intermediates are involved they must be extremely short lived, and in no sense "free" radicals.

Experimental Section[9]

Starting Materials.—Compounds 1 and 3 (Table I) were commercial samples and were purified prior to use. Compounds 2 and 4–8 were prepared by bimolecular coupling of the appropriate ketones with anhydrous magnesium iodide according to the procedure described by Gomberg and Bachmann.[10]

General Procedure for Glycol Cleavage with TTN.—A mixture of 2.74 mmol of the glycol and 2.74 mmol of TTN in 25 ml of acetic acid was stirred and heated at 75° for 30 min. The reaction mixture was then cooled, diluted with 50 ml of water, and extracted with chloroform, and the extracts were washed with saturated aqueous sodium bicarbonate solution. Evaporation of the dried chloroform extract gave the crude product, which was freed from traces of inorganic thallium salts by passage through a short column of alumina using chloroform as eluent. The pure ketone was then obtained by crystallization or distillation of the concentrated eluent.

General Procedure for Glycol Cleavage Using Thallium(I) Ethoxide.—Thallium(I) ethoxide (2.74 mmol) was added to a suspension of 2.74 mmol of the glycol in 25 ml of ethanol and the mixture was gently heated to about 50°. After a few seconds thallium metal was deposited. After 5 min excess powdered potassium iodide was added to remove traces of thallium(I) salts as thallium(I) iodide. The reaction mixture was filtered, concentrated, and passed through a short column of alumina using chloroform as eluent. Concentration of the eluate gave the crude product, which was purified as described above.

Direct nmr examination of the crude reaction product obtained after chromatography showed in some cases a small peak at *ca.* τ 4.5 due to the methine proton of the corresponding benzhydrol. The amount of this by-product was easily determined from the relative integrations of the aromatic and methine proton areas. Standard control experiments established that benzhydrols are oxidized to benzophenones only very slowly by thallium(I) ethoxide; the alcohol did not therefore serve as precursor to the ketone.

Registry No.—$Tl(NO_3)_3$, 13746-98-0; $TlOC_2H_5$, 20398-06-5.

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[9] Melting points were determined on a Kofler hot-stage melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model PE 237 grating infrared spectrophotometer using the normal liquid film and Nujol mull techniques. Nuclear magnetic resonance spectra were recorded in carbon tetrachloride solution, using tetramethylsilane as internal standard, on a Perkin-Elmer R12 60-MHz spectrometer.

[10] M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, **49**, 236 (1927).

Ethyl 3-Oxo-2,2-dimethylcyclobutanecarboxylate

K. Parameswar Sivaramakrishnan,
Lawrence H. Brannigan, and Carl S. Marvel*

Department of Chemistry, The University of Arizona, Tucson, Arizona 85721

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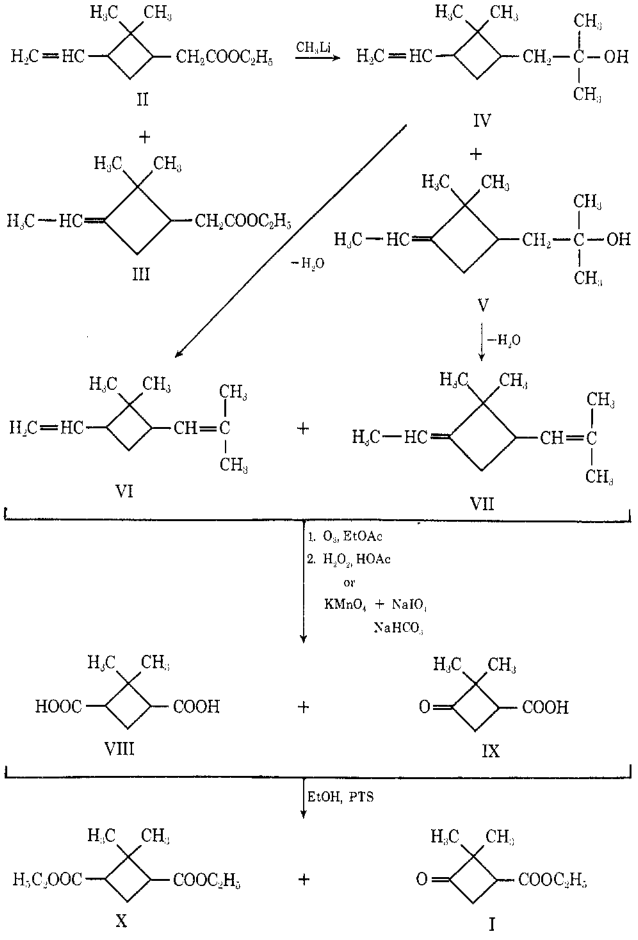
In connection with work toward the synthesis of bridgehead-substituted bicyclobutanes[1] as monomers for polymers containing cyclobutane rings, the synthesis of ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate (I) from readily accessible α-pinene and its degradation products was investigated.

A mixture of ethyl pinenates [ethyl 2,2-dimethyl-3-vinylcyclobutaneacetate (II) and ethyl 2,2-dimethyl-3-ethylidene cyclobutaneacetate (III)] described by Park, *et al.*,[2] formed the starting material for the synthesis of ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate. Reaction of a 60:40 mixture of ethyl pinenates with methyllithium afforded a mixture of 1-(2-methyl-2-hydroxypropyl)-3-vinyl-2,2-dimethylcyclobutene (IV) and 1-(2-methyl-2-hydroxypropyl)-3-ethylidene-2,2-dimethylcyclobutane (V). The mixture of alcohols was dehydrated using anhydrous oxalic acid to give a mixture of 1-(2,2-dimethylvinyl)-3-vinyl-2,2-dimethylcyclobutane (VI) and 1-(2,2-dimethylvinyl)-3-ethylidene-2,2-dimethylcyclobutane (VII). Oxidation of this mixture with sodium periodate–potassium permanganate[3] as well as by ozonolysis followed by cleavage of the ozonide with hydrogen peroxide and acetic acid afforded a mixture of norpinic acid (VIII) and 3-oxo-2,2-dimethylcyclobutanecarboxylic acid (IX), which was esterified with ethanol and *p*-toluenesulfonic acid to give a mixture of diethyl norpinate (X) and ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate (I). Separation was effected by fractional distillation and the keto ester was characterized as its 2,4-dinitrophenylhydrazone derivative.



Experimental Section

Mixture of 1-(2-Methyl-2-hydroxypropyl)-3-vinyl-2,2-dimethylcyclobutane (IV) and 1-(2-Methyl-2-hydroxypropyl)-3-ethylidene-2,2-dimethylcyclobutane (V).—Methyllithium was prepared by the addition of methyl iodide (42.6 g, 0.3 mol) in anhydrous ether (75 ml) to lithium wire (4.2 g, 0.6 g-atom) in anhydrous ether (150 ml). The lithium was contained in a three-necked

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[1] H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Sieja, *J. Amer. Chem. Soc.*, **93**, 121 (1971).

[2] J. D. Park, R. L. Settine, and G. W. Hedrick, *J. Org. Chem.*, **27**, 902 (1962).

[3] R. V. Lemiux and E. Von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

500-ml flask equipped with mechanical stirrer, Dry Ice condenser, nitrogen inlet–outlet, and an addition funnel. The addition of methyl iodide to lithium was performed at ice–salt temperature in about 2 hr. After an additional 2 hr all lithium had reacted. The methyllithium solution was cooled in an acetone–Dry Ice bath and a solution of a 60:40 mixture of ethyl 2,2-dimethyl-3-vinyl- and ethyl 3-ethylidene-2,2-dimethylcyclobutaneacetate (19.6 g, 0.1 mol) in anhydrous ether (25 ml) was added dropwise with rapid stirring. After addition was complete, the mixture was allowed to warm to room temperature and stirred in a nitrogen atmosphere overnight. The reaction slurry was poured onto 300 g of crushed ice containing 100 ml of concentrated ammonia. The mixture was stirred rapidly for 1 hr. The ether layer was separated and the aqueous layer was extracted with 2 × 100 ml of ether. The combined ether solutions were washed with water and dried over anhydrous sodium sulfate. Removal of ether under reduced pressure yielded a colorless liquid (17.5 g, 96% yield). Distillation of this liquid afforded 16.3 g, bp 58° (0.4 mm). The infrared spectrum of this liquid exhibited hydroxyl absorption at 3400 cm^{-1} and absorptions due to *gem*-dimethyl groups at 1355 and 1375 cm^{-1}; the nmr ($CDCl_3$) was consistent for the mixture of alcohols.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.05; H, 12.16. Found: C, 78.80; H, 12.01.

Mixture of 1-(2,2-Dimethylvinyl)-3-vinyl-2,2-dimethylcyclobutane (VI) and 1-(2,2-Dimethylvinyl)-3-ethylidene-2,2-dimethylcyclobutane (VII).—To a mixture of alcohols (12.0 g) contained in a 50-ml distilling flask was added anhydrous oxalic acid (4.5 g). The flask was fitted with a 4 by 0.5 ft Vigreux column equipped with distillation head, condenser, and receiving flask. The system was connected to the water aspirator and the pressure was held at 45–50 mm. The reaction flask was heated and the water began to distil. After water ceased to distil the reaction flask was cooled and the residue in the pot was taken up in ether. The ether extract was washed with sodium bicarbonate solution and then with water and finally dried over anhydrous sodium sulfate. Removal of ether and distillation of the residual liquid afforded colorless liquid, 10.3 g (94% yield), bp 94–96° (42 mm). The infrared spectrum exhibited no hydroxyl absorption and had bands at 3050 (m, vinyl CH), 1668 (m, C=C), and 1375 and 1355 cm^{-1} (s, *gem*-dimethyl doublet).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.64; H, 12.48.

Ozonolysis of This Mixture of Diolefins (VI and VII).—A mixture of diolefins (9.0 g) was taken up in 150 ml of ethyl acetate and ozonized oxygen was passed through the solution at 0° for 2 hr until the exit gas turned acidified potassium iodide solution brown. To this solution was added acetic acid (15 ml) and hydrogen peroxide (30%, 10 ml) and this mixture was allowed to stand at room temperature overnight. The reaction mixture was taken up in ether and the acidic components were extracted with 2 *N* Na_2CO_3 solution. The ether layer yielded a neutral fraction of 3.2 g, whereas acidification of the sodium carbonate extract with sulfuric acid and extraction with ether gave a viscous oil, 4.5 g. The infrared spectrum of this oil exhibited carboxylic acid absorption at 2900–2550 cm^{-1} (broad) and two different bands due to keto absorption as well as the acid carbonyl. On standing with a small amount of ether this oil afforded 1.2 g of white powder, mp 160–163° (mp of *cis*-norpinic acid ~170°). The residual oil in its ir exhibited two different carbonyls at 1785 and 1740 cm^{-1}.

Ethyl 3-Oxo-2,2-dimethylcyclobutanecarboxylate (I) and Diethyl Norpinate (X).—The mixture of diolefins (11.1 g, 0.068 mol) in *tert*-butyl alcohol (50 ml) was added dropwise to a stirred mixture of sodium bicarbonate (33.6 g, 0.39 mol), sodium periodate (150 g, 0.069 mol), and potassium permanganate (3 g) in water (1000 ml). After this mixture was stirred for 48 hr, it was acidified with dilute sulfuric acid and filtered to remove insoluble salts and the oxidate was extracted with ether. The ether solution was extracted with 2 *N* Na_2CO_3 solution. The ether layer yielded a neutral 2.2 g, identified as unreacted starting material, whereas acidification of the sodium carbonate extract with sulfuric acid and extraction with ether gave viscous oil (5.8 g). The infrared spectrum of this oil exhibited absorptions due to carboxylic acid and two carbonyl absorptions at 1780 and 1730 cm^{-1}. This crude acid (4.5 g) was dissolved in benzene (75 ml) and esterified with ethanol using *p*-toluenesulfonic acid (0.50 g) as catalyst. Benzene was removed and the crude product was taken up in ether. The ether solution was washed with sodium carbonate solution and then with water and finally dried over anhydrous sodium sulfate. Removal of ether afforded brownish colored liquid (4.2 g). The infrared spectrum exhibited two different carbonyl absorptions at 1790 and 1735 cm^{-1}. This liquid (3.65 g) was distilled to give two main fractions: (1) 1.02 g of ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate (I), bp 57–60° (0.3 mm), and (2) 2.20 g of diethyl norpinate (X), bp 86–89° (0.3 mm).

Ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate (I) in its ir spectrum exhibited two carbonyl absorptions at 1805 (keto) and 1755 cm^{-1} (ester). Its nmr spectrum ($CDCl_3$) exhibited signals at δ 4.1 (octet, 2 H, $-CH_2-$), 3.4 (m, 2 H, $CH_2C{=}O$), 2.2–1.6 [m, 1 H, $-CHC({=}O)O$], and 1.1–1.4 (m, 9 H, *gem*-methyls, $-CH_3$).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.53; H, 8.24. Found: C, 64.01; H, 9.10.

These analyses indicates that the keto ester may contain a small amount of the diester.

The 2,4-dinitrophenylhydrazone was obtained as a yellow precipitate, mp 118–120°, which was purified by chromatography on alumina, using benzene as an eluent. The yellow band was eluted with benzene. After removal of benzene, crystallization from ethanol gave a yellowish powder, mp 122–123°.

Anal. Calcd for $C_{15}H_{18}N_4O_6$: C, 51.43; H, 5.14; N, 16.00. Found: C, 51.68; H, 5.37; N, 15.81.

Registry No.—I, 36611-75-3; I DNP, 36611-76-4; IV, 36611-77-5; V, 36611-78-6; VI, 36611-79-7; VII, 36611-80-0.

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Ditetrazolylbenzene Dianions. Potential Precursors of the Phenylenedimethylenes[1]

P. SCHEINER,* E. STOCKEL, D. CRUSET, AND R. NOTO

Department of Chemistry,
York College of the City University of New York,
Jamaica, New York 11432

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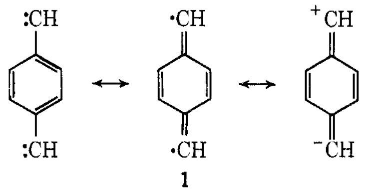
Arylmethylenes have received attention from the synthetic[2] and theoretical[3] viewpoints. Of particular interest are arylpolycarbene systems, few of which have as yet been generated.[3] Molecule **1** (*p*-phenylenedimethylene), for example, presents intriguing possibilities with regard to electronic distribution,



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[1] This research was supported by grants from the Petroleum Research Fund, administered by the American Chemical Society, and the Research Foundation of the City University of New York.

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