Experimental[13]

Diethyl 3-Methyl-3-cyclopentenedicarboxylate (3a).—Diethyl (2-oxopropyl)malonate[11] (0.047 mole) was treated with sodium hydride (0.047 mole) in 200 ml. of anhydrous ether with stirring. Once the hydrogen evolution had stopped, the mixture was cooled with an ice–water bath and vinyltriphenylphosphonium bromide[8] (0.049 mole) was added directly *via* a flexible rubber tube. An exothermic reaction was observed. After stirring at room temperature for 48 hr., the reaction mixture was poured into water and the ether layer was separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was fractionally distilled *in vacuo* to give 7.3 g. (69% yield) of **3a**, b.p. 95° (0.5 mm.), $n^{26}D$ 1.4494.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.71; H, 7.96. Found: C, 63.81; H, 8.10.

The n.m.r. spectrum of **3a** (neat) showed $=\overset{|}{C}-CH_3$ (unresolved multiplet, 1.69 p.p.m., weight 3.0), $-CH_2-HC=\overset{|}{C}-CH_2-$ (unresolved multiplet, 2.94 p.p.m., weight 3.9), $=CH-$ (unresolved multiplet, 5.25 p.p.m., weight 0.8), $-CO_2CH_2CH_3$ (quadruplet, 4.20 p.p.m., weight 3.9), and $-CO_2CH_2CH_3$ (triplet, 1.22 p.p.m., weight 6.5). The infrared spectrum was in agreement with the assigned structure.

Diethyl (4-Methyl)-3-cyclohexenedicarboxylate (3b).—Diethyl (3-oxobutyl)malonate[7] (0.1 mole) was treated with sodium hydride (0.1 mole) in 150 ml. of anhydrous ether with stirring. Once the hydrogen evolution had stopped the mixture was cooled with an ice–water bath and vinyltriphenylphosphonium bromide[8] (0.9 mole) was added directly. An exothermic reaction was observed. After stirring at room temperature for 12 hr., the reaction mixture was filtered, the filtrate was concentrated under reduced pressure, and the residue was fractionally distilled *in vacuo* to give 12 g. (51% yield) of **3b**, b.p. 90–92° (0.5 mm.), $n^{23}D$ 1.4570 (lit.[9] b.p. 127° at 6 mm., $n^{25}D$ 1.456). The n.m.r. spectrum of **3b** (neat) showed $=\overset{|}{C}-CH_3$ (multiplet, 1.58 p.p.m., weight 2.9), $=CH-$ (unresolved multiplet, 5.30 p.p.m., weight 0.9), $-CH_2-CH_2-\overset{|}{C}=$ (unresolved multiplet, 2.02 p.p.m., weight 4.0), $>C=CH-CH_2-$ (unresolved multiplet, 2.47 p.p.m., weight 1.9), $-CO_2CH_2CH_3$ (quadruplet, 4.12 p.p.m., weight 3.9), and $-CO_2CH_2CH_3$ (triplet, 1.18 p.p.m., weight 6.0). The infrared spectrum was in agreement with the assigned structure.

A portion of **3b** was saponified in 20% NaOH, acidified, and decarboxylated at 200° to give the known 4-methyl-3-cyclohexenecarboxylic acid, m.p. 100–101° (from H_2O) (lit.[10] m.p. 100°).

Isolation of Triphenylphosphine Oxide (4).—Diethyl (3-oxobutyl)malonate (0.026 mole), sodium hydride (0.025 mole), and vinyltriphenylphosphonium bromide were subjected to essentially the same conditions as above. The resulting reaction mixture was poured into water; the ether layer was extracted, dried over anhydrous Na_2SO_4, and concentrated on a steam bath. Triphenylphosphine oxide, 5 g. (71% yield), melting point and mixture melting point with an authentic sample unchanged, was recovered by filtration. The remaining ether in the filtrate was removed under reduced pressure and the residue was fractionally distilled *in vacuo* to give 1.6 g. (27% yield) of **3b**.

Diethyl (4-Oxopentyl)malonate (2c).—Diethyl malonate (0.31 mole) was slowly added to a stirred mixture of sodium hydride (0.25 mole) and 200 ml. of 3:1 benzene–DMF solvent. Once the hydrogen evolution had ceased, 5-bromo-2-pentanone[12] (0.30 mole) was added over a period of 0.5 hr. and refluxed for 24 hr. The reaction mixture was filtered, and the solvent was removed under reduced pressure. The residue was fractionally distilled *in vacuo* to give 30 g. (49% yield) of **2c**, b.p. 115° (0.5 mm.), $n^{26}D$ 1.4380.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 59.01; H, 8.14. Found: C, 58.83; H, 8.24.

The n.m.r. spectrum for **2c** (neat) showed $H_3C-\overset{|}{C}=O$ (singlet, 2.20 p.p.m., weight 3.2), $O=\overset{|}{C}-CH_2CH_2CH_2-$ (triplet, 2.62 p.p.m., weight 2.0), $O=\overset{|}{C}-CH_2CH_2CH_2-$ (unresolved multiplet, 1.80 p.p.m., weight 3.8), H–C< (triplet, 3.53 p.p.m., weight 1.0), $-CO_2CH_2CH_3$ (quadruplet, 4.39 p.p.m., weight 4.0), and $-CO_2CH_2CH_3$ (triplet, 1.29 p.p.m., weight 6.3). The infrared spectrum was consistent with the assigned structure.

Attempt to Prepare Diethyl (4-Methyl)-3-cycloheptenedicarboxylate (3c).—The reaction conditions described here are essentially those employed by House and Babad.[6]

A solution of 0.036 mole of diethyl (4-oxopentyl)malonate, 0.054 mole of vinyltriphenylphosphonium bromide, and 300 ml. of anhydrous *t*-butyl alcohol was placed in a flask fitted with a Soxhlet extractor containing 0.036 g.-atom of potassium. The mixture was refluxed under a nitrogen atmosphere for 48 hr. The reaction mixture was concentrated under reduced pressure. A portion of the resulting viscous residue was chromatographed on a 20-cm. Florsil column using 10% $CHCl_3$–benzene eluent. Triphenylphosphine oxide (melting point and mixture melting point unchanged, infrared spectrum superimposable on the spectrum of an authentic sample) was isolated. Another portion of the residue was analyzed by thin layer chromatography using silica gel H and 20% MeOH–$CHCl_3$ eluent. Triphenylphosphine, triphenylphosphine oxide, an unknown substance, and vinyl salt were detected by spot enhancement and identical retention times with authentic samples. The unknown material, m.p. 208–210° [recrystallized from petroleum ether (b.p. 90–100°)], was isolated by boiling the residue in a large amount of high-boiling (b.p. 90–100°) petroleum ether and then decanting and evaporating the solvent

Anal. Found: C, 79.32; H, 5.79; P, 9.85.

The vapor phase chromatograph (12-ft. Dow silicone 300 on firebrick column at 250°) of a portion of the viscous residue dissolved in chloroform showed traces of starting malonate, triphenylphosphine, and triphenylphosphine oxide which were identified by peak enhancement and identical retention times with authentic samples. No other volatile product was detected.

Acknowledgment.—The authors wish to thank the donors of the Petroleum Research Fund of the American Chemical Society for their kind support.

(13) Melting points and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Infracord 137 and n.m.r. spectra on a Varian A-60 spectrometer employing tetramethylsilane as a standard. Analyses were by Micro-Analyses, Inc., Wilmington, Del.

Formation of a Cyclopropane Ring from an α,β-Unsaturated Carboxylic Acid[1]

ROY T. UYEDA AND DONALD J. CRAM

Department of Chemistry, University of California, Los Angeles 24, California

Received February 4, 1965

In the course of the preparation of 3-phenyl-1-butanol (III) by reduction of β-methylcinnamic acid (I) with lithium aluminum hydride,[2] besides the expected alcohol, considerable quantity of 1-methylphenylcyclopropane (II) was isolated. Table I records the con-

TABLE I

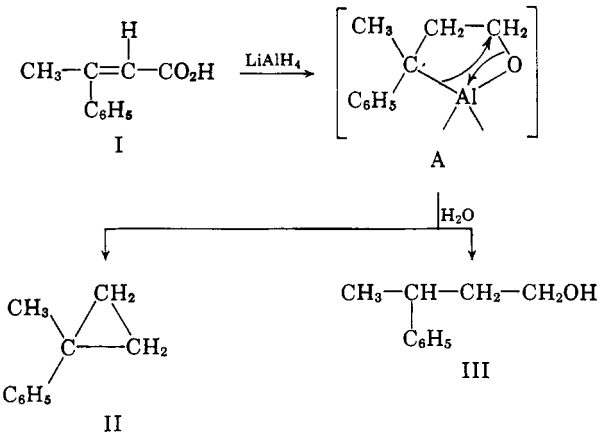
REDUCTION OF β-METHYLCINNAMIC ACID WITH LITHIUM ALUMINUM HYDRIDE IN TETRAHYDROFURAN AT 65°

Run	Moles of I/ml. of THF	Moles of $LiAlH_4$/ml. of THF	Time, hr.	III, %	II, %
1	0.03/30	0.07/30	3	80	3
2	0.03/50	0.07/40	6	75	6
3	0.03/40	0.07/30	16	61	13
4	0.06/30	0.10/20	36	...	35
5	0.06/40	0.13/35	185	8	69

(1) This research was supported by the Directorate of the Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR 124-63. The authors wish to express their thanks for this support.

(2) (a) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947); (b) F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

ditions that favor one or the other of these two products. The pattern of results indicates that the two products have a common precursor, and that the relative yields are controlled by the amount of time the reaction is allowed to go before the reaction mixture is quenched. This fact coupled with the structures of starting materials and products indicates that the intermediate in question has structure A.[2b]



I A II III

Numerous examples of reduction of α,β-unsaturated carbonyl compounds have appeared in the literature,[3] but the formation of cyclopropane derivatives has not been reported.

The over-all conversion of I to II resembles a number of known preparations of cyclopropane compounds.[4] Thus treatment of β-methylallyl chloride with diborane gave methylcyclopropane.[4a] Similarly, 1-chloro-3-methyl-1,2-butadiene and lithium aluminum hydride gave 1,1-dimethylcyclopropane.[4b] Finally, 2-methylallyl ethyl ether and diisobutylaluminum hydride gave methylcyclopropane.[4c] The critical ring-closing steps in all of these preparations resemble one another in the sense that they are intramolecular nucleophilic substitution reactions.

The scope and limitations of our reaction have not been examined, but, in principle, the reaction might be applicable to a broad range of α,β-unsaturated carbonyl compounds.

Experimental

1-Methyl-1-phenylcyclopropane (II).—Run 5 will be described. To a stirred suspension of 5.0 g. of lithium aluminum hydride in 35 ml. of tetrahydrofuran (distilled from lithium aluminum hydride) at −78° under an atmosphere of dry nitrogen was added 10 g. of *trans*-β-methylcinnamic acid[5] (m.p. 98°) in 40 ml. of tetrahydrofuran (distilled from lithium aluminum hydride). The reaction mixture was allowed to warm to 20°, and was stirred under reflux for 185 hr. The excess lithium aluminum hydride was decomposed with 10 ml. of cold water, then with 100 ml. of cold 12 *N* sulfuric acid. The resulting mixture was extracted four times with 50 ml. of ether, and the combined organic layers were in turn washed with 50 ml. of saturated sodium bicarbonate solution and twice with 50 ml. of water. The ether layer was dried, and the solvent was slowly evaporated through a Vigreux column. The residual oil was chromatographed on 250 g. of silica gel with pentane as the eluent for the hydrocarbon, then with methanol to strip the column. The pentane fraction was evaporated, and the residual oil was distilled at 85° (32 mm.) to give 5.4 g. (69%) of 1-methylphenylcyclopropane, $n^{25}D$ 1.5139 (lit.[6] $n^{20}D$ 1.5160). Analysis of this material by vapor phase chromatography (4-methyl-4-nitropimelonitrile column at 90°) demonstrated purity.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.88; H, 9.21.

The infrared spectrum was almost identical with that found in the literature[7] for 1-methylphenylcyclopropane with the characteristic absorption at 9.85 μ. The phenyl protons appeared in the nuclear magnetic resonance spectrum at τ 2.89, the methyl protons as a singlet at 8.78 and the methylene protons as a multiplet centered at 9.32. These absorptions integrated to give a ratio of 5:3:4.

The methanol fraction was evaporated, and the residual oil was flash distilled at 7 mm. to give 1 g. of material, which was analyzed by vapor phase chromatography (5% *m*-phenyl ether on Fluoropak at 170°) to be 80% of 3-phenyl-1-butanol and five other components totaling 20%. The major product had a retention time identical with authentic 3-phenyl-1-butanol.[8]

(3) For example: (a) M. J. Jorgenson, *Tetrahedron Letters*, 559 (1962); (b) L. Li and W. H. Elliott, *J. Am. Chem. Soc.*, **74**, 4089 (1952); (c) G. E. Benedict and R. R. Russell, *ibid.*, **73**, 5444 (1951); (d) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954); (e) J. S. Meek and R. D. Stacy, *J. Org. Chem.*, **26**, 300 (1961).

(4) (a) M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 1886 (1960); (b) T. L. Jacobs and R. D. Wilcox, *ibid.*, **86**, 2240 (1964); (c) L. I. Zakharkin and L. A. Savina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1693 (1963).

(5) D. Lipkin and T. D. Stewart, *J. Am. Chem. Soc.*, **61**, 3295 (1939).

(6) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *ibid.*, **65**, 1469 (1943).

(7) F. S. Bridson-Jones, G. D. Buckley, L. H. Cross, and A. P. Driver, *J. Chem. Soc.*, 2999 (1951).

(8) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2138 (1952).

Furano Compounds. VI. The Synthesis of Linear Furanoxanthones[1]

Y. S. AGASIMUNDIN AND S. RAJAGOPAL

Department of Chemistry, Karnatak University, Dharwar, India

Received December 3, 1964

In general the fusion of the furan ring in the various naturally occurring furano compounds is of two types, *viz.*, angular or linear, the most typical examples being angelicin (angular furanocoumarin) and psoralen (linear furanocoumarin). The synthesis of a number of furanoxanthones of the angular type has been recorded from these laboratories.[2-4] It is common knowledge that, while the synthesis of these angular furano compounds is fairly simple, the synthesis of their linear isomers is more difficult. A convenient method which has been developed for the synthesis of linear furanocoumarins is the one due to Kaufman.[5] This involves the use of a blocking group, like an acetyl group (introduced by the Fries rearrangement), so that the Claisen rearrangement of an allyloxycoumarin produces an appropriate intermediate for the synthesis of a linear furano compound. This has been adopted for the synthesis of linear furanoxanthones for the first time.

Thus the furan ring has been built on two typical xanthones, *viz.*, on 3-hydroxyxanthone[3] (an analog of the naturally occurring 7-hydroxychromone) and on 3-hydroxy-7-methylxanthone[4] (an analog of the widely distributed 6-methylchromone derivatives). These

(1) This article forms part of the material for the Ph.D. thesis to be submitted by Y. S. Agasimundin to the Karnatak University.

(2) G. S. Puarnik and S. Rajagopal, *Ber.*, **96**, 976 (1963).

(3) G. S. Puranik and S. Rajagopal, *J. Org. Chem.*, **29**, 1089 (1964).

(4) Y. S. Agasimundin and S. Rajagopal, *Ber.*, in press.

(5) K. D. Kaufman and L. R. Worden, *J. Org. Chem.*, **26**, 4721 (1961).