22815-39-0; diethyl *p*-chloroanilinomalonate, 5203-01-0; diethyl *p*-bromoanilinomalonate, 5500-48-1; diethyl *p*-ethoxycarbonylanilinomalonate, 28268-31-7; dimethyl anilinomalonate, 35757-92-7; dimethyl *p*-chloroanilinomalonate, 62851-37-0; dimethyl *p*-bromoanilinomalonate, 62851-38-1; dimethyl *p*-ethoxycarbonylanilinomalonate, 62851-39-2.

References and Notes

(1) A. K. Bose and M. S. Manhas, *J. Org. Chem.*, **27**, 1244 (1962).
(2) A. K. Bose, M. S. Manhas, and R. M. Ramer, *Tetrahedron*, **21**, 449 (1965).
(3) G. H. Cocolas and W. H. Hartung, *J. Am. Chem. Soc.*, **79**, 5203 (1957).
(4) F. Zymalkowski and P. Pachaly, *Chem. Ber.*, **100**, 1137 (1967); P. Pachaly, *ibid.*, **101**, 2176 (1968); **102**, 2153 (1969); **104**, 412 (1971); **104**, 421 (1971); *Arch. Pharm. (Weinheim, Ger.)*, **309**, 98 (1976).
(5) B. G. Chatterjee and R. F. Abdulla, *Chem. Ber.*, **102**, 421 (1969).
(6) A. K. Bose, *J. Indian Chem. Soc.*, **31**, 108 (1955).
(7) M. Artico, G. Filacchioni, V. Nacci, and F. Chimenti, *Farmaco, Ed. Sci.*, **26**, 411 (1971).
(8) M. S. Manhas, S. Jeng, and A. K. Bose, *Tetrahedron*, **24**, 1237 (1968).
(9) J. E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silberman, and R. C. Thomas, *J. Chem. Soc., Chem. Commun.*, 736 (1976).
(10) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).
(11) "NMR Spectra Catalog", Vol. 2, Varian Associates, Palo Alto, Calif., 1963, p 497.
(12) Melting points are uncorrected.
(13) O. Grummitt, E. I. Becker, and C. Miesse, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1962, p 109.
(14) W. H. Perkin, *J. Chem. Soc.*, **31**, 388 (1877).
(15) E. J. Wayne and J. B. Cohen, *J. Chem. Soc.*, **127**, 459 (1925).

Exploitation of the Vinylogous Wolff Rearrangement. An Efficient Total Synthesis of (±)-Mayurone, (±)-Thujopsene, and (±)-Thujopsadiene

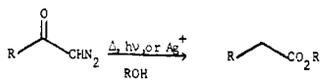
Stephen J. Branca, Robert L. Lock, and Amos B. Smith III*

The Department of Chemistry and The Monell Chemical Senses Center, University of Pennsylvania, Philadelphia, Pennsylvania 19104

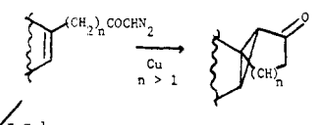
Received March 4, 1977

A synthetic route to (±)-mayurone, (±)-thujopsene, and (±)-thujopsadiene employing in turn a vinylogous Wolff rearrangement, a photochemical Wolff rearrangement, and an intramolecular copper-catalyzed cyclopropanation reaction is described.

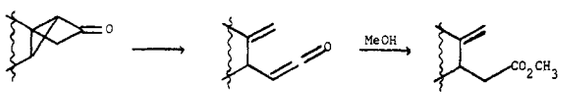
Since the pioneering studies of Arndt and Eistert in the early 1940's α-diazo ketones have found wide application in organic syntheses.[1] Principal among the synthetically useful reactions of this functionality are the Wolff rearrangement (eq 1) and the intramolecular insertion into olefinic bonds (eq 2). The former transformation can be effected thermally,[2] photochemically,[3] and by silver ion[1] catalysis, while the latter is best effected by copper.[4] Recently, we and others have described what appears, formally at least, to be a special case of the latter reaction.[5-7] Specifically, β,γ-unsaturated diazo ketones in the presence of a nucleophile and under the influence of copper lead efficiently via skeletal rearrangement to γ,δ-unsaturated acid derivatives (eq 3). This transformation, a synthetic alternative to the Claisen rearrangement (eq 4),



(1)



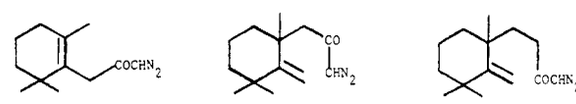
(2)



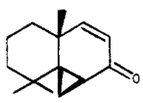
(3)

(4)

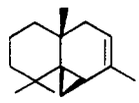
was termed[5] the vinylogous Wolff rearrangement and was suggested to involve the intermediacy of a bicyclo[2.1.0]pentanone, which under the reaction conditions fragments to a β,γ-unsaturated ketene (eq 3).[5-7] In order to illustrate dramatically the synthetic flexibility of the diazo ketone functionality in general, and the use of the vinylogous Wolff rearrangement in particular, we describe here an efficient route to the thujopsene class of sesquiterpenes including mayurone, thujopsene, and thujopsadiene (**1-3**). Our approach, employing the three diazo ketones listed below, exploits in turn a vinylogous Wolff rearrangement, a photochemical Wolff rearrangement, and an intramolecular copper-catalyzed cyclopropanation reaction.



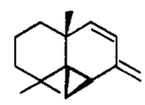
The salient structural feature of the thujopsene class of sesquiterpenes is the cis disposition of the angular methyl group and the cyclopropane ring. Dihydromayurone (**4**) occupies a central place in any synthetic strategy to this class of natural products as it embodies the requisite stereochemical features and furthermore is easily transformed to each member of this class. The first solution of this interesting architectural problem was achieved in 1963 by Dauben and Ashcraft through application of their then recent discovery: the hydroxyl-mediated stereospecific Simmons–Smith reaction (**5** → **6**).[8] Subsequent oxidation yielded (±)-dihydromayurone (**4**), which was transformed into (±)-thujopsene. The second approach, solely to (±)-thujopsene and avoiding the intermediacy of dihydromayurone, was elegantly conceived by Buchi to involve intramolecular cyclization of the carbene derived from tosyl hydrazone **7**.[9] Finally, Anderson[10a] and more recently Mori[10b] and McMurry[11] demonstrated that the intramolecular cyclization of δ,ϵ-unsaturated diazo ketones



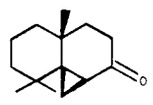
MAYURONE (1)



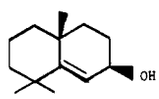
THUJOPSENE (2)



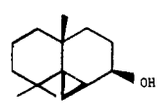
THUJOPSADIENE (3)



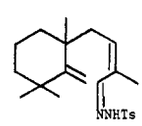
DIHYDROMAYURONE (4)



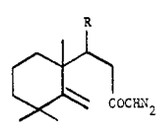
5



6



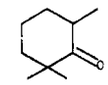
7



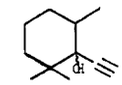
8

a) R = H

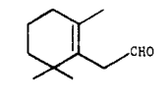
b) R = CO_2CH_3



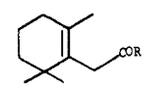
9



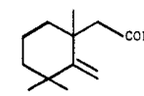
10



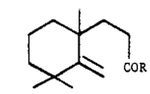
11



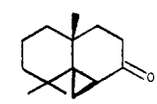
12



13



14



4

a) R = OH c) R = Cl

b) R = OCH_3 d) R = CHN_2

8a and 8b leads efficiently to dihydromayurone and its β-carbomethoxy derivative.

Our approach to the thujopsene class, envisioned to incorporate in turn the vinylogous Wolff rearrangement, the photochemical Wolff rearrangement, and the intramolecular cyclopropanation reaction, called initially for preparation of the β,γ-unsaturated acid **12a.** This acid appeared at the outset to be easily available by dehydration of the epimeric mixture of alcohols derived from the addition of the lithium enolate of ethyl acetate[12] to 2,2,6-trimethylcyclohexanone. Unfortunately, all attempts (ca. 12 in all) at this dehydration led only to complex mixtures consisting of various amounts of the two α,β-, the β,γ-, and the two γ,δ-unsaturated acid derivatives. Successful acquisition of the desired β,γ-unsaturated acid (**12a**) was finally achieved via Jones oxidation[13] of aldehyde **11**,[14] now readily available through application of the vanadium(V)-catalyzed Meyer–Schuster rearrangement[14,15] of α-acetylenic alcohol **10.**[16] Successive treatment of this crystalline carboxylic acid (**12a**) (mp 55–58 °C) with oxalyl chloride and excess diazomethane afforded diazo ketone **12d** in 65% overall yield.

At this point we were ready to exploit the various diazo ketone transformations discussed above. The first, the vinylogous Wolff rearrangement [i.e., $Cu(acac)_2$; C_6H_{12}–MeOH (0.2% v/v); Δ], afforded ester **13b** in 55% yield. This ester proved to be identical in all respects with that prepared previously by McMurry and Blaszczak via a Claisen rearrangement sequence.[11] With this ester in hand homologation to the corresponding chain lengthened methyl ester (**14b**) via a photochemical Wolff rearrangement, the second utilization of a diazo ketone, was now straightforward. To this end, **13a** was converted in the usual manner [(a) ClCOCOCl; (b) CH_2N_2] to diazo ketone **13d** in 87% yield. Subsequent irradiation of **13d** in methanol through Pyrex (λ ≥ 2800 Å) gave the desired methyl ester (**14b**) in 75% yield. The stage was now set for the third and final diazo ketone transformation, namely the previously reported Mori–McMurry copper-catalyzed intramolecular cyclopropanation reaction.[10,11] This reaction sequence proceeded without event to yield (±)-dihydromayurone (**4**) in 47% yield.

With completion of this efficient approach to dihydromayurone (i.e., 8% overall from 2,2,6-trimethylcyclohexanone), there remained only the conversions to (±)-mayurone, (±)-thujopsene, and (±)-thujopsadiene to fulfill our synthetic goal. To this end dihydromayurone was readily transformed to (±)-thujopsene and (±)-thujopsadiene in 72 and 58% yield, respectively, as originally outlined by Dauben[8] and McMurry.[11] The synthetic samples were identical in all respects (IR, NMR, and VPC retention data) with the natural products.[17,18] Transformation of dihydromayurone to mayurone, on the other hand, had not previously been described. Initial attempts here to utilize the Sharpless–Reich selenoxide elimination[19] sequence lead only to partial conversion. Efforts at this point to effect separation of (±)-dihydromayurone and (±)-mayurone proved unsuccessful. (±)-Mayurone, identical in all respects with natural mayurone,[17] was finally prepared in 75% yield by selenium dioxide oxidation of dihydromayurone.

Experimental Section

Materials and Methods. Vapor-phase chromatography (VPC) was performed with a Varian Aerograph Model 920 gas chromatograph on one of the following columns: A, 25% QF-1, 10 ft × 0.375 in.; B, 6% SE-30, 10 ft × 0.375 in.; C, 25% SE-30, 10 ft × 0.375 in.; D, 6% DEGS, 10 ft × 0.375 in.; E, 12.5% OV 101, 10 ft × 0.375 in. The helium carrier gas flow rate was 100–120 mL/min and the oven temperature ranged from 160 to 190 °C. Compounds isolated by preparative VPC were obtained as either colorless oils or white solids. Melting points were taken on a Thomas Hoover capillary melting point apparatus and are corrected. Boiling points are uncorrected. Solutions were dried over $MgSO_4$ unless specified otherwise. IR and NMR spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer Model 337 spectrophotometer and the latter on either a Varian A-60 (60 MHz) or HR-220 (220 MHz) spectrometer. Photochemical experiments were carried out with a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well using Pyrex 7740 as filter.

2,2,6-Trimethylcyclohexanone was readily prepared from 2-carbethoxycyclohexanone.[21] The lithium acetylide–ethylenediamine complex was obtained from Research Organic/Inorganic Chemicals Co. and was stored under N_2. Samples of triphenylsilanol and tris(triphenylsiloxy)vanadate were kindly supplied by Hofmann-La Roche. Triphenylsilanol is commercially available from Arapahoe Chemicals and tris(triphenylsiloxy)vanadate can be conveniently prepared from V_2O_5 and Ph_3SiOH.[22]

2,6,6-Trimethyl-1-cyclohexeneacetaldehyde (11). To a suspension of 10.8 g (1.5 equiv) of $LiC{\equiv}CH{\cdot}(CH_2NH_2)_2$ in 60 mL of anhydrous C_6H_6–THF (1:1) warmed to 39 °C under N_2 was added a solution of 11.1 g (79.2 mmol) of ketone **9** in 25 mL of C_6H_6–THF (1:1). During the course of the addition (~10 min) the reaction temperature was maintained at 39 °C by slight cooling. The resulting mixture was then stirred at room temperature for 10 h. After careful addition of 15 mL of H_2O the mixture was refluxed for 1 h. The reaction mixture

was then poured into saturated aqueous NH_4Cl and extracted with Et_2O. The organic phase was separated, washed with H_2O and brine, and dried. Removal of the solvent in vacuo followed by distillation of the residue afforded 11.9 g (90%) of an oily liquid boiling at 56–58 °C (1.4 torr) which consisted of a 75:25 (NMR; relative area for acetylenic hydrogen's) epimeric mixture of the corresponding propynols (10): IR 3650 (m), 3550–3400 (w, br), 3310 (m), 2970 (s), 2940 (s), 1460 (m), 1030 (s) cm^{-1}.

A solution consisting of 3.87 g (23.3 mmol) of the propynols and 1.44 g of Ph_3SiOH in 20 mL of paraffin oil ($d^{20} = 0.86$) was heated to 144 °C under N_2. To this was added 450 mg of tris(triphenylsiloxy) vanadate (91%). The resulting solution was stirred for 5 h at 144–146 °C under N_2, cooled to 40 °C, and then distilled under reduced pressure. The colorless oil [3.42 g, 88%, 75–82 °C (1.0 Torr)] obtained was found to be a 9:1 mixture (VPC on column A) of **11** and the α,β-unsaturated isomers, respectively. An analytical sample of **11** obtained by VPC on column A had the following spectral data: IR 2940 (s), 2860 (s), 2830 (s), 2720 (m), 1720 (s), 1460 (m) cm^{-1}; NMR (60 MHz) δ 0.95 (s, 6 H), 1.33–2.30, 1.58 (m, s, 9 H), 3.05 (s, 2 H), 9.50 (t, J = 2.5 Hz, 1 H).

2,6,6-Trimethyl-1-cyclohexeneacetic acid (12a). A solution of 330 mg (2.0 mmol) of aldehyde **11** in 15 mL of acetone was chilled to 0–5 °C and then treated with 740 μL (1.0 equiv) of CrO_3–H_2SO_4 (2.7 M). After stirring at 0–5 °C for 30 min the reaction mixture was poured into water and extracted with Et_2O. The organic phase was washed with two 25-mL portions of 5% (w/v) aqueous NaOH. The aqueous phase was separated, acidified (dilute HCl), and extracted with ether. The organic phase was washed with H_2O and brine, and dried. Removal of the solvent in vacuo yielded 300 mg (83%) of crude crystalline **12**. An analytical sample was obtained by recrystallization from petroleum ether (30–60 °C) at low temperature. The resulting white, crystalline solid had mp 55–58 °C and the following spectral data; IR 3500–2600 (s, br), 1705 (s), 1455 (m), 1405 (m), 1380 (w), 1360 (w), 1290 (m), 1220 (m) cm^{-1}; NMR (60 MHz) δ 0.97 (s, 6 H), 1.30–2.50, 1.62 (m, s, 9 H), 3.06 (s, 2 H), 11.0 (br s, 1 H); *m/e* 182.1298 (M^+, calcd for $C_{11}H_{18}O_2$, 182.1306).

Methyl 1,3,3-Trimethyl-2-methylenecyclohexaneacetate (13b). A solution consisting of 3.00 g (16.7 mmol) of acid **12a** in 20 mL of dry benzene was treated with 2.20 mL (1.50 equiv) of oxalyl chloride and then stirred at room temperature for 8 h. The resulting solution was concentrated in vacuo and the residue distilled (Kuglerohr), yielding 2.77 g (83%) of the corresponding acid chloride (**12c**) [IR 2940 (s), 2870 (s), 1800 (s), 1460 (m), 1360 (m), 950 (s) cm^{-1}].

A solution of 2.17 g (10.8 mmol) of **12c** in 50 mL of anhydrous ether was added dropwise with stirring to a chilled, ethereal solution of CH_2N_2 (5–6 equiv). After the addition, the resulting solution was allowed to stand overnight at room temperature. The excess diazomethane was then removed on a steam bath and the remaining solution was dried and concentrated in vacuo to yield 2.23 g (100%) of diazo ketone **12d** [IR 3130 (w), 2940 (s), 2105 (s), 1640 (s), 1350 (s) cm^{-1}]. This diazo ketone (435 mg, 2.12 mmol) was dissolved in 56 mL of cyclohexane and then treated with 40 mg of $Cu(acac)_2$ and 112 μL of MeOH (1.1 equiv). The resulting mixture was heated at reflux for 1 h, cooled, washed with three 50-mL portions of 2 N HCl, and dried. Removal of the solvent in vacuo yielded 395 mg of a dark oil which contained 244 mg (55%, VPC) of ester **13b**. An analytical sample obtained by VPC on column A possessed the following spectral data which were identical in all respects with the spectral data provided by Prof. McMurry for this ester: IR 3110 (w), 2960 (s), 2940 (s), 2875 (m), 1740 (s), 1630 (w), 1460 (m), 1440 (m), 1190 (m), 1005 (m), 902 (m) cm^{-1}; NMR (60 MHz) δ 0.92–2.10, 1.10, 1.22 (m, s, s, 15 H), 2.43 (s, 2 H), 3.53 (s, 3 H), 4.83 (s, 1 H), 4.96 (s, 1 H).

Methyl 1,3,3-Trimethyl-2-methylenecyclohexanepropionate (14b). A solution of 1.47 g (7.0 mmol) of ester **13b** in 15 mL of MeOH was treated with 10 mL of 5% (w/v) aqueous NaOH and refluxed for 2 h under a N_2 atmosphere. The reaction mixture was then cooled, poured into water, and extracted with ether. The aqueous phase was separated, acidified (dilute HCl), and extracted with ether. The resulting organic phase was washed with H_2O and brine, and dried. Removal of the solvent in vacuo afforded 1.27 g (93%) of carboxylic acid **13a** [IR 3700–2600 (s, br), 1705 (s), 1610 (w), 1460 (m), 1400 (m), 1295 (m), 1235 (m), 902 (m) cm^{-1}].

This acid (1.27 g, 6.5 mmol) was dissolved in 5 mL of benzene and treated with 1.0 mL (1.8 equiv) of oxalyl chloride. The resulting solution was then stirred for 5 h at room temperature, concentrated under reduced pressure, and distilled (Kuglerohr) to yield 1.29 g (93%) of acid chloride **13c** [3100 (w), 2960 (s), 2945 (s), 1800 (s), 1620 (w), 908 (m) cm^{-1}].

A solution of this acid chloride (1.29 g, 6.00 mmol) in 50 mL of anhydrous ether was added dropwise with stirring to a chilled, ethereal solution of CH_2N_2 (4.5 equiv). The resulting solution was allowed to stand overnight at room temperature and then after removal of excess diazomethane on a steam bath, the remaining solution was concentrated in vacuo to yield 1.38 g (100%) of diazo ketone **13d** [IR 3120 (w), 2970 (s), 2945 (s), 2110 (s), 1645 (s), 1350 (s), 900 (m) cm^{-1}]. Without further purification diazo ketone **13d** was dissolved in 70 mL of MeOH and irradiated for 1.3 h. The photolysate was poured into H_2O and extracted with ether. The organic phase was washed with H_2O and brine, and dried. Removal of the solvent in vacuo afforded 1.23 g of a yellow oil which on distillation (Kuglerohr, 110–115 °C) afforded 1.05 g (75%) of ester **14b**. An analytical sample obtained by VPC on column B had the following spectral characteristics: IR 3100 (w), 2950 (s), 2870 (s), 1740 (s), 1670 (m), 1460 (m), 1440 (m), 1380 (m), 1360 (m), 1200 (s), 1175 (s), 902 (s) cm^{-1}; NMR (60 MHz) δ 1.00–2.40, 1.06, 1.11 (m, s, s, 19 H), 3.59 (s, 3 H), 4.83 (s, 1 H), 5.03 (s, 1 H).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78, Found: C, 74.77; H, 10.74.

Dihydromayurone (4). A solution consisting of 545 mg of diazo ketone **14d** [IR 3100 (w), 2960 (s), 2100 (s), 1645 (s), 1350 (s), 900 (m) cm^{-1}], prepared in 86% overall yield [NaOH, MeOH; $(ClCO)_2$, C_6H_6; CH_2N_2, Et_2O] from ester **14b**, in 10 mL of cyclohexane was added dropwise to a refluxing suspension of 720 mg of Cu powder, 214 mg of $CuSO_4$ (anhydrous), and 60 mL of cyclohexane. The resulting mixture was stirred at reflux for 1 h following the addition. After cooling, the reaction mixture was washed with three 50-mL portions of 2 N HCl, dried, and concentrated in vacuo to afford 525 mg of a dark oil. This oil was chromatographed on silica gel. Elution with hexane–benzene (1:1) and then hexane–benzene (3:7) yielded 224 mg (47%) of crystalline ketone **4**. An analytical sample obtained by VPC on column D had a mp of 100 °C and the following spectral data which were in good agreement with literature data[10] for this ketone: IR 3075 (w), 3020 (m), 2950 (s), 2870 (s), 2860 (s), 1680 (s), 1470 (m), 1275 (s), 1100 (m), 910 (m), 870 (m) cm^{-1}; NMR (60 MHz) δ 0.64 (s, 3 H), 0.91 (m, 1 H), 1.04–2.32, 1.13, 1.21 (m, s, s, 18 H).

(±)-Thujopsene (2). A solution of 42 mg (0.2 mmol) of ketone **4** dissolved in 5 mL of anhydrous ether under a nitrogen atmosphere was first treated with 5 equiv of MeMgI and then refluxed for a period of 40 min. The reaction mixture was cooled to room temperature and carefully treated with 2.0 mL of saturated aqueous NH_4Cl. The resulting suspension was poured into ether and water and the aqueous phase was separated. The organic phase was washed with H_2O and brine, and dried. Removal of the solvent in vacuo yielded 48 mg of a yellow oil which consisted mainly of thujopsene (**2**) and a small amount (12%; VPC) of ketone **4**. The yield based on recovered **4** was 72% (VPC). A sample obtained by preparative VPC on column C was identical [VPC retention properties, IR, NMR] with an authentic sample of natural (±)-thujopsene.[17]

(±)-Mayurone (1). A solution consisting of 32.2 mg (0.16 mmol) of ketone **4**, 112 mg of SeO_2, and 15 mL of *t*-BuOH was heated at reflux under an atmosphere of N_2 for 41 h. After filtration, the mixture was evaporated in vacuo and the residual material was dissolved in 15 mL of MeOH and agitated for 3 h in the presence of 450 mg of Raney Ni (deactivated).[23] The mixture was then filtered and the filtrate evaporated under reduced pressure. The remaining residue was washed with three 10-mL portions of ether. The ether washings were combined, washed with brine, and dried. Removal of the solvent in vacuo afforded 44.5 mg of a dark oil which contained 24.5 mg (75%; VPC) of enone **1**. An analytical sample obtained by VPC on column D was found to be identical (IR, 220 MHz NMR, and VPC retention properties) with an authentic sample of mayurone.[17]

(±)-Thujopsadiene (3). A solution containing 41.2 mg (0.2 mmol) of enone **1** in 5 mL of dry ether (distilled from $LiAlH_4$) was first treated with 4 mL (36.8 equiv; 1.84 M) of methyllithium and then gently refluxed under a nitrogen atmosphere for 3 h. After cooling to 0–5 °C 15 mL of saturated aqueous NH_4Cl was then added. The resulting mixture was poured onto water–pentane (1:1 v/v) and the aqueous layer separated. The organic phase was washed with H_2O and brine, and dried. Removal of the solvent in vacuo afforded 41 mg of an oil containing 31.9 mg (78.5%; VPC) of diene **3**. An analytical sample obtained by VPC on column E possessed spectral data (IR and NMR) which were identical in all respects with those provided by Professor McMurry for (±)-thujopsadiene.[18]

Acknowledgments. It is a pleasure to acknowledge the support of this investigation by Research Corporation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. In addition, we thank Mr. S. T. Bella for the microanalyses, The Rockefeller University Mass Spectrometry Laboratory (NIHDRR No. RR00862) for the high resolution mass spectra, and the Middle Atlantic

Regional NMR Facility (NIH No. RR542) at the University of Pennsylvania, where the 220-MHz NMR spectra were obtained.

Registry No.—**1**, 51446-90-3; **2**, 17974-52-6; **3**, 51446-91-4; **4**, 28890-28-0; **9**, 62861-88-5; *cis*-**10**, 62861-89-6; *trans*-**10**, 62861-90-9; **11**, 472-66-2; **12a**, 472-68-4; **12c**, 62861-91-0; **12d**, 62861-92-1; **13a**, 62861-93-2; **13b**, 51417-31-3; **13c**, 62861-94-3; **13d**, 62861-95-4; **14b**, 62861-96-5; **14d**, 62861-97-6.

References and Notes

(1) For review articles, see W. E. Bachmann and W. S. Struve, *Org. React.* **1**, 38 (1942); B. Eistert, "New Methods in Preparative Organic Chemistry", Vol. 1, Interscience, New York, N.Y., 1948, p 513; F. Weygand and H. J. Bestmann, *ibid.*, Vol. 3, p 451.
(2) L. Wolff, *Justus Liebigs Ann. Chem.*, **394**, 23 (1912); H. Krzikalla and B. Eistert, *J. Prakt. Chem.*, **143**, 50 (1935); A. L. Wilds and A. L. Meader, *J. Org. Chem.* **13**, 763 (1948).
(3) L. Horner and E. Spietschka, *Chem. Ber.*, **88**, 934 (1955).
(4) G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961).
(5) A. B. Smith III, *J. Chem. Soc., Chem. Commun.*, 695 (1974); A. B. Smith III, B. H. Toder, and S. J. Branca, *J. Am. Chem. Soc.*, **98**, 7458 (1976).
(6) J. P. Lokensgard, J. O'Dea, and E. A. Hill, *J. Org. Chem.*, **39**, 3355 (1974).
(7) H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **96**, 4623 (1974).
(8) W. G. Dauben and A. C. Ashcraft, *J. Am. Chem. Soc.*, **85**, 3673 (1963).
(9) G. Buchi and J. D. White, *J. Am. Chem. Soc.*, **86**, 2884 (1964).
(10) (a) P. L. Anderson, Ph.D. Dissertation, *Chem. Abstr.*, **68**, 13186 (1968); (b) K. Mori, M. Ohki, A. Kobayashi, and M. Matsui, *Tetrahedron*, **26**, 2815 (1970).
(11) J. E. McMurry and L. C. Blaszczak, *J. Org. Chem.*, **39**, 2217 (1974).
(12) M. W. Rathke, *J. Am. Chem. Soc.*, **92**, 3222 (1970).
(13) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39, (1946).
(14) G. L. Olson, H. C. Cheung, K. D. Morgan, R. Borer, and G. Saucy, *Helv. Chim. Acta*, **59**, 567 (1976); also see H. Pauling, D. A. Andrews, and N. C. Hindley, *ibid.*, **59**, 1233 (1976).
(15) We are grateful to Dr. G. L. Olson (Hoffmann-La Roche Inc., Nutley, N.J.) for generous samples of triphenylsilanol and tris(triphenylsiloxy)vanadate.
(16) S. W. Pelletier and N. V. Mody, *J. Org. Chem.*, **41**, 1069 (1976).
(17) We thank Dr. A. R. Hochstetler (Givaudan Corporation) for samples of natural thujopsene and mayurone.
(18) We thank Professor J. E. McMurry for IR and NMR spectra of authentic **13b** and (±)-thujopsadiene.
(19) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Am. Chem. Soc.*, **95**, 6137 (1973); H. J. Reich, I. L. Reich, and J. M. Renga, *ibid.*, **95**, 5813 (1973); H. J. Reich, J. M. Renga, and I. L. Reich, *J. Org. Chem.*, **39**, 2133 (1974); H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975), and references cited therein.
(20) S. Bernstein and R. Littell, *J. Am. Chem. Soc.*, **82**, 1235 (1960).
(21) C. L. Stevens and A. J. Weinheimer, *J. Am. Chem. Soc.*, **80**, 4072 (1958).
(22) H. Pauling, D. A. Andrews, and N. C. Hindley, *Helv. Chim. Acta*, **59**, 1233 (1976).
(23) P. L. Julian, C. C. Cochrane, A. Magnani, and W. J. Karpel, *J. Am. Chem. Soc.*, **78**, 3153 (1956).

A Conformational Analysis of Cyclopropanodecalin Derivatives by Carbon-13 Nuclear Magnetic Resonance Spectroscopy[1]

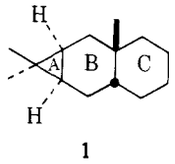
Francesco Fringuelli,[2a] Edward W. Hagaman,[2b] Louis N. Moreno,[2b] Aldo Taticchi,[2a] and Ernest Wenkert*[2b]

Istituto di Chimica dell' Università, Perugia, Italy, and the Department of Chemistry, Rice University, Houston, Texas 77001

Received January 25, 1977

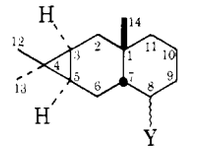
The ^{13}C NMR spectra of 18 cyclopropanodecalins based on the carane skeleton and containing a *cis*-decalin configuration have been recorded and all carbon shifts assigned. The β-deuterium isotope effect of some multiply deuterated compounds aided the shift assignment. On the basis of the shift data the hydrocarbons, alcohols, and acetates could be classified in terms of the two possible *cis*-decalin conformations.

The stereochemical and conformational features of a series of tricyclic substances derived from (−)-*cis*-caran-3-one have been the subject of recent chemical[3] and spectroscopic[3,4] studies, circular dichroism,[3] ^1H NMR,[3] IR,[3] and, in one instance, x-ray crystallographic, data[4] having been gathered on trimethylcyclopropanodecalin derivatives (**1**). The present communication represents an extension of the earlier ^{13}C NMR investigation of bicyclic carane derivatives[5] and reports the chemical shift assignment and conformational assessment of tricycles based on structure **1**.

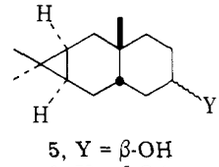


1

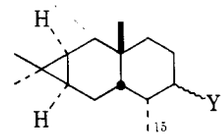
The compounds chosen for study consisted of the hydrocarbon **1**, nine derivatives possessing a single methyl, hydroxy, or acetoxy substituent on ring C (**2–6** and **15–18**) and eight derivatives containing two of these functions on ring C (**7–14**). For four of these substances, **1**, **5**, **15**, , and **16**, the assignment of seven of the decalin ring carbons has been obtained by a minimum number of deuteration experiments, making extensive use of the deuterium β-effect.[5,6] This technique has permitted the characterization of the conformationally impure members of this class of compounds.



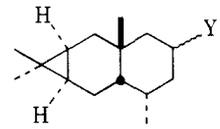
1, Y = H
2, Y = α-Me
3, Y = α-OH
4, Y = α-OAc
17, Y = β-OH
18, Y = β-OAc



5, Y = β-OH
6, Y = β-OAc
15, Y = α-OH
16, Y = α-OAc



7, Y = β-OH
8, Y = β-OAc
11, Y = α-OH
12, Y = α-OAc



9, Y = α-OH
10, Y = α-OAc
13, Y = β-OH
14, Y = β-OAc

The B/C cis ring junction of these substances allows the skeleton to adopt conformation A or B or exist as a mixture of the two forms.[7] On the basis of conformational analysis, A is expected to be of lower energy in view of its avoidance of the severe nonbonded interaction of C(12) and C(14) in B. Furthermore, in the monofunctional derivatives possessing either