Gas chromatography was effected on 8-ft columns of 25% Dow Corning 200 (at 80°) and 25% Carbowax 20 M (at 80°) for separation of compounds **2** to **6**, and 25% Dow Corning 200 (at 210°) for separation of compounds **7** to **12**.

Authentic samples of **2**, **4**, **5**, **6**, **7**, **10**, and **13** were commercially available. Monoethyl oxalate (**8**) was prepared by acidification of the potassium salt, hydroquinone monoacetate (**9**) by acetylation of hydroquinone α-(4-acetylphenoxy)acetone (**11**) from α-chloroacetone and the sodium salt of 4-hydroxyacetophenone in dry benzene and ethyl 4-acetylphenyl oxalate (**12**) from 4-hydroxyacetophenone and ethyl oxalyl chloride.

Acknowledgment.—The authors wish to thank Mr. J. H. Lugert, for the gas chromatography, Mr. D. P. Maier, for the mass spectrometry, and Miss T. J. Davis, for the infrared spectroscopy.

An Improved Synthesis of 3-Cyclopentene-1-Carboxylic Acid from 1,4-Dichlorobutene-2[1a]

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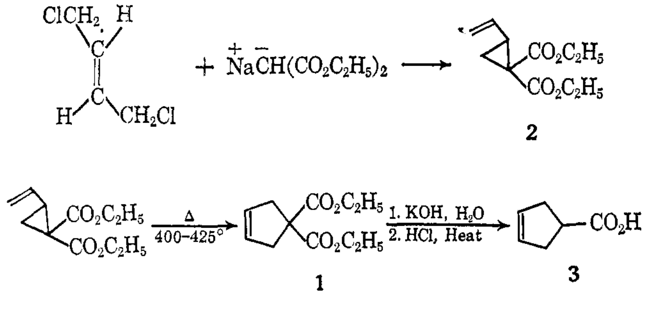
Received September 19, 1966

Several approaches to the preparation of 1-substituted 3-cyclopentenes are reported in the literature.[2-5] Of these only the cycloalkylation of malonic ester with *cis*-1,4-dichlorobutene-2 gives a reasonable yield of the desired product (**1**). However this synthesis also results in the formation of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2**) as an undesirable side product. Separation of **1** and **2** can be accomplished by hydrolysis to the dicarboxylic acid and followed by fractional crystallization.[2] The purpose of this communication is to report a modification of this synthetic scheme which results in an improvement in the yield of **1**.

This improvement can be accomplished by means of the thermal vinylcyclopropane rearrangement.[6]



Thus the cycloalkylation of malonic ester with *cis*-1,4-dichlorobutene-2 gives a 59% yield of a mixture of 58% **1** and 42% **2**. The per cent of **1** and **2** can readily be determined by nmr since the vinyl protons of **2** are a multiplet centered at $\delta = 5.20$ ppm while those of **1** are a singlet located at $\delta = 5.57$ ppm.

The mixture of **1** and **2** was directly pyrolyzed at 400–425° to form diethyl 3-cyclopentene-1,1-dicarboxylate (**1**). Subsequent hydrolysis and decarboxylation gave the desired 3-cyclopentene-1-carboxylic acid (**3**) in 72% yield. The cycloalkylation of malonic ester with *trans* 1,4-dichlorobutene-2 yielded only diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2**) in 63% yield. Again pyrolysis followed by hydrolysis and decarboxylation gave 3-cyclopentene-1-carboxylic acid (**3**) in 52% yield.

This simple modification permits the preparation of 3-cyclopentene-1-carboxylic acid in good yield from the commercially available *trans*-1,4-dichlorobutene-2.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer. Nmr spectra were taken on a Varian A-60 spectrometer on the neat compounds with tetramethylsilane as internal standard. Microanalyses were carried out by A. B. Gygli Microanalyses Laboratory, Toronto, Ontario.

Diethyl 2-vinylcyclopropane-1,1-dicarboxylate (2) was prepared by the method of Murdock and Angier[2] from *trans*-1,4-dichlorobutene-2 (Eastman Kodak) in 63% yield, bp 116–119° (16 mm) [lit.[2] bp 88–92° (0.8 mm)]. The nmr spectrum showed a quartet at $\delta = 4.14$ ppm (4 H) and a triplet at $\delta = 1.23$ ppm (6 H) due to the ethyl group and multiplets at $\delta = 5.20$ ppm ($CH_2{=}CH$ 3 H), $\delta = 2.50$ ppm (cyclopropylmethine H, 1 H), and $\delta = 1.48$ ppm (cyclopropyl methylene protons, 2 H); the infrared spectrum showed $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.34, 5.78, 6.09, 8.30, 10.10, and 10.93 μ (vinyl).

Preparation of Diethyl 3-Cyclopentene-1,1-dicarboxylate (1) by the Thermal Rearrangement of Diethyl 2-Vinylcyclopropane-1,1-dicarboxylate.—A total of 128.6 g of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**2**) was introduced dropwise from a dropping funnel into a Pyrex column packed with 6-mm porcelain berl saddles (available from Fisher Scientific Co.) heated to between 400 and 425° in an electric combustion furnace. A stream of dry nitrogen swept the vapors through the furnace, into a 300-ml, three-necked, round-bottom flask equipped with a Dry Ice condenser and beyond it to a trap immersed in an acetone–Dry Ice bath and a mineral oil gas counter. After all the material was added the column was cooled and washed with ether. The ether was removed under reduced pressure to constant weight. The resulting reddish brown oil weighed 122.7 g (95.5% recovery). The nmr spectrum showed singlet peaks at $\delta = 2.97$ ppm and $\delta = 5.57$ ppm, characteristic of the vinyl and allylic protons of a 1,1-disubstituted 3-cyclopentenyl ring.

Hydrolysis and Decarboxylation of Diethyl 3-Cyclopentene-1,1-dicarboxylate (1).—A solution of 102 g of potassium hydroxide and 122.7 g of the above reddish brown oil in 1150 ml of 80% ethanol was heated under reflux for 11 hr. The ethanol was removed under reduced pressure. A small amount of benzene was added to codistill the remaining traces of ethanol. Hydrochloric acid (6 *N*) was added with cooling until the solution was acid to congo red indicator paper. The solution was extracted with 150-ml portions of diethyl ether until the ether extracts remained colorless. The ether extracts were combined and the ether was evaporated to give 89 g of a brown solid (99%). The solid was decarboxylated by heating in an oil bath at 180° for 2 hr. The liquid was distilled to give 35.3 g (52%) of product, bp 118–121° (20 mm) [lit.[2] bp 83–85° (2 mm)].

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.58; H, 7.59.

The infrared and nmr spectra were identical with that of **3** prepared by the method of Murdock and Angier.[2] The nmr spectrum showed a singlet at $\delta = 5.70$ ppm ($CH{=}CH$, 2 H), a singlet at $\delta = 10.53$ ppm (carboxyl proton, 1 H), and a complex multiplet at $\delta = 2.73$ ppm (allyl and methine protons of the cyclopentene ring, 5 H).

An anilide of **3** was prepared according to the procedure of Shriner, Fuson, and Curtin,[7] mp 137.5–138° (lit.[3] mp 139–140°).

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.98; H, 7.05; N, 7.40.

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(1) (a) This research was supported by the National Research Council of Canada. (b) Holder of a National Research Council Bursary, 1966–1967.

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