

The Reactions of Ethyl *cis*- β -Chloroacrylate with Aminomalonate Derivatives¹⁾

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Treatment of ethyl propiolate (I) with diethyl acetamidomalonate (II) gave cyclized product, 1-acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (III). Analogously, III was obtained from ethyl *cis*- β -chloroacrylate (VIII) and the same reagent in good yield. VIII was treated with ethyl acetamidocyanoacetate (XIII) and diethyl carbobenzyloxyaminomalonate (XIV) to afford cyclized products, 1-acetyl-2-oxo-5-cyano-5-ethoxycarbonyl-3-pyrroline (XVII) and 1-carbobenzyloxy-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (XVIII), respectively. On the other hand, the reactions of VIII with diethyl benzamidomalonate (XV) and diethyl trifluoroacetamidomalonate (XVI) afforded open chain products, diethyl 4-benzamido-4-ethoxycarbonylglutaconate (XIX) and diethyl 4-trifluoroacetamido-4-ethoxycarbonylglutaconate (XX), respectively.

In an earlier paper,³⁾ it was reported that ethyl propiolate, *cis*-3-chloroacrylic acid ester and propiolonitrile derivatives react with thiourea or ammonium dithiocarbamate to afford sulfide derivatives, and that 3-substituted propiolic acid esters react with the same reagents to give 1,3-thiazine derivatives.

The ease with which activated acetylenic compounds undergo Michael type addition reaction is well documented.^{4,5)}

In this paper the authors wish to report Michael type addition reactions of active methylene groups, including those having substituted amino grouping to activated acetylenic compound and *cis*-3-chloroacrylic acid ester.

Ethyl propiolate (I) was allowed to react with diethyl acetamidomalonate (II) in the presence of potassium *tert*-butoxide at room temperature to afford a pale yellow oil (III) of 114–115° (0.0001 mmHg) in 5.6% yield. In the infrared spectrum of III, the absorption bands due to the triple bond and the secondary amide group were absent. The nuclear magnetic resonance (NMR) spectrum in deuteriochloroform showed a AB type quartet at 6.25 ppm and 7.20 ppm ($J_{AB}=7$ cps) for olefinic protons, a singlet at 2.50 ppm due to acetyl group, and a triplet and a quartet at 1.30 and 4.25 ppm, respectively, due to two ethyl ester groups.

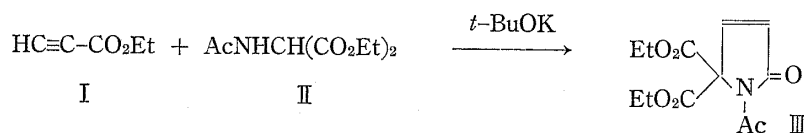


Chart 1

From these spectroscopic data coupled with the elemental analysis ($\text{C}_{12}\text{H}_{15}\text{O}_6\text{N}$), the compound, III, was assigned to 1-acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline. Moreover, the assignment was confirmed by the conversion of an independent route of III into *dl*-N-acetyl glutamic acid (V) and its dimethyl ester (VI) as shown in Chart 2 (see Experiments).

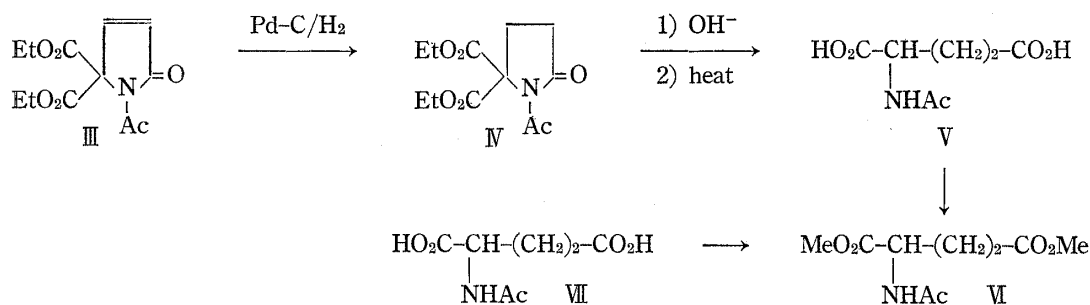
1) The 86th Annual Meeting of Pharmaceutical Society of Japan, Sendai, Oct. 1966.

2) Location: *Hiromachi, Shinagawa-ku, Tokyo*.

3) Y. Kishida and A. Terada, *Chem. Pharm. Bull.* (Tokyo), **16**, 1351 (1968).

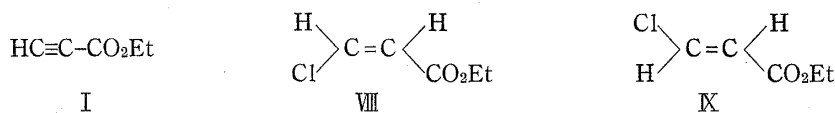
4) A.W. Johnson, "The Chemistry of the Acetylenic Compounds," Vol. II, London, 1950.

5) R.A. Raphael, "Acetylenic Compounds in Organic Synthesis," London, 1955.

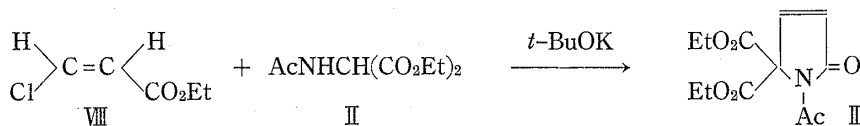


Since the yield of Michael addition reaction of ethyl propiolate (I) and diethyl acetamidomalonate was very poor (5.6%, *loc. cit.*) we turned our attention to improving the reaction.

The reaction⁶⁾ of active methylene compounds with potential Michael acceptors⁸⁾ such as ethyl *cis*- or *trans*-3-chloroacrylate (VIII) (IX)^{9,10)}, instead of ethyl propiolate (I), was carried out.



Thus ethyl *cis*-3-chloroacrylate (VIII) was allowed to react with diethyl acetamidomalonate in the presence of potassium *tert*-butoxide and we obtained the same product, 1-acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (III) in 61% yield (Chart 4).



Treatment of III with 1N sodium hydroxide under drastic conditions afforded 2-acetamidoglutaconic acid (X), mp 175—176°, which separated from the acidified aqueous reaction mixture. The structure, X, was supported by the elemental analysis and spectroscopy. The infrared (IR) spectrum showed secondary amide bands at 1665, 1555 cm^{-1} and the NMR in deuteriochloroform showed a doublet at 3.15 ppm ($J=8$ cps) due to methylene group, a triplet

- 6) H.O. House, W.F. Roelofs and B.M. Trost⁷⁾ have reported, independently, Michael reaction of various active methylenes with methyl *cis*- and *trans*-3-chloroacrylate in the presence of potassium *tert*-butoxide.
- 7) H.O. House, W.F. Roelofs and B.M. Trost, *J. Org. Chem.*, **31**, 646 (1966).
- 8) a) F. Scotti and E.J. Frazza, *J. Org. Chem.*, **29**, 1800 (1964); b) R.B. Woodward and F. Singh, *J. Am. Chem. Soc.*, **72**, 494 (1950); c) P.R. Hills and F.J. McQuillin, *J. Chem. Soc.*, **1953**, 4060; d) G.N. Walker, *J. Am. Chem. Soc.*, **76**, 309 (1954); e) N.K. Kochetkov, L.J. Kudryashov and B.P. Gottich, *Tetrahedron* **12**, 63 (1961); f) D.E. Jones, R.O. Morris, C.A. Vernon and R.F. White, *J. Chem. Soc.*, **1960**, 2349; g) D.E. Jones and C.A. Vernon, *Nature*, **176**, 791 (1955); h) W.R. Benson and A.E. Pohland, *J. Org. Chem.*, **29**, 385 (1964).
- 9) T.H. Vaughn, Belg. 631355.
- 10) Usually, nucleophilic replacement of halogen in simple vinyl halides is known to be difficult. Nevertheless, there are numerous reports of apparent nucleophilic replacement of vinylic halogen atom, and a summary of these has been given by S.I. Miller and P.K. Yonan,¹¹⁾ and A.E. Pohland and W.R. Benson.¹²⁾
- 11) S.I. Miller and P.K. Yonan, *J. Am. Chem. Soc.*, **79**, 5931 (1957).
- 12) A.E. Pohland and W.R. Benson, *Chem. Rev.*, **66**, 161 (1966).

at 6.40 ppm ($J=8$ cps) for vinyl proton, a singlet at 1.95 ppm due to acetyl group and a singlet at 9.75 ppm for carboxylic acid. Thus X was the fate of an exhaustive hydrolysis of III.

On the other hand, hydrolysis of III with 1*N* sodium hydroxide under mild conditions gave a small amount of crystalline substance (XI), mp 69—73°. From the absorption data, this compound was considered to be 4-acetamido-4,4-diethoxycarbonyl-2-butenic acid, resulted from the hydrolytic fission of the amide bond of ring. This compound, however, was not subjected to investigation.

Treatment of III with *p*-toluenesulfonic acid in boiling ethanol yielded 2-oxo-5,5-diethoxycarbonyl-3-pyrroline (XII), mp 72—76°, resulted from the hydrolysis of the N-acetyl bond. The IR spectrum of XII showed an α,β -unsaturated five membered lactam band at 1725 cm^{-1} and an amino band at 3300 cm^{-1} .

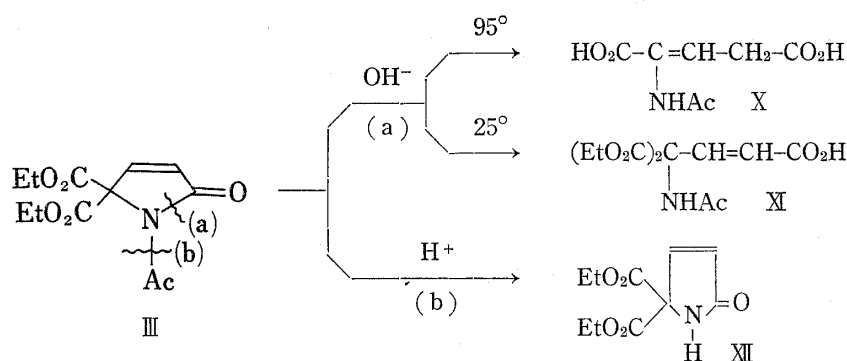


Chart 5

The direction of the bond fission of III may be pH-dependent, as was observed; under the basic conditions, the cleavage (a) preceded and under the acidic conditions, the cleavage (b) occurred predominantly (see Chart 5).

Then we extended the reaction by changing the nucleophile to ethyl acetamidocyanoacetate (XIII), diethyl carbobenzyloxyamidomalonate (XIV), diethyl benzamidomalonate (XV) and diethyl trifluoroacetamidomalonate (XVI).

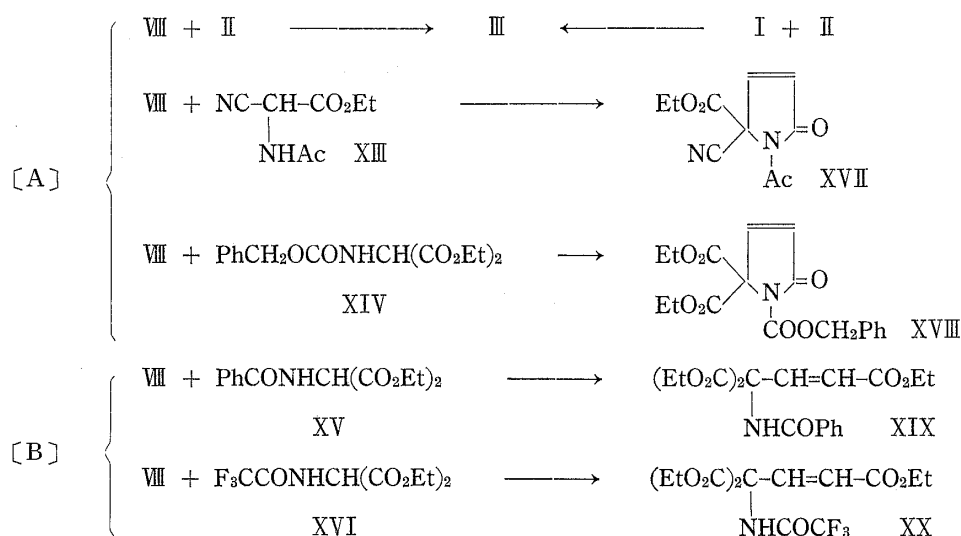


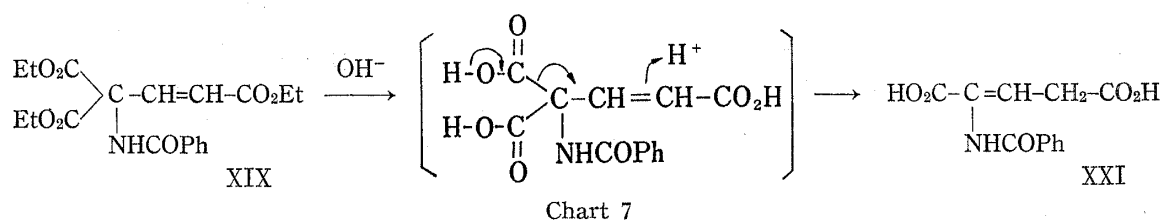
Chart 6

In these reactions, two kinds of reaction products were obtained. On the reaction of VIII with XIII in the presence of potassium *tert*-butoxide, an oily substance (bp 115—120° (0.0003 mmHg)), 1-acetyl-2-oxo-5-cyano-5-ethoxycarbonyl-3-pyrroline (XVII), was obtained.

Similarly, VIII and XIV gave 1-carobenzyloxy-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (XVIII) of bp 160—165° (0.0001 mmHg) (type A). These results, including the reaction of

II and VIII, indicate that usual Michael type addition reaction firstly occurred and was followed by cyclization to afford pyrroline derivatives.

When VIII reacted with XV in the same conditions described above, however, an open chain substance (XIX) of bp 165—168° (0.0002 mmHg) was obtained, whose elemental analysis corresponded to $C_{19}H_{23}O_7N$. The IR spectrum showed secondary amide bands at 1660 and 1520 cm^{-1} and the NMR in deuteriochloroform showed a AB type quartet at 7.35 and 5.90 ppm ($J_{AB}=12$ cps) due to olefinic protons and a triplet at 1.20 ppm and a quartet at 4.20 ppm due to three ethyl ester groups. From these results, XIX was not a cyclized product, but evidently diethyl 4-benzamido-4-ethoxycarbonylglutaconate. Similarly, VIII and XVI gave an open chain product, diethyl 4-trifluoroacetamido-4-ethoxycarbonylglutaconate (XX) of bp 104—105° (0.0001 mmHg) (type B). In the latter's cases, there occurred only Michael type addition reactions giving the open chain glutaconic acid derivatives. Confirmingly, hydrolysis of XIX with 2.5% sodium hydroxide at room temperature afforded 2-benzamidoglutaconic acid (XXI) of mp 158—160° as shown in Chart 7.

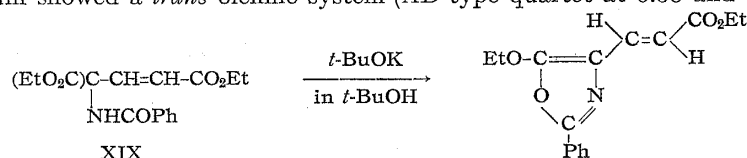


Although the configurations of XIX and XX are not desicively clear as either *cis* or *trans*, owing to the coupling constants of 12 and 13 cps, respectively, in the NMR, these may have *trans* configuration. One of the reasons is that these reactions gave no cyclized product and the plausible deduction would be reinforced by the following reported facts.¹³⁾

Many workers¹⁴⁾ have concluded that the reactions of *cis*-3-haloacrylate derivatives with hetero anions such as thiols or amines proceed largely with retention of geometric configuration, although they have not concluded either retention or inversion about the reactions with carbanions as nucleophile.

The differences of the formation between A and B may be considered to be governed by the negativity of amino groups. The amino groups protected with acetyl- and carbobenzyloxy groups could yield the cyclized products, because the electron density at the amino groups were not decreased so much as compared with those having benzoyl- and trifluoroacetyl groups. In the preceding discussion, we have assumed that the configurations of XIX and XX may be *trans*. The most stable products would predominate, that is, the course of the reactions may proceed with a thermodynamic control to afford *trans* configuration products.

- 13) Y. Kishida and N. Nakamura, *Chem. Pharm. Bull.* (Tokyo), **17**, 2424 (1969). Treatment of XIX with *tert*-butoxide in boiling *tert*-butanol gives ethyl 3-(2-phenyl-5-ethoxy-4-oxazolyl)acrylate whose NMR spectrum showed a *trans* olefinic system (AB type quartet at 6.38 and 7.40 ppm, $J=16$ cps).



- 14) a) W. Autenrith, *Chem. Ber.*, **29**, 1639 (1896); b) H. Scheiber and J. Vors, *ibid.*, **53**, 379 (1920); c) D. E. Jones, R.O. Morris, C.A. Vernon and R.E.M. White, *J. Chem. Soc.*, **1960**, 2349; d) F. Montanari, *Bull. Sci. Fac. Chim. Ind.*, **31**, 16 (1958); e) G. Modena, *Ric. Sci.*, **28**, 341 (1958); f) L. Maioli and G. Modena, *Gazz. Chim. Ital.*, **89**, 854 (1959); g) G. Modena and P.E. Todesco, *ibid.*, **89**, 856 (1959); h) G. Modena, P.E. Todesco and S. Tonti, *ibid.*, **89**, 878 (1959); i) F. Montanari, *Tetrahedron Letters*, **1960**, 18.

The plausible reaction path for the formation of A and B are thought to be addition-elimination mechanism as shown in Chart 8, wherein the addition of the nucleophiles are followed by loss of chloride ion, just as proposed by Jones, *et al.*,^{14c)} in the similar reactions. It can proceed with either synchronous way or the formation of an intermediate adduct. The activated complex may be represented by XXII in Chart 8.

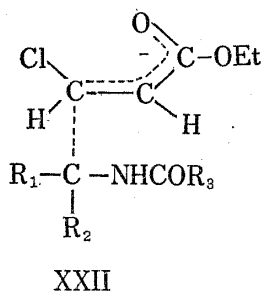
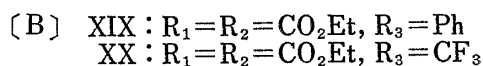
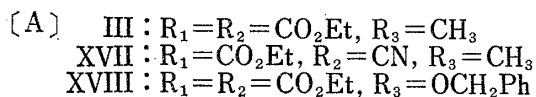
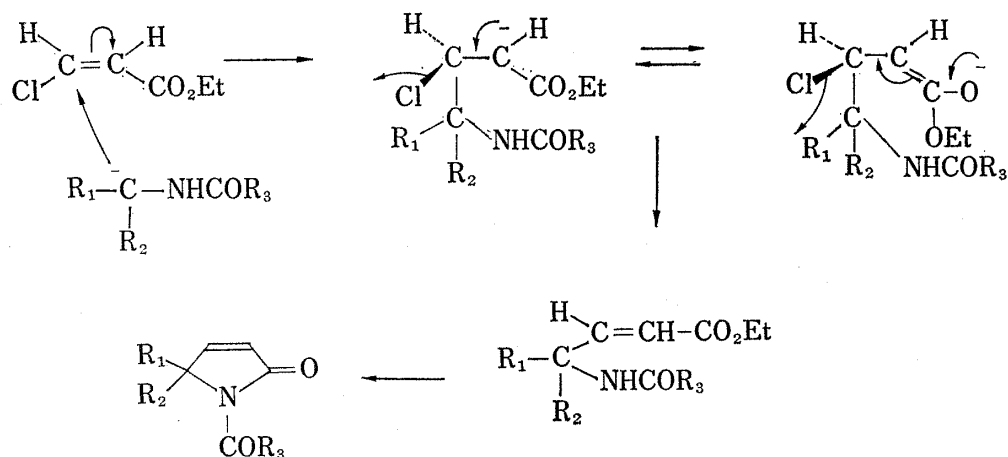


Chart 8

From these results it is clear that ethyl *cis*-3-chloroacrylate is more reactive to carbanion than ethyl propiolate in Michael addition reactions.

Experimental¹⁵⁾

1-Acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (III) from I—To a mixture of *t*-BuOK in *t*-BuOH, prepared from K (0.6 g) and 45 ml of abs. *t*-BuOH, and diethyl acetamidomalonate (9.3 g) was added dropwise a solution of ethyl propiolate (4.9 g) in 10 ml of *t*-BuOH at room temperature. After standing overnight at room temperature, the reaction mixture was acidified with 2N AcOH. The solvent was removed under reduced pressure and the residue was dissolved in H₂O and ether. The ethereal layer was separated and aqueous layer was extracted with ether. The combined ethereal solution was washed successively with H₂O, satd. NaCl solution and then dried over Na₂SO₄. Evaporation of the solvent gave an oily substance (10.5 g) which was dissolved in a minimum amount of hexane-benzene (5:2) and was adsorbed on Al₂O₃.

15) All boiling points and melting points were uncorrected. NMR spectra were taken on Varian A-60 spectrometer with Me₄Si as the internal standard.

(300 g) (Woelm, grade II). Elution with hexane-benzene (1:2) gave an oily substance (0.88 g). Vacuum distillation of an oil gave 1-acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (III) of bp 114–115° (0.0001 mmHg) (bath temp.). *Anal.* Calcd. for $C_{12}H_{15}O_6N$: C, 53.53; H, 5.62; N, 5.20. Found: C, 53.82; H, 5.79; N, 5.07. IR ν_{\max}^{liq} cm^{-1} : 1765, 1760, 1720. UV λ_{\max}^{EtOH} (e): 228.5 (6700).

1-Acetyl-5,5-diethoxycarbonyl-2-pyrrolidone (IV)—Pd-C (5%) (200 mg) in EtOH (6 ml) was stirred in H_2 atmosphere until no more hydrogen was absorbed. Then 1-acetyl-5,5-diethoxycarbonyl-2-oxo-3-pyrroline (400 mg) in EtOH (3 ml) was added and the mixture was stirred in H_2 atmosphere at 29°. 37.5 ml of H_2 gas was absorbed (calculated volume is 37 ml). The solid substance was filtered off, and washed with EtOH. The combined filtrate was evaporated under reduced pressure. The oily residue was distilled under diminished pressure to give 1-acetyl-5,5-diethoxycarbonyl-2-pyrrolidone of bp 112–115° (0.02 mmHg) (bath temp.) (0.382 g). *Anal.* Calcd. for $C_{12}H_{17}O_6N$: C, 53.13; H, 6.32; N, 5.16. Found: C, 53.04; H, 6.44; N, 5.06.

Dimethyl N-Acetyl-glutamate (VI)—1-Acetyl-5,5-diethoxycarbonyl-2-pyrrolidone (84 mg) was dissolved in EtOH (0.7 ml) and to this solution was added 47 mg of NaOH in H_2O (0.3 ml). The reaction mixture was stirred at room temperature for 20 hr. The solution was diluted with H_2O (10 ml) and passed through a column packed with IRC-50 resin (wet, 7 ml). The column was eluted with H_2O (40 ml) and then with EtOH (40 ml). The eluate was evaporated under reduced pressure (0.1 mmHg) for 15 min. The product thus obtained was a white crystalline substance, which was very hygroscopic. The substance was dissolved in H_2O (3 ml) and 1N HCl solution was added until pH value of the solution reached about 3. The solution was evaporated under reduced pressure at room temperature to give an oily substance (100 mg), 84 mg of which was covered with 3 ml of ether and an ethereal solution of diazomethane (1.2 ml; it contained 0.000201×2 mole of CH_2N_2) was added under ice-water cooling. The reaction mixture was stirred at 2–4° for 1 hr. Then 4 ml of MeOH was added and stirring was continued at 2–4° for further 3 hr (at this point yellow color disappeared). The solution was filtered in order to remove a small amount of solid substance. The filtrate was evaporated under reduced pressure to give an oil (35 mg). Distillation of this oil gave dimethyl N-acetylglutamate of bp 130–135° (0.001 mmHg) (bath temp.) (15 mg), whose IR spectrum was superimposed on that of the authentic sample. *Anal.* Calcd. for $C_9H_{15}O_5$: C, 49.76; H, 6.96. Found: C, 49.51; H, 6.86.

1-Acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (III) from VIII—To a mixture of *t*-BuOK in *t*-BuOH, prepared from K (2 g) and 80 ml of abs. *t*-BuOH, and diethyl acetamidomalonate (11.1 g) was added a solution of ethyl *cis*-3-chloroacrylate (7.73 g) in 16 ml of *t*-BuOH at room temperature. The reaction mixture was stirred for a night at room temperature and then was acidified with AcOH. The solvent was removed under reduced pressure, the residue was dissolved in H_2O and ether and the organic layer was separated. The aqueous layer was extracted with ether, and the combined ethereal solution was washed with H_2O , satd. NaCl solution and dried over Na_2SO_4 . Evaporation of the solvent gave an oily substance, which distilled *in vacuo* to afford a pale yellow oil (11.0 g), 1-acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline, bp 114–115° (0.0001 mmHg) whose IR spectrum was superimposed on that of the product from I.

2-Acetamidoglutaconic Acid (X)—A mixture of 1-acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (1.345 g) and 1N NaOH (15 ml) was refluxed for 2 hr. After cooling, 1N HCl (15 ml) was added to this reaction mixture, and then the solvent was evaporated under reduced pressure to give a crystalline substance. Recrystallization from H_2O gave 2-acetamidoglutaconic acid of mp 175–176° (decomp.) (0.59 g). *Anal.* Calcd. for $C_7H_9O_5N$: C, 44.92; H, 4.85; N, 7.48. Found: C, 44.46; H, 4.91; N, 7.16. IR ν_{\max}^{NaJol} cm^{-1} : 1665, 1555.

2-Oxo-5,5-diethoxycarbonyl-3-pyrroline (XII)—A mixture of 1-acetyl-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (1.35 g), *p*-toluene sulfonic acid (0.1 g) and 30 ml of EtOH was refluxed for 44 hr. The reaction mixture was evaporated under reduced pressure to dryness to afford a crystalline substance. Recrystallization from ether-hexane (1:1) gave 2-oxo-5,5-diethoxycarbonyl-3-pyrroline of mp 72–76° (0.985 g). *Anal.* Calcd. for $C_{10}H_{13}O_5N$: C, 52.86; H, 5.77; N, 6.17. Found: C, 52.94; H, 5.90; N, 5.99. IR ν_{\max}^{NaJol} cm^{-1} : 3300, 1745, 1725.

1-Acetyl-2-oxo-5-cyano-5-ethoxycarbonyl-3-pyrroline (XVII)—To a mixture of *t*-BuOK in *t*-BuOH, prepared from K (0.8 g) and 50 ml of abs. *t*-BuOH, and ethyl acetamidocyanoacetate (3.4 g) was added a solution of ethyl *cis*-3-chloroacrylate (2.7 g) in 5 ml of *t*-BuOH at room temperature. After standing overnight at room temperature, the reaction mixture was acidified with 2N AcOH. The solvent was removed under reduced pressure and the residue was dissolved in H_2O and ether. The ethereal layer was separated and aqueous layer was extracted with ether. The combined ethereal solution was washed successively with H_2O , satd. NaCl solution and dried over Na_2SO_4 . The evaporation of ether gave a pale yellow oil, which was distilled *in vacuo* to afford 1-acetyl-2-oxo-5-cyano-5-ethoxycarbonyl-3-pyrroline of bp 115–120° (0.0003 mmHg) (bath temp.) (0.25 g). *Anal.* Calcd. for $C_{10}H_{10}O_4N_2$: C, 54.05; H, 4.54; N, 12.61. Found: C, 53.78; H, 4.48; N, 12.87. IR ν_{\max}^{liq} cm^{-1} : 2220 (–CN), 1740, 1700, 1630.

1-Carbobenzoyloxy-2-oxo-5,5-diethoxycarbonyl-3-pyrroline (XVIII)—To a mixture of *t*-BuOK in *t*-BuOH, prepared from K (0.8 g) and 50 ml of abs. *t*-BuOH, and diethylcarbobenzoyloxyamidomalonate (6.2 g) was added a solution of ethyl *cis*-3-chloroacrylate (2.7 g) in 10 ml of *t*-BuOH at room temperature.

The reaction mixture was treated as described above. 1-Carbobenzyloxy-2-oxo-5,5-diethoxycarbonyl-3-pyrroline was purified by distillation, bp 160—165° (0.0001 mmHg) (4.2 g). *Anal.* Calcd. for $C_{18}H_{19}O_7N$: C, 59.83; H, 5.30; N, 3.88. Found: C, 59.46; H, 5.75; N, 4.03. IR ν_{\max}^{liq} cm^{-1} : 1800, 1760, 1755, 1620.

Diethyl 4-Benzamido-4-ethoxycarbonylglutaconate (XIX)—To a mixture of *t*-BuOK in *t*-BuOH, prepared from K (1.6 g) and 140 ml of abs. *t*-BuOH, and diethyl benzamidomalonate (11.2 g) was added a solution of ethyl *cis*-3-chloroacrylate (5.4 g) in 20 ml of *t*-BuOH at room temperature. After standing overnight at room temperature, the reaction mixture was acidified with AcOH. The solvent was removed under reduced pressure and the residue was dissolved in H_2O and ether. The ethereal layer was separated and aqueous layer was extracted with ether. The combined ethereal solution was washed with H_2O , satd. NaCl solution and dried over Na_2SO_4 . Evaporation of ether gave an oily substance, which was distilled *in vacuo* to afford diethyl 4-benzamido-4-ethoxycarbonylglutaconate of bp 165—168° (0.0002 mmHg) (10.5 g). *Anal.* Calcd. for $C_{19}H_{23}O_7N$: C, 60.47; H, 6.14; N, 3.71. Found: C, 60.21; H, 6.28; N, 3.70. UV $\lambda_{\max}^{\text{EtOH}}$ $m\mu$ (ϵ): 225 (15500).

Diethyl 4-Trifluoroacetamido-4-ethoxycarbonylglutaconate (XX)—To a mixture of *t*-BuOK in *t*-BuOH, prepared from K (0.312 g) and abs. *t*-BuOH (30 ml), and diethyl trifluoroacetamidomalonate (2.17 g) was added a solution of ethyl *cis*-3-chloroacrylate (1.08 g) in 5 ml of *t*-BuOH at room temperature. The reaction mixture was stirred for a night at room temperature and then was acidified with AcOH. The solvent was removed under reduced pressure and the residue was dissolved in H_2O and ether. The organic layer was separated and aqueous layer was extracted with ether. The combined ethereal solution was washed with H_2O , satd. NaCl solution and dried over Na_2SO_4 . After evaporation of the solvent, the residue was submitted to vacuum distillation to give diethyl 4-trifluoroacetamido-4-ethoxycarbonylglutaconate, bp 104—105° (0.0001 mmHg) (2.1 g). *Anal.* Calcd. for $C_{14}H_{18}O_7NF_3$: C, 45.53; H, 4.88; N, 3.79; F, 15.45. Found: C, 45.47; H, 5.01; N, 4.05; F, 15.67.

2-Benzamidoglutaconic Acid (XXI)—A mixture of diethyl 4-benzamido-4-ethoxycarbonylglutaconate (1 g) and 2.5% NaOH (40 ml) was stirred vigorously for 30 hr at room temperature. The reaction mixture was acidified with conc. HCl. The solvent was evaporated under reduced pressure to give a crystalline substance. Recrystallization from H_2O gave 2-benzamidoglutaconic acid, mp 155—160° (0.5 g). *Anal.* Calcd. for $C_{12}H_{11}O_5N$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.42; H, 4.59; N, 5.56. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 3220, 2630 (broad), 1640, 1505.