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The Reduction of Stereoisomeric 6-*tert*-Butyl-3-methoxy-3-methylcyclohexenes with Lithium in Ethylamine

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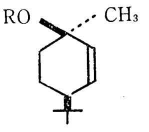
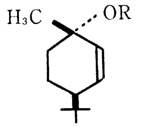
The synthesis and reduction with lithium in ethylamine of the entitled stereoisomeric allyl ethers **1** and **2** are described. The reaction of both the isomers occurred very readily with concomitant cleavage of the methoxy groups, and gave the same products, 4-*tert*-butyl-1-methylcyclohexene (**13**), and *c*- and *t*-3-*tert*-butyl-6-methylcyclohex-1-enes (**14** and **15**), in the same ratio (87 : 4 : 9), indicating that the respective reactions involved a common intermediate (**16**). Moreover, the reduction of the *cis*-isomer **1** with an axial methoxy group proceeded much more rapidly than that of the *trans*-isomer **2** with an equatorial methoxy.

Although the metal-in-ammonia reduction of aromatic carbocycles or heterocycles has been extensively investigated,[1] comparatively little is known about the corresponding reduction of allyl ethers and, especially, its stereochemistry.[2] In the studies aimed at establishment of C_9-configuration of jervine,[3] we found that "jervine-11β-ol" or 11-deoxojervine produced both Δ^{12}-olefin with 17β-hydrogen[4] and $\Delta^{13(17)}$-olefin with 12α-hydrogen[3] by the Birch reduction, but not any stereoisomers of the olefins. This result led us to have interest in and examine the relevant reaction of simpler, stereoisomeric allyl ethers. In this paper we describe the synthesis and chemical behavior under the Birch conditions of *c*- and *t*-6-*tert*-butyl-*r*-3-methoxy-3-methylcyclohex-1-enes (**1** and **2**).[5]



1 R=CH_3, with Δ
8 R=H, with Δ
11 R=H, without Δ



2 R=CH_3, with Δ
9 R=H, with Δ
12 R=H, without Δ

Treatment of 4-*tert*-butylanisole[6] (**3**) with lithium in liquid ammonia[7] followed by distillation afforded a mixture of dihydro compounds (**4**), bp 86—87°C/8 mmHg, in 74% yield. This on acid hydrolysis gave a 4 : 1 mixture (checked by gas chromatography; abbr., vpc) of $\alpha\beta$- and $\beta\gamma$-unsaturated ketones (**5** and **6**) in 91% yield, from which **5**, bp 101—102°C/11 mmHg, and **6**, bp 95—97°C/9 mmHg, were isolated in 42 and 14% yields, respectively, by column chromatography over silicic acid.[8] In accordance with the assigned structures, the former **5** exhibited absorptions at 224 mμ (ε 10500), at 1691 and 1618 cm^{-1}, and at τ 3.99 and 2.98 (two olefinic protons) in the UV, IR and NMR spectra, while the latter **6** those at 1720 cm^{-1} and at τ 4.48 (only one olefinic proton).

$\beta\gamma$-Unsaturated ketone **6** manifested itself to be untenable to oxidation. When allowed to stand in the air at room temperature, **6** spontaneously formed a beautiful crystalline compound (**7**), mp 106—107°C, which was analyzed for $C_{10}H_{16}O_3$, a molecular formula

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[1] For the recent references concerning the Birch reductions, see: A. J. Birch, E. G. Hutchinson, and G. S. Rao, *J. Chem. Soc., C*, **1971**, 637; W. A. Remers, G. J. Gibs, C. Pidacks, and M. J. Weiss, *J. Org. Chem.*, **36**, 279 (1971); S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **93**, 430 (1971); B. C. Newman and E. L. Eliel, *J. Org. Chem.*, **35**, 3641 (1970); E. J. Eisenbraun, R. C. Bansal, D. V. Hertzler, and W. P. Duncan, *ibid.*, **35**, 1265 (1970); P. W. Rabideau and R. G. Harvey, *Tetrahedron Lett.*, **1970**, 4139, and also literatures cited in these papers.

[2] A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *J. Chem. Soc.*, **1957**, 1969.

[3] T. Masamune, K. Kobayashi, M. Takasugi, Y. Mori, and A. Murai, *Tetrahedron*, **24**, 4193 (1969).

[4] A. Murai, K. Arita, and T. Masamune, unpublished observations.

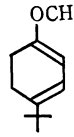
[5] For nomenclature, see: *J. Org. Chem.*, **35**, 2849 (1970).

[6] W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodnan, I. Hart, J. H. Lamneck, Jr., and L. C. Gibbons, *J. Amer. Chem. Soc.*, **69**, 2451 (1947).

[7] M. D. Soffer and M. J. Jevnik, *ibid.*, **77**, 1003 (1955).

[8] Lewis and Williams recently prepared these ketones **5** and **6** to determine the equilibrium ratio between them. However, the authors reported no physical constants to characterize the compounds and also the ratio in question to be 1 to 1 (vpc). K. G. Lewis and G. J. Williams, *Tetrahedron Lett.* **1965**, 4573.

corresponding to the sum of **6** and an oxygen molecule. In the IR spectrum absorption maxima appeared newly at 3200 and 1660 cm^{-1} instead of that at 1720 cm^{-1} of **6**. Similarly, in the NMR spectrum one-proton singlet and doublet were observed at τ 1.10 and 3.06 instead of the triplet at τ 4.48 of **6**. While compound **7** resisted acetylation under the usual conditions, it was reduced with sodium borohydride to give a mixture, from which a glycol (**7a**), mp 108.5—109.5°C, could be isolated in good yield by preparative tlc. This was readily converted into the acetonide (**7b**), oil, in 60% yield by treatment with acetone and silica gel (Wakogel Q-23). These findings indicated the compound to be formulated by structure **7**.



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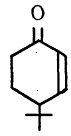
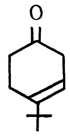
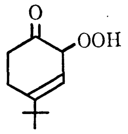


5



6

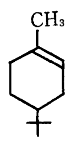


7

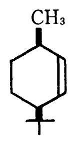
$\alpha\beta$-Unsaturated ketone **5** was treated with methyl lithium in ether[9] to produce a mixture of stereoisomeric tertiary alcohols, which were separated by column chromatography over alumina to give *cis*- and *trans*-alcohols (**8** and **9**), mp 36—37°C and 57—58°C, in 32 and 43% yields, respectively. The same treatment of $\beta\gamma$-unsaturated ketone **6** afforded the corresponding tertiary alcohol (**10**), mp 64—66°C, only in a low yield. The configurations of **8** and **9** were tentatively assigned on the basis of the R_f values on tlc or the elution sequence in column chromatography[10] as well as the predominant axial attack by Grignard reagents on unhindered ketones.[11] This assignment proved to be correct by derivation of these alcohols to the known compounds; hydrogenation of **8** and **9** over platinum yielded quantitatively the corresponding saturated alcohols (**11** and **12**), mp 65.5—67°C and 95—96°C, which were identified as *c*- and *t*-4-*tert*-butyl-1-methyl-*r*-1-cyclohexanols.[12] The olefinic alcohols **8** and **9** were then converted with methyl iodide and sodium hydride into the respective methyl ethers **1** and **2**, bp 76—78°C/25 mmHg and 88—89°C/17 mmHg, in 60 and 70% yields.

The reduction of *cis*-ether **1** with excess of lithium in ethylamine at *ca.* −70°C for 1 hr produced a 87 : 4 : 9 mixture (vpc) of three compounds (**13**, **14** and **15**), which were separated by preparative vpc into the main product **13** and the mixture of minor products **14** and **15** in 72 and 10% yields. Compound **13** was identified as 4-*tert*-butyl-1-methylcyclohexene by comparison of the authentic sample.[13] The mixture in question displayed in the NMR spectrum a broad multiplet and a sharp singlet at τ 4.43 and τ 9.13 due to *two* olefinic and *tert*-butyl protons, indicating that it consisted of stereoisomeric 3-*tert*-butyl-6-methylcyclohex-1-enes. Hydrogenation of the mixture over palladium followed by examination of the resulting saturated hydrocarbons[13] by vpc proved the minor and major components to be *cis*- and *trans*-isomers **14** and **15**, respectively.

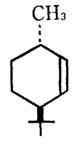
The same reaction of *trans*-ether **2** led to the same result; formation of a 87 : 4 : 9 mixture of **13**, **14** and **15**, indicating the products to be formed through a *common* intermediate (**16**) from both the ethers **1** and **2**.



13



14 with Δ
21 without Δ



15 with Δ
22 without Δ

The reduction was next followed by vpc with time. Thus, excess of lithium was added to a solution of *trans*-ether **2** in ethylamine at *ca.* −70°C, and a small portion of the mixture was picked up and the product components were determined in a short interval of time, after the blue color appeared. It was found that (1) the reduction was extremely fast; while 25% of the starting ether remained unchanged after 30 sec, the reaction had been completed after 50 sec, and (2) the ratio of the reaction products **13**, **14** and **15** was constant (87 : 4 : 9) before and after the starting ether reacted completely. As expected, the compound **13** or the mixture of **14** and **15** itself was recovered unchanged on treatment for 2 hr under the conditions used.

Finally it was attempted to examine the relative rates of *cis*- (**1**, axial methoxy) and *trans*-ether (**2**, equatorial methoxy); that is, equal amounts of **1** and **2** in ethylamine were reacted with excess of lithium. Interestingly, the reduction of *cis*-isomer **1** proceeded much more fast, at least with the rate of 50 times, than that of *trans*-isomer **2**, although the ratio could not be determined quantitatively owing to the extreme rapidness. These results were summarized as shown in Scheme 1.

In this Scheme, the processes of **1** or **2** to allyl radical **19** or allyl anion **16**[14] must involve the rate-determining step and would probably contain some complexes formed between metal or electron and allyl ethers such as **17** or **18**, since the reactions of **1** and **2** proceeded with the different rates and led to the same results. In view of the difficulty of reduction of an isolated double bond and of reductive cleavage of a saturated alkyl ether, it would be very improbable that the processes either consisted of two steps, addition

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[9] *Cf.*, G. Stork and F. H. Clarke, Jr., *J. Amer. Chem. Soc.*, **83**, 3114 (1961).

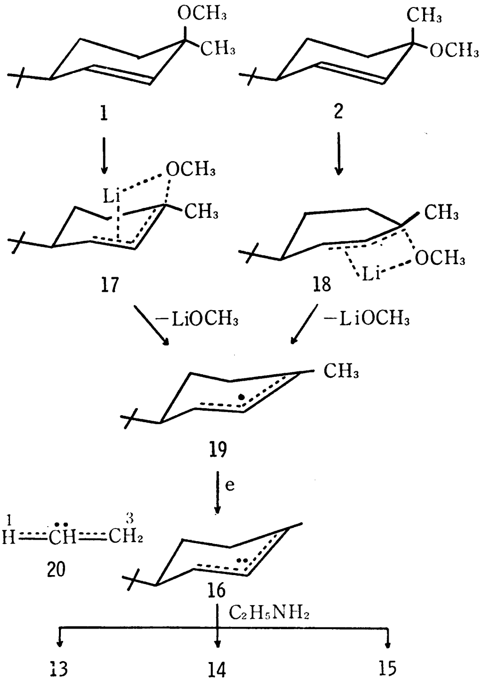
[10] *Cf.*, D. H. R. Barton and R. C. Cookson, *Quart. Rev.*, **10**, 44 (1956).

[11] M. Chérest and H. Felkin, *Tetrahedron Lett.*, **1971**, 383, and literatures cited there; J. C. Richter, *J. Org. Chem.*, **30**, 324 (1965). *Cf.*, E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970); D. C. Wigfield and D. J. Phelps, *Chem. Commun.*, **1970**, 1152; D. N. Kirk, *Tetrahedron Lett.*, **1969**, 1727.

[12] B. Cross and G. H. Whitham, *J. Chem. Soc.*, **1960**, 3895.

[13] F. G. Bordwell, P. S. Landis, and G. S. Whitney, *J. Org. Chem.*, **30**, 3764 (1965).

[14] The transformation of **19** to **16** would proceed very readily, as the energy level of the highest half-occupied orbital of methylallyl radical corresponding to the anion **20** would be very low ($-0.10\sim-0.20\beta$). We are indebted to Mr. H. Kashiwagi in our Department for calculation as to methylallyl radical.



Scheme 1

of an electron to the double bond (the energy of lowest unoccupied molecular orbital,[15] -1.0β) and subsequent removal of the methoxy anion, or direct expulsion of the methoxy group by metal or an electron. The following step, the irreversible protonation of anion **16**, would occur most preferably at the site with the highest total π-electron density.[16] The distribution of π-electron of methylallyl anion **20** was calculated[17] by the Hückel MO orbital method, using more or less standard parameters.[18] The result showed that the site in question was the carbon atom (C_3 of **20**) unsubstituted by the methyl group (the difference in total π-electron density between C_1 and C_3, 0.15—0.25 electron). Thus the predominant formation of compound **13** would be reasonably interpreted by assuming that the afore-mentioned calculation with model **20** could be applied for the present intermediate **16**. On the other hand, the difference in formation of **14** and **15** might be rationalized on the basis of the difference in continued maximum overlap[19] between the axially oriented π-orbitals at C_1, C_2 and C_3 of **16** on approach of the proton of ethylamine, or of that in steric hindrance between the transition states leading to the products **14** and **15** from **16**. Further investigations concerning which factor is generally more or exclusively important are now in progress.

Experimental

The melting points were measured in open capillaries and uncorrected. Homogenity of each compound was always checked by tlc on silica gel (Wakogel B-5) and/or alumina (Merck G), and also by vpc (PEG-6000) with Hitachi Gas Chromatograph Model K53. The UV and IR spectra were taken in 99% ethanol and in liquid state, unless otherwise stated. The NMR spectra were measured in deuterochloroform at 60 and/or 100 MHz, TMS being used as an internal standard, unless otherwise stated. The abbreviations "s, d, t, q, br and m" in the NMR spectra denote "singlet, doublet, triplet, quartet, broad and multiplet," respectively.

*4-*tert*-Butylanisole (**3**).* 4-*tert*-Butylphenol was converted into **3** in 80% yield by the method of Olson *et al.*,[6] bp 87—88°C/8 mmHg (lit,[6] bp 232.2°C/760 mmHg); IR, $\nu_{\max}$ 1610, 1247, 1183 and 1039 cm^{-1}; NMR, τ 8.71 (9H, s, *tert*-butyl), 6.23 (3H, s, OC$\underline{H}_3$), and 3.17 and 2.71 (each 1H, ABq J=9 Hz, $\underline{H}$ at C_2 and C_3).

*4-*tert*-Butyldihydroanisole (**4**).* Compound **3** was reduced under the conditions similar to those of the Birch reduction of the corresponding isopropyl derivative;[7] small pieces of lithium (6 g) were added under vigorous stirring to a solution of liquid ammonia (300 m*l*) containing **3** (20 g) in dry ether (130 m*l*) cooled with dry ice-acetone. The mixture was stirred for 30 min after the blue color appeared. The color gradually disappeared on addition of ethanol (70 m*l*). After removal of ammonia, the residue was mixed with water and extracted with ether. The ether solution was dried over anhydrous sodium sulfate, evaporated and then distilled to give **4** (14.8 g), which was used for the next reaction without further purification, bp 86—87°C/8 mmHg; IR, $\nu_{\max}$ 1695, 1658 and 1608 cm^{-1}; NMR, τ 8.94 (9H, s, *tert*-butyl), 7.78 (4H, s, $\underline{H}$ at C_5 and C_6), 6.43 (3H, s, OC$\underline{H}_3$), and 5.08 and 4.37 (each 1H, ABq J=6.5 Hz, $\underline{H}$ at C_2 and C_3). The NMR spectrum indicated that the product (a single peak by vpc) would be the 5,6-dihydro derivative rather than the expected compound, 4-*tert*-butyl-3,6-dihydroanisole.

*4-*tert*-Butylcyclohex-2-en-1-one (**5**) and 4-*tert*-Butylcyclohex-3-en-1-one (**6**).* Compound **4** (7.4 g) was refluxed in 5% hydrochloric acid (bath temperature, 140°C) for 10 hr.[8,20] After being cooled, the mixture was treated with ether. The ether solution was washed with 5% sodium carbonate solution and water, dried and evaporated to leave oily residue, which proved to be a 79 : 21 mixture of **5** and **6** by vpc. The residue (6.27 g) was submitted to column chromatography over a mixture of silicic acid (120 g) and celite (35 g), each fraction being checked by vpc. Fractions eluted with benzene, showing a single peak, were collected and purified by distillation to give $\beta\gamma$-unsaturated ketone **6** (1.0 g), bp 95—97°C/9 mmHg; IR, $\nu_{\max}$ 1720 and 809 cm^{-1}; NMR, τ 8.90 (9H, s, *tert*-butyl), 7.20 (2H, d, J= 3.5 Hz, $\underline{H}$ at C_2), and 4.48 (1H, t, J=3.5 Hz, $\underline{H}$ at C_3).

Found: C, 78.65; H, 10.88%. Calcd for $C_{10}H_{16}O$; C, 78.89; H, 10.59%.

Fractions eluted withb enzene - ether (4 : 1), showing a single peak, were treated in the same manner as mentioned above and afforded $\alpha\beta$-unsaturated ketone **5** (3.0 g), bp 101—102°C/11 mmHg; UV, $\lambda_{\max}$ 224 mμ (ε 10500); IR, $\nu_{\max}$ 1691 and 1618 cm^{-1}; NMR, τ 9.12 (9H, s, *tert*-butyl), 3.99 (1H, double d, J=10.5 and 2.5 Hz, $\underline{H}$ at C_2), and 2.98 (1H, dobule t, J=10.8, 2.0 and 2.0 Hz, $\underline{H}$ at C_3).

Found: C, 78.77; H, 10.63%. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59%.

The composition ratio of **5** and **6** in the product was about 1 to 1 after 5 hr reflux in 5% hydrochloric acid, and changed

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[15] *Cf.*, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y. (1962).

[16] H. E. Zimmerman, *Tetrahedron*, **16**, 169 (1961).

[17] H. Kashiwagi, private communication.

[18] T. Yonezawa, C. Nagate, H. Kato, A. Imamura, and K. Morokuma, "Ryoshi Kagaku Nyumon," Kagaku Dozin, Kyoto (1968), p. 56 and 173.

[19] *Cf.*, H. E. Zimmerman and A. Mais, *J. Amer. Chem. Soc.*, **81**, 4305 (1959), and their previous papers.

[20] *Cf.*, A. J. Birch, *J. Chem. Soc.*, **1946**, 595; *ibid.*, **1944** 430.

to 4 to 1 after 10 hr reflux. This ratio (4 : 1) was obtained after 3 hr reflux in 7.5% hydrochloric acid.

*4-*tert*-Butyl-2-hydroperoxycyclohex-3-en-1-one (7).* When compound **6** was allowed to stand in the air at room temperature, a crystalline substance gradually separated out. After one month compound **6** became completely crystalline. Recrystallization from carbon tetrachloride afforded hydroperoxide **7**, mp 106—107°C, UV, λ_{max} 216 mμ (ε 12600); IR (Nujol), ν_{max} 3200, 1660 and 871 cm^{-1}; NMR, τ 8.91 (9H, s, *tert*-butyl), 3.78 (1H, d, J=10.5 Hz, $\underline{H}$ at C_2), 3.06 (1H, d, J=10.5 Hz, $\underline{H}$ at C_3), and 1.10 (1H, s, $OO\underline{H}$).

Found: C, 65.13; H, 8.84%. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

A solution of **7** (300 mg) in methanol (20 m*l*) was treated with sodium borohydride (100 mg) under cooling with ice-water and stirring for 1 hr. After addition of acetic acid (0.6 m*l*) and water (50 m*l*), the mixture was extracted with ether. The ether solution was dried and evaporated to leave crystalline substance, which showed two spots on tlc. The main product (**7a**) was obtained by preparative tlc, had mp 108.5—109.5°C, and amounted to 160 mg. Recrystallization from ether afforded an analytical sample, mp 108.5—109.5°C; IR (Nujol), ν_{max} 3250, 1050 and 951 cm^{-1}.

Found: C, 70.21; H, 11.03%. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66%.

Compound **7a** (40 mg) dissolved in a small volume of acetone was poured onto a column filled with silica gel (Wakogel Q-23, 5.0 g) freshly washed with acetone and then with *n*-hexane, and eluted successively with *n*-hexane, and *n*-hexane - acetone (97 : 3, 95 : 5 and 92 : 8). Eluates from the solvent mixtures were purified by preparative tlc (chloroform) to give the acetonide (**7b**, 26 mg), oil; IR, ν_{max} 1060, 1030, 882, and 856 cm^{-1}; NMR, τ 8.90 (9H, s, *tert*-butyl), 8.64 (6H, s, *gem*-$C\underline{H}_3$), 5.80 and 5.57 (each 1H, br, m, $\underline{H}$ at C_4 and C_3), and 4.55 (1H, br, d, J=4 Hz, $\underline{H}$ at C_2).

Found: C, 74.56; H, 10.34%. Calcd for $C_{13}H_{22}O_2$; C, 74.24; H, 10.54%.

c- and t*-4-*tert*-Butyl-1-methylcyclohex-2-en-*r*-1-ol (8 and 9).* To a cooled, suspended mixture of small pieces of lithium (7.3 g) in dry ether (200 m*l*) was added methyl iodide (30 m*l*) in dry ether (40 m*l*) under stirring and under a stream of nitrogen. The mixture was refluxed for 4 hr and then filtered rapidly through glass-wool.[9] After dropwise addition of $\alpha\beta$-unsaturated ketone **5** (10.1 g) dissolved in ether (50 m*l*) to the filtrate, the whole mixture was stirred at room temperature for 1 hr, then treated with a solution of sodium sulfate (8.0 g) and sodium thiosulfate (0.5 g) in water (100 m*l*) under cooling to decompose excess of the lithium, and extracted with ether. The ether solution was dried and evaporated to leave oily residue (11.8 g), showing two spots on tlc (benzene - ether, 5 : 1 or 4 : 1). This was separated by column chromatography over alumina (standard, active II—III, 130 g). Fractions eluted with *n*-hexane and *n*-hexane - benzene (10 : 1), showing a single spot with higher R_f value were collected and evaporated to give crystalline *cis*-alcohol (**8**, 3.45 g), which on sublimation had mp 36—37°C; IR (CS_2), ν_{max} 3620, 3400, 1100, 902 and 735 cm^{-1}; NMR, τ 9.04 (9H, s, *tert*-butyl), 8.75 (3H, s, $C\underline{H}_3$ at C_1), and 4.28 (2H, br s, $\underline{H}$ at C_2 and C_3).

Found: C, 78.29; H, 11.91%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

Fractions eluted with *n*-hexane - benzene (10 : 1, 8 : 2, 6 : 4 and 1 : 1) showed two spots on tlc. The following fractions eluted with benzene showed a single spot with lower R_f value on tlc and afforded *trans*-alcohol **9** (4.7 g), which on sublimation had mp 57—58°C; IR (CS_2), ν_{max} 3620, 3400, 1120, 918 and 752 cm^{-1}; NMR, τ 9.09 (9H, s, *tert*-butyl), 8.76 (3H, s, $C\underline{H}_3$ at C_1), and 7.81 (1H, s, $O\underline{H}$), and 4.41 (2H, s, $\underline{H}$ at C_2 and C_3).

Found: C, 78.49; H, 11.97%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

cis-Alcohol **8** (50 mg) was hydrogenated over rhodium-platinum (30 mg) in ethanol (5 m*l*) for 24 hr. After filtration of the catalysis the solution was evaporated and then extracted with ether. The ether solution was washed with water, dried and evaporated to leave oily residue, which crystallized on trituration with *n*-hexane, had mp 61—63°C and amounted to 48 mg. This was distilled for purification to give *c*-4-*tert*-butyl-1-methyl-*r*-1-cyclohexanol (**11**), mp 65.5—67°C (lit,[12] mp 66—67°C); IR (CS_2), ν_{max} 3600, 1198, 1098, 1026, 990, 925, and 904 cm^{-1} (lit,[12] ν_{max} 1200, 1100, 1031, 995, 923, and 909 cm^{-1}); NMR, τ 9.14 (9H, s, *tert*-butyl) and 8.87 (3H, s, $C\underline{H}_3$ at C_1).

trans-Alcohol **9** (50 mg) was hydrogenated over platinum (50 mg as PtO_2–H_2O) in methanol (5 m*l*) for 2 hr. The mixture was worked up as usual to give *t*-4-*tert*-butyl-1-methyl-*r*-1-cyclohexanol[12] (**12**, 48 mg), mp 91—93°C, which on recrystallization from aqueous methanol had mp 95—96°C (lit,[12] mp 89—90°C); IR (CS_2), ν_{max} 3600, 3340, 1137, 1100, 977, and 913 cm^{-1} (lit,[12] ν_{max} 1142, 1103, 979, and 914 cm^{-1}); NMR, τ 9.14 (9H, s, *tert*-butyl) and 8.88 (3H, s, $C\underline{H}_3$ at C_1).

*4-*tert*-Butyl-1-methylcyclohex-3-en-1-ol (10).* To methyl lithium, prepared from methyl iodide (20 g), lithium (2.0 g) and dry ether (60 ml) was dropwise added $\beta\gamma$-unsaturated ketone **6** (1.0 g) in dry ether (20 m*l*). The mixture was refluxed for 25 hr under stirring and then worked up in the same manner as the case of **5** to give oily substance (1.18 g). A part (380 mg) of the oil was purified by preparative tlc (benzene - ether, 4 : 1) to yield crystalline alcohol **10** (137 mg), mp 38—40°C, which on further purification by sublimation had mp 64—66°C and amounted to 82 mg; IR (Nujol), ν_{max} 3320, 1128, 1104, and 884 cm^{-1}; NMR, τ 8.96 (9H, s, *tert*-butyl), 8.82 (3H, s, $C\underline{H}_3$ at C_1), and 4.66 (1H, m, $\underline{H}$ at C_3).

Found: C, 78.35; H, 11.85%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

c- and t*-6-*tert*-Butyl-*r*-3-methoxy-3-methylcyclohex-1-enes (1 and 2).* A mixture of *cis*-alcohol **8** (2.7 g) and sodium hydride (2.5 g), washed with *n*-hexane repeatedly, was stirred vigorously in dry ether (180 m*l*) at room temperature for 19 hr under a stream of nitrogen. After addition of methyl iodide (50 m*l*), the whole mixture was refluxed overnight under stirring and then filtered. The filtrate was washed with water, dried, evaporated, and then distilled to give the methyl ether (**1**, 1.75 g), showing a single peak by vpc, bp 76—78°C/25 mmHg; IR ($CHCl_3$), ν_{max} 1371, 1110, 1073, 868, and 822 cm^{-1}; NMR, τ 9.10 (9H, s, *tert*-butyl), 8.81 (3H, s, $C\underline{H}_3$ at C_3), 6.80 (3H, s, $OC\underline{H}_3$), and 4.34 and 4.08 (each 1H, ABq, J=11 Hz, $\underline{H}$ at C_1 and C_2 or *vice versa*).

Found: C, 79.35; H, 11.98%. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%.

trans-Alcohol **9** (3.2 g) was treated in the same manner (sodium hydride 2.6 g, methyl iodide 50 m*l*, and ether 200 ml) as **8**, and afforded the methyl ether (**2**, 2.40 g) after distillation, bp 88—89°C/17 mmHg; IR, ν_{max} 1368, 1110, 1078, 868, and 830 cm^{-1}; NMR, τ 9.11 (9H, s, *tert*-butyl), 8.79 (3H, s, $C\underline{H}_3$ at C_3), 7.80 (3H, s, $OC\underline{H}_3$), and 4.43 and 4.18 (each 1H, ABq, J=11 Hz, $\underline{H}$ at C_3 and C_2).

Found: C, 79.30; H, 11.87%. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%.

Reduction of cis- *and* trans-*ethers* ***1*** *and* ***2***. To a solution of *cis*-ether **1** (2.2 g) in ethylamine (70 m*l*) cooled with dry ice - acetone (*ca.* −70°C) were added small pieces of lithium (1.0 g) under stirring, and the blue color appeared after 10 min. The mixture was further stirred for 1 hr and the reaction was stopped by addition of ammonium chloride. After removal of the ethylamine, the residue was treated with ether and water, and the ether solution was dried and evaporated carefully to leave oily substance (1.7 g), which was decolorized by passing through alumina column and proved to be a 87 : 4 : 9 mixture of three components by vpc (PEG-6000, 70°C, and nitrogen 0.9 kg/cm^2). A part (1.0 g) of the oily product was separated into the main product (0.59 g) and the mixture of two minor products (84 mg) by preparative vpc with Varian Aerograph Autoprep 700, using DGSP and helium gas (60 m*l*/min) at 60°C. The former was identified as 4-*tert*-butyl-1-methylcyclohex-1-ene (**13**) by comparison (vpc and NMR) with the authentic sample;[13] NMR, τ 9.15 (9H, s, *tert*-butyl), 8.37 (3H, br s, $C\underline{H}_3$ at C_1), and 4.70 (1H, br, $\underline{H}$ at C_2). This compound **13** (290 mg) was hydrogenated over palladium charcoal (12 mg) in ethanol (5 m*l*) according to the known procedure.[13] The vpc analysis showed the product to be a 32 : 68 mixture of *c*- and *t*-*r*-1-*tert*-butyl-4-methylcyclohexanes (**21** and **22**) (lit,[13] the ratio, 27 : 73).

The latter mixture was supposed to consist of stereoisomeric 3-*tert*-butyl-6-methylcyclohex-1-enes (**14** and **15**) on the basis of the NMR spectrum: τ 9.13 (9H, s, *tert*-butyl), 9.07 (3H, d, J=6 Hz, $C\underline{H}_3$ at C_6), and 4.43 (2H, br m, $\underline{H}$ at C_1 and C_2). This was supported in the following: hydrogenation of the mixture (20 mg) in the same manner as **13** produced a 31 : 69 (*ca.* 4 : 9) mixture (vpc) of the corresponding saturated *cis*- and *trans*-hydrocarbons **21** and **22**.

The reduction of *trans*-ether **2** was carried out in the same manner as that of the *cis*-isomer **1** and gave a 87 : 4 : 9 mixture of **13**, **14**, and **15**. Hydrogenation of the relevant mixture of two minor products afforded a 27 : 73 (*ca.* 4 : 9) mixture (vpc) of **21** and **22**.

To a solution of *trans*-ether **2** (2.2 g) in ethylamine (100 m*l*) cooled at *ca.* −70°C were added small pieces of lithium (0.8 g). A small fraction of the mixture was picked up in a small interval of time (30 and 50 sec, 1, 5, 10, 15, and 20 min, 1 and 1.5 hr) after the blue color appeared, and the composition of each fraction was checked by vpc. The first fraction, picked up after 30 sec, was found to contain **2**, **13**, **14**, and **15** in the ratio of *ca.* 25, 65, 3, and 7. All other fractions consisted only of **13**, **14**, and **15** with the ratio of 87, 4, and 9.

To a solution of equal amounts (150 mg) of *cis*- and *trans*-ethers (**1** and **2**) in ethylamine (30 m*l*) cooled at *ca.* −70°C was added lithium (300 mg) under vigorous stirring. A part of the mixture was taken up as soon as the blue color appeared and the components were determined by vpc, when *cis*-ether **1** practically disappeared and the ratio in area of **2** and **1** was over 50.