immersion exhibited in every case a single major peak of λ_{max} 241 mμ with an α value as listed in Table I. For any one acid, the height of the abietic acid peak did not change appreciably from 2 to 30 min. of immersion time. The four reactions were repeated with immersion times of only 2 min. Each reaction mixture was allowed to cool to room temperature under a nitrogen sweep, treated with an excess of a saturated aqueous solution of boric acid, and ether extracted five times; the ether extract was washed with water five times and evaporated to dryness. The yield of mixed acids was quantitative. The acid mixture was treated with an excess of diazomethane and the ether solution was stripped to dryness. The residue was analyzed by g.l.c. on a 10% Versamid 900 column (on Chromosorb W) 15 ft. long and 0.25 in. in diameter. The analysis of the pine gum resin acids on this substrate has been studied previously.[5] The analyses were run at 240° with a helium gas flow of 200 cc./min. The results of the analyses are given in Table I. Several of the peaks were collected and the ultraviolet spectra were determined. The results are given in Table I. The identity of the various resin acids was based upon emergence time (ratios with the added marker methyl primarate) as compared with emergence time ratios of mixtures of the known resin acids.[5]

Extensive refluxing of solutions of levopimaric acid in the following solvents containing the indicated basic catalysts did not result in any significant change in the ultraviolet spectrum of the solutions: potassium *t*-butoxide in dimethylformamide, sodium methylate in dimethylformamide, sodium methylate in dimethyl sulfoxide, and potassium *t*-butoxide in *t*-butyl alcohol.

Blank Run.—A solution of 0.50 g. of levopimaric acid in dry dimethyl sulfoxide exhibited λ_{max} 272 mμ (α 18.8). After a 20-min. nitrogen purge, the flask containing the solution and equipped as described previously was lowered into a 230° oil bath for 2 min. and then removed and an aliquot was taken. This exhibited λ_{max} 272 mμ (α 19.1).

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Reactions of Phosphorus Compounds. VI. A General Synthesis of Cycloalkenes

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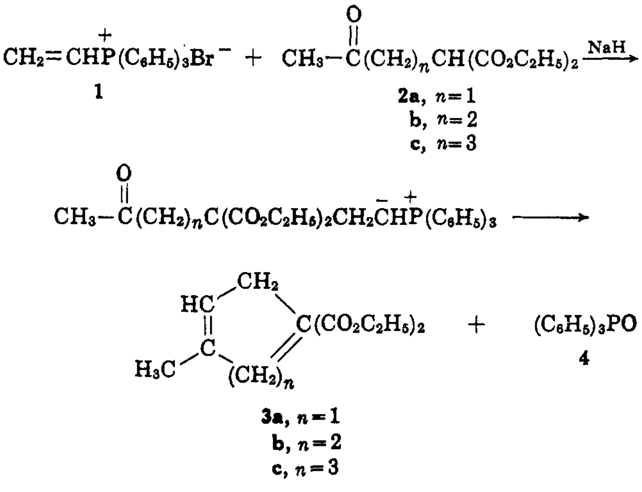
In a recent communication[1] we have outlined a new general ring synthesis whose common feature was the use of vinyltriphenylphosphonium bromide (**1**). The synthetic usefulness of this reaction has been demonstrated in the published reports of the preparation of a dihydrofuran,[1] a chromene,[1] and a pyridizine.[2] In this paper we wish to demonstrate the utility of this general reaction for the preparation of certain cycloalkenes.

The preparation of 1-phenylcyclopentene[3] and 1-phenylcyclohexene[4] has been accomplished in 24 and 10% yields, respectively, employing the corresponding ω-benzoylalkyltriphenylphosphonium salts as precursors. Other phosphorus ylid cyclizations giving cycloalkylphosphonium salts and ketophosphoranes have been reported.[5,6]

We have prepared diethyl (4-methyl)-3-cyclopentenedicarboxylate (**3a**) in 69% yield and diethyl (4-methyl)-3-cyclohexenedicarboxylate (**3b**) in 51% yield as shown by the following equations. All attempts to synthesize



the comparable seven-membered system **3c** following the above reaction scheme were unsuccessful.

Diethyl (3-oxobutyl)malonate (**2b**) prepared according to Spencer, *et al.*,[7] was treated with sodium hydride and vinyltriphenylphosphonium bromide[8] in ether and gave the known[9] diethyl (4-methyl)-3-cyclohexenedicarboxylate (**3b**) in 51% yield. Saponification and decarboxylation of **3b** gave the known[10] 4-methyl-3-cyclohexenecarboxylic acid. In a separate experiment 71% triphenylphosphine oxide (**4**) was recovered along with **3b**. Diethyl (3-methyl)-3 cyclopentenedicarboxylate (**3a**) (69%) was prepared in a similar manner using diethyl (2-oxopropyl)malonate[11] (**2a**) as its precursor.

When 5-bromo-2-pentanone, prepared according to Bachetti and Fiecchi,[12] was treated with sodio diethylmalonate, the expected diethyl (4-oxopentyl)malonate (**2c**) was isolated in 49% yield. Attempts to cyclize **2c** with the vinyl salt **1** to give **3c** were unsuccessful. Numerous attempts were made using sodium hydride in ether, sodium hydride in a 3:1 benzene–DMF mixture, sodium hydride in acetonitrile, and potassium *t*-butylate in *t*-butyl alcohol. The last method listed was a variation on the procedure employed by House and Babad to prepare their seven-membered cyclic ketophosphorane.[6] A viscous polymer-like material was obtained in all cases, and in the *t*-butyl alcohol experiment traces of the starting materials **2c**, **1**, triphenylphosphine, and triphenylphosphine oxide were detected by thin layer and vapor phase chromatography.

Thus, five- and six-membered cycloalkenes are readily available utilizing this new procedure. Work is in progress to include activating groups other than carboxylic esters in order to expand the scope of this reaction to include larger ring sizes.

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[11] C. D. Hurd and M. L. McAuley, *J. Am. Chem. Soc.*, **70**, 1650 (1948).

[12] T. Bachetti and A. Fiecchi, *Gazz. chim. ital.*, **83**, 1037 (1953).

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.

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[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]

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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

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[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.

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