After 22.5 hr, the recovered product was unchanged in optical rotation. Similarly, with *l*-4-chloride, the rotation was constant over 5 hr.

Acknowledgment. We appreciate the assistance, in the preparation of this work for publication, graciously given by Professor C. J. Collins, of the University of Tennessee and the Oak Ridge National Laboratory.

Registry No.—(+)-4, 5978-70-1; (−)-4, 6169-06-8; 5, 71-36-3; 6, 78-92-2; 7, 75-65-0; 8, 108-93-0; zinc chloride, 7646-85-7; thionyl chloride, 7719-09-7; thionyl bromide, 507-16-4.

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Oxymercuration of Nitrogen Heterocycles. II.[1] Syntheses of Novel Nitrogen Heterocycles and Cycloheptatriene Carboxaldehydes from *N*-Benzyldihydroazabullvalene and Dihydro-9-azabicyclo[4.2.2]deca-2,4,7-triene

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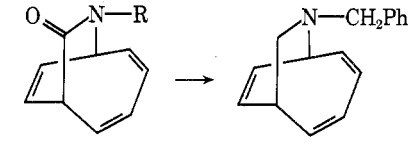
June 19, 1974

Solvomercuration–demercuration provides a convenient synthetic route for conversion of olefins into Markovnikov alcohols and ethers. An advantage of this synthetic approach is that additions generally occur without rearrangements.[2] However, there are a few alicyclic substrates which, because of their ground state strain or because they are precursors of stabilized carbonium ions, can rearrange either directly upon the addition of mercuric ions or following loss of free mercury from unstable hydroxymercurial ions. Most notably, rearranged oxymercurials are formed from bullvalene,[3,4] bicyclo[4.2.2]decatetraene,[4,5] and several 1-alkylidene-2-alkoxycyclopropanes,[6] while cyclobutene and 1-methylcyclobutene,[7] hexamethyl(Dewar benzene),[8] and cyclooctatetraene[9] undergo rearrangement with concomitant oxidative demercuration. Although mercuric acetate is capable of coordination with olefins in the presence of amines,[10,11] there have been no reports of rearrangements during the oxymercuration of heterocyclic structures. We here report two heterocyclic molecules **3** and **4** which can exhibit both of the above types of anomalous behavior during oxymercuation. In anhydrous media rearranged products of oxymercuration afford azabicyclic structures **5** and **6a** upon reduction, while in aqueous media, oxidative demercuration of hydroxymercurial product ions results in the synthesis of novel cycloheptatriene carboxaldehydes **7** and **8**.

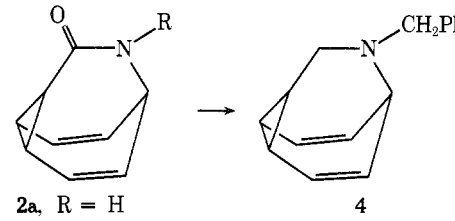
Discussion

The lactam **1a**[12] was benzylated with benzyl chloride–sodium hydride in dimethylformamide and the resulting *N*-benzyl lactam **1b** was treated with trimethyloxonium fluoroborate–sodium borohydride[13] to give amine **3**. Similar benzylation of lactam **2a** followed by aluminum hydride[14] reduction of **2b** afforded amine **4**. Detailed nmr analysis[15] of homotropilidene structure **4** has indicated the tautomeric structure is preferred in which nitrogen is not adjacent to cyclopropane.



1a, R = H
b, R = CH_2Ph

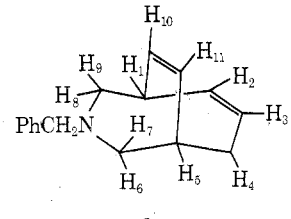
3



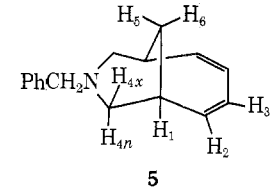
2a, R = H
b, R = CH_2Ph

4

Table I
Pmr Spectra of Azabicyclics 5 and 6a



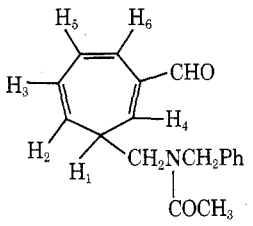
6a



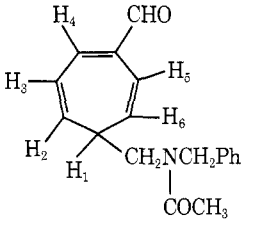
5

Proton	δ	Appearance, *J*, Hz	Proton	δ	Appearance, *J*, Hz
H_1	2.74	m, $J_{1,10}$ = 8.5	H_1	2.54	m, $J_{1,4x}$ = 3.5
H_2, H_3	5.72	m	H_{4x}	2.16	dd, $J_{4x,4n}$ = 11
H_4, H_5	2.26	br	H_{4n}	2.84	dd, $J_{1,4n}$ = 1.0
H_6, H_8	2.18, 2.30	d, $J_{8,9} = J_{6,7}$ = 11	H_5, H_6	1.80	br
H_7, H_9	2.60, 2.84	dd, $J_{5,7} = J_{1,9}$ = 4	H_2, H_3	5.86	br
H_{10}, H_{11}	5.90, 6.20	t, $J_{5,11}$ = 8.5			
CH_2Ph	3.60, 7.30	s, br	CH_2Ph	3.46, 7.20	s, s

Table II
Pmr Spectra of Cycloheptatriene Carboxaldehydes 7b and 8b



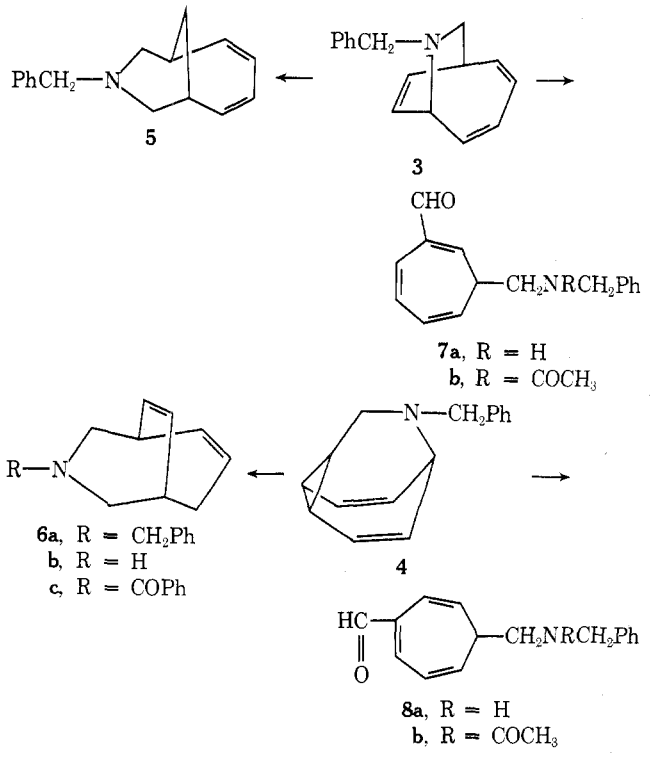
7b



8b

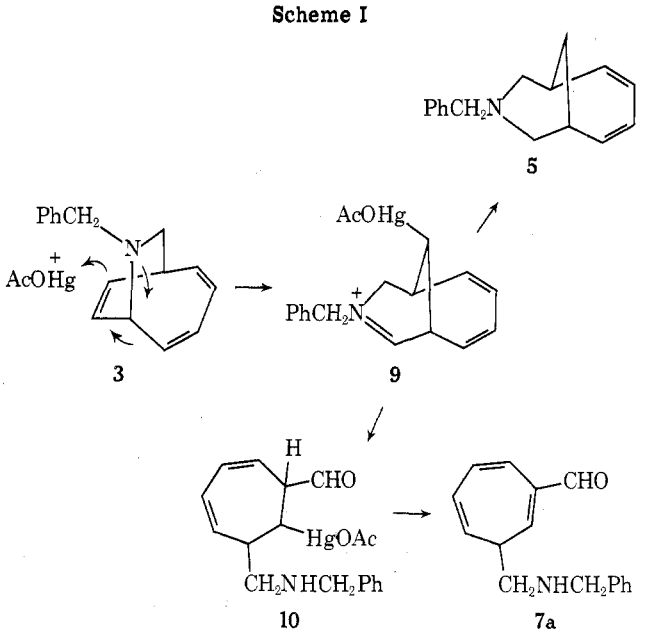
Proton	δ	Appearance, J, Hz	Proton	δ	Appearance, J, Hz
CH_3	2.14	s	CH_3	2.08	s
H_1	2.31	br, $J_{1,2} = 5$	H_1	2.30	m, $J_{1,2} = 4$
H_2	5.30	dd, $J_{2,3} = 9$	H_2	5.65	dd, $J_{2,3} = 10$
H_3	6.22	dd, $J_{3,5} = 6$	H_3	6.22	dd, $J_{3,4} = 6$
H_4	6.11	d, $J_{1,4} = 6$	H_4	7.06	d
H_5	6.70	dd, $J_{5,6} = 11$	H_5	6.69	d, $J_{5,6} = 10$
H_6	6.99	d	H_6	5.46	dd, $J_{1,6} = 5$
CH_2N	3.80	br	CH_2N	3.74	m, $J_{vic} = 5$; $J_{gem} = 14$
CH_2Ph	4.60, 7.09	s, s	CH_2Ph	4.48, 7.26	br, br
CHO	9.53	s	CHO	9.58	s

Treatment of amine **3** with mercuric acetate is anhydrous methanol followed by sodium borohydride demercuration afforded the rearranged amine **5.** Under these conditions amine **4** rearranged to afford amine **6a.** The structures of amines **5** and **6a** were determined on the basis of spectral data including nmr spin decoupling (Table I). Structure **6a** was confirmed by independent synthesis from **6b.**[12] If, however, amine **3** was stirred with mercuric acetate in aqueous tetrahydrofuran, elemental mercury was formed along with the novel rearranged ring cleavage product, cycloheptatriene carboxaldehyde (**7a**). Amine **4** afforded cycloheptatriene carboxaldehyde **8a** under these latter conditions. The rearrangements could also be effected in acetic acid–acetic anhydride solution to afford upon addition of water the aldehydes **7b** and **8b.** The structures of **7b** and **8b** were readily determined from their special data (Table II and Experimental Section).



The most plausible mechanisms for the formation of **5** and **7** from **3** are shown in Scheme I. Coordination of a mercuric ion with the olefinic bridge is followed by bond migration to form the stabilized immonium ion **9.** This ion **9,** or its amino ketal equivalent, is reduced in methanol by sodium borohydride to form bicyclic amine **5,** However, in water ion **9** hydrolyzes to give cycloheptadiene **10,** which upon loss of mercury and acetic acid affords cycloheptatriene carboxaldehyde **7a.**

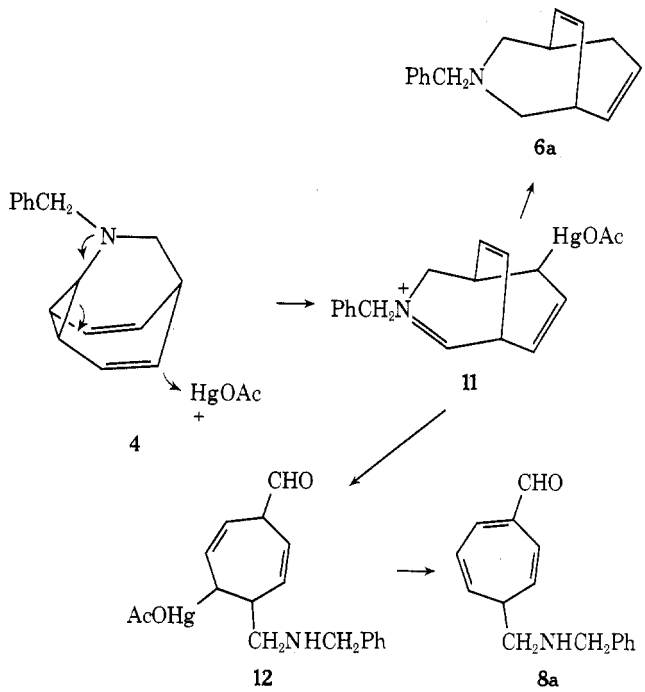
Scheme I



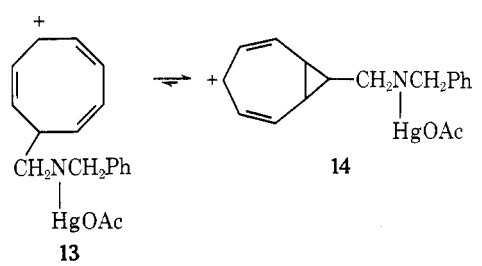
In Scheme II pathways for formation of **6a** and **8** from **4** are depicted. Coordination of a mercuric ion with an olefinic bond of **4** is followed by ring opening with nitrogen participation from the less stable tautomeric form of **4** to afford immonium ion **11.** In methanol ion **11,** or its amino ketal equivalent, is reduced by sodium borohydride to bicyclic amine **6a.** In water ion **11** hydrolyzes to cycloheptadiene **12,** which upon oxidative demercuration yields cycloheptatriene carboxaldehyde **8a.**

Alternatives to Schemes I and II involving coordination of mercuric acetate with nitrogen followed by carbon–ni-

Scheme II



trogen bond cleavage and generation of a homotropylium cation are unlikely. The cation **13** formed from amine **3** should readily convert to its valence tautomer **14** formed from **4**. Thus, product overlap would be expected if a ring cleavage process had occurred.



Experimental Section

The nmr spectra were determined on a Varian Associates XL-100-15 spectrometer using tetramethylsilane as internal standard. Couplings and coupling constants were determined with the aid of spin-decoupling experiments; where necessary several solvents were employed to improve resolution of individual peaks. Uv spectra were recorded on a Cary 14 spectrometer. Melting points and boiling points are uncorrected. Microanalyses were performed by Microanalysis, Wilmington, Del.

***N*-Benzyl-9-azabicyclo[4.2.2]deca-2,4,7-triene (3).** A magnetically stirred solution of lactam **1a**[12] (4.0 g, 27 mmol) in sodium hydride–57% oil dispersion (1.16 g, 28 mmol) in dry dimethylformamide (100 ml) was heated at 65° for 1 hr and cooled to 45°, and benzyl chloride (3.8 g, 30 mmol) was added. After 8 hr at 45°, the reaction mixture was filtered to remove sodium chloride, solvent was removed *in vacuo* and the oily residue was washed with pentane. The oil solidified to give *N*-benzyl lactam **1b** (6 g, 93%): mp 117.5–119° (tetrahydrofuran–pentane); nmr ($CDCl_3$) δ 7.24 (Ph), 6.06 and 5.62 (olefinic), 5.02 (d, J = 15 Hz, CHPh), 4.14 (d, J = 15 Hz, CHPh), 4.00 (CHN), and 3.82 (CHCO); ir ($CHCl_3$) 1640 cm^{-1}; uv (95% ethanol) λ_{max} 268 (ϵ 3900), 259 mμ (3900).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.99; H, 6.37; N, 5.90. Found: C, 80.79, H, 6.39, N, 5.90.

To lactam **1b** (23 g, 97 mmol) in methylene chloride (200 ml) was added trimethyloxonium fluoroborate[13] (19 g, 100 mmol) under nitrogen. After 20 hr at 25°, solvent was removed *in vacuo*, and the residue was dissolved in anhydrous methanol (100 ml). Sodium borohydride (3.8 g) was added in small portions to the solution which was maintained below 5° during addition. After 12 hr at ambient temperature ether (300 ml) was added and the solution was washed with 10% sodium carbonate and dried (magnesium sulfate). Removal of solvent afforded a tan oil. Digestion with cold pentane and filtration removed unreacted amide **1b** (4 g). Removal of solvent gave amine **3** (14.5 g, 67%): bp 97–102° (0.5 mm); nmr ($CDCl_3$) δ 7.72 (Ph), 6.50 and 6.24 (olefinic), 4.14 (s, CH_2Ph), 3.94 (CHN), and 3.34 (CH_2N, $CH(C{=}C)_2$); uv (95% ethanol) λ_{max} (appear as shoulders) 277 mμ (ϵ 900), 265 (1600), 247 (2050); picrate, mp 139–140° (ethanol).

Anal. Calcd for picrate $C_{22}H_{20}N_4O_7$: C, 58.40; H, 4.46; N, 12.38. Found: C, 58.53, H, 4.47, N, 12.29.

***N*-Benzyl-4-azatricyclo[3.3.2.0^{2,8}]deca-6,9-diene (4).** Lactam **2a**[12] (8g) was benzylated as above for **1a** to afford *N*-benzyl lactam **2b** (9.5 g, 74%), mp 260°, unless placed in a bath preheated to 240°: nmr ($CDCl_3$) δ 7.24 (Ph), 6.04 (m), 5.74 (dd, J = 8 Hz), 4.74 (CH_2Ph, s), 3.54 (t, J = 8 Hz), 3.04 (t, J = 9 Hz), 2.44 (m, two protons).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.99; H, 6.37; N, 5.90. Found: C, 80.72, H, 6.37; N, 6.01.

A 1.5 *M* solution of lithium aluminum hydride in tetrahydrofuran (50 ml) was added to dry ether (100 ml). This solution was cooled to 0° and 100% sulfuric acid (2.1 ml) was added dropwise keeping the temperature below 10°.[14] To this cold solution lactam **2b** (7.4 g) was added. The reaction mixture was stirred for 6 hr at 25° and then excess aluminum hydride was quenched with 10% sodium hydroxide solution until hydrogen evolution ceased. Filtration of solid, drying (magnesium sulfate), and removal of solvent afforded amine **4** (6.0 g, 90%) as an oil which crystallized from petroleum ether to give white crystals, mp 47–48.5°, nmr reported previously,[15] picrate, mp 131.5–133 (ethanol).

Anal. Calcd for picrate $C_{22}H_{20}N_4O_7$: C, 58.40; H, 4.46; N, 12.38. Found: C, 58.20; H, 4.56; N, 12.40.

***N*-Benzyl-8-azabicyclo[4.3.1]deca-2,4-diene (5).** A solution of **3** (530 mg, 2.4 mmol) and mercuric acetate (755 mg, 2.4 mmol) in dry methanol (25 ml) was stirred for 0.5 hr. Sodium borohydride (0.3 g) was then added to the solution cooled in an ice bath. Filtration through Celite removed mercury. Ether (100 ml) was added and the organic phase was washed with water and dried (magnesium carbonate). Removal of solvent afforded amine **5** (340 mg, 50%): purified by gc (1 m, 3% XF1150 Chromosorb W, 180°); uv (95% ethanol) λ_{max} 263 mμ (ϵ 5200), 252 (8600), 243 (8400);[4] nmr ($CDCl_3$, Table I).

Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.43; H, 8.55; N, 6.05.

***N*-Benzyl-3-azabicyclo[3.3.2.]deca-6,9-diene (6a).** A solution of **4** (580 mg, 2.6 mmol) and mercuric acetate (8.15 mg, 2.6 mmol) in dry methanol (25 ml) was reacted as above to afford after work-up amine **6a** (600 mg, 83%), purified by gc (1 m, 3% XF1150 Chromosorb W, 180°), nmr ($CDCl_3$, Table I).

Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.17; H, 8.52; N, 6.26.

Alternate Synthesis of 6a. Amine **6b**[12] (0.9 g) was allowed to react with benzoyl chloride (1 g) in pyridine (10 ml) on a steam bath to afford upon routine work-up benzamide **6c** (1.4 g), mp 78–79.5° (petroleum ether).

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.42; H, 7.21; N, 5.88.

Benzamide **6c** (100 mg) in tetrahydrofuran (10 ml) was reduced for 8 hr at 25° with lithium aluminum hydride (25 mg). Usual work-up afforded amine **6a** (85 mg) identical with that obtained above.

Cycloheptatriene 2-Carboxaldehyde 7b. Route A. A solution of **3** (320 mg, 1.4 mmol) in 50% aqueous tetrahydrofuran (20 ml) containing mercuric acetate (460 mg, 1.4 mmol) was stirred for 10 hr at 25°. Free mercury formed in 10–20 min. The reaction mixture was basified and extracted with ether to afford amine **7a** (260 mg, 76%), which could be purified by tlc on alumina (R_f 9.0, 70–30 pentane–ether), or converted in 90% yield with acetic anhydride in methylene chloride to oily acetamide **7b**: uv (ethanol) λ_{max} 231 mμ (ϵ 3000), 204 (5200); ir (CCl_4) 1690 1650 cm^{-1}; nmr (acetone-d_6, Table II). The amine **7a** was analyzed as its methanesulfonamide 2,4-dinitrophenylhydrazone, mp 149–150° (ethanol).

Anal. Calcd for $C_{23}H_{23}N_5O_6S$: C, 55.53; H, 4.66; N, 14.08. Found: C, 55.67; H, 4.77; N, 13.89.

Route B. A solution of **3** (600 mg, 2.6 mmol) in acetic acid (20 ml) containing acetic anhydride (1 ml) and an excess of mercuric acetate (1.68 g, 5.25 mmol) was stirred at room temperature for 10 hr. During this time a small quantity of elemental mercury precipitated. The reaction mixture was concentrated to 5 ml, neutralized with sodium hydroxide, and extracted with ether to afford after drying ($MgSO_4$) and removal of solvent an oil **7b** (380 mg, 55%).

Cycloheptatriene 3-Carboxaldehyde 8b. Amine **4** (580 mg, 2.5

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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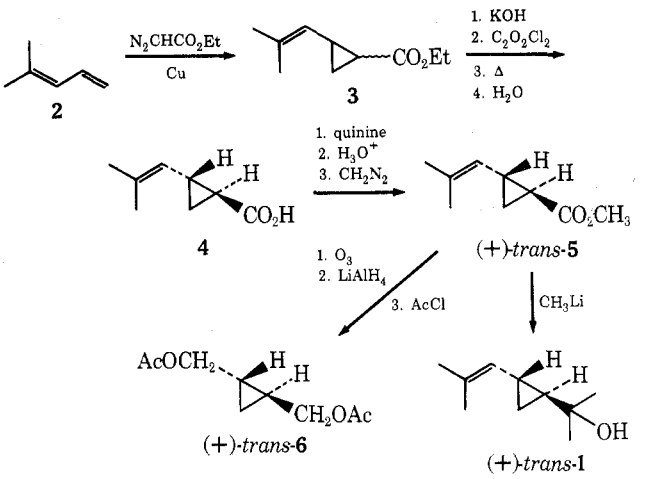
Received July 23, 1974

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