14,300); in ethanol it showed λ_{max} 261 mμ (ε 16,300) and 230 mμ (shoulder).

Anal. Calcd for $C_{14}H_{17}N_5O_5$: C, 50.14; H, 5.11; N, 20.89. Found: C, 50.41; H, 5.38; N, 20.76.

9-(2′-Deoxy-β-D-ribopyranosyl)adenine (II).—In 20 ml of absolute methanol, 0.33 g of I was dissolved and 3.2 ml of a solution of barium methoxide in methanol (1 *N*) was added. The mixture was kept at room temperature overnight and refluxed for 40 min. The solution was neutralized with carbon dioxide. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. Recrystallization of the residue from water gave II, mp 267–268°, $[\alpha]^{23}D$ −16.5 (*c* 0.53, water). Ultraviolet absorption at pH 1 showed λ_{max} 258 mμ (ε 15,000); at pH 11 it showed λ_{max} 261 mμ (ε 14,600); in ethanol it showed λ_{max} 260.5 mμ (ε 16,000) and 231 mμ (shoulder).

Anal. Calcd for $C_{10}H_{13}N_5O_3$: C, 47.8; H, 5.2; N, 27.9. Found: C, 47.74; H, 5.45; N, 27.84.

The Reaction of Diphenylcyclopropenone with Alkaline Hydrogen Peroxide

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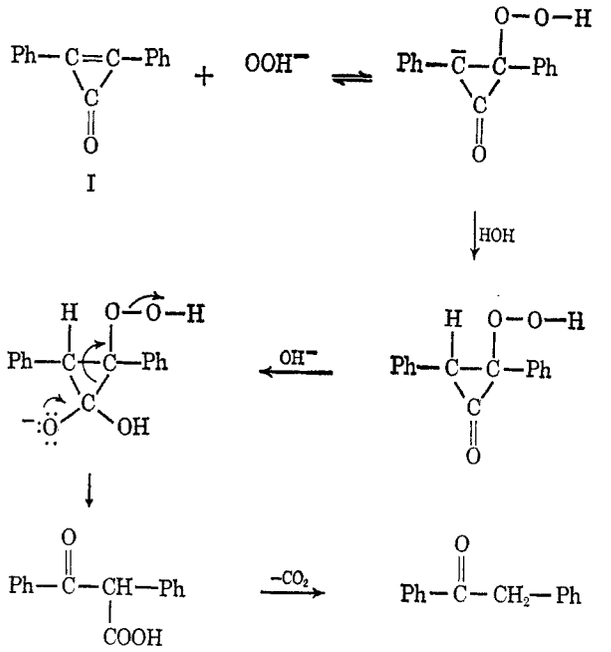
Although the preparation of bicyclobutane or derivatives has been reported,[2] the heterocyclic analog, oxabicyclobutane, or its derivatives have never been made. Epoxidation of diphenylcyclopropenone (I) appeared to be a convenient method for the preparation of a derivative of oxabicyclobutane.

The reaction of diphenylcyclopropenone with hydrogen peroxide and sodium carbonate or sodium hydroxide afforded desoxybenzoin as the major product. A small amount of an intensely yellow, oily material, which was not identified, was also produced. Breslow, *et al.*,[3,4] have found that I reacts with alcoholic sodium hydroxide to form *cis*-1,2-diphenylpropenoic acid, indicating an initial attack of hydroxide ion on the carbonyl carbon atom. It is postulated that the hydroperoxide ion, on the other hand, reacts at the carbon–carbon double bond, as in the case of an "ordinary" α,β-unsaturated carbonyl compound.[5] However, the succeeding steps, in which ring closure to the epoxide is effected, could not take place because of unfavorable steric factors. Consequently, an alternate pathway is followed; one possible route is depicted in Scheme I.

Attempts were made to oxidize diphenylcyclopropenone with peroxyacetic acid but in each instance the starting material was recovered unchanged. Reaction of I with hydroxylamine resulted in the formation of desoxybenzoin oxime[4] as one of the products, which points to the involvement of the carbon–carbon double bond, rather than the carbonyl group, in the first step. Attempts to oxidize I with hypochlorite ion (in aqueous dioxane) were unsuccessful, starting material

SCHEME I



being recovered each time. The hypochlorite–pyridine reagent[6] was ineffective because of the rapidity of the reaction of I with the pyridine.[4]

Experimental Section

Reaction of Diphenylcyclopropenone with Alkaline Hydrogen Peroxide.—To a solution of 2 g (0.01 mole) of diphenylcyclopropenone[4] in 25 ml of purified dioxane was added 4 ml of 3 *M* NaOH (or 10 ml of 5% Na_2CO_3). Two milliliters of 25% hydrogen peroxide was then added dropwise to the stirred mixture. The temperature of the reaction mixture was maintained at 25–30° during the addition and for 30 min thereafter. The addition of 60 ml of ice–water caused the separation of a yellow solid, which was filtered and allowed to air dry. The yield of the crude product was 1.5 g. Recrystallization from methanol afforded white crystals, mp 55–56°, whose infrared spectrum was identical with that of an authentic sample of desoxybenzoin.

The mother liquor from the recrystallization was evaporated and the residual solid was recrystallized again. After another such operation a yellow, oily residue (less than 0.5 g) remained.

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(2) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959); W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961); D. M. Lemal, F. Menger, and G. W. Clark, *ibid.*, **85**, 2529 (1963).

(3) R. Breslow and R. Peterson, *ibid.*, **82**, 4426 (1960).

(4) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965).

(5) C. Bunton and G. Minkoff, *J. Chem. Soc.*, 665 (1949).

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Preparation of Ethyl α-Aryloxyacetoacetates and the Decomposition of Ethyl α-(4-Acetylphenoxy)acetoacetate

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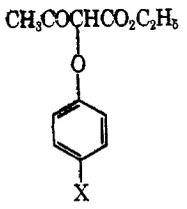
Several ethyl α-aryloxyacetoacetates have been described in the literature as intermediates in the preparation of benzofurans and naphthofurans.[1] Among the analogous compounds (**1a** to **1f**) prepared in this laboratory was ethyl α-(4-acetylphenoxy)acetoacetate (**1c**). It was observed that this compound, originally ob-

(1) (a) A. Hantzsch, *Ber.*, **19**, 1290, 1298, 1301 (1886); (b) R. Royer and E. Bisagni, *Bull. Soc. Chim. France*, 526 (1959); (c) W. R. Boehme, *Org. Syn.*, **33**, 43 (1953).

TABLE I
PROPERTIES OF

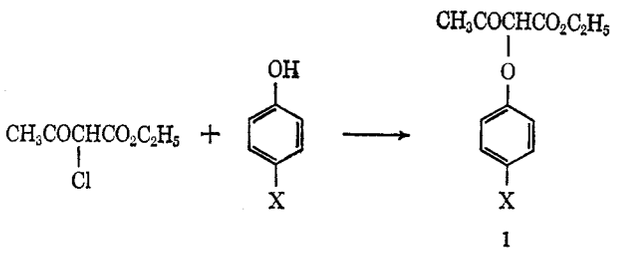


No.	X	Mp, °C	Bp, °C (mm)	Yield, %	Mp, °C, of 2,4-DNP	Calcd, % C	Calcd, % H	Calcd, % N (S)	Found, % C	Found, % H	Found, % N (S)
1a	NO_2	69–72		38		53.9	4.9	5.2	53.7	4.9	5.4
1b	SO_2CH_3	108–109		40		52.1	5.4	(10.7)	52.2	4.9	(10.7)
1c	$COCH_3$	60–61.5		39		63.6	6.1		63.4	6.2	
1d	H[a,b]		110–115 (0.5)	47	109–111	53.7	4.5	13.9	53.9	4.6	14.0
1e	CH_3[b]		132–134 (0.2)	45	107–108	54.8	4.8	13.5	54.6	4.9	13.2
1f	OCH_3[b]		150–153 (0.1)	43	135–136	52.8	4.7	13.0	52.8	4.6	12.6

[a] Reference 1. [b] Analysis refers to the 2,4-dinitrophenylhydrazone.

tained as a crystalline solid, became a syrup after 6 weeks and ultimately developed a crystalline precipitate on standing for 3 months. When a sample was stored *in vacuo* or under nitrogen, this change did not occur, indicating that the compound was undergoing an oxidative and/or hydrolytic decomposition. It was also observed that all the compounds in this series, although odorless at the time of preparation, developed a sharp odor after several months. Since no explanation of these observations could be found in the literature, we undertook a detailed study of the decomposition of **1c**.

All the ethyl α-aryloxyacetoacetates in this series were prepared by a modified Williamson ether synthesis from ethyl α-chloroacetoacetate and the appropriate phenol in the presence of triethylamine in refluxing acetonitrile. With the exception of **1d**, these ethyl α-aryloxyacetoacetates have not been described in the



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literature. The properties of the pure esters are therefore given in Table I. Those compounds which are liquids were difficult to obtain absolutely pure by vacuum distillation and were therefore characterized as the 2,4-dinitrophenylhydrazones.

The gas chromatogram of a decomposed sample of **1c** exhibited 14 distinct peaks; we have been able to assign structures to 11 of these products and to one additional product (**13**) not detected by gas chromatography (gc). The products identified are acetic acid (**2**), water (**3**), ethyl formate (**4**), ethyl acetate (**5**), ethanol (**6**), diethyl oxalate (**7**), monoethyl oxalate (**8**), hydroquinone monoacetate (**9**), 4-hydroxyacetophenone (**10**), α-(4-acetylphenoxy)acetone (**11**), ethyl 4-acetylphenyl oxalate (**12**), and oxalic acid (**13**). Each of the compounds except **13** was identified by a gc comparison with an authentic sample. In addition, the structures of compounds **7**, **8**, **9**, **11**, and **12** were confirmed by mass spectrometry. Based on the area of the gas chromatogram peak, the compounds identified account for approximately 95% of the decomposition products present in the original sample. Except for 4-hydroxyacetophenone (**10**) which accounted for approximately 50% of the mixture, the compounds were present in quantities varying from 1.5 to 6%.

A crystalline precipitate, formed after **1c** had been allowed to stand for 3 months, was isolated by washing it with chloroform and was determined to be oxalic acid (**13**) by comparison of its infrared spectrum with that of an authentic sample. As stated earlier, this component of the decomposition mixture could not be detected by gc.

When a freshly prepared sample of ethyl α-(4-acetylphenoxy)acetoacetate was purified to a constant melting point (60–61.5°) by recrystallization from ethanol and examined immediately by gc, only one broad, tailing peak, identical in shape and retention time with the broad peak previously seen in the gas chromatogram of partially decomposed **1c**, was observed. Mass spectrometry and gc comparison of the eluate which was collected in a cold trap established that this material consisted mainly of α-(4-acetylphenoxy)acetone (**11**). However, no peak corresponding in retention time to an authentic sample of **11** was observed in the chromatogram of decomposed **1c**; this indicates that **11** is not present in the original decomposition mixture, but rather arises by thermal decomposition of **1c** on the column at the time of chromatography.

Experimental Section

Synthesis of Ethyl α-(4-Acetylphenoxy)acetoacetate (1c).—To a solution of 68.0 g (0.5 mole) of 4-hydroxyacetophenone in 500 ml of acetonitrile was added 56 g (0.55 mole) of triethylamine, followed by 82.5 g (0.5 mole) of ethyl α-chloroacetoacetate. After refluxing for 18 hr, the solution was cooled in an ice bath, and the precipitated triethylamine hydrochloride was removed by filtration. The filtrate was evaporated *in vacuo* to a syrup, which was triturated with 200 ml of ethyl acetate; the extract was filtered and evaporated. The resulting syrup was crystallized from 50 ml of ethanol to give 51 g of crude ethyl α-(4-acetylphenoxy)acetoacetate.

Compounds **1a**, **1b**, **1d**, **1e**, and **1f** were prepared in the same manner as **1c**. In the case of the liquid samples (**1d**, **1e**, and **1f**), the crude syrup was distilled *in vacuo* and the 2,4-dinitrophenylhydrazine derivative was prepared[2] for elemental analysis.

(2) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 111.

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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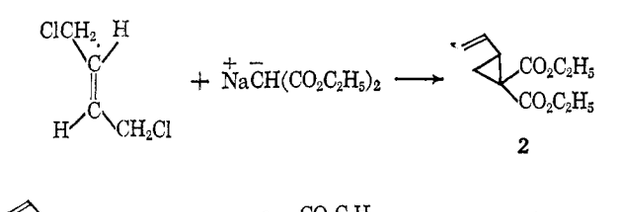
Several approaches to the preparation of 1-substituted 3-cyclopentenes are reported in the literature.[2-5] Of these only the cycloalkylation of malonic ester with *cis*-1,4-dichlorobutene-2 gives a reasonable yield of the desired product (**1**). However this synthesis also results in the formation 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 δ = 5.20 ppm while those of **1** are a singlet located at δ = 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 Angiers[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 δ = 4.14 ppm (4 H) and a triplet at δ = 1.23 ppm (6 H) due to the ethyl group and multiplets at δ = 5.20 ppm (CH_2=CH 3 H), δ = 2.50 ppm (cyclopropylmethine H, 1 H), and δ = 1.48 ppm (cyclopropyl methylene protons, 2 H); the infrared spectrum showed $\lambda_{max}^{CCl_4}$ 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 δ = 2.97 ppm and δ = 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 δ = 5.70 ppm (CH=CH, 2 H), a singlet at δ = 10.53 ppm (carboxyl proton, 1 H), and a complex multiplet at δ = 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.

(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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(5) E. L. Alfred, J. Sonnenberg, and S. Winstein, *ibid.*, **25**, 25 (1960).
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(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 236.