Chromatography on polyamide (eluant light petroleum) gave only the triazole V.

Heating of Triazoline III at 35°.

The above solution (A) was heated at 35° for 60 hours and analyzed by nmr. Molar ratio IV:V:VI was *ca.* 1.5:1:1 on the basis of relative areas of the signals at τ 3.91 (NH of IV), at τ 1.85-2.30 (2′ and 6′ phenyl protons of V) and at τ 5.28 (Ph-CH-O of VI); moreover I, VIII (2), IX and traces of benzalazine (13) were also present. All the compounds were identified by comparison with authentic samples.

The reaction mixture was chromatographed on alumina BIV (14) (20 g.). Elution with 100 ml. of light petroleum/benzene (3:2) and with 50 ml. of light petroleum/benzene (1:1) gave methyl phenylacetate (from ketene acetal I) and ester XII (15) (from imino-ether VI); elution with 150 ml. of light petroleum/benzene (3:7) afforded impure diazoamide acetal IV (90 mg.); elution with 150 ml. light petroleum/benzene (1:4) gave ester XIV (13 mg.) (from aziridine VII); elution with 150 ml. of benzene-ether (19:1) gave urethane XV (2) (6 mg.) (from imidocarbonate VIII); elution with 150 ml. of benzene-ether (9:1) gave triazole X (from triazole V) contaminated with urethane

XIII (from imino-ether VI); finally elution with ether gave urethane XIII. All the compounds were identified by comparison (ir and nmr spectra) with authentic samples.

Impure IV (90 mg.) recovered from the alumina column was chromatographed in light petroleum on polyamide (100 g., ϕ column 16 mm); 150 ml. fractions were collected. Fractions 1-3 contained a mixture (15 mg.) of methyl phenylacetate, ester XII and oxazoline IX (nmr); fraction 4 afforded diazoamide acetal IV (75 mg) as red crystals, m.p. 63-66°; uv λ max (chloroform) 285 (log ϵ 4.29) and 480 mμ (log ϵ 1.76); ir ν max (carbon tetrachloride) 3390 (NH), 2067 (C=N_2), 1722 and 1715 (NH-C=O), 1087-1081 cm^{-1} (C$\begin{smallmatrix}\text{O-C}\\ \text{O-C}\end{smallmatrix}$); nmr τ 2.60-3.20 (m, 5H, aromatic), 3.91 (bs, 1H, NH), 6.01 (q, J = 7 Hz, 2H, CH_2), 6.74 (s, 6H, 2 OCH_3), 8.90 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{13}H_{17}N_3O_4$: C, 55.90; H, 6.14; N, 15.05. Found: C, 56.14; H, 6.29; N, 15.32.

Heating of Triazoline III at 90°.

A solution (A) of triazoline III in ketene acetal I, prepared as above from 33.86 mmoles of both reagents, was heated at 90°. During the heating, evolution of nitrogen was observed in *ca.* 80% of the theoretical amount. After 2 hours the solution was analyzed by nmr. Molar ratio VI:VIII:V was *ca.* 10:3:1, on the basis of relative areas of the signals at τ 5.28 (Ph-CH-O of VI), at τ 6.16 (OCH_3 of VIII) and at τ 1.85-2,30 (2′ and 6′ phenyl protons of V); moreover I and traces of oxazoline IX and benzalazine were identified by comparison with authentic samples.

A portion of the reaction mixture (574 mg.) was chromatographed on alumina BIII (28 g.). Elution with 250 ml. of light petroleum/benzene (7:3) yielded methyl phenylacetate and ester XII; elution with 100 ml. of light petroleum/benzene (1:1) gave oxazoline IX (few mg.); elution with 150 ml. of light petroleum/benzene (1:4) yielded ester XIV [23 mg., 10% (16)]; elution with 375 ml. of benzene-ether (19:1) yielded urethane XV [26 mg., 17% (16)]; elution with ether gave triazole X and urethane XIII. All the compounds were identified by comparison (ir and nmr spectra) with authentic samples.

A solution of the reaction mixture (986 mg.) in dioxane (2 ml.) and 2*N* hydrochloric acid (0.15 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 (70 g.). Elution with 1250 ml. of light petroleum/ether (9:1) gave methyl phenylacetate (from I), elution with 700 ml. of the same solvents gave triazole V [26 mg., 6% (16)], elution with 700 ml. of light petroleum/ether (4:1) afforded ester XIV [40 mg. 10% (16)] (from VII), elution with 980 ml. of light petroleum/ether (1:1) gave a mixture (265 mg.) of amide XI [56% (16)] (from VI) and urethane XV [17% (16)] (from VIII) in a molar ratio of *ca.* 10:3 (nmr). All the compounds were identified by comparison (ir and nmr spectra) with authentic samples.

Preparation of Imino-ether VI.

Ketene acetal I (60 mmoles) was heated at 90° and azide II (60 mmoles) was added slowly dropwise; the nitrogen evolution, after 4 hours was *ca.* 90% of theoretical. Distillation of the oily residue *in vacuo* gave the imino-ether VI, b.p. 104-106°/0.2 mm, yield 45%; ir ν max (carbon tetrachloride) 1724 and 1707 (C=N-C=O) cm^{-1}; nmr τ 2.50-2.90 (m, 5H, aromatic), 5.28 (s, 1H, Ph-CH-O), 5.90 (q, J = 7 Hz, 2H, CH_2), 6.43 (s, 3H, OCH_3), 6.75 (s, 3H, OCH_3), 8.75 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.28; H, 6.79; N, 5.28.

Imino-ether VI is very sensitive to hydrolysis: chromatography on alumina column under the same experimental conditions as described above, gave only ester XII and urethane XIII in 25% yield. Mild acid hydrolysis (imino-ether VI 630 mg., dioxane 1.2 ml., 2*N* hydrochloric acid, 0.11 ml. for 30 minutes at room temperature) gave amide XI (98% yield), b.p. 124°/0.4 mm; ir ν max (carbon tetrachloride) 3320 (NH), 1786 and 1723 (O=C-NH-C=O) cm^{-1}; nmr τ 1.75 (bs, 1H, NH), 2.70 (s, 5H, aromatic), 5.35 (s, 1H, Ph-CH-O), 5.86 (q, J = 7 Hz, 2H, CH_2), 6.63 (s, 3H, OCH_3), 8.70 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.56; H, 6.51; N, 6.15.

Preparation of Diazoamide Acetal IV and Oxazoline IX.

A mixture of ketene acetal I (23.77 mmoles) and azide II (23.77 mmoles) was kept at 35° for 8 days. On the basis of the intensity of absorption band at 480 mμ the yield of diazoamide acetal IV was close to 20%.

A portion of the reaction mixture (5.0 g.) was chromatographed on alumina (100 g., BIV) (14). Elution with 150 ml. of light petroleum/benzene (4:1) afforded azide II and methyl phenylacetate; elution with increasing concentrations of benzene in light petroleum (from 1:4 up to 7:3), 400 ml., afforded a mixture (1.85 g.) of methyl phenylacetate, ester XII, oxazoline IX, triazole V and diazoamide acetal IV (nmr). Further elution of the column with ether gave ester XIV, urethanes XIII and XV, triazole X (from hydrolysis of compound IV and triazole V). The second fraction (1.85 g.) was rechromatographed in light petroleum on polyamide (140 g., ϕ column 16 mm); 50 ml. fractions were collected. Fractions 1-10 contained a mixture (900 mg.) of methyl phenylacetate, ester XII and oxazoline IX; fraction 11 contained a mixture (78 mg.) of compound IV and triazole V; fractions 12-20 gave diazoamide acetal IV (710 mg.).

Fractions 1-10 (900 mg.) from the polyamide chromatography were successively chromatographed on alumina (30 g., BIII). Elution with 300 ml. of light petroleum/benzene (7:3) afforded first methyl phenylacetate followed by ester XII; further elution with 180 ml. light petroleum/benzene (1:1) afforded oxazoline IX (50 mg.), m.p. 60-62° from light petroleum; ir ν max (carbon tetrachloride) 1661 (C=N) cm^{-1}; nmr τ 2.79 (s, 5H, aromatic), 4.78 (s, 1H, Ph-CH-O), 5.68 (q, J = 7 Hz, 2H, CH_2), 6.72 (s, 3H, OCH_3), 7.16 (s, 3H, OCH_3), 8.64 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.42; H, 7.06; N, 5.46.

Oxazoline IX by mild acid hydrolysis (IX, 280 mg., dioxane, 3 ml; 1*N* hydrochloric acid, 0.05 ml., for 30 minutes at room temperature) gave oxazolidine-2,4-dione XVI (90 mg.) and ester XVII (12 mg.) which were separated on TLC (chloroform-ethylacetate 97:3, uv-light). Compound XVI was identified by comparison with authentic material (9), XVII with synthetic material (ir and nmr spectra). Ester XVII was prepared by treatment of *O*-ethoxycarbonyl-α-hydroxy-α-phenylacetic acid (17) with diazomethane (96% yield), b.p. 95°/0.2 mm; ir ν max (carbon tetrachloride 1760, 1745 cm^{-1}; nmr τ 2.50-2.80 (m, 5H aromatic), 4.30 (s, 1H, Ph-CH-O), 5.80 (q, J = 7 Hz, 2H, CH_2), 6.31 (s, 3H, OCH_3), 8.67 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.78; H, 6.06.

Heating of Diazoamide Acetal IV at 35°.

A solution of IV (430 mg.) in ketene acetal (505 mg.) (10) was heated at 35° for 20 days and submitted to nmr analysis. Molar

ratio IV:V:VI was *ca.* 3:1:1 on the basis of relative areas of the signals at τ 3.91 (NH of IV), at 1.85-2.30 (2′ and 6′ phenyl protons of V) and at 5.28 (Ph-CH-O of VI); moreover I, VIII, IX and traces of benzalazine were present. All the compounds were identified by comparison with authentic samples.

The reaction mixture was chromatographed on alumina BIV (30 g.). Elution with light petroleum/benzene (4:1) gave methyl phenylacetate and ester XII, elution with 60 ml. of light petroleum/benzene (1:1) and 90 ml. of light petroleum/benzene (3:7) afforded impure IV (230 mg.); elution with 180 ml. of light petroleum/benzene (3:7) gave ester XIV (33 mg.); elution with 300 ml. of benzene-ether (19:1) afforded urethane XV (6 mg.); elution with 300 ml. of benzene-ether (9:1) gave triazole X and urethane XIII; elution with ether afforded urethane XIII. All the compounds were identified by comparison (ir and nmr spectra) with authentic samples.

Heating of Diazoamide Acetal IV at 90°.

A solution of IV (1.82 g.) in ketene acetal I (2.37 g.) (10) was heated at 90° for 72 hours. Inspection of the nmr spectrum of the reaction mixture showed the presence of triazole V (main product), triazole X and very small quantities of VI, VIII, IX and benzalazine, in addition to the ketene acetal I. Molar ratio (V+X):VI was *ca.* 10:1 on the basis of relative areas of the signals at τ 1.85-2.30 (2′ and 6′ phenyl protons of triazoles V and X) and at 5.28 (Ph-CH-O of VI).

A portion of the reaction mixture (1 g.) was chromatographed on alumina BIII (30 g.). Elution with 300 ml. of light petroleum/benzene (7:3) gave methyl phenylacetate and traces of ester XII, elution with 150 ml. of light petroleum/benzene (1:1) gave oxazoline IX (few mg.), elution with 180 ml. of light petroleum/benzene (1:4) gave ester XIV (11 mg., 3%), elution with 300 ml. of benzene-ether (19:1) gave urethane XV (6 mg., 3%), elution with ether gave triazole X.

A solution of the reaction mixture (2.80 g.) in acetone (3 ml.) and 2*N* hydrochloric acid (0.28 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 (120 g.). Elution with 2350 ml. of light petroleum/ether (45:1) and with 705 ml. of light petroleum/ether (9:1) gave methyl phenylacetate; elution with 705 ml. of light petroleum/ether (9:1) afforded triazole V (178 mg.) and with 1040 ml. afforded a mixture of triazole V [302 mg. (18)] and triazole X [50 mg. (18)]; elution with 2350 ml. of the same solvents yielded a mixture of triazole V [215 mg. (18)], triazole X [65 mg. (18)] and ester XIV [37 mg. (18), 3%]; elution with 1175 ml. of light petroleum/ether (1:4) gave a mixture (110 mg.) of amide XI and compounds XV and XVI that by TLC (chloroform-ethyl acetate 45:1, uv light) afforded pure amide XI (80 mg., 8%); yield of triazole V, 65%, of triazole X, 15%.

Triazole V was recrystallized from light petroleum to give white crystals, m.p. 66-68°; ir ν max (carbon tetrachloride) 1767 ($COOC_2H_5$) cm^{-1}; nmr τ 1.85-2.30 (m, 2H, 2′ and 6′ phenyl H); 2.50-2.85 (m, 3H, 3′, 4′ and 5′ phenyl H); 5.52 (q, J = 7 Hz, 2H, CH_2); 5.88 (s, 3H, OCH_3); 8.52 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{13}N_3O_3$: C, 58.29; H, 5.30; N, 17.00. Found: C, 58.39; H, 5.32; N, 17.30.

Triazole V was quantitatively recovered after treatment with hydrochloric acid under the conditions employed above. Alumina BIII chromatography afforded triazole X; heating at 90° for 72 hours gave some triazole X, m.p. 104-106° from light petroleum; ir ν max (carbon tetrachloride) 3400-3120 (NH) cm^{-1}; nmr τ 1.85-2.30 (m, 2H, 2′ and 6′ phenyl H); 2.50-2.85 (m, 3H, 3′, 4′ and 5′ phenyl H); 5.98 (s, 3H, OCH_3).

Anal. Calcd. for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.52; H, 5.27; N, 24.28.

Methyl *N*-Ethoxycarbonyl-α-amino-α-phenylacetate (XIV).

A suspension in water (5 ml.) of methyl α-aminophenylacetate hydrochloride (3 g.), prepared by refluxing α-aminophenylacetic acid (19) in methanolic hydrogen chloride solution for 3 hours, was cooled at 0° and treated, under stirring, with ethyl chlorocarbonate (1.65 g.) and 2*N* sodium carbonate (16 ml.). Usual workup gave the ester XIV (3.26 g.) yield 92% m.p. 51.53° from light petroleum; ir ν max (carbon tetrachloride) 3350 (NH), 1750, 1725 cm^{-1}; nmr τ 2.76 (s, 5H, aromatic), 4.50 (br s, 1H, NH), 4.80 (d, J = 8 Hz, 1H, Ph-CH-N), 5.97 (q, J = 7 Hz, 2H, CH_2), 6.32 (s, 3H, OCH_3), 8.78 (t, J = 7 Hz, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.65; H, 6.28; N, 6.18.

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(17) A. McKenzie and M. S. Lesslie, *Ber.*, **61**, 153 (1928).

(18) Estimated on the basis of TLC (benzene-ether 99:1, uv light).

(19) R. E. Steiger, "Organic Syntheses," Coll. Vol. III, p. 84 (1955).