Synthesis of Ethyl 2-Vinylcyclopropane-1-carboxylate via Half-Ester Decarboxylation

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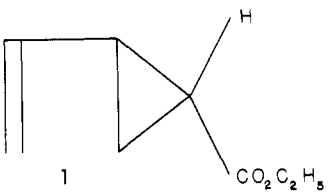
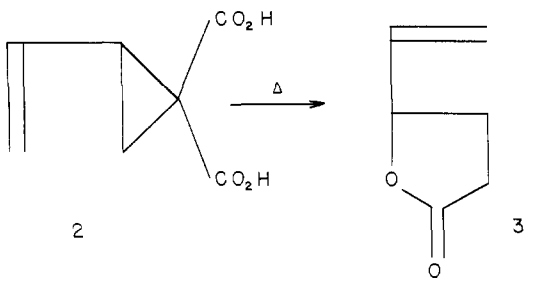
Thermal decarboxylation of 2-vinylcyclopropane-1,1-dicarboxylic acids results in formation of cyclic lactones. Thermal decarboxylation of the half esters of 2-alkenyl cyclopropane-1,1-dicarboxylic acids proceeds without skeletal rearrangement, forming the desired cyclopropanecarboxylic acid. The synthesis of ethyl 2-vinylcyclopropane-1-carboxylate by this technique is described.

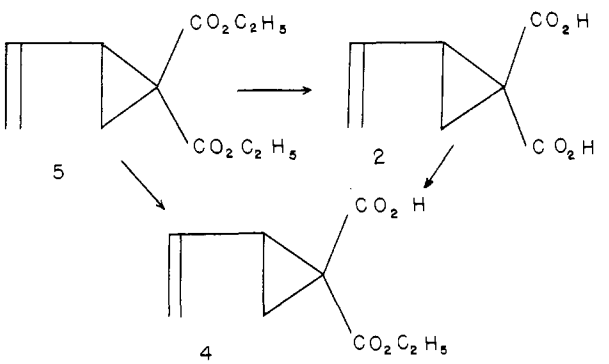
A NEW convenient synthesis of ethyl 2-vinylcyclopropane-1-carboxylate (1) by a novel decarboxylation procedure is reported. This compound has been previously prepared via the reaction of ethyldiazoacetate and 1,3-butadiene (*5, 7*).



Attempted synthesis by the decarboxylation of 2-vinylcyclopropane-1,1-dicarboxylic acid (2) has resulted only in the formation of the cyclic lactone, γ-vinyl-γ-butyrolactone (3) (*1, 2, 6*). However, thermal decarboxylation of the half ester, 2-vinylcyclopropane-1-carbethoxy-1-carboxylic acid (4), proceeds, without skeletal rearrangement to the lactone, forming ethyl 2-vinylcyclopropane-1-carboxylate (1). Decarboxylation via the half ester of 1,1-cyclopropanedicarboxylic acids is therefore a useful procedure for synthesis of substituted cyclopropane carboxylic acids and the lactone formation may be successfully avoided.



Lactone formation is the usual course of decarboxylation of 2-alkenylcyclopropane-1,1-dicarboxylic acids. To our knowledge, this is the first reported example where formation of an undesired loctone is prevented by decarboxylation of a 2-alkenylcyclopropane-1-carbethoxy-1-carboxylic acid instead of the more usual 1,1-diacid. Furthermore, the preparation of 2-vinylcyclopropane-1-carboxylic acid by the procedure described by Vogel and Erb (*7*) involves use of expensive ethyldiazoacetate. The preparation described here involves inexpensive reagents, and appears to be general for synthesis of 2-alkenylcyclopropane-1-carboxylic acids.



The half ester (4) may be synthesized by two different synthetic routes: partial saponification of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (5) or partial esterification of 2-vinylcyclopropane-1,1-dicarboxylic acid (2).

Preparation of the half ester (4) from the diester (5) is stereospecific, producing predominantly one isomer, hydrolysis occurring trans to the vinyl group.

The cis configuration of ethyl 2-vinylcyclopropane-1-carboxylate was assigned on the basis of gas chromatography data. Lishanskii (*5*) has shown that the isomer having the longer retention time is the cis form. The mixture of *cis*- and *trans*-ethyl 2-vinylcyclopropane-1-carboxylates was successively treated with base and thionyl chloride, and the cis isomer of the carbonyl chloride was thermally converted to the trans isomer. The carbonyl chloride was converted back to the ester by the reaction with sodium ethoxide. The gas chromatogram now showed a decrease in area of the peak of the longer retention time. Chromatography of the ester (1) prepared from 5 showed the peak of longer retention time having the larger area, giving evidence that the decarboxylation of the half ester (4) prepared from the diester (5) gave a mixture of predominantly *cis*-ethyl 2-vinylcyclopropane-1-carboxylate. The preparation of 2-vinylcyclopropane-1-carbethoxy-1-carboxylic acid (4) from 2-vinylcyclopropane-1,1-dicarboxylic acid (2) produces a mixture of the cis and trans isomers, as shown by NMR and gas chromatography data.

2-Vinylcyclopropane-1-carbethoxy-1-carboxylate (4) produced from diethyl 2-vinylcyclopropane-1,1-dicarboxylic acid (5) was decarboxylated and formed predominantly the cis isomer, the cis : trans ratio being 83 to 17. The half ester (4) produced by partial esterification of the diacid

(2), decarboxylated to a mixture of *cis*- and *trans*-ethyl 2-vinylcyclopropane-1-carboxylate (1) in 45 to 55 ratio. Attempts to prepare 1 by partial decarbethoxylation of 5 using sodium cyanide in refluxing dimethylsulfoxide, a procedure developed by Krapcho (*4*), were unsuccessful. This reaction fails as a method of decarboxylation of 1,1-carbethoxycyclopropanes (*3*).

EXPERIMENTAL

All boiling points are uncorrected. Gas chromatograms were taken using a 10% QF-1 Chromosorb W, acid-washed, 10-foot × $^3/_{16}$-inch analytical column.

Relative retention volumes are: diethyl 2-vinylcyclopropane-1,1-dicarboxylate (5), 1.00; *cis*-ethyl 2-vinylcyclopropane-1-carboxylate, 0.50; *trans*-ethyl 2-vinylcyclopropane-1-carboxylate, 0.45. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer, using neat samples with tetramethylsilane as an internal standard.

Diethyl 2-Vinylcyclopropane-1,1-dicarboxylate (5) was prepared by the method of Murdock and Angier (*6*) from *trans*-1,4-dichloro-2-butene in 75% yield [b.p. 78–79° C (0.1 mm of Hg), n_d^{20} = 1.4519]. The increased yield resulted from careful drying of absolute ethanol.

2-Vinylcyclopropane-1,1-dicarboxylic Acid (2). Saponification of 45.2 grams of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (5) with 10% excess KOH in 80% ethanol gave 21.1 grams (48%) of the diacid. Purification of the crystals was not attempted.

2-Vinylcyclopropane-1-carbethoxy-1-carboxylic Acid (4). FROM 2. In a 250-ml distilling flask, containing 21.1 grams of 2, equipped with a Dean-Stark trap were placed 51 ml of benzene, 10 grams of 95% ethanol, and 0.5 ml of concentrated sulfuric acid. This mixture was refluxed until water was no longer being collected in the trap. The reaction mixture was made basic with 20% Na_2CO_3 and placed in a separatory funnel. The lower layer was made acidic to litmus paper, extracted with ether, and dried (Na_2SO_4). A total of 8.0 grams of product was recovered upon removal of the excess ether.

The NMR spectrum showed a triplet at δ = 1.24 ppm (3*H*), a quartet at δ = 4.26 ppm (2*H*), and a singlet at δ = 10.17 ppm (1*H*), with multiplets at δ = 1.73 ppm (2*H*), δ = 2.65 ppm (1*H*), and δ = 5.30 ppm (3*H*).

FROM 5. A solution of 800 ml of 80% ethanol and 22.0 grams of KOH was added to a 1-liter distilling flask, containing 83.0 grams of 5, equipped with a Friedrich condenser. The mixture was refluxed for 17 hours. The ethanol was removed by distillation. The crude residue was transferred to a separatory funnel containing 40 ml of saturated NaCl solution. The mixture was made basic with 50 ml of 20% Na_2CO_3, then extracted twice with 80-ml portions of ether. The etheral extracts were combined and dried over sodium sulfate and the ether was removed under vacuum. The aqueous layer was made acidic to Congo Red paper with the addition of 25 ml of concentrated HCl, and extracted three times with 100-ml portions of ether. The extracts were combined and dried over sodium sulfate and the excess ether was removed. A total of 18.2 grams of unreacted diester was recovered from the basic extract. The acid solution yielded 46.7 grams of product (73%), n_d^{20} = 1.4683. The infrared spectrum showed λ_{max} at 3.38, 5.80, 5.35, and 10.85 microns. The NMR spectrum was virtually identical to that obtained from 2. Equivalent weight by neutralization was 185.5.

Ethyl 2-Vinylcyclopropane-1-carboxylate (1). A total of 8.0 grams of 4, prepared from 2, was decarboxylated by heating in an oil bath for 4 hours. Decarboxylation began at 125° C; the final temperature was 180° C. Distillation of the residue yielded 4.8 grams (60%) of product [b.p. 72–75° C (15 mm of Hg), n_d^{23} = 1.4648]. The NMR spectrum shows a triplet at δ = 1.24 ppm (3*H*) and a quartet at δ = 4.18 ppm (2*H*) with multiplets centered around δ = 2.50 ppm (1*H*), δ = 5.25 ppm (3*H*), and δ = 1.85 ppm (3*H*). Decarboxylation of 4 prepared from 5 gave a product, the NMR spectrum of which was virtually identical to that of 1 prepared as described above.

LITERATURE CITED

(1) Birch, S., Dean, R., Hunter, N., *J. Org. Chem.* **23**, 1390 (1958).
(2) Bus, J., Steinberg, H., deBoer, Th. J., *Tetrahedron Letters* **1966**, 1979.
(3) Krapcho, A.P., Department of Chemistry, University of New Hampshire, Durham, N.H., private communication, 1969.
(4) Krapcho, A.P., Glynn, G., Grenon, B., *Tetrahedron Letters* **1967**, 215.
(5) Lishanskii, I.S., Zak, A.G., D'Yakonov, I.A., *Zh. Org. Khim.* **1**, 1189 (1965).
(6) Murdock, K., Angier, R., *J. Org. Chem.* **27**, 2395 (1962).
(7) Vogel, E., Erb, R., *Angew. Chem.* **74**, 76 (1962).

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