

*abdominis* muscle were made as described by MacIntosh and Perry.<sup>8</sup>

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(8) F. C. MacIntosh and W. L. M. Perry in *Methods in Medical Research*, Vol. III, 78, Year Book Publishers, New York, 1950.

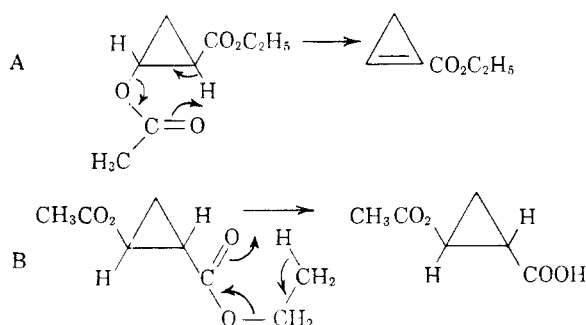
## Cyclopropene. II. The Pyrolysis of *trans*-2-Acetoxy-cyclopropanecarboxylates<sup>1</sup>

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The results obtained in the attempted dehydrobromination of ethyl 2-bromocyclopropanecarboxylate<sup>2</sup> indicate that ethyl cyclopropenecarboxylate is particularly reactive towards Michael addition of nucleophilic agents. It would then be desirable to try to prepare this compound using a reaction which may be effected in the absence of any nucleophilic agents. A particularly attractive reaction is the thermal elimination of acetic acid from an acetate ester.

D'yakonov<sup>3</sup> found that the reaction of ethyl diazoacetate with vinyl acetate gave an ethyl 2-acetoxy-cyclopropanecarboxylate (I). This probably has the *trans*-configuration in analogy with other compounds prepared by this method.<sup>4</sup> The pyrolysis of acetates probably proceeds *via* a cyclic activated complex<sup>5</sup> giving *cis*-elimination. Ethyl 2-acetoxy-cyclopropanecarboxylate thus has the proper stereochemistry for this type of elimination, and



(1) Taken from part of a thesis submitted by R. K. Barnes to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree, 1955. Shell Oil Co. fellow 1953-5.

(2) K. B. Wiberg, R. K. Barnes, and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957).

(3) I. A. D'yakonov, *Zhur. Obshchei Khim.*, **20**, 2289 (1950).

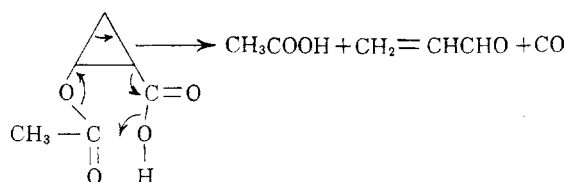
(4) Ethyl acrylate, vinyl bromide, and *t*-butyl vinyl ether all give predominantly the *trans* isomer on reaction with ethyl diazoacetate (*cf.* ref. 2).

(5) C. D. Hurd and F. H. Blunck, *J. Am. Chem. Soc.*, **60**, 2419 (1938).

should give a cyclopropenecarboxylic ester as the product of the pyrolysis if the ease of introducing a double bond into the cyclopropane ring is greater than that of introducing a double bond into the ethyl group. It is known that the pyrolysis of 2° acetates proceeds much faster than that of 1° acetates and this one factor will favor the desired course.

The pyrolysis was first effected at 500°C.<sup>6</sup> using a short contact time, giving starting material, acrolein, acetic acid, ethylene and a small amount of acetic anhydride as the main products. There was also obtained a small amount of a solid acid with an empirical formula C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>, which had carbonyl bands in its infrared spectrum at 5.69 μ and 5.87 μ, and also had a broad absorption at 8.12-8.19 μ. The 5.69 μ and 8.12-8.19 μ bands probably correspond to an acetoxy group, and the 5.87 μ band probably corresponds to the carboxylic acid function. The small amount of material available precluded a more thorough investigation, but the available data, and the method of preparation suggest that it is 2-acetoxy-cyclopropanecarboxylic acid formed by path B.

The other products could arise from this acid as follows:



A *cis*-configuration would appear desirable for this reaction. It is possible that at the reaction temperature the *trans*-compound may be converted to *cis*, or under these conditions, a direct reaction of the *trans*-compound may be possible.

Since the difficulty with this reaction might have been a consequence of initial elimination of ethylene from the ester, followed by decomposition of the acid, the methyl ester which could not lead to the acid was prepared. The pyrolysis of the methyl ester led to the same mixture of products as did the ethyl ester, except that instead of ethylene and acetic acid, methyl acetate was obtained. Thus, this mode of ring cleavage is possible even with an ester.

In connection with other experiments, the methyl ester was subjected to acid catalyzed cleavage. The expected product, methyl β-formylpropionate was formed.

### EXPERIMENTAL

*Ethyl 2-acetoxy-cyclopropanecarboxylate.* The procedure of D'yakonov<sup>3</sup> was used. A mixture of 290 ml. of freshly dis-

(6) At lower temperatures, considerable starting material was recovered and the course of the reaction was unchanged. It should be noted that the observed products could not be formed by a route involving the formation of the cyclopropenecarboxylic ester followed by the decomposition of the latter.

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.<sup>7</sup>

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  $\mu$  and 5.79  $\mu$  and a strong band at 8.09  $\mu$  presumably due to the acetate group.<sup>8</sup>

*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  $\mu$  and 5.85–5.89  $\mu$ , as well as broad absorption at 8.12–8.19  $\mu$ . 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  $\beta$ -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 sample<sup>2</sup> on admixture.

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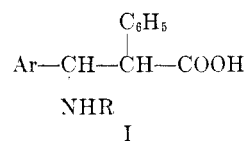
(10) C. G. Moses and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 2101 (1932) reported the m.p. of the *p*-bromophenacyl ester as 86°.

### Addition of Phenylacetic Acid to a Schiff Base with Formation of a $\beta$ -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).