

tilled vinyl acetate (b.p. 72–73°) and 1.0 g. of powdered anhydrous cupric sulfate was stirred and heated to boiling. A cold mixture of 58 g. of ethyl diazoacetate (0.51 mole) and 58 g. of vinyl acetate was added to the boiling solution at such a rate as to maintain gentle refluxing. The addition required approximately 35 min. The solution was then heated for an additional 15 min., cooled, and filtered. The solvent was removed at atmospheric pressure, and the residue was distilled under reduced pressure giving 55.5 g. (67%) of ethyl 2-acetoxycyclopropanecarboxylate, b.p. 72–78° at 2 mm., n_D^{25} 1.4345.

The unsaturated impurities were removed as follows. The ester (20 g.) was stirred with 250 ml. of 0.15 *M* sodium bicarbonate solution and a stream of carbon dioxide was passed through the solution during the oxidation reaction. Solid potassium permanganate was added in small portions to the buffered solution until an excess had been added. The solution was stirred for 10 min. and then extracted with four 100 ml. portions of ether. The ether solution was dried over calcium sulfate and distilled giving an 80–95% recovery of the acetoxy ester. The pure ester had b.p. 105–106° at 13 mm., n_D^{25} 1.4330.⁷

The methyl ester was prepared by the same method, giving 32% of purified ester b.p. 90° at 10 mm., n_D^{25} 1.4358.

Anal. Calcd. for $C_6H_{11}O_4$: C, 53.2; H, 6.4. Found: C, 52.9; H, 6.6.

The infrared spectrum of the ethyl ester contained two peaks of equal intensity in the carbonyl region at 5.69 μ and 5.79 μ and a strong band at 8.09 μ presumably due to the acetate group.⁸

Pyrolysis of ethyl 2-acetoxycyclopropanecarboxylate. All pyrolysis experiments were carried out in a dry, oxygen free, nitrogen atmosphere. A 24 × 1 inch glass column, packed with glass helices and mounted in a vertical position, was used as the reaction chamber. Ethyl 2-acetoxycyclopropanecarboxylate (5 g.) was dropped into the column which was heated to 500°. The addition required 30 min. during which time a nitrogen flow of approximately 26 l. per hour was maintained. The effluent vapors were collected in a Dry Ice-acetone cooled trap, and in a liquid nitrogen cooled trap. There was obtained 2.2 ml. of a strongly acidic and lachrymatory liquid. Distillation, followed by infrared analysis of the lower boiling fractions indicated the presence of acetic acid, acrolein, and acetic anhydride. The higher boiling fraction was distilled under reduced pressure giving a small amount of starting material, and a small amount of a solid. The solid was recrystallized twice from carbon tetrachloride, m.p. 97.5–98.5°, a total of 10 mg. being obtained.

Anal. Calcd. for $C_6H_5O_4$: C, 50.0; H, 5.6. Found: C, 49.7; H, 5.7.

The solid was acidic to bicarbonate and contained two bands in the carbonyl region of the infrared spectrum, at 5.69 μ and 5.85–5.89 μ , as well as broad absorption at 8.12–8.19 μ . The small amount of this material precluded a more thorough investigation, but these data suggest that it was 2-acetoxycyclopropanecarboxylic acid.

Pyrolysis of the ester at 520° with a flow rate of 3.3 l. per hour was carried out, and the low boiling material was distilled and identified. Ethylene from the liquid nitrogen trap was identified by its characteristic infrared absorption spectrum. The approximate yield estimated from the pressure produced by the gas in a vessel of known volume was 61%. Acrolein, b.p. 50–53°, n_D^{23} 1.3987, was characterized by its infrared spectrum and by its 2,4-dinitrophenylhydrazone, m.p. 163–163.9°, mixed m.p. with an authentic sample, 164–165°. The yield of acrolein was 18%, and a considerable amount of this material probably polymerized in the reaction tube. Acetic acid, obtained in 62% yield,

(7) Ref. 3 reported b.p. 90–92.5° at 7 mm., n_D^{25} 1.433.

(8) A. W. Thompson and P. Torkington, *J. Chem. Soc.* 640 (1945).

(9) C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2955 (1930) reported the 2,4-dinitrophenylhydrazone, m.p. 165°.

was characterized by its infrared spectrum and by the melting point of the *p*-bromophenacyl ester, m.p. 84–85°. Acetic anhydride was detected in the middle boiling fraction by its characteristic infrared spectrum. Only a trace of this compound was obtained.

In another pyrolysis experiment, a 4 l. gas fraction was collected over water. The ethylene and water vapor were trapped from the gas, and the infrared spectrum of the remaining gas showed the presence of carbon monoxide. The yield, estimated using the intensity of the spectrum, was 39%.

Pyrolysis of methyl 2-acetoxycyclopropanecarboxylate. The methyl ester was pyrolyzed at 520° with a flow rate of 3 l. per hour. The products were found to be methyl acetate, acrolein, acetic acid, and a small amount of acetic anhydride. No attempt was made to identify carbon monoxide in this case.

Hydrolysis of methyl 2-acetoxycyclopropanecarboxylate. A solution of 4.76 g. (30 mmoles) of the ester, 100 ml. of methylene chloride, 10 ml. of concentrated hydrochloric acid, and 30 ml. of methanol was heated under reflux for 26 hr. The solution was cooled, the organic layer was separated, washed with water, 5% sodium bicarbonate solution and water, and dried over anhydrous magnesium sulfate. After removal of the solvent, the product was distilled giving 3.20 g. (92%) of methyl β -formylpropionate, b.p. 78–80° at 13 mm., n_D^{25} 1.4168–1.4153. The infrared spectrum of this material corresponded to that of an authentic sample, and the 2,4-dinitrophenylhydrazone, m.p. 130–131.5° gave no depression of the m.p. of an authentic sample² on admixture.

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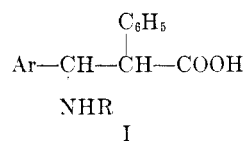
(10) C. G. Moses and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 2101 (1932) reported the m.p. of the *p*-bromophenacyl ester as 86°.

Addition of Phenylacetic Acid to a Schiff Base with Formation of a β -Amino Acid

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Beta amino acids of general formula I have, according to recent reports, been synthesized by the



following methods involving addition reactions to the carbon-nitrogen double bond of Schiff bases.

(a) Addition of $\text{C}_6\text{H}_5-\text{CH}(\text{MgCl})-\text{COONa}^2$ (sodium phenylacetate plus a Grignard reagent), of $\text{C}_6\text{H}_5-\text{CHNa}-\text{COONa}^3$ (sodium phenylacetate

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(2) B. I. Kurtev and St. Robev, *Doklady Bolgar. Akad. Nauk*, **4**, 37 (1951); *Chem. Abstr.*, **49**, 958g (1955).

(3) A. Spasov and St. Robev, *Doklady Akad. Nauk S.S.S.R.*, **95**, 817 (1954).

plus sodamide) or of $C_6H_5-CHLi-COONa^4$ to Schiff bases. (b) Addition of ethyl phenylacetate to Schiff bases in the presence of aluminum chloride, followed by alkaline hydrolysis.⁵⁻⁷

We wish to report that a simple mixture of phenylacetic acid and *N*-benzylidenemethylamine, after being heated at about 100°, affords I, Ar = C_6H_5 , R = CH_3 . No catalyst is necessary. A discussion of possible reaction mechanisms is postponed until we have determined the stereochemical nature (DL-erythro, DL-threo, or some mixture of these) of products formed by the various methods. Only malonic acid has previously been reported capable of adding without catalyst to a carbon-nitrogen double bond to give a beta amino acid.⁸

EXPERIMENTAL

2,3-Diphenyl-3-methylaminopropanoic acid. Equimolecular quantities of phenylacetic acid and *N*-benzylidenemethylamine^{9,10} are heated at 100° for 2 hr. in a flask equipped with a calcium chloride drying tube. The reaction mixture, which is almost completely solid at the end of the heating period, is cooled and treated with a 0.1M NaOH solution. Any alkali-insoluble material is removed by filtration. A stream of carbon dioxide gas is then passed through the alkali solution until the β -aminoacid precipitates. After being filtered, washed with water, and dried it melts at 200°.

Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 74.81; H, 6.85; N, 5.30.

Yields are variable but may reach approximately 75%. Polymerization reactions of the imine, which appear to reduce the yield, may possibly be minimized by the use of an inert diluent.

The β -aminoacid dissolves in very dilute hydrochloric acid. When concentrated hydrochloric acid is added to such a solution, then the hydrochloride of the β -aminoacid precipitates. This substance is easily water soluble but only slightly soluble in fairly concentrated (3M or higher) hydrochloric acid. It melts sharply, but with decomposition, anywhere between 194.5° and 198°, depending on the rate of heating.

Anal. Calcd. for $C_{16}H_{18}ClNO_2$: C, 65.86; H, 6.22; Cl, 12.15; N, 4.80. Found: C, 65.89; H, 6.34; Cl, 11.99; N, 4.69.

A sample of β -aminoacid hydrochloride prepared by Mollov according to method (b) was reported to melt with decomposition at 190–191°. The free β -aminoacid was not described by Mollov.

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Levulinic Acid. II.¹ Some Derivatives of 2-Aminoethyl Levulinate

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In connection with other studies a series of esters of levulinic acid were required; most of these have been described previously. Attempts to prepare 2-aminoethyl levulinate by azeotropic esterification of a mixture of levulinic acid and ethanolamine only yielded a viscous gum which could not be distilled; hydrogenation of the same mixture gives 1-(ethan-2-ol)-5-methyl-2-pyrrolid-one.^{2,3} Using the azeotropic method, levulinic acid was successfully esterified with 2-dimethylaminoethanol, 2-diethylaminoethanol, and *N*-2-hydroxyethylphthalimide.

EXPERIMENTAL⁴

2-Dimethylaminoethyl levulinate. Levulinic acid (116 g., 1.0 mole), 2-dimethylaminoethanol (89 g., 1.0 mole), and benzene (100 ml.) were refluxed in a flask fitted with a Dean and Stark adaptor; water (18 ml.) separated in 24 hrs. The reaction product was washed with water, sodium bicarbonate, and dried. After removal of the solvent the ester had b.p. 156–158°/30 mm.; n_D^{23} 1.4395; yield 61 g. (33%).

Anal. Calcd. for $C_9H_{17}O_3N$: C, 57.73; H, 9.15; N, 7.49. Found: C, 57.32; H, 9.08; N, 6.90%.

2-Diethylaminoethyl levulinate. This ester was prepared in a similar manner and had b.p. 172–176°/30 mm., n_D^{27} 1.4435; yield 46%.

Anal. Calcd. for $C_{11}H_{21}O_3N$: C, 61.37; H, 9.83; N, 6.51. Found: C, 61.54; H, 9.45; N, 6.32%.

2-Phthalimidoethyl levulinate. *N*-2-hydroxyethyl phthalimide⁶ (95.5 g., 0.5 mole.) and levulinic acid (58 g., 0.5 mole.) in benzene (100 ml.) were refluxed for 48 hrs. in a flask fitted with a Dean and Stark adaptor; water (9.5 ml.) separated. After cooling the reaction mixture was washed twice with 2N sodium carbonate; at this stage the product crystallized and was collected by filtration. The dried product was recrystallized from ethanol m.p. 90–93°; yield 89 g. (62%).

Anal. Calcd. for $C_{15}H_{15}O_5N$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.58; H, 5.35; N, 4.91%.

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Monomeric and Polymeric Compositions from Carbethoxymethyl Isocyanate¹

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Recent work in the field of synthetic polypeptides has provided improved techniques for the

(1) Communication No. 1915 from the Kodak Research Laboratories.