115. An Efficient Approach to Patchouli Alcohol Analogues

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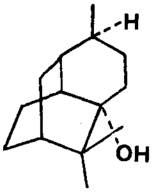
Summary

A short approach to the tricyclo [5.3.1.$0^{3,8}$] undecane derivatives **1, 10, 11** and **12** and to the tricyclo [4.3.1.$0^{3,7}$] decane derivative **2**, starting from industrially available intermediates, is described. Of the compounds **1**, **10**, **11**, and **12**, which possess the ring system of patchouli alcohol, **12** also exhibits a woody, patchouli-like note. The ^{1}H-NMR.-spectra of **1**, **2** and **8–12** are discussed.

Continuing our efforts toward a facile access to patchouli alcohol [1] and its analogues we realized that, in view of the low price of natural patchouli oil (50–70 Sfr/kg), only an extremely short synthesis from the cheapest starting materials would be competitive. If a highly organized compound, such as patchouli alcohol, has to be made by a minimum of operations, then the search for synthetic methods allowing the regio- and stereoselective formation of more than one bond per operation becomes a main objective in synthetic planning. Examples of such methods are *e.g.* the *Diels-Alder* reaction, biogenetic-type polyene cyclizations [2], and our 'methylating cyclization of oxo-enones' [3]. Although intramolecular *Diels-Alder* reactions [4] and biogenetic-type cyclizations may lead in one operation, and with remarkable regio- and stereoselectivity, to complex molecules, the corresponding precursors are often accessible only with difficulty. Their lengthy preparation not only diminishes the beauty of the syntheses, but moreover, makes them unattractive for industrial application.



patchouli alcohol

In the present work we report two examples of a one-pot cycloaddition-rearrangement process leading from cheap starting materials to the tricyclo[5.3.1.$0^{3,8}$]-undec-9-ene or tricyclo[4.3.1.$0^{3,7}$]dec-8-ene skeleton. Some of the compounds prepared in this context not only resemble patchouli alcohol from a structural point of view, but also exhibit similar olfactive properties.

Condensation of the methylheptenones **3** or **4** with cyclopentadiene (**5**) [5] using sodium ethylate in ethanol gave the fulvenes **6** or **7** in good yield. Epoxidation of **6** and **7** with 35% aqueous hydrogen peroxide in methanolic KOH[1]) afforded the epoxide-dimers **8** and **9** respectively. The monomeric epoxides were never detected, even after rapid work-up and immediate NMR. analysis of the reaction mixture. Purification of the crude dimers **8** or **9** was, due to their high molecular weight, only possible by bulb distillation: column chromatography on silica gel, using wet ether/hexane, destroyed the epoxides completely. For these reasons it was fortunate that the crude products could be used directly for the next step. When a degassed solution of **8** and **9** in anhydrous toluene was heated in the presence of a little hydroquinone for 2 h at 270–280° in a sealed glass tube (or in an Inox autoclave) the tricyclic ketones **1** (71% yield) and **2** (55% yield) were obtained. By running the same reactions at lower temperature or during shorter reaction times, only starting materials and end products, but no intermediates, could be detected.

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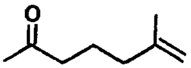

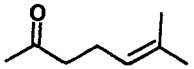

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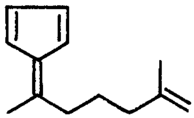

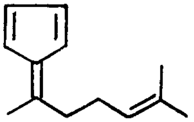

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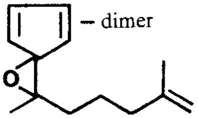

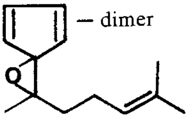

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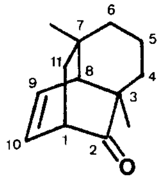

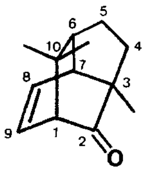

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Pursuing the perfumistic aim of this work, namely to make simple, patchouli-like structures, the ketone **1** was further transformed into the alcohols **10**, **11** and **12**. When ketone **1** was reduced with lithium aluminium hydride in ether (4 h under reflux) the *exo* alcohol was isolated exclusively, due to the preferential attack of the hydride from the less hindered side. Reduction of **1** with sodium in ethanol, on the other hand, gave a 1:1 mixture of the two epimeric alcohols **10** and **11**. Reaction of ketone **1** with methyllithium in ether (5 h under reflux) yielded the *exo* alcohol **12**.

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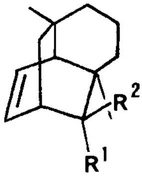
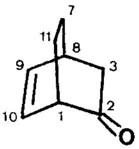
[1]) By analogy with the epoxidation of 6,6-dimethylfulvene [6].

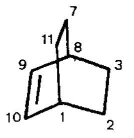
Of the compounds prepared in this work both alcohols **10** and **12** exhibit a woody, leathery note, **12** being stronger and also having a patchouli-type odour. Alcohol **11** displays a much weaker odour of the less desirable borneol-camphor type.



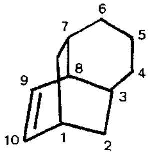
$R^1 = H$ $R^2 = OH$: **10**
$R^1 = OH$, $R^2 = H$: **11**
$R^1 = CH_3$, $R^2 = OH$: **12**



13²)



14²)



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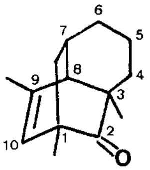

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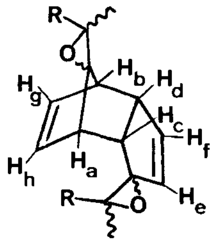
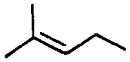
Structure assignment by NMR. - *The cyclopentadiene dimers* **8** *and* **9**. - 90-MHz-^{1}H-NMR. spectra, with the aid of double resonance decoupling, established the dimeric structures **8** and **9**. While the *endo* orientation of the two cyclo-adducts is secured by the H_a-H_c or the H_b-H_d coupling constants ($J_{a,c} = J_{b,d} = 4$ Hz) by analogy with the values of dicyclopentadiene [7], the relative configuration at the four chiral epoxide carbonatoms remains unknown (for the attribution of the chemical shifts and the coupling constants, see *Table 1*).



R=  :**8**

R=  :**9**

The tricyclo[5.3.1.0^{3,8}]undecanes **1**, **10**, **11** *and* **12**. - The present structure assignments are based on (1) chemical shifts, (2) multiplicities, and (3) coupling constants, making extensive use of double irradiation technique (see *Table 2* and Experimental Part). To further support the structures and to understand better some noteworthy features of the tricyclo[5.3.1.0^{3,8}]undecane derivatives, the known compounds **13**²) [9], **14**²) [10], **15** [11], and **16** [8a, d] have also been included in *Table 2* and in the discussion. Firstly, homoconjugation between the carbonyl group and the double bond, a well established phenomenon in the related bicyclo[2.2.2]-

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²) To simplify *Table 2* and the discussion, the carbonatoms in the bicyclo[2.2.2]octanes **13** and **14** are numbered, despite their names, as in the tricyclo[5.3.1.0^{3,8}]undecanes **10**-**12** and **16**.

Table 1. *90-MHz-^1H-NMR. spectra ($CDCl_3$) of* **8** *and* **9**

a) Chemical shifts (δ) in ppm downfield from TMS

	8	**9**
H_a	2.45	2.45
H_b	2.65	2.66
H_c	3.05	3.05
H_d	3.58	3.59
H_e	5.52	5.52
H_f } H_g }	5.93	5.95
H_h	6.27	6.27
$=CH_2$	4.71	
$=C-CH_3$	1.71	1.6/1.69
$=CH-$		5.10
tert CH_3	1.30	1.30
(minor)	1.36	1.37

b) Coupling constants J (Hz)

	8	**9**
$J_{a,c}$	4	4
$J_{a,h}$	4	4
$J_{a,g}$	~2	
$J_{b,d}$	4	4
$J_{b,g}$	4	4
$J_{b,h}$	2	
$J_{c,d}$	8	8
$J_{d,f}$	2	2
$J_{d,e}$	1.6	2
$J_{e,f}$	6	6
$J_{g,h}$	6	6

Table 2. *^1H-NMR. spectra ($CDCl_3$) of* **1** *and* **10–16**

a) Chemical shifts (δ) in ppm downfield from TMS

	H_1	H_2	H_8	H_9	H_{10}	H_{11}	$H_3C-C(1)$	$H_3C-C(3)$	$H_3C-C(7)$	$H_3C-C(9)$	$H_3C-C(2)$	ref./ remarks
1	3.02		2.08	6.51	6.15	1.72		0.97	0.97			[b])
16			2.07		5.43		1.13		0.94	1.85		[8a, d][b])[d])
13	3.15		3.01	6.51	6.22							[9][b])[d])
14	2.49		2.49	6.25	6.25	1.27 1.5						[10][a])
15	2.4		1.96	6.27	6.16	1.17						[11][c])
10	2.45	3.36	1.54	6.21	6.08			0.84	0.81			[b])
11	2.63	3.61	1.58	6.46	6.1	0.96 1.44		0.77	0.82			[b])
12	2.23			6.26	6.13			0.82	0.82		1.15	[b])

b) Coupling constants J (Hz)

	$J_{1,2}$	$J_{1,9}$	$J_{1,10}$	$J_{1,11A}$	$J_{1,11B}$	$J_{8,9}$	$J_{8,10}$	$J_{9,10}$	$J_{11,11}$	ref./ remarks
1		1.2	6.4	2.8	2.8	6.4	1.8	8	14	[b])
13		1.2	5.6			5.1	1.6	8.1		[9][b])[d])
14		1.5	6.5	1.6		6.5	1.5	8.8		[10][a])
15		1.4	5.6			5.8	1.2	8.2		[11][c])
10	2.4	1.6	6.5	2.4	2.2	6.5	1.6	8.1		[b])
11	2.8	1.0	6.0	4	4	6	1	8	13	[b])

[a]) 60 MHz spectrum.

[b]) 90 MHz spectrum.

[c]) 300 MHz spectrum.

[d]) Values measured by us using a sample prepared according to the reference quoted.

octenone **13** [9], makes H–C(10) resonate at a higher field than H–C(9). However, in the corresponding alcohols **10** and **11**, as well as in the bicyclo[2.2.2]octene **14** and tricyclo[$5.3.1.0^{3,8}$]undec-9-ene (**15**), the olefinic hydrogens have similar chemical shifts. Secondly, the carbonyl group in **1** not only imposes a $\Delta\delta \cong 0.6$ ppm downfield shift upon the hydrogen at C(1) (being at $\delta = 3.02$ ppm in **1**, but at $\delta = 2.4$ ppm in **15**), but, surprisingly, also upon the bridgehead hydrogen at C(8). The same deshielding effect by the carbonyl group is observed in the bicyclo[2.2.2]-octenone **13** (H–C(8) at $\delta = 3.01$ ppm) with respect to bicyclo[2.2.2]octene **14** (H–C(8) at $\delta = 2.49$ ppm).

A third feature typical of the 3,7-dimethyltricyclo[$5.3.1.0^{3,8}$]undecane skeleton is the strong shielding effect upon the bridgehead hydrogen atom at C(8) ($\Delta\delta = -1$ ppm), probably by the trimethylene bridge from C(3) to C(7) (*cf.* tricyclo-[$5.3.1.0^{3,8}$]undec-9-ene (**15**), $\delta_{H-C(1)} = 2.4$ and $\delta_{H-C(8)} = 1.96$ ppm) and by the two methyl groups at C(3) and C(7)[3]). This shielding with respect to bicyclo[2.2.2]octene **14** is directly recognized in the compounds **10**, **11** and **12**, whereas in the ketone **1** a $\Delta\delta = 1$ ppm upfield shift is partially compensated by the aforementioned carbonyl downfield shift of $\Delta\delta \cong -0.6$ ppm. A further peculiarity is the pronounced chemical shift difference between the two olefinic hydrogen atoms in the *endo* alcohol **11** with respect to the two *exo* alcohols **10** and **12**. This phenomenon is also encountered in the two epimeric bicyclo[2.2.2]oct-5-en-2-ols [11]. It is quite possible that in alcohol **11** the hydrogen atom at C(9) feels a homoconjugation effect between the *endo* C–O bond and the C(9)–C(10) double bond. The hydrogen atom at C(2) is also significant for the stereochemical assignment of the two epimers: H–C(2) in the *exo* alcohol occurs at a higher field than in the *endo* alcohol ($\Delta\delta = 0.25$ ppm). This is again in agreement with the observed values in *endo* and *exo* bicyclo[2.2.2]oct-5-en-2-ol [13]. The stereochemical assignment of the *tert.* alcohol **12** is based on the close analogy of its NMR. spectrum with that of the *sec. endo* alcohol **10**. Of the coupling constants measured (see *Table 2b*) all values are within expectation (*cf. e.g.* [9] and [10]). The vicinal couplings between H–C(1) and H–C(2) in the two epimers **10** and **11** were nearly identical and could therefore not be used in support of the configurational assignment.

3,10,10-Trimethyltricyclo[$4.3.1.0^{3,7}$]dec-8-en-2-one (**2**). - The olefinic hydrogen atoms at C(8) ($\delta = 6.31$ ppm) and C(9) ($\delta = 6.12$ ppm) are, as in ketone **1**, almost $\delta\Delta = 0.2$ ppm apart from each other, reflecting the homoconjugative influence of the carbonyl group. The bridgehead hydrogen atoms, H–C(1) and H–C(7), have identical chemical shifts ($\delta = 2.65$ ppm), and the multiplicities of these two signals, which are important for the structure proof, were made visible by the addition of $Eu(fod)_3$ shift agent (see Experimental Part).

Apart from our approach, an elegant construction of the tricyclo[$5.3.1.0^{3,8}$]undecane skeleton from readily accessible, cheap starting material and *via* a one-pot sequence of a *Claisen* rearrangement and an intramolecular *Diels-Alder* reaction has been achieved by *Greuter, Fráter and Schmid* [8].

We wish to express our gratitude to Dr. *G. Ohloff* for valuable discussions and helpful advice.

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[3]) Shielding of an axial hydrogenatom in a six-membered ring by two vicinal, equatorial methyl groups is reported to be $\Delta\delta = -2 \times (0.3 \ldots 0.5 \text{ ppm}) = -0.6 \ldots -1$ ppm [12].

Experimental Part

(with the collaboration of *Chantal Chappuis*)

General remarks. - Column chromatography was carried out on *Merck* silica gel (0.05-0.2 mm). Melting points are not corrected. For bulb distillation a *Büchi* apparatus, type KR-3, with external temperature measurement was used. The 90-MHz-^{1}H-NMR. spectra were measured on a *Bruker* instrument, type HX 90/15″, using $CHCl_3$ as solvent and TMS ($\delta = 0.00$ ppm) as internal standard; abbreviations: s = singulet, d = doublet, t = triplet, q = quartet, m = multiplet, J = spin-spin coupling constant (Hz). IR. spectra: *Perkin Elmer* 125, typical max in cm^{-1}. Mass spectra (MS.): *Atlas* CH_4, inlet temp. ~150°, electron energy ~70 eV; fragment ions (highest peak of each group) are given as *m/e* with rel. peak intensity in % of the most abundant peak (base peak). Other abbreviations: RT. = room temperature, anh. anhydrous.

Fulvene **6**. 6-Methyl-6-heptene-2-one[4]) (63 g; 0.5 mol), freshly distilled cyclopentadiene (44 g; 0.66 mol) [5] and anh. ethanol (100 ml) were treated with a solution of sodium (11.5 g; 0.5 mol) in anh. ethanol (200 ml) at 0-5° for 1 h (slightly exothermic reaction). After the reaction mixture had been stirred for 4 h at RT., the solvent was removed under reduced pressure. The concentrate was poured onto a mixture of acetic acid (32 ml) and crushed ice and extracted with ether.

The ethereal phase was washed (brine), dried ($MgSO_4$) and distilled at 50-64°/0.07 Torr to give 64.1 g (73%) of pure fulvene **6**. - IR. (neat): 3100, 3065, 1635, 1612, 1365, 882, 760 cm^{-1}. - ^{1}H-NMR. (60 MHz): 1.7 (*s* with long range fine splitting, 3H); 2.18 (*s*, 3H); 2.5 (*t*, J = 7 Hz, 2H); 4.7 (br. *s*, 2H); 6.43 (*s*, 4H) ppm. - MS.: 174 (M^+, 31), 159 (9), 145 (14), 131 (16), 117 (40), 106 (64), 91 (100), 77 (24), 65 (13), 51 (9), 41 (37), 27 (14).

Fulvene **7**. Using the reaction conditions described in the previous experiment, fulvene **7**, b.p. 57-64°/0.1 Torr, was obtained in 78% yield from 6-methyl-5-heptenone (**4**) and cyclopentadiene. - IR. (neat): 3110, 3075, 1640, 1616, 1370, 765 cm^{-1}. - ^{1}H-NMR. (60 MHz): 1.6 ('*s*', 3H); 1.67 ('*s*', 3H); 2.18 (*s*, 3H); 5.13 (*t* with fine splitting, 3H); 6.43 (*s*, 4H) ppm. - MS.: 174 (M^+, 11), 159 (13), 154 (1), 131 (63), 117 (7), 106 (9), 91 (25), 77 (11), 69 (100), 53 (6), 41 (80), 27 (9).

Dimer **8**. Aq. 35% hydrogen peroxide (21.4 g; 0.2 mol) was added dropwise, over a 1 h period, to a stirred solution of fulvene **6** (34.8 g; 0.2 mol) in anh. methanol (100 ml) containing KOH (4 g) at 0-5° (exothermic reaction!). After stirring at 0° for 1 h, ether and water were added, and the two layers were separated. The aqueous phase was reextracted with ether, and the two organic extracts were washed (brine), dried ($MgSO_4$) and concentrated. Of the crude product (37.1 g) obtained, 1 g was bulb distilled at 180-215°/0.03 Torr for analysis. For the following step the crude dimer was used without additional purification. - IR. (neat): 3080, 1650, 890, 770 cm^{-1}. - ^{1}H-NMR. (90 MHz): see *Table 1.*

Dimer **9**. Using the reaction conditions described in the previous experiment, the crude dimer of **9** was obtained which was used without additional purification for the following step. For spectral data 1 g was purified by bulb distillation at 180-210°/0.02 Torr. - IR. (neat): 3020, 1655 (weak), 755 cm^{-1}. - ^{1}H-NMR. (90 MHz): see *Table 1.*

3,7-Dimethyltricyclo[5.3.1.0^{3,8}]undec-9-en-2-one (**1**). Crude dimer **8** (2.5 g, > 90% pure by NMR.; ~6.5 mmol), anh. toluene (40 ml) and hydroquinone (50 mg) were degassed by passing a slow stream of dry argon and then heated in a sealed glass tube at 270-280° for 2 h. The cold reaction product was concentrated under reduced pressure, taken up in ether and washed successively with 1N NaOH, 1N HCl, and diluted $NaHCO_3$-solution. After drying ($MgSO_4$), the product was concentrated and buld distilled at 90-140°/0.01 Torr to give 1.6 g (64%) of ketone **1** (residue: ~1.1 g). One gram of this product was chromatographed on silica gel (40 g). Hexane/ether 98:2 eluted 0.86 g of pure ketone **1** which, after bulb distillation at 80-100°/0.01 Torr, crystallized; m.p. 82-83°. The same yield was obtained with a bulb distilled samples (3.5 g) of starting material **8**. - IR. (CCl_4): 3060, 1720, 1615 (weak) cm^{-1}. - ^{1}H-NMR. (90 MHz): see *Table 2*. - MS.: 190 (M^+, 15), 175 (1), 162 (60), 147 (46), 133 (9), 119 (30), 105 (71), 91 (100), 77 (29), 65 (11), 55 (14), 41 (35), 26 (16).

3,10,10-Trimethyltricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (**2**). Crude dimer **9** (400 g, 90% pure by NMR.; ~0.95 mol), anh. toluene (2.9 l), and hydroquinone (5 g) were degassed and then heated in two subsequent batches (~1.4 l each batch) in an inox autoclave (2 lt) at 270-280° for 2 h. The cold reaction mixture was concentrated under reduced pressure and distilled in a *Vigreux* apparatus at ~63°/0.01 Torr to give 199 g (~55%) of ketone **2** (residue ~200 g). A 58% yield was obtained with a bulb distilled

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[4]) BASF, Ludwigshafen.

sample (3.8 g) of starting material **9**. - IR. (neat): 3020, 1705, 1605 cm^{-1}. - ^1H-NMR. (90 MHz): 0.88 (*s*, 3H, CH_3); 0.94 (*s*, 3H, CH_3); 1.09 (*s*, 3H, CH_3); 2.65 (*m*, 2H, H–C(1) and H–C(7)), addn. of Eu$(fod)_3 \rightarrow$ H–C(1): *d*×*d*, $J_{1,9}=6$, $J_{1,8}=1.6$ Hz, and H–C(7): *d*×*d*×*d*, $J_{7,8}=6$, $J_{7,9}=2$, $J_{7,6}=2$ Hz; 6.12 (*d*×*d*×*d*, $J_{9,8}=8$, $J_{9,1}=6$, $J_{9,7}=2$ Hz, 1H, H–C(9)); 6.31 (*d*×*d*×*d*, $J_{8,9}=8$, $J_{8,7}=6$, $J_{8,1}=2$ Hz, 1H, H–C(8)); the present assignment of spin-spin couplings was obtained by irradiation of the Eu$(fod)_3$ shifted spectrum at H–C(1), H–C(7), H–C(8) and H–C(9). - MS.: 190 (M^+, 22), 175 (< 1), 162 (9), 147 (51), 133 (6), 119 (24), 105 (100), 91 (32), 82 (48), 67 (11), 55 (16), 41 (37), 27 (15).

Alcohol **10**. A solution of ketone **1** (15.2 g; 80 mmol) in anh. ether (50 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (3.8 g; 100 mmol) in anh. ether (50 ml) at – 10 to 0°. The reaction mixture was stirred under reflux for 4 h and then decomposed at – 10° to 0° by careful, successive addition of water (10 ml) and aq. 10% sulfuric acid. The resulting two layers were separated and the aqueous layer was reextracted with ether. The combined organic phases were washed ($NaHCO_3$ and water), dried ($MgSO_4$) and concentrated to give 14.2 g of crude alcohol. Subsequent *Vigreux* distillation afforded 12.45 g of a semicrystalline fraction, boiling at 65–85°/0.01 Torr.

This fraction was further purified by column chromatography on silica gel with hexane/ether 95:5 to 90:10 as solvent followed by crystallization (twice) from hexane, yielding 7.7 g of pure **10**, m.p. 101–102°. - IR. (CCl_4): 3640, 3055 cm^{-1}. - ^1H-NMR. (90 MHz): see *Table 2*. - MS.: 192 (M^+, 27), 174 (3), 159 (6), 149 (5), 131 (4), 118 (31), 105 (17), 93 (100), 77 (25), 71 (22), 55 (15), 41 (29), 27 (13).

Mixture of alcohols **10** *and* **11** *by sodium reduction of* **1**. Ketone **1** (0.95 g; 5 mmol) in 2-propanol (20 ml) was heated to 80–90° and small pieces of sodium (0.57 g; 25 mmol) were added with stirring over a 4 h period. After dissolution of the metal the reaction mixture was cooled to RT., poured onto ice-water and extracted with ether. The ethereal extract was washed (1N HCl, diluted $NaHCO_3$-solution, H_2O), dried ($MgSO_4$) and concentrated. The crude material (1.04 g) was bulb distilled at 90–95°/0.05 Torr yielding 0.79 g of semicrystalline material. Column chromatography on silica gel (40 g) using the ether/hexane 9:1 gave first 0.27 g of crystalline **10**, m.p. 103–104° (once from pentane), followed by 0.43 g of crystalline **11**, m.p. 84–85° (once from pentane). - IR. (CCl_4): 3605, 3050 cm^{-1}. - ^1H-NMR. (90 MHz): see *Table 2*. - MS.: 192 (M^+, 29), 174 (1), 159 (3), 149 (3), 131 (1), 118 (25), 105 (13), 97 (32), 93 (100), 77 (16), 71 (14), 55 (8), 41 (29), 27 (20).

Alcohol **12**. Ketone **1** (15.2 g; 80 mmol) in anh. ether (50 ml) was treated with a 1.15N ethereal solution of methyllithium (100 ml; 115 mmol). The resulting solution was stirred under reflux for 5 h and then poured onto crushed ice. Extraction with ether gave 16.35 g of crude product which was distilled in a *Vigreux* apparatus, and the fraction boiling at 76–100°/0.1 Torr (13.6 g, semicrystalline) was further purified by chromatography on silica gel (125 g). Hexane/ether 95:5 eluted 8.09 g of crystalline **12**, m.p. (rec. from hexane) 88°. - IR. (CCl_4): 3630, 3055 cm^{-1}. - ^1H-NMR. (90 MHz): see *Table 2*. - MS.: 206 (M^+, 21), 188 (6), 173 (5), 163 (12), 145 (8), 131 (8), 118 (56), 111 (76), 105 (31), 93 (100), 85 (47), 71 (31), 55 (21), 43 (95), 29 (14).

REFERENCES

[1] *F. Näf & G. Ohloff*, Helv. *57*, 1868 (1974).

[2] For some recent reviews see *e.g.* a) *W.S. Johnson*, Angew. Chem. Int. Ed. *15*, 9 (1976); b) *E.E. van Tamelen*, Accounts chem. Res. *8*, 152 (1975); c) *idem, ibid. 1*, 111 (1968): *W.S. Johnson*, Accounts chem. Res. *1*, 1 (1968).

[3] a) *F. Näf, R. Decorzant & W. Thommen*, Helv. *58*, 1808 (1975); b) *A.F. Thomas, M. Ozainne, R. Decorzant, F. Näf & G. Lukacs*, Tetrahedron *32*, 2261 (1976).

[4] For a recent excellent review see: *W. Oppolzer*, Angew. Chem. Int. Ed. *16*, 10 (1977).

[5] *R.B. Moffet*, Org. Synth. *32*, 41 (1952).

[6] *K. Alder, F.H. Flock & H. Lessenich*, Chem. Ber. *90*, 1709 (1957).

[7] *K.C. Ramey & D.C. Lini*, J. magn. Res. *3*, 94 (1970).

[8] a) *H. Greuter, G. Fráter & H. Schmid*, Helv. *55*, 526 (1972); b) *H. Greuter*, Dissertation, University of Zürich, 1973; c) *H. Greuter & H. Schmid*, Helv. *55*, 2382 (1972); d) *H. Greuter, G. Fráter & H. Schmid*, Germ. Offen. *2*, 252, 865 (1971); e) *idem*, ibid. *2*, 252, 864 (1971).

[9] *S. Geribaldi, G. Torri & M. Azzaro*, Bull. Soc. chim. France *1973*, 2836.

[10] *K. Tori, Y. Takano & K. Kitahonoki*, Chem. Ber. *97*, 2798 (1964).

[11] *A. Krantz & C.Y. Lin*, J. Amer. chem. Soc. *95*, 5662 (1973).

[12] *H. Booth*, Tetrahedron *22*, 615 (1966).

[13] *R.R. Fraser & S. O'Farrell*, Tetrahedron Letters *1962*, 1143.