mmol) and mercuric acetate (820 mg, 2.5 mmol) in acetic acid (10 ml) containing acetic anhydride (1 ml) were stirred for 10 hr. Addition of water and work-up as above for **7b** resulted in formation of acetamide **8b**: uv (95% ethanol) λ_{max} 291 mμ (ε 4100), 226 (7400);[16] ir (CH_2Cl_2) 1690, 1650 cm^{-1}; nmr ($CDCl_3$, Table II). Amine **8a**, prepared as **6a** above, was analyzed as its methanesulfonamide 2,4-dinitrophenylhydrazone, mp 240–241° (ethanol).

Anal. Calcd for $C_{23}H_{23}N_5O_6S$: C, 55.53; H, 4.66; N, 14.08. Found: C, 55.34, H, 4.70, N, 14.04.

Registry No.—**1a**, 17198-06-0; **1b**, 52895-39-3; **2a**, 17303-53-6; **2b**, 52895-40-6; **3**, 52895-42-8; **3** picrate, 52928-64-0; **4**, 49542-98-5; **4** picrate, 52895-41-7; **5**, 52928-65-1; **6a**, 52895-43-9; **6b**, 52895-44-0; **6c**, 52895-45-1; **7a** methanesulfonamide 2,4-dinitrophenylhydrazone, 52895-46-2; **7b**, 52895-47-3; **8a** methanesulfonamide 2,4-dinitrophenylhydrazone, 52895-48-4; **8b**, 52895-49-5.

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Model Studies of Terpene Biosynthesis. Synthesis of (+)-2-[*trans*-2′-(2″-Methylpropenyl)cyclopropyl]-propan-2-ol[1]

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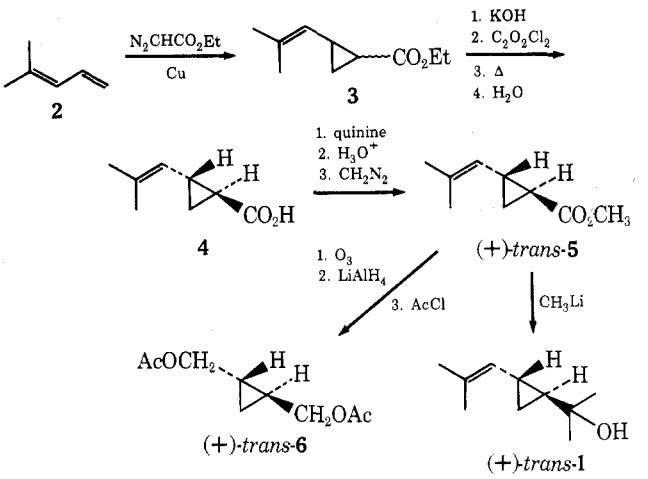
Received July 23, 1974

Tertiary cyclopropylcarbinyl cations have been proposed as intermediates in the rearrangements of C_{30} and C_{40} cyclopropylcarbinyl pyrophosphates to squalene and phytoene, respectively.[2] In this note we describe the synthesis of a C_{10} alcohol, (+)-2-[*trans*-2′-(2″-methylpropenyl)cyclopropyl]propan-2-ol, of known absolute configuration and optical purity, which serves as a precursor of the tertiary cation in model studies.[2e]

The synthesis of and optical correlations for (+)-*trans*-**1** are outlined in Scheme I. A 57:43 trans:cis mixture of ethyl ester **3** was obtained by copper-catalyzed addition of ethyl diazoacetate to 4-methyl-1,3-pentadiene (**2**).[3] The reaction was regiospecific (>98%) for the monosubstituted double bond.

The trans:cis ratio was increased from 57:43 in **3** to 95:5 in carboxylic acid **4** by the method of Smejkal and Farkas.[4] Saponification of **3** followed by treatment with oxalyl chloride gave a mixture of acid chlorides which were heated at

Scheme I



145° for 45 min. The acid obtained by hydrolysis of equilibrated acid chlorides was mostly (95%) trans.

Acid **4** was partially resolved by multiple recrystallization of its quinine salt. Although recrystallization was complicated by a small amount of salt from *cis*-**4**, quinine salts of *trans*-**4** were obtained free of cis contamination. The carboxylic acid was liberated from its quinine salt with hydrochloric acid and treated with diazomethane. The resulting ester, (+)-*trans*-**5**, was a single isomer, as judged by glpc and nmr.

The absolute configuration and optical purity of (+)-*trans*-**5**, $[\alpha]^{25}D$ +103° (*c* 2.3, $CHCl_3$), was determined by converting a portion of the ester to (+)-*trans*-1,2-diacetoxymethylcyclopropane (*trans*-**6**), $[\alpha]^{25}D$ +9.60° (*c* 1.6, EtOH). Since the maximum rotation of (1*R*,2*R*)-**6** is $[\alpha]^{25}D$ −17.75° (*c* 2.0, EtOH),[5] our sample of (+)-*trans*-**5** was 54% optically pure and predominately the 1*S*,2*R* enantiomer. Addition of methyllithium to (+)-*trans*-**5** gave (+)-*trans*-**1**.[3] Based on correlations with (1*R*,2*R*)-**6**, (1*S*,2*R*)-**5** and (1*S*,2*R*)-**1** should have maximum rotations of $[\alpha]^{25}D$ +191 and +33.5°, respectively, in chloroform.

Experimental Section

General. Boiling points are uncorrected. Nmr spectra were recorded on a Varian A-60 spectrometer using tms as an internal standard. Analytical gas chromatography was carried out on a Varian Model 1200 gas chromatograph with a flame ionization detector, using a 500 ft × 0.03 in. open tubular column coated with Carbowax 20M. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

Ethyl *cis*- and *trans*-2-(2′-Methylpropenyl)cyclopropanecarboxylate, *cis*- and *trans*-3. Ethyl diazoacetate was prepared by the method of Moser.[6] In a typical run, 20.0 g (0.244 mol) of 4-methyl-1,3-pentadiene and 2.3 g of copper dust, which had been dried overnight under aspirator vacuum in a drying pistol heated by refluxing toluene, were placed in a dry 100-ml three-necked flask. To this was added, dropwise with stirring under a nitrogen atmosphere, 27.9 g (0.244 mol) of ethyl diazoacetate. Addition was as slow as possible, consistent with maintaining a gentle reflux of the reaction mixture. Complete addition took approximately 3 hr, after which the mixture was heated to reflux for an additional 15 min.

Unreacted diene was removed by distillation and the residue was filtered. Distillation of the filtrate at aspirator pressure gave 13.9 g (36%) of a colorless oil, bp 89–92°. An nmr spectrum of the distillate was similar to that reported by Robinson.[3]

(+)-*trans*-2-(2′-Methylpropenyl)cyclopropanecarboxylic acid, (+)-*trans*-4. A methanol solution of 12.8 g (76.2 mmol) of *cis*- and *trans*-**3** and 6.3 g of sodium hydroxide was heated at reflux for 3 hr. After cooling, the solution was added to 400 ml of water, acidified with hydrochloric acid, and extracted with three 150-ml portions of ether. The combined ether fractions were washed with brine, filtered through anhydrous sodium sulfate, and

dried over molecular sieves. Rotary evaporation of solvent gave 10.3 g (96%) of a syrupy residue which was dissolved in 45 ml of dry benzene. To the resulting solution was added 11.2 g (88.5 mmol) of oxalyl chloride. Gas evolution continued for 45 min and stirring was maintained for an additional hour. Solvent was removed at reduced pressure and the residue was heated at 145° for 45 min. The reaction was followed by quenching samples in methanol and determining the cis:trans ratio of methyl esters by glpc. At the end of the isomerization the mixture was 95% trans and 5% cis. The acid chloride was allowed to cool before water was added. The trans acid was isolated as described above; yield 6.3 g (61%).

Samples of *trans*-4 from several isomerizations, 9.6 g (68 mmol), were allowed to react with 22.0 g (68 mmol) of quinine, and the resulting salt was partially resolved by recrystallization from 40:60 ethyl acetate–diethyl ether. After four recrystallizations, treatment of a less soluble fraction with dilute hydrochloric acid followed by extraction with diethyl ether yielded 1.54 g of optically active carboxylic acid, $[\alpha]^{25}D$ +72.5° (*c* 4.95, CH_3OH). From a more soluble fraction of the quinine salt, (−)-*trans*-**4**, $[\alpha]^{25}D$ −90.7° (*c* 4.84, CH_3OH), was obtained: nmr δ ($CDCl_3$) 0.7–2.3 (4, m, H at C_1, C_2, and C_3), 1.67 and 1.74 (6, two d, methyls at $C_{2'}$, $J \simeq$ 1.5 Hz), and 4.63 ppm (1, d of septets, H at $C_{1'}$, $J_{2,1'}$ = 9 Hz).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.80; H, 8.75.

(+)-Methyl *trans*-2-(2′-Methylpropenyl)cyclopropanecarboxylate, (+)-*trans*-5. *N*-Methyl-*N*-nitrosourea, 3.0 g (29 mmol), was stirred with 9 ml of 50% aqueous KOH and 36 ml of diethyl ether in an acetone–ice bath for 7 min, before the resulting yellow ether layer was decanted into a flask containing 1.54 g (11.0 mmol) of (+)-*trans*-**4**, $[\alpha]^{25}D$ + 72.5°. The reaction mixture was allowed to stand in the hood until the ether had evaporated, fresh ether was added, and the resulting organic fraction washed successively with saturated sodium bicarbonate and brine solutions. The organic layer was dried, and the ether evaporated, yielding 1.46 g (87%) of a colorless oil. Samples for spectra and analysis were purified by glpc (Carbowax 20M): $[\alpha]^{25}D$ +103° (*c* 2.33, $CHCl_3$); nmr δ 0.6–2.2 (4, m, cyclopropyl H), 1.63 and 1.70 (6, two d, methyls at $C_{2'}$, $J \simeq$ 1.5 Hz), 3.57 (3, s, carbomethoxy), and 4.52 ppm (1, d of septets, H at $C_{1'}$, $J_{2,1'}$ = 9 Hz); ir (CCl_4) 2950, 2900, 1725, 1660, 1450, 1180, and 1040 cm^{-1}.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.13; H, 9.28.

(+)-*trans*-1,2-Diacetoxymethylcyclopropane, (+)-*trans*-6. Ozone was passed through a solution of 107 mg (6.7 mmol) of (+)-*trans*-**5** in 15 ml of dry methylene chloride at −78° until a pale blue color persisted. Excess ozone was removed at −78° with a stream of dry nitrogen, and solvent was removed at reduced pressure. The residue was dissolved in 30 ml of dry ether to which was added 150 mg of $LiAlH_4$, and the mixture was allowed to stir overnight. Excess hydride was decomposed by addition of a saturated solution of NH_4Cl, and addition continued until the inorganic salts precipitated. The clear ether layer was decanted, and the precipitate was washed repeatedly with ether. The combined ether fractions were dried over anhydrous $MgSO_4$ and solvent was removed at reduced pressure, leaving 73 mg (100%) of a colorless oil:[5] nmr ($CDCl_3$) δ 0.1–1.4 (4, m, H at C_1, C_2, and C_3) 3.0–4.0 (4, m, hydroxymethyls at C_1 and C_2), and 4.25 ppm (2, br s, OH).

To a solution of 73 mg (0.70 mmol) of the trans diol and 500 mg (6.5 mmol) of pyridine in 10 ml of dry benzene was added 256 mg (3.26 mmol) of acetyl chloride. Heat was evolved and a white precipitate formed. After 30 min the reaction was diluted with 30 ml of ether and extracted with successive 10-ml portions of water, 3 *N* HCl, water, and saturated $NaHCO_3$. The ether layer was dried, and solvent removed at reduced pressure, yielding 101 mg (79%) of (+)-*trans*-**6**.[5] Analytical samples were purified by glpc (Carbowax 20M): $[\alpha]^{25}D$ +9.60° (*c* 1.57, EtOH); nmr ($CDCl_3$) δ 0.47–0.75 (2, m, H at C_3), 0.97–1.35 (2, m, H at C_1 and C_2), 2.13 (6, s, acetate methyls), and 4.08 ppm (4, d, acetoxymethyl at C_1 and C_3, J = 7 Hz).

(+)-2-[*trans*-2′-(2″-Methylpropenyl)cyclopropyl]propan-2-ol, (+)-*trans*-1. In a 100-ml three-necked flask with condenser, addition funnel, and N_2 inlet was placed 1.08 g (7.0 mmol) of (+)-*trans*-**5**, $[\alpha]^{25}D$ +103°, in 25 ml of anhydrous ether, and 10 ml of 1.5 *M* MeLi (15 mmol) was added dropwise. After stirring for an hour, 2 ml of saturated NH_4Cl was carefully added, and the clear ether layer was decanted and washed with brine. The ether solution was filtered through sodium sulfate and dried over molecular sieves. The solvent was evaporated at reduced pressure, leaving 0.97 g (90%) of a colorless, fragrant oil. Samples for analysis were collected by glpc: $[\alpha]^{25}D$ +18.1° (*c* 2.28, $CHCl_3$); nmr ($CDCl_3$) δ 0.6–2.2 (4, m, cyclopropyl H), 1.18 (6, s, H at C_1 and C_3), 1.63 and 1.70 (6, pair of d, CH_3's at $C_{2''}$, $J \simeq$ 1 Hz), and 4.58 ppm (1, d of septets, H at $C_{1''}$, $J_{2',1''}$ = 8 Hz); ir (CCl_4) 3500, 2900, 1660, 1440, 1370, 1160, and 910 cm^{-1}. Our spectra are similar to those reported by Robinson for racemic trans-1.[3]

Registry No.—(+)-*trans*-**1**, 52152-29-1; **2**, 926-56-7; *cis*-**3**, 53166-49-7; *trans*-**3**, 53166-50-0; *trans*-**4**, 53166-51-1; (+)-*trans*-**4**, 53187-84-1; (−)-*trans*-**4**, 53187-85-2; (+)-*trans*-**5**, 53187-86-3; (+)-*trans*-**6**, 53166-30-6; (+)-*trans*-**6** free diol, 53187-82-9; ethyl diazoacetate, 623-73-4.

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Homolysis of Methyl Phenylazo Sulfones

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Received September 3, 1974

Kice and Gabrielsen studied the thermolysis of methyl phenylazo sulfone (Ia) and concluded that the decomposition is homolytic on the basis of the product studies.[1] However, thermolysis of azo sulfones tends to contain some acid-catalyzed ionic decomposition because of the production of sulfinic or sulfonic acids.

When Ia was decomposed in nitrobenzene, the nitrobiphenyls formed were rich in its meta isomer, as shown in Table I. The isomer distribution suggests that both homolysis and heterolysis are taking place. In the decompositions of phenylazo *p*-tolyl sulfone (II), acid-catalyzed heterolysis was effectively prevented by the addition of a base.[2a] Therefore, I was decomposed in the presence of pyridine. When 2 mol of pyridine per mol of I was present, the isomer distribution found indicated that the decomposition is

Table I
Products of Decomposition of Azo Sulfones in Nitrobenzene

Azo sulfone	Pyridine, mol/mol I	Temp, °C	Nitrobiphenyls: Yield, %	Orientation, % Ortho	Meta	Para	Nitrogen, %
I_a	0	80.5	*a*	33	41	26	38
I_a	2/1 I_a	80.2	77.1	67.0	10.0	23.0	86
I_a	3/1 I_a	80.1	75.3	68.3	9.4	22.3	95
II[b]	2/1 II	60.0	54.4	64.5	7.7	27.8	*a*

[a] Not determined. [b] In ref 2.