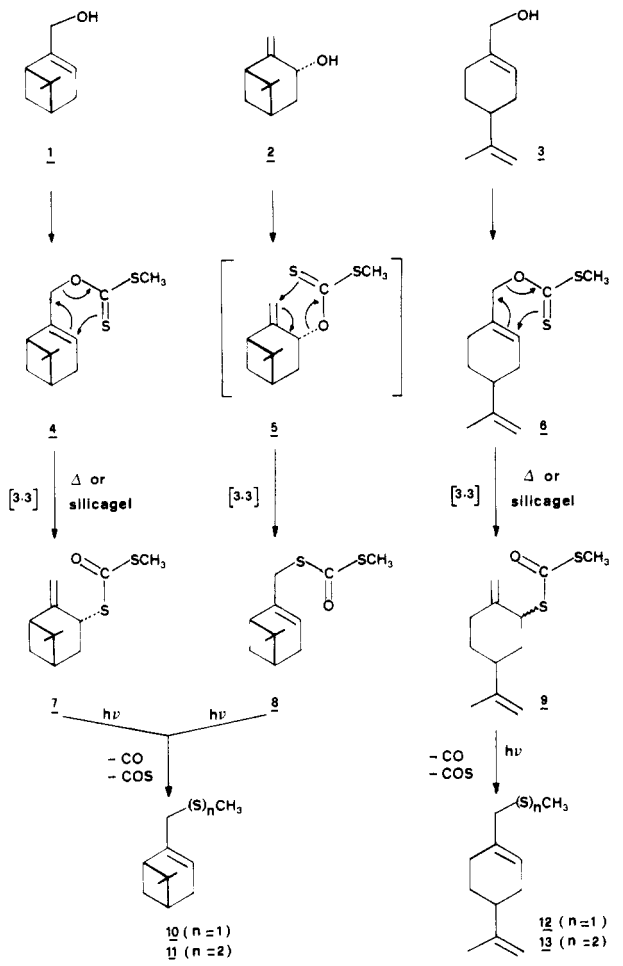
Scheme I



(for $\lambda > 313$ nm). The Me_2SO was freshly distilled from sodium hydride.

Xanthation or Alcohols 1, 2, and 3. Myrtenol (1) is a Fluka commercial product (purity 99%). *trans*-Pinocarveol (2) was prepared following a described method[16] from commercial pinene epoxide (Aldrich; purity 95%). Perillyl alcohol (3) was an EGA-CHEMIE commercial product (purity 90%).

Ethylenic alcohol (1.7 g, 11 mmol) was stirred for 30 min between 10 and 15 °C with a suspension of 1.65 g of powdered KOH in 30 mL of dry Me_2SO. Then 1.98 g (or 1.56 mL) of dry CS_2 were added dropwise such that the temperature never rised above 10 °C. After 30 min of stirring, 3.3 g (1.45 mL) of ICH_3 were added to the orange solution. The mixture was stirred at about 5 °C for 4.5 h for **1** and **2** and 1 h for **3** to limit aromatization reaction.[17] The solution was poured onto a small amount of ice water to avoid emulsion. The organic phase was extracted with ether. The etheric layer was washed with a saturated NaCl solution until pH 7 was obtained and then dried. The solvent was removed under reduced pressure. The yellow liquid residue (2.3 g, yield 85%) was subjected to column chromatography on silica gel with gradual eluting: (1) Hexane, afforded 100 mg of $(CH_3S)_2C{=}S$; NMR (CCl_4) 2.70 ppm; (2) 90 hexane/10 methylene chloride afforded 1.8 g of dithiocarbonate **7** or **8** (yield 80%), and 1.2 of g dithiocarbonate **9** (yield 65%) (IR, NMR, MS, molecular centesimal formulae; analyses of **7**, **8**, and **9**, see Tables I and III).

***S*-Methyl *O*-α-pinenyl dithiocarbonate (4) (crude)**: IR (film) ν 1120 and 1250 cm^{-1} (COC + C=S), 1650 (C=C); ^1H NMR ($CDCl_3$) δ 5.00 (s, 2 H, CH_2-10), 5.70 (m, 1 H, H-3), 2.45 (s, 3 H, CH_3-12).

***S*-Methyl *O*-dithiocarbonate (6) (crude)**: IR (film) ν 1200 and 1060 cm^{-1} (COC + C=S), 1640 (C=C); ^1H NMR ($CDCl_3$) δ 5.90 (m, 1 H, CH-2), 4.90 (s large, 2 H, CH_2-7), 4.70 (s large, 2 H, CH_2-9), 1.70 (s large, 3 H, CH_3-10), 2.40 (s, 3 H, CH_3-11).

Thermolysis of Xanthates 4 and 6. The crude product (2.3 g) obtained by xanthation of **1** and **3** was heated in 40 mL of dry Me_2SO at 85 °C under a nitrogen atmosphere for 2.5 h. Me_2SO was removed by etheric extraction. After drying and solvent removal under reduced pressure, 2 g of dithiocarbonate **7** or **9** were obtained and subjected to column chromatography of silica gel with gradual eluting (hexane, 90 hexane/10 methylene chloride): 1.8 g of **7** (yield 80%) and 1.2 g of **9** (yield 50% after two necessary consecutive elutions on silica gel) were isolated.

Photolysis of Dithiocarbonates 7-9. A sample of 40 mL of 5×10^{-2} M **7**, **8**, or **9** (484 mg) in methanol was poured into a quartz tube under a nitrogen stream. The whole solution was irradiated $\lambda = 254$ nm or $\lambda > 313$ nm. The reaction was followed by gas chromatography and stopped when the percentage of starting product did not vary.

***S*-Methyl *S*-β-pinenyl dithiocarbonate (7)**: λ_{max_1} 251 nm (ϵ_1 7200) and λ_{max_2} 203 nm (ϵ_2 12400) (ethanol). (1) λ 254 nm; time of irradiation 3.5 h in methanol. After removal of the solvent under reduced pressure, 350 mg of crude product was obtained and subjected to column chromatography on silica gel (eluent 95 hexane/5 methylene chloride), 80 mg of disulfide **11** (28%), 200 mg of thioether **10** (67%), and 15 mg of dithiocarbonate **7** (5%) were separated in this order. (2) For $\lambda > 313$ nm; time of irradiation 8 h in methanol. The solvent was removed under reduced pressure: 356 mg of crude product were obtained and subjected to column chromatography as described previously; 220 mg of thioether **10** (70%) and dithiocarbonate **7** (30%) were separated.

***S*-Methyl *S*-α-pinenyl dithiocarbonate (8)**: λ_{max_1} 249 nm, ϵ_1 6000; λ_{max_2} 206 nm, ϵ_2 10400 (ethanol). For λ 254 nm; time of irradiation 6 h in methanol. The solvent was removed under reduced pressure: 320 mg of crude product was obtained and subjected to column chromatography on silica gel (eluent 95 hexane/5 methylene chloride); 200 mg of disulfide **11** (80%), 46 mg of thioether **10** (10%), and 50 mg of dithiocarbonate **8** (10%) were separated. For $\lambda > 313$ nm; no reaction after 40 h of irradiation.

***S*-Methyl *S*-isocarveyl dithiocarbonate (9)**: λ_{max_1} 250 nm, ϵ_1 2600; λ_{max_2} 203 nm, ϵ_2 6000 (ethanol). (1) λ 254 nm (solvent methanol, time of irradiation 4 h). 425 mg of irradiated compound **9** afforded 330 mg of crude product. The mixture was subjected to successive column chromatographies on silica gel (eluent, 95 hexane/5 methylene chloride). Finally, 160 mg of thioether **12** (85%), 20 mg of disulfide **13** (10%), and 20 mg of dithiocarbonate **9** (5%) were separated without further purification. (2) $\lambda > 313$ nm. The results were analogous to those obtained with λ 254 nm, and with cyclohexane as solvent, longer irradiation times were necessary.

Registry No. 1, 515-00-4; 2, 1674-08-4; 3, 536-59-4; 4, 93040-75-6; 5, 93040-76-7; 6, 93040-77-8; 7, 93040-78-9; 8, 93040-79-0; 9, 74940-37-7; 10, 93040-80-3; 11, 93040-81-4; 12, 93040-82-5; 13, 93040-83-6; CS_2, 75-15-0; CH_3I, 74-88-4.

(16) Bessiere, Y.; Montheard, J. P. *Bull. Soc. Chim. Fr.* **1968**, 336.
(17) Bates, R. B.; Caldwell, E. S.; Klein, H. P. *J. Org. Chem.* **1969**, *34*, 2615.

(2*R*,5*R*)-(-)-2,5-Dimethylcyclopentanone and (5*S*)-(+)-2,5-Dimethyl-2-cyclopenten-1-one by Microbiological Reduction of Racemic 2,5-Dimethyl-2-cyclopenten-1-one

Jean-Claude Gramain, Alain Kergomard,* Michel F. Renard, and Henri Veschambre

ERA 392 du CNRS, Université de Clermont II, B.P. 45, 63170 Aubiere, France

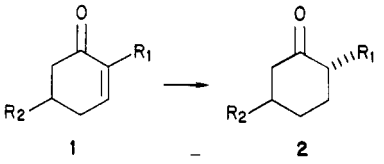
Received April 25, 1984

We reported in a previous work[1] that microbiological reduction of an α-substituted α,β-unsaturated ketone such as **1** gives the corresponding optically active saturated

(1) Kergomard A.; Renard, M. F.; Veschambre, H. *J. Org. Chem.* **1982**, *47*, 792.

0022-3263/85/1950-0120$01.50/0

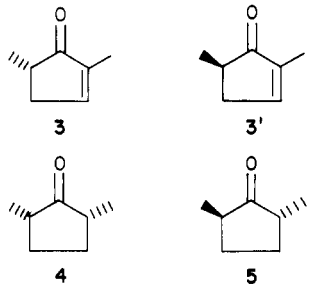
ketone 2 of 100% optical purity (e.g., 1 with $R_1 = CH_3$ and $R_2 = H$).



1 2

If the starting material is racemic (e.g., 1 with $R_1 = H$ and $R_2 = CH_3$) and if the reaction is incomplete, the saturated ketone obtained and the unreacted starting material are both optically active, indicating that preferential attack occurs on one of the enantiomers of 1.

As expected, reduction of racemic 2,5-dimethyl-2-cyclopenten-1-one (3 and 3′) with *Beauveria sulfurescens* (ATCC 7159) gave pure *cis*- or *trans*-2,5-dimethylcyclopentanone (4 and 5) along with some optically active starting material. Neither pure 4 and 5 nor pure 3 and 3′ had been obtained hitherto.



3 3′ 4 5

We report here the results of work carried out to determine the absolute configuration of the reaction products. This involved determining first the stereochemistry of 2,5-dimethylcyclopentanone for which conflicting data had been reported. The influence of the reaction time on the composition of the product mixture is discussed.

Stereochemistry of 2,5-Dimethylcyclopentanone. Commercial 2,5-dimethylcyclopentanone is a mixture of cis and trans isomers 4 and (±)-5 at the thermodynamic equilibrium, one of the isomers makes up about two-thirds of the mixture. Contrary to Brown et al.,[2] Rei[3] reported that the more abundant was trans. We have reexamined part of the work of Rei in order to determine which of the two isomers is in fact preponderant. We studied the mixture of cyclopentanols obtained on one hand by reduction with $LiAlH_4$ of a commercial mixture of 2,5-dimethylcyclopentanones and on the other hand by hydroboration of 1,3-dimethylcyclopentene. The stereochemistry of each of the three alcohols obtained was determined by high-field ^1H NMR (250 MHz) (cf. Experimental Section).

These findings corroborate those of Rei. Hence, commercial 2,5-dimethylcyclopentanone consists of about 67% trans isomer 5 and 33% cis isomer 4.

Microbiological Reduction of (±)-2,5-Dimethyl-2-cyclopenten-1-one. Microbiological reduction of racemic 2,5-dimethyl-2-cyclopenten-1-one by *B. sulfurescens* is never total. Unreacted α,β-unsaturated ketone is always found along with the reduction products, even after prolonged contact.

The composition of the reaction mixture was studied after 5 and 10 days contact time.

The results are given in Table I.

Composition of reaction mixture after 5 and 10 days contact time.

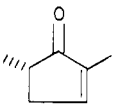
Table I. Composition of Reaction Mixture after 5 and 10 Days Contact Time

reactn time, days	3	3′	4	5
5	50% $[\alpha]^{25}_J$ +30°	20%[a]	0%	30% $[\alpha]^{25}_J$ −144°
10	40% $[\alpha]^{25}_J$ +65.2°	0%	18%	36% of 5[b] 6% of 5′[c] $[\alpha]^{25}_J$ −71°

[a] Percentages calculated from optical activities of optically pure enantiomers. [b] Percentages calculated from NMR data (cis/trans ratio) and from optical activities of optically pure enantiomers. [c] 5′ enantiomer of 5.

(a) Five-Day Reaction Time. The residue obtained consists of 30% 2,5-dimethylcyclopentanone and 70% unreacted 2,5-dimethyl-2-cyclopenten-1-one (GPC).

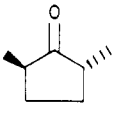
Comparison of the ^{13}C NMR spectrum of isolated 2,5-dimethylcyclopentanone with that of the commercial mixture shows that it is a pure trans isomer. This isomer has a very high optical activity $[\alpha]^{25}_J$ −144° which shows that it must be the trans isomer given that the cis isomer must perforce be inactive. We showed previously that the microbiological reduction of cyclic α,β-unsaturated ketones with *B. sulfurescens* always gives a 2-carbon with *R* configuration. The *trans*-2,5-dimethylcyclopentanone obtained here would thus be expected to have the 2*R*,5*R* configuration shown below:



The ^1H NMR spectrum of isolated unreacted 2,5-dimethyl-2-cyclopenten-1-one recorded in the presence of chiral shift reagent showed that a mixture of the isomers 3 and 3′ (double doublet for 5-CH_3) had been obtained. Composition and characteristics are given in Table I.

(b) Ten-Day Reaction Time. After 10 days the reaction has gone to 60% completion. ^{13}C NMR spectrum of the 2,5-dimethylcyclopentanone showed it to be a mixture of cis and trans isomers similar to the commercial mixture.

The recovered 2,5-dimethyl-2-cyclopenten-1-one had an optical activity of $[\alpha]^{25}_J$ +65.2° and was optically pure. Its NMR spectrum recorded in the presence of a chiral shift reagent showed a single doublet for the 5-CH_3 (coupling with the C_5-H). A double doublet (Figure 1) was obtained with the racemic ketone. Given the results obtained after 5 days reaction, this product is presumably the isomer 3 of configuration 5*S*.



This result is at variance with that reported by Bertrand et al.,[4] who obtained an optically active 2,5-dimethyl-2-cyclopenten-1-one with $[\alpha]^{20}_D$ −1.24° by oxidation of a partially resolved enallene. In order to determine the absolute configuration of this ketone, these authors carried out an oxidative ozonolysis which gave (−)-(*S*)-methylsuccinic acid with $[\alpha]^{25}_D$ −1.38°. The literature value of (−)-(*S*)-methylsuccinic acid is $[\alpha]^{20}_D \simeq 9.2°$. Bertrand et al. concluded that their unsaturated ketone was of configuration 5*S* which is inconsistent with our results.

(2) Brener, L.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2702.
(3) Rei, M. Hon. *J. Org. Chem.* **1978**, *43*, 2173.
(4) Bertrand, M.; Dulcere, J. P.; Gil, G. *Tetrahedron Lett.* **1977**, 4403.
(5) Schreiber, K.; Ripperger, H. *Liebigs Ann. Chem.* **1962**, *655*, 114.

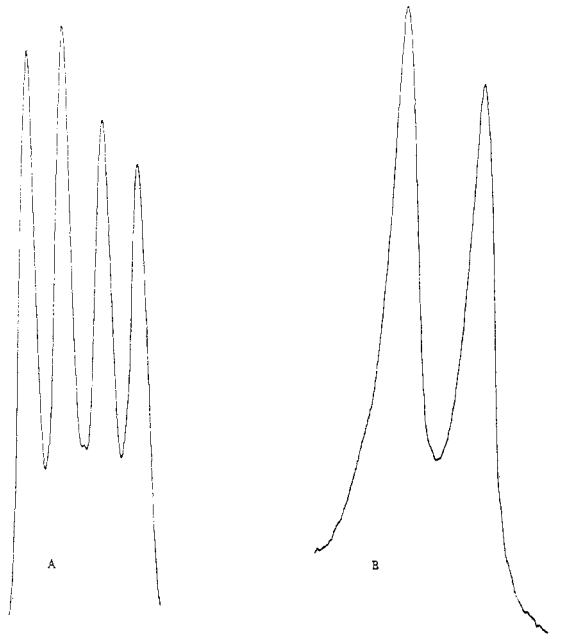


Figure 1. ^1H NMR spectrum of the 5-methyl of 2,5-dimethyl-2-cyclopenten-1-one in the presence of tris[3-[(trimethylfluoromethyl)hydroxymethylene]-*d*-camphorato]europium(III): A, racemate; B, isomer **3**.

We carried out the same oxidative ozonolysis on the optically pure unsaturated ketone **3** with $[\alpha]^{25}_J$ +65.2°. The methylsuccinic acid obtained had $[\alpha]^{25}_J \simeq 7.5°$, corresponding to an optical purity of 80% and an *S* configuration. (The slight loss of optical purity may result from racemization through enolization of 2,5-dimethyl-2-cyclopenten-1-one.) This result confirms the attribution of the absolute configuration 5*S* to 2,5-dimethyl-2-cyclopenten-1-one (**3**).

The inconsistency between our results and those of Bertrand et al. is probably due to the low optical activities of the compounds isolated and used by these authors. There is indeed an inconsistency in the optical purities of their 2,5-dimethyl-2-cyclopenten-1-one (1.9%) and of the methylsuccinic acid they obtained by oxidative ozonolysis (15%).

In addition, like 2-methylcyclopentanone, 2,5-dimethylcyclopentanone (**5**) racemizes rapidly via **4**. Similarly, the reaction product of the reduction of **3** at 10 days also underwent racemization; the trans saturated ketone obtained was partially racemized with an enantiomeric excess of about 70% (Table I).

Given the evidence detailed above, the absolute configuration of the two optically pure ketones obtained here can be confidently attributed, namely (−)-(2*R*,5*R*)-2,5-dimethylcyclopentanone (**5**) and (+)-(5*S*)-2,5-dimethyl-2-cyclopenten-1-one (**3**) and their optical activity are respectively $[\alpha]^{25}_J$ −144° and $[\alpha]^{25}_J$ +65.2°.

The same is not the case, however, for 5-methyl-2-cyclohexen-1-one,[1] with which no optically pure products were obtained even at low completion.

Experimental Section

Optical rotations were measured with a Perkin-Elmer 141 polarimeter at the yellow mercury line (λ 578 nm) at 25°.

^1H NMR spectra were obtained with JEOL C 60 HL and CAMECA 250 MHz spectrometers and ^{13}C NMR with a JEOL FX 60 spectrometer for $CDCl_3$ solutions. Chemical shifts are given relative to Me_4Si as internal standard. Column chromatography was performed on 70–230-mesh Merck silica gel with pentane/ether as the mobile phase. Gas chromatography was performed with an Intersmat IGC 12M chromatograph equipped with a catharometer. Columns were 10 ft × 0.125 in. stainless steel packed with 20% Carbowax 20 M on Chromosorb W. Hydrogen was used as carrier gas, oven temperature 90 °C.

2,5-Dimethylcyclopentanone. Commercial mixture: ^{13}C NMR (15.08 MHz) δ 223.65 (C1-cis), 223.25 (C1-trans), 43.70 (C2 + C5 trans), 42.70 (C2 + C5 cis), 30.10 (C3 + C4 trans), 28.85 (C3 + C4 cis), 15.30 (CH_3 cis), 14.70 (CH_3 trans).

2,5-Dimethyl-2-cyclopenten-1-one (3 and 3′). 2,5-Dimethyl-2-cyclopenten-1-one was prepared from commercial 2,5-dimethylcyclopentanone by the method of V. A. Mironov et al.[6]

General Methods. The following two bioconversion methods were used: (a) Reduction was carried out with growing microorganisms according to the procedure described previously.[1] Reaction time was 5 or 10 days. (b) *B. sulfurescens* was grown under the same conditions as for (a) except for aeration rate which was 500 mL/min/L. After 24 h, the mycelium was filtered and thoroughly washed with water. The bioconversion was carried out by suspending 50 g of washed mycelium in 500 mL of 20 g/L aqueous glucose and then adding 100 mg of 2,5-dimethyl-2-cyclopenten-1-one. The mixture was left for 5 days at 20 °C with occasional agitation. Extraction of the reaction products was performed under the same conditions as those previously described.[1]

Microbiological Reduction of 2,5-Dimethyl-2-cyclopenten-1-one (3 and 3′). (a) Five-Day Reaction Time. The residue obtained after evaporation of the solvent contained 70% 2,5-dimethyl-2-cyclopenten-1-one and 30% 2,5-dimethylcyclopentanone. These were separated by chromatography on a silica gel column using 90/10 v/v pentane/ether as eluant.

***trans*-2,5-Dimethylcyclopentanone (5):** $[\alpha]^{25}_J$ −144.4° (*c* 0.075, $CHCl_3$); ^1H NMR (60 MHz) δ 1.12 (d, 6 H, 6 Hz), 2.6 to 0.9 (m, 6 H); ^{13}C NMR (15.08 MHz) δ 223.25 (C_1), 43.70 (C_2 + C_5), 30.10 (C_3 + C_4), 14.70 (CH_3).

2,5-Dimethyl-2-cyclopenten-1-one: $[\alpha]^{25}_J$ +30° (*c* 0.096, $CHCl_3$); ^1H NMR (60 MHz) δ 1.14 (d, 3 H, 6.75 Hz), 1.76 (m, 3 H), 1.9–2.55 (m, 2 H), 2.55–3.20 (m, 1 H), 7.25–7.45 (m, 1 H).

In the presence of tris[3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato]europium(III), the methyl signal at 1.14 ppm was split into two doublets.

(b) Ten-Day Reaction Time. The residue obtained contained 40% 2,5-dimethyl-2-cyclopenten-1-one and 60% 2,5-dimethylcyclopentanone (GPC). These were separated as above.

***cis*- and *trans*-2,5-Dimethylcyclopentanone:** $[\alpha]^{25}_J$ −71° (*c* 0.0675, $CHCl_3$); ^1H NMR (60 MHz) δ 1.05 and 1.08 (two doublets, J = 6 Hz, 6 H), 2.6–0.9 (m, 6 H).

2,5-Dimethyl-2-cyclopenten-1-one 3: $[\alpha]^{25}_J$ +65.2° (*c* 0.0854, $CHCl_3$); circular dichroism $(\theta)_{max}$ +1300 at 345 nm; ^1H NMR identical with that obtained above. In the presence of tris[3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato]europium-(III), the methyl signal at 1.14 ppm remained unaffected.

Oxidative Ozonolysis of 2,5-Dimethyl-2-cyclopenten-1-one 3′. A 0.275-g sample of 2,5-dimethyl-2-cyclopenten-1-one obtained by microbiological reduction (reaction time 10 days) was dissolved in 5 mL of CH_2Cl_2. The solution was placed in a bath kept at −30 °C and a stream of ozone-enriched oxygen was passed through until a solution of KI placed downstream of the reaction vessel turned dark brown. The solution was then allowed to return to ambient temperature while a stream of nitrogen was bubbled through it. Water (5 mL) was then added and the solution was shaken for 30 min before being refluxed for 40 min. The organic phase was decanted and evaporated down under reduced pressure. Acetone (3 mL) and 3 mL of 30% hydrogen peroxide were added to the residue. More acetone was added until a homogeneous solution was obtained. After stirring for 2 h at ambient temperature, sodium bicarbonate was added to bring the pH up to 8 and the solution was extracted with methylene dichloride, acidified with dilute HCl, and finally extracted several times with ether. The ether extracts were dried and evaporated to dryness. The residue was purified by preparative thin layer chromatography on silica gel using 9/1 v/v ethanol/concentrated ammonia as eluant. White crystals were obtained: mp 110–115 °C (lit.[7]

(6) Mironov, V. A.; Fadeeva, T. M.; Kuz'yants, G. M.; Akhrem, A. A. *Izv. Akad. Nauk. SSSR Ser* Khim **1966**, *12*, 2211.

(7) Rappoport, Z. "Handbook of Table for Organic Compounds Identification", 3rd ed.; CRC Press: Cleeveland, 1967; p 199.

mp 115 °C); $[\alpha]^{25}_J$ -7.5° (c 0.01, CH_3OH); lit.[5] $[\alpha]^{20}_D$ -9.2°; ^{13}C NMR (15.08 MHz, D_2O) δ 181.67, 177.77, 38.40, 36.90, 17.15.

Stereochemistry of the 2,5-Dimethylcyclopentanones. Commercial 2,5-dimethylcyclopentanone was reduced by $LiAlH_4$ by usual method.[9] 1,3-Dimethylcyclopentene was prepared by the method of Rei.[3] The hydroboration was carried out by the procedure of Brown et al.[8]

^1H NMR (250 MHz) (δ) follow.

cis,cis-2,5-Dimethylcyclopentanol: 3.71 (t, 3.7, 1-H), 2-CH_3 and 5-CH_3 are not visible (too small concentration).

trans,trans-2,5-Dimethylcyclopentanol: 3.00 (t, 3.0, 1-H), 1.03 (d, 6.5, 2-CH_3 and 5-CH_3).

cis,trans-2,5-Dimethylcyclopentanol: 3.57 (q, 4.5 and 6, 1-H), 0.97 (d, 7, 2-CH_3), 0.99 (d, 7, 5-CH_3).

Acknowledgment. We thank Mme M. Bon (Laboratoire des Composés Azotés Polyfonctionnels, Université P. Sabatier, Toulouse) for NMR spectra at 250 MHz and Dr. A. Collet (Collège de France) for CD curve.

Registry No. (±)-**3**, 93301-81-6; **3**, 66166-86-7; **3'**, 93184-37-3; **4**, 6672-39-5; **5**, 93301-79-2; **5'**, 93301-80-5; *cis,cis*-2,5-dimethylcyclopentanol, 65404-79-7; *trans,trans*-2,5-dimethylcyclopentanol, 63057-29-4; *cis,trans*-2,5-dimethylcyclopentanol, 65378-78-1.

(8) Brown, H. C.; Zweifel, C. *J. Am. Chem. Soc.* **1959**, *91*, 4106.
(9) Gannon, W. F.; House, H. O. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. 5, p 294.

Intramolecular Simmons-Smith Reaction and Other Synthetic Alternatives to Cyclopropanation of Dienic Diazoketones. Parallel Decomposition Pathways of a Sterically Congested Diazoketone and Its Vinylcyclopropane under Thermal, Photolytic, Acid-Catalyzed, and Radical-Release Conditions

Tomas Hudlicky*[1] and Brindaban C. Ranu

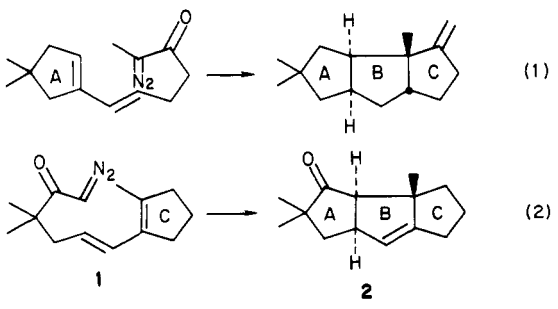
Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Saiyid M. Naqvi and Ana Srnak

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

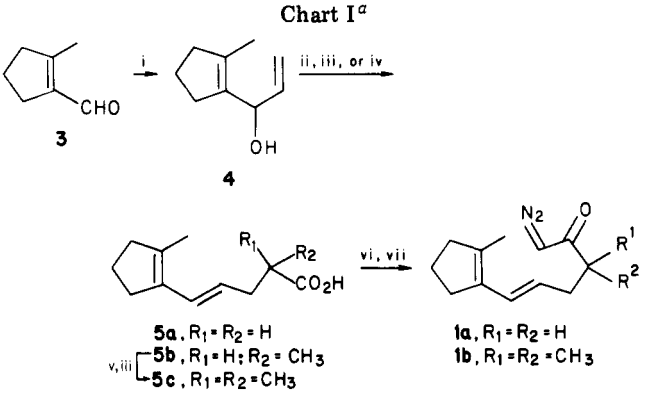
Received May 8, 1984

The linearly fused triquinane sesquiterpene hirsutene has been synthesized in our laboratory by the cyclopropanation and subsequent rearrangement of a dienic diazoketone using the [4 + 1] annulation strategy shown



(1) (a) Fellow of the Alfred P. Sloan Foundation, 1981-1985; Recepient of the Research Cancer Development Award, 1984-1989 (NIH-AI-00564). (b) Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, IL 60616.
(2) Hudlicky, T.; Kutchan, T. M.; Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6351.

Chart I[a]



[a] Reagents: (i) $CH_2CHMgBr/THF$; (ii) $RCH_2C(OEt)_3/H^+/\Delta$; (iii) KOH/H_2O; (iv) $(CH_3)_2CHCOCl/Et_3N$, then LDA/THF (-78 °C → 25 °C); (v) LDA, THF/MeI; (vi) $(COCl)_2$/benzene; (vii) CH_2N_2/Et_2O.

in eq 1.[2] We assumed that the reversal of the order of the ring-closing sequence of this methodology applied to the diazoketone **1** depicted in eq 2 would eventually lead to the tricyclic ketone **2** containing the necessary ring A oxygenation for eventual elaboration to coriolins.

During the past few years, we have developed a reliable method of intramolecular cyclopentene annulation via the cyclopropanation-cyclopentene rearrangement[3] or the acid-catalyzed decomposition[4] of dienic diazoketones. We were especially interested in testing the conditions of sequential radical release of dihalides such as **6** (Chart II) anticipating two consecutive carbon-carbon bond forming steps in direct parallel to the behavior of diazoketones under the conditions of acid catalysis. Since the literature contained examples of radical closures elicited by the interaction of olefins with halides using the $R_3SnH/AIBN$ system[5] or photolysis,[6] the extrapolation to a diene-geminal dihalide system seemed a logical one. The cyclopentene portion of diazoketone **1** and cyclopropane **7** contains unfavorable steric disposition, and since the rearrangements of *congested* vinylcyclopropanes to cyclopentenes tend to be sluggish,[8] we had hoped to test alternate methods of carbon-carbon bond formation on these substrates. In this paper we report on the parallel behavior of this diazoketone and its derivatives under a variety of conditions.

Diazoketones **1** were prepared as outlined in Chart I. The dimethylated dienic acid **5c** was prepared by the application of Claisen rearrangement of the enolate anion derived from the isobutyrate of alcohol **4** under conditions developed by Ireland[7] or by the methylation (LDA/MeI) of the ester of the monomethyl acid **5b** obtained by the rearrangement of **4** in refluxing triethyl orthopropionate

(3) For recent examples of this methodology, see: (a) Short, R. P.; Revol, J. M.; Ranu, B. C.; Hudlicky, T. *J. Org. Chem.* **1983**, *48*, 4453. (b) Govindan, S. V.; Hudlicky, T.; Koszyk, F. J. *J. Org. Chem.* **1983**, *48*, 3581. (c) Hudlicky, T.; Govindan, S. V.; Reddy, D. B.; Kulp, T.; Still, B.; Sheth, J. P. *J. Org. Chem.* **1983**, *48*, 3422. (d) Short, R. P.; Hudlicky, T. *J. Org. Chem.* **1982**, *47*, 1522. (e) Hudlicky, T.; Koszyk, F. J.; Dochwat, D.; Cantrell, G. L. *J. Org. Chem.* **1981**, *46*, 2911. (f) Hudlicky, T.; Kutchan, T. M.; Koszyk, F. J.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020.
(4) For application of this methodology to total synthesis of filifolone, see: Hudlicky, T.; Kutchan, T. M. *Tetrahedron Lett.* **1980**, *21*, 691.
(5) Hart, D. J.; Tsai, Y. M. *J. Am. Chem. Soc.* **1982**, *104*, 1430. Curran, D. P.; Rakiewicz, D. M. 187th National Meeting of the American Chemical Society St. Louis, MO, April 1984; Abstract 30.
(6) Kropp, P. J.; Pienta, N. J. *J. Org. Chem.* **1983**, *48*, 2084.
(7) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.
(8) Ketley, A. D.; Berlin, A. J.; Fischer, L. P. *J. Org. Chem.* **1966**, *31*, 2648. Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React. (N.Y.)* **1984**, *33*, 247.

0022-3263/85/1950-0123$01.50/0