the decomposition of spirohexane is controlled by the stage of the C_2H_4 elimination. The liquid-phase decompositions favor the ring contraction over the 1,2-hydrogen shift. The opposite situation is encountered under our conditions, where the methylenecyclopropane:1,3-butadiene ratio (Table I) ranges between 0.2 and 0.4. The observed invariance of this ratio at different laser outputs (different T_{eff}'s) can be consistent with very similar activation energies of both cyclobutylidene pathways.

The closeness in the E_a values for the decomposition of spiropentane and spirohexane seems to be supportive of the suggested reaction scheme in which the three-membered ring is cleaved first. Low yields of methylenecyclopentane at only higher temperatures can, however, indicate that this product arises via a higher energy process which can be initiated by a cleavage of the four-membered ring and consecutive migration and peripheral C_1–C_2 cleavage (see Scheme I).

The yield of ethylene is always higher than the total of yields of methylenecyclopropane and 1,3-butadiene. This indicates that 1,3-butadiene partly polymerizes. The 1,3-butadiene depletion upon the irradiation (8-W output) of 1,3-C_4H_6 (3.7 kPa)–SF_6 (1.9 kPa) mixture is, indeed, corroborating such a statement, since only traces of ethylene and a few percent of propene are formed after the expositions 7–10 times longer than those needed to drive the decomposition of spirohexane to completion.

Triplet carbenes can be detected via their conversion into long-lived iminoxyl radical by reaction with nitric oxide[17] or via their fast exothermic dimerization.[18,19] Our attempts to detect intermediary cyclobutylidene failed. No traces of dicyclobutyleneethylene were found among the reaction products. We also observed that spirohexane reacts with nitric oxide at ambient temperatures to produce liquid polymeric substance.

Surprising difference in behavior of intermediary diradicals postulated in the decomposition of both spiroalkanes might be associated with a higher stability of cyclobutylidene compared to cyclopropylidene. The examination of laser-driven decompositions of spiro[2.*n*]alkanes (*n* = 4–6) along with the study of deuterium labeled spiroalkanes are believed to bring more understanding to this problem.

Experimental Section

Experiments were carried out with a 1.4 cm long stainless-steel optical cell (internal diameter, 3.6 cm) equipped with one needle valve, two NaCl windows, and a side arm with a rubber septum. Mixtures of spirohexane (3.7 kPa) and sulfur hexafluoride (1.9 kPa) were prepared directly in the cell by using a standard vacuum line and were irradiated at measured intervals with slightly focused laser beam. A cw CO_2 laser[20] operated at the P(20) line of the 10.6-μm transition with the output covering the range of 4–8 W.

The extent of the spirohexane decomposition was followed by periodical analyses of gaseous mixtures on a Chrom-4 gas chromatograph (flame ionization, 3 m long column packed with alumina deactivated with silicon oil) coupled with a computing integrator (Model CI 100) and on a GC–MS spectrometer (Shimadzu Model QP 1000 equipped with a 3 m long column packed with 10% OV-101 silicone elastomer on Chromaton Super). For the identification of the decomposition products the GC–MS system was used. The products were identified by comparison with authentic samples (methylenecyclopentane (Fluka), methylenecyclopropane (laboratory stock), ethylene and 1,3-butadiene (both Chemapol)) both for the retention time and mass spectrum.

The decomposition progress was calculated as the ratio ethylene + methylenecyclopentane/ethylene + methylenecyclopropane + spirohexane. The amount of 1,3-butadiene formed prior to its polymerization was assessed as the difference between the amounts of ethylene and methylenecyclopropane. For the estimation of the effective mean temperatures and the Arrhenius parameters of the spirohexane decomposition, the technique for noninteracting systems[12] using isopropyl acetate as a chemical thermometer (marker) was used. The mixtures of spirohexane (3.7 kPa)–isopropyl acetate (2.9 kPa) and SF_6 (1.9 kPa) were irradiated with mildly focused laser beam with the output ranging from 4 to 8 W. Prior to the analysis of the reaction mixtures for the products of the spirohexane decomposition, the depletion of isopropyl acetate was monitored by recording the IR spectra at 1240 cm^{-1}. For this purpose a Perkin-Elmer Model 621 infrared spectrometer was used. The effective temperatures were calculated on the grounds of the Arrhenius parameters for isopropyl acetate decomposition taken from ref 21.

Sulfur hexafluoride (Fluka, purum) and isopropyl acetate (Lachema, purum) were commercial samples. Spirohexane[22] and nitric oxide[23] were prepared as reported earlier.

Acknowledgment. We thank Dr. E. B. Poztnych for the gift of the sample of spirohexane.

Registry No. Spirohexane, 157-45-9; ethylene, 74-85-1; 1,3-butadiene, 106-99-0; methylenecyclopropane, 6142-73-0; methylenecyclopentane, 1528-30-9.

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Simple One-Step Synthesis of 1,4-Diketones: A New Approach to Dihydrojasmone

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Many biologically active natural products are characterized by a cyclopentenone moiety as a main structural feature, hence an increasing interest exists in developing new synthetic routes to substituted cyclopentenones.[1] In this context 1,4-diketones represent the most widely employed intermediates and efforts to find new efficient syntheses of these compounds are continuing.[2,3]

Since triorganoalanes (AlR_3 or $AlR_3{\cdot}OEt_2$) react with α-nitro olefins **1** to give the corresponding saturated nitro compounds **2** in high yields (Scheme I),[4] and **2** can be easily converted into carbonyl derivatives[5] **3**, the reaction of AlR_3 or $AlR_3{\cdot}OEt_2$ with a suitable nitro olefin such as **4** could represent a useful approach for the preparation of unsymmetrical 1,4-diketones **6** "via" the saturated nitrocompound **5** (Scheme II).

Results and Discussion

The reaction of 5-hexen-2-one (**7**) with $HgCl_2/NaNO_2$[6] followed by acid-catalyzed (TsOH) ketalization with

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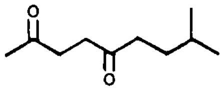
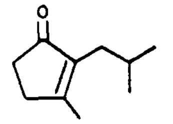
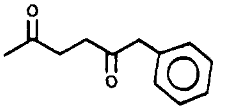
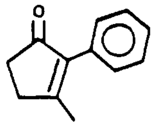
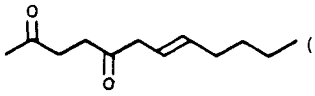
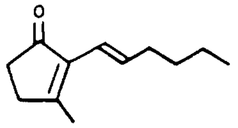
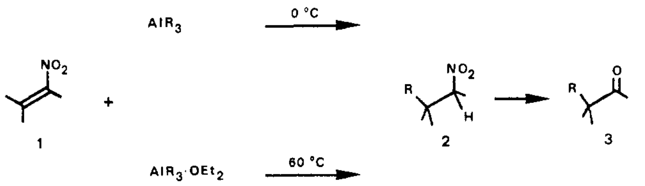
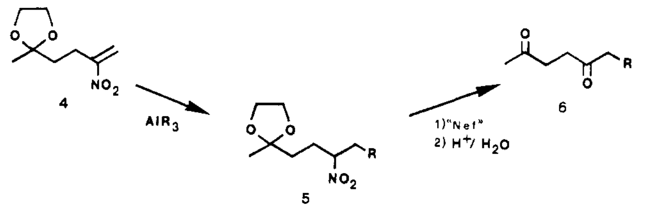
Table I. Recovered Yields of Diketones 6 and Cyclopentenones 10

AlR_3	1,4-diketone (%)		cyclopentenone (%)	
$AlBu^i_3$	 6a	(91)	 10a	(93)
$AlPh_3 \cdot OEt_2$	 6b	(93)	 10b	(94)
Bu^i_2Al 	 6c	(96)	 10c	(88)

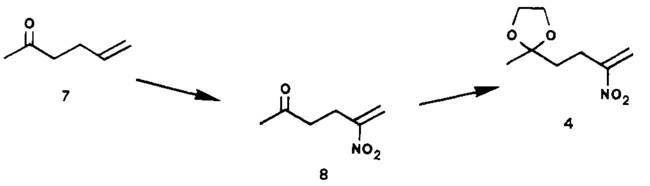
Scheme I



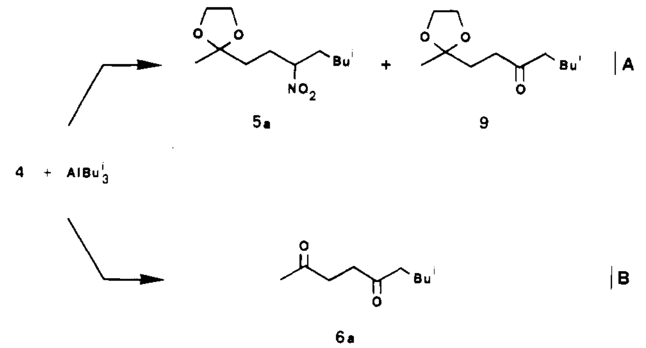
Scheme II



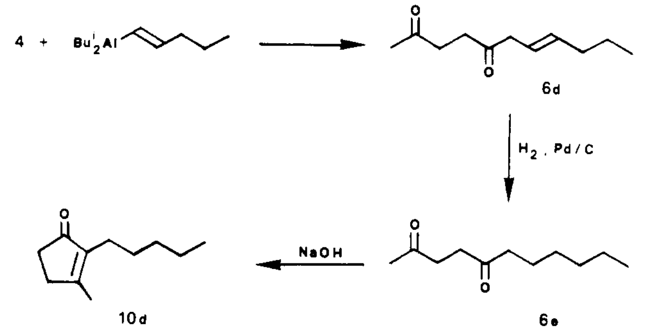
Scheme III



Scheme IV



Scheme V



ethylene glycol of the intermediate **8** (Scheme III) gave **4** (40%).

Since in a preliminary test the hydrolysis (0.2 N HCl[4]) of the reaction mixture of **4** and Al-*i*-Bu_3 furnished, in addition to **5a**, appreciable quantities of **9** (Scheme IV, A), in subsequent runs hydrolysis conditions were employed (3.0 N HCl, see Experimental Section) so as to effect both the Nef reaction of the intermediate nitronate and the deblocking of the acetalic protective group (Scheme IV, B). In this way, **6a** was recovered with a nearly quantitative yield (Table I).

As nitro olefins successfully react with many aluminum derivatives in addition to triisobutylaluminum,[4] **4** was treated also with triphenylaluminum etherate and with diisobutyl-1-hexenylaluminum. Under the same experimental conditions (3.0 N HCl) the corresponding diketones **6b** and **6c** were isolated with a very good yield (Table I). All the obtained compounds **6a–c** were successively cyclized to the cyclopentenones **10a–c** through reaction with NaOH[7] (Table I).

In accordance with our previous results[4b] the reaction of **4** with diisobutyl-1-hexenylaluminum proceeds with high

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chemoselectivity (hexenyl/isobutyl transfer ≈ 95/5) and with retention of the double bond configuration. Moreover, considering that either mono-, di-, and trisubstituted and functionalized dialkylalkenylalanes can be obtained "via" hydroalumination of the corresponding alkynes,[8] the use of these reagents allows the preparation of a wide number of 2-substituted cyclopentenones.

The remarkable versatility of the reaction of AlR_3 with **4** is well illustrated by the synthesis of the dihydrojasmone **10d**. Following the procedure described above for the preparation of **10a**, the synthesis of **10d** could have been effected starting from **4** and tri-*n*-pentylaluminum; however, since the preparation of this organometallic reactive proves troublesome and time consuming,[9] **10d** was obtained according to the alternative procedure outlined in Scheme V).

Starting from **4** and diisobutyl-1-pentenylaluminum, easily prepared "in situ" from 1-pentyne and DIBAL, the crude β,γ-unsaturated diketone **6d** was obtained and subsequently hydrogenated to give the undecane-2,5-dione (**6e**) (85% overall yield); the cyclization of this latter compound yielded (90%) the dihydrojasmone **10d**.

Experimental Section

Materials and Instrumentation. All the reactions of **4** with triorganoalanes were performed in dry apparatus under argon. Triisobutylaluminum (Fluka A.G. Co.) was distilled under argon and stored in sealed capillary glass vials in weighed amounts. Triphenylaluminum etherate was prepared according to the reported procedure.[10] Diisobutyl-1-hexenylaluminum and diisobutyl-1-pentenylaluminum were obtained "in situ" from 1-hexyne and 1-pentyne (Aldrich) respectively and diisobutylaluminum hydride (Aldrich, 1.0 M hexane solution) as previously reported.[9] Hexane and benzene were purified by means of standard methods and redistilled from $LiAlH_4$ before use.

GLC analyses were performed on a Perkin-Elmer F-30 instrument (SE-30, 2 m × 0.29 cm columns) equipped with flame ionization detectors and N_2 as carrier gas.

IR spectra (ν, cm^{-1}) were obtained on a Perkin-Elmer FT IR 1750 spectrophotometer using liquid films (20 μm).

^1H NMR spectra were recorded on a Varian T-60 (60 MHz) and, unless otherwise stated, on a Varian VXR-300 (300 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian VXR-300 (75.2 MHz) spectrometer. All NMR data were obtained in $CDCl_3$ solution and chemical shifts are reported as δ values referred to Me_4Si (TMS) as internal reference.

Mass spectra [m/e, (relative intensity)] were taken on a VG-Analytical 7070 GC-MS instrument.

All the compounds described in this paper gave satisfactory elemental analyses (0.2%).

Analytical TLC were performed on silica gel (Merck, SiO_2 60); all the crude products were purified by means of flash chromatography on a silica gel column (Merck, 230–400 mesh), eluent, ethyl acetate/light petroleum (20/80).

4-(2-Methyl-1,3-dioxolan-2-yl)-2-nitrobutene (4). 5-Hexen-2-one (20 g, 204 mmol; Aldrich) was reacted with $HgCl_2/NaNO_2$ as reported.[6] The resulting gummy precipitate was decanted, repeatedly washed with water, then dissolved in CH_2Cl_2, and treated with NEt_3.[6] The obtained crude **8** (16 g) was dissolved in benzene (500 mL) together with 20 g of ethylene glycol and 0.1 g of *p*-toluenesulfonic acid and refluxed for 6 h with a water separator. After the mixture was cooled, ether (300 mL) was added and the mixture washed subsequently with 5% $NaHCO_3$ solution, water, and brine; the organic phase was then dried with Na_2SO_4 and evaporated in vacuo. The residue was purified through flash chromatography (ethyl acetate/petroleum ether, 40/60) to give 15.2 g of pure **4**: IR 1527, 1346; ^1H NMR (60 MHz) 6.37 (d, J = 1.5 Hz, 1), 5.53 (s, 1), 3.90 (s, 4), 2.73 (t, J = 7 Hz, 2), 1.95 (t, J = 7 Hz, 2), 1.33 (s, 3).

Preparation of 6a–d. General Procedure. To a cooled (−15 °C) solution of 13 mmol of the triorganoalane reagent in hexane[11] (40 mL) was added dropwise 2 g (10.7 mmol) of the nitro olefin **4** in 20 mL of hexane/benzene (1/1, v/v) mixture. The resulting solution was then stirred at room temperature[12] for 30 min and then poured into a flask containing 250 mL of a cold (ca. −10 °C) 3.0 N HCl solution saturated with NaCl and ether (50 mL). The mixture was vigorously stirred at room temperature for 2–3 h, then the aqueous layer was further extracted with 3 × 50 mL of ether, and the collected organic phases were dried on Na_2SO_4. The solvent was removed at reduced pressure, and the crude residue was purified by means of flash chromatography (yields are reported in Table I).

Preparation of 6e. The product **6d**, arising from diisobutyl-1-pentenylaluminum, was hydrogenated in ethyl acetate at atmospheric pressure on 10% Pd/C (50 mg/mmol). When the required amount of H_2 was consumed the catalyst was filtered off, and the solvent was removed at reduced pressure (20 mmHg). The obtained crude undecane-2,5-dione (**6e**) was then purified by flash chromatography.

The recovered products **6a–e** showed the following.

6a ($C_{10}H_{18}O_2$): MS, 127 (2), 114 (23), 99 (41), 81 (18), 71 (49), 43 (100); IR 1715; ^1H NMR (60 MHz) 2.66 (s, 4), 2.43 (t, J = 7 Hz, 2), 2.18 (s, 3), 1.65–1.20 (m, 3), 0.86 (d, J = 5 Hz, 6); ^{13}C NMR 209.08, 206.59, 40.69, 36.78, 35.89, 32.52, 29.78, 27.56, 22.21 (2 C).

6b ($C_{12}H_{14}O_2$): MS, 190 (1, M^+), 99 (100), 91 (31), 71 (13), 43 (62); IR 1710, 1603, 1497, 789, 701; ^1H NMR (60 MHz) 7.27–7.03 (m, 5), 3.63 (s, 2), 2.60 (s, 4), 2.05 (s, 3); ^{13}C NMR 206.32, 206.17, 133.89, 129.09, 128.25, 126.56, 49.64, 36.85, 35.33, 29.54.

6c ($C_{12}H_{20}O_2$): MS, 196 (1, M^+), 99 (100), 71 (11), 55 (12), 43 (45); IR 1715, 1638, 972; ^1H NMR 5.66–5.50 (m, 2), 3.14 (d, J = 5.3 Hz, 2), 2.69 (s, 4), 2.18 (s, 3), 2.06–2.01 (m, 2), 1.40–1.27 (m, 4), 0.89 (t, J = 6.9 Hz, 3); ^{13}C NMR 207.07, 206.25, 134.84, 121.36, 46.56, 36.75, 35.39, 32.16, 31.27, 29.76, 22.11, 13.86.

6d ($C_{11}H_{18}O_2$): MS, 182 (1, M^+), 99 (100), 71 (13), 55 (8), 43 (55).

6e ($C_{11}H_{20}O_2$): MS, 184 (2, M^+), 141 (6), 127 (8), 114 (85), 99 (83), 85 (19), 71 (94), 57 (13), 43 (100); IR 1713; ^1H NMR 2.73–2.64 (m, 4), 2.45 (t, J = 7.4 Hz, 2), 2.18 (s, 3), 1.63–1.51 (m, 2), 1.34–1.21 (m, 6), 0.88 (t, J = 6.5 Hz, 3); ^{13}C NMR 209.05, 206.66, 42.75, 36.84, 35.99, 31.55, 29.85, 28.83, 23.79, 22.44, 13.99.

Preparation of 10a–d. General Procedure. Following the previously reported procedure,[7] 14 mL of 0.5 N NaOH solution were added to a solution of 8 mmol of the diketone in ethyl alcool (15 mL) and refluxed for 6 h. The cooled mixture was then diluted with water (100 mL) and extracted with ether (3 × 50 mL). The extracts were washed with brine and dried with Na_2SO_4; evaporation of the solvent gave the crude **10a–d**, which were then purified through flash chromatography (yields are reported in Table I).

The recovered products showed the following.

10a ($C_{10}H_{16}O$): MS, 152 (46, M^+), 137 (44), 110 (100), 95 (20), 81 (13), 67 (24); IR 1699, 1645, 1385; ^1H NMR 2.55–2.49 (m, 2), 2.38–2.33 (m, 2), 2.05 (s, 3), 2.04 (d, J = 5.0 Hz, 2), 1.86–1.72 (m, 1), 0.85 (d, J = 6.6 Hz, 6); ^{13}C NMR 208.95, 170.08, 139.36, 34.14, 32.01, 31.45, 27.65, 22.52 (2 C), 17.46.

10b ($C_{12}H_{12}O$): MS, 172 (100, M^+), 157 (6), 143 (13), 129 (79), 115 (37), 91 (8); IR 1696, 1637, 1599, 1495, 1380, 1133, 763, 701; ^1H NMR (60 MHz) 7.33–7.20 (m, 5), 2.75–2.40 (m, 4), 2.13 (s, 3); ^{13}C NMR 206.87, 171.22, 139.96, 131.52, 128.78, 127.89, 127.23, 34.73, 31.70, 18.23.

10c ($C_{12}H_{18}O$): MS, 178 (96, M^+), 163 (27), 149 (75), 135 (66), 122 (83), 110 (100), 91 (76), 79 (94); IR 1700, 1649, 1603, 1384, 976; ^1H NMR 6.70 (dt, J = 15.8, 7.0 Hz, 1), 6.06 (d, J = 15.8 Hz, 1), 2.54–2.48 (m, 2), 2.40–2.34 (m, 2), 2.18–2.08 (m, 2), 2.12 (s, 3), 1.46–1.26 (m, 4), 0.90 (t, J = 7.0 Hz, 3); ^{13}C NMR 207. 73, 158.83, 135.59, 134.95, 118.36, 34.70, 33.65, 31.38, 31.33, 22.26, 17.46, 13.91.

10d ($C_{11}H_{18}O$): MS, 166 (14, M^+), 151 (47), 137 (26), 123 (21), 110 (100), 95 (13), 81 (16), 67 (20); IR 1699, 1650, 1386; ^1H NMR

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[11] Triphenylaluminum etherate is only slight soluble so a mixture of benzene/hexane (1/1, v/v) was employed as solvent.

[12] In the case of triphenylaluminum etherate a reaction temperature of 60 °C is required to obtain a complete conversion of **4** in the same time.

J. Org. Chem. 1988, 53, 2617-2620

2.58–2.52 (m, 2), 2.44–2.38 (m, 2), 2.16 (t, J = 7.4 Hz, 2), 2.06 (s, 3), 1.48–1.25 (m, 6), 0.87 (t, J = 6.9 Hz, 3); ^{13}C NMR 209.04, 169.47, 140.41, 34.26, 31.75, 31.44, 28.03, 22.95, 22.47, 17.17, 13.99.

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Registry No. 4, 113810-80-3; **6a**, 60721-34-8; **6b**, 32776-14-0; **6c**, 113810-81-4; **6d**, 113810-82-5; **6e**, 7018-92-0; **8**, 113810-79-0; **10a**, 72474-00-1; **10b**, 50397-92-7; **10c**, 113810-83-6; **10d**, 1128-08-1; AlBu-i_3, 100-99-2; $AlPh_3{\cdot}OEt_2$, 58482-37-4; $i\text{-}Bu_2AlCH{=}CH(CH_2)_3CH_3$, 26076-75-5; $i\text{-}Bu_2AlCH{=}CH(CH_2)_2CH_3$, 83021-61-8; 5-hexene-2-one, 109-49-9.

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exo,endo-3-((Dimethylamino)methyl)-*d*-camphor: *d*-Camphor Mannich Products

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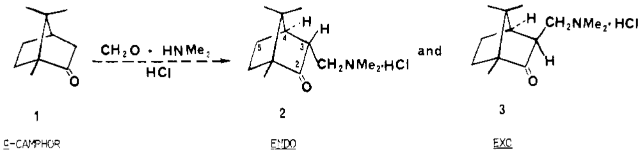
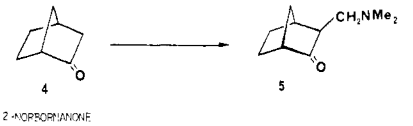
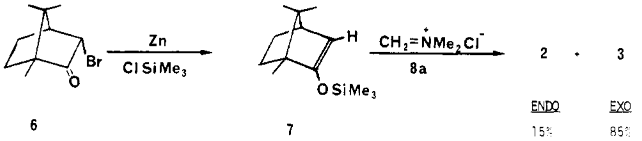
Of the two 3-((dimethylamino)methyl) Mannich products from *d*-camphor (**1**), the endo product (**2**) has been described by Hine and co-workers.[3,4] Several other reports[5] on reactions to give these products fail to consider the stereochemistry of the reaction and do not adequately characterize the product or product mixtures. It appears, however, that the exo compound **3** has not been previously described. Here we consider the synthesis and properties of this exo diastereomer **3**, its configurational assignment, and its equilibration with the endo isomer via the enolate anion.

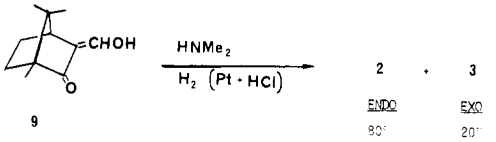
Although the classical conditions for the Mannich condensation[6] ($CH_2O + HNMe_2{\cdot}HCl$) work well for the unsubstituted 2-norbornanone[7] (**4**) to give the less hindered exo isomer **5**, these conditions are not applicable to the more hindered camphor. *exo*-3-((Dimethylamino)methyl)-*d*-camphor (**3**) has now been prepared by the reaction of dimethylmethyleneammonium chloride[8] (**8a**) or dimethylmethyleneammonium iodide (**8b**, Eschenmoser's salt[9]) in acetonitrile solvent with the trimethylsilyl enol ether[10] (**7**) of *d*-camphor, which was prepared from *endo*-(+)-3-bromo-*d*-camphor (**6** → **7**). The crude product from the reaction of **7** with **8a** ($CH_2{=}NMe_2{}^+Cl^-$) is a mixture of endo and exo isomers (**2** and **3**) in approximately 15:85 ratio (as determined from the well-separated 400-MHz NMR signals of the H-3 and H-4 protons of the exo and endo isomers as either the salts or free bases; cf. Table I). Crystallization gave the purified exo isomer (mp 219–220 °C) in an isolated yield of 66%. The same reaction using dimethylmethyleneammonium iodide (**8b**, Eschenmoser's salt) gave an 86% yield of crude *exo*-hydroiodide (**3**·HI) that contained less than 3% of the endo isomer.







The procedure used by Hine and co-workers,[3,4,5b] in which 3-(hydroxymethylene)-*d*-camphor[11] (**9**) was treated with dimethylamine followed by hydrogenation in the presence of platinum oxide and hydrochloric acid,[12] gave a 90% yield of a 4:1 mixture of isomers (**2**·HCl/**3**·HCl). Repeated crystallizations of these hydrochlorides gave a single product, mp 208–209 °C. Hine and co-workers assigned the endo configuration, **2**, to this product based on its proton NMR spectra. We have verified this assignment and have made the exo assignment to the other isomer based on decoupling studies on the hydrochlorides and free bases of both **2** and **3** as given in Table I. The rigid camphor system permits the application of the Karplus equation[13a] to these isomers with confidence. The dihedral angle between H-3 and H-4 in the exo isomer is close to 90° and no appreciable coupling of these protons would be expected. This is observed for the major isomer prepared from the silyl enol ether, **7**, and the minor isomer obtained from the hydroxymethylene derivative **9**. The corresponding angle between H-3 and H-4 in the endo isomer is about 30° for which a coupling constant of 3–4 Hz would be expected, as is observed for the major isomer obtained from **9**. Furthermore, as expected, a long-range coupling between H-3 and H-5β was observed in the endo isomer (as the base **2** or salt **2**·HCl or **2**·HI) by virtue of the "W" configuration[14] of these protons. No such coupling was observed for the major isomer (**3**) prepared from the silyl enol ether.



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