more easily attacked by electrophiles like ozone, in agreement with experimental results on the ozonolysis of acetals [12].

Stereoelectronic or conformational effects, which are believed to influence the decomposition of tetrahedral intermediates [1] [2], are thus present in isolated species. Such effects as well as orientation effects [6] [10] may well be important in determining the stereochemical and other specificity of hydrolytic enzymes. Extension to the case of amide hydrolysis should allow to check and to generalize these results [11].

We thank Prof. *J. D. Dunitz* for helpful discussion.

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55. The Reaction of some Carbonyl and Thiocarbonyl Compounds with Prenyl- and Crotyllithium in Tetrahydrofuran Solution

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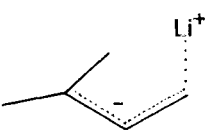
(11 XII 73)

Summary. Prenyllithium (3-methylbut-2-enyl-lithium) (**1**) and *cis*-crotyllithium (*Z*-but-2-enyl-lithium) (**2**) in tetrahydrofuran solution, prepared according to the method of *Eisch & Jacobs,* react with carbonyl compounds to give the branched alcoholates with moderate to high selectivity, unless access to the carbonyl group is strongly hindered (see the Table). Adamantanethione (**12**) reacts with **1** to give the unbranched thiolate.

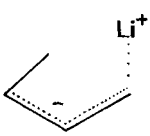
Allyllithiums can now be prepared readily, and often more conveniently than the corresponding *Grignards,* by the method of *Eisch & Jacobs* [1–4], by cleavage of allyl phenyl ethers with lithium in tetrahydrofuran. We have studied the reactions of two simple substituted allyllithiums, 'prenyllithium' (3-methylbut-2-enyl-lithium) (**1**) and *cis*-crotyllithium (*Z*-but-2-enyl-lithium) (**2**), made in this way, with a few aldehydes and ketones. These simple addition reactions interested us as possible synthetic steps; prenyllithium (**1**) is a potentially useful synthetic 'isoprene unit'. We also wished to compare these reactions with the related ether [5] [6] and thioether

[7] [8] 'anion' rearrangements; in this context we have also examined the reaction of **1** with adamantanethione (**12**).

To the best of our knowledge there is only one related work in the literature; *Miginiac & Bouchoule* have studied the reaction of pent-2-enyl-lithium (**3**) in tetrahydrofuran solution with seven aliphatic ketones [3]. The allyllithium **3** was likewise prepared by *Eisch-Jacobs* cleavage. The preparation of prenyllithium (**1**) according to this method has been described by *Birch et al.* [4] and the crotyllithium (**2**) was prepared analogously [2].



1



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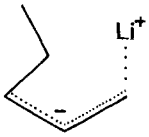


3

The aldehydes and ketones were treated at –60° to –70° with an excess of the solutions of **1** and **2** (containing *ca.* 1 equiv. of lithium phenolate and a catalytic amount of biphenyldilithium [1]). After 25 min at this temperature, the products were quenched into water. The results are summarized in the Table.

Both **1** and **2** are seen to give mainly the branched adducts, with moderate to high selectivity[1]), unless access to the carbonyl group is strongly hindered. These results are similar to those obtained by *Miginiac & Bouchoule.* The various adducts are formed under kinetic control [3] [5]. We have checked this for two systems; the lithium alcoholates of **16** and **20** in tetrahydrofuran solution are stable at room temperature. In the reaction of **1** with benzaldehyde, the temperature was varied; the additions are significantly more selective at low temperature. The reactions with ketones are 'cleaner' than the reactions with aldehydes; base (lithium phenolate)–catalyzed self-condensation seems to compete with the reactions with **1** and **2.** The reaction between **1** and the α,β-unsaturated aldehyde **7** was particularly 'unclean' giving rise to at least six by-products (together *ca.* 35% of the distilled mixture). Analysis of the products was carried out by gas chromatography. Structures were assigned on the basis of spectral data (see Exper. Part).

At present the mechanism of these simple addition reactions is unclear; we briefly list related structural problems and several possible mechanisms.

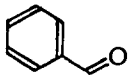
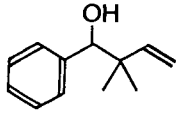
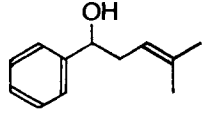
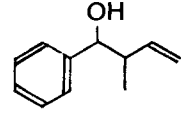
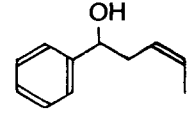
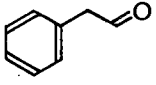
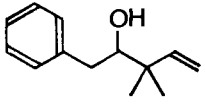
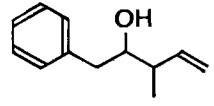
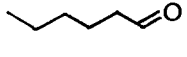
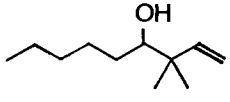
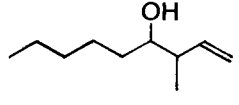
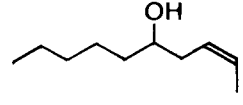
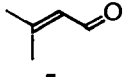
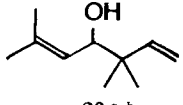
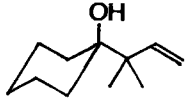
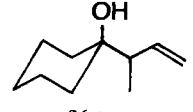
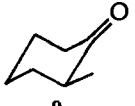
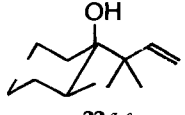
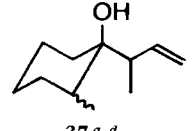
The structures of **1** and **2** in tetrahydrofuran solution are not known [9][2]). By extrapolation from what is known about the parent compound, allyllithium (**40**)[3]),

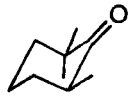
[1]) Essentially the opposite orientation of addition was observed in the reaction of **1** with the lithium salts of carboxylic acids [4].

[2]) No direct information on the structure of **1** and only limited information [10] [11] on the structure of **2** is available.

[3]) The structure of allyllithium (**40**) has been investigated extensively [12–16] but is not yet completely understood. In donor solvents such as ether or tetrahydrofuran, the available data [13–16], in particular the temperature dependent NMR. spectrum [12], seem to be best in accord with ionic contact pair structures; aggregates may be playing an essential role in the dynamic behaviour, although **40** in tetrahydrofuran solution is essentially monomeric [14–16] and has been found to react in some reactions, in an approximately first order manner [15] [16].

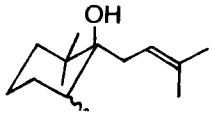
Table. *Reactions of Prenyllithium* (**1**) *and* cis-*Crotyllithium* (**2**) *with Carbonyl and Thiocarbonyl Compounds*

 **4**		 **16**	 **17**		 **31**[d]	 **32**
	−79°	**16:17** = 6:1			**31:32** = 55:1	
	−25°	4.5:1				
	+23°	3:1				
 **5**	−65°	 **18**[a]		−70°	 **33**[d,f]	
 **6**	−65°	 **19**[a]		−70°	 **34**[d] **34:35** = 7.5:1	 **35**
 **7**	−25°	 **20**[a,b]				
 **8**	−70°	 **21**[a]		−70°	 **36**[a]	
 **9**	−70°	 **22**[a,c]		−70°	 **37**[a,d]	



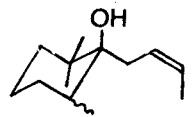
10

−65°

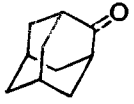


23 [a,d]

−70°

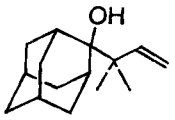


38 [a,d]



11

−75°



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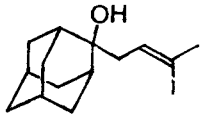
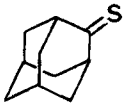


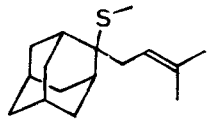
25

24:25 = 4:1



12

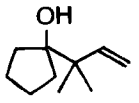
−75°



26 [a,e]

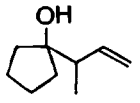
13

−70°

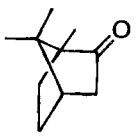


27 [a]

−70°

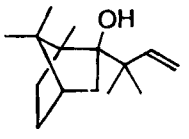


39 [a]

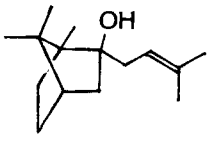


14

−70°



28

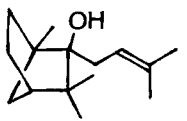


29

28:29 = 1.2:1

15

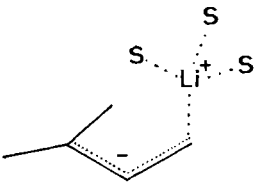
−70°



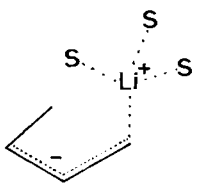
30 [a]

[a]) The isomeric adduct was not found: *ca.* 5% or less present. [b]) The aldehydes which would result from conjugate addition and hydrolysis were not found: *ca.* 5% or less present. [c]) At least 90% of one diastereoisomer only. [d]) Mixture of diastereoisomers. [e]) After methylation of the corresponding thiolate. [f]) The isomeric adduct was not identified, *ca.* 20% may have been present.

methyl derivatives **1** and **2** in tetrahydrofuran solution are probably best viewed as monomeric contact ion pair species. Contact between anion and cation is probably preferred at the primary ends of the allyl anions, because electron density is highest there, and simply for steric reasons (the peripheral solvation shell of the lithium cation probably contains three molecules of tetrahydrofuran), the lithium cation being located above the π-cloud [17] [18]. These assumptions lead to hypothetical monomeric structures **1** and **2** – or **1a** and **2a** if symbols for the solvent (S) tetrahydrofuran are added – as the preferred species.



1a

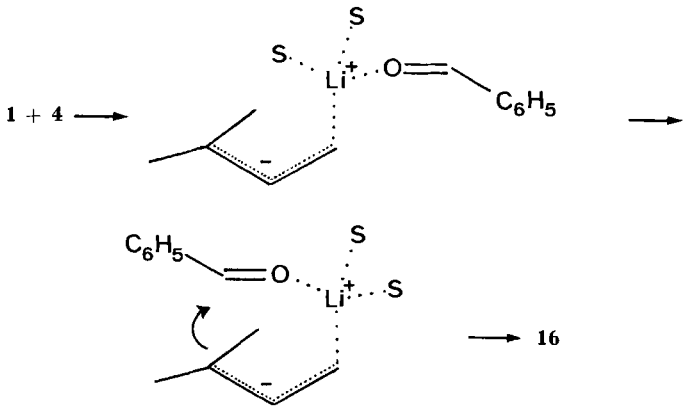


2a

The assignment of *cis*-geometry to **2** is only based on the structures of the derived, unbranched adducts **32**, **35** and **38** (see the Table) which of course does not provide strict proof, and on analogy with the geometries of several vinylogs in ammonia solution [19] [20]. The weakest point of the following mechanisms is that invoke only monomers of **1** and **2**; it is quite possible that aggregates play a role.

One mechanism for the reaction of monomeric **1** and **2** with carbonyl compounds is the classical one[4]) involving, sequentially, exchange of a solvent molecule of the solvation shell of **1** and **2** against a molecule of the carbonyl compound, *i.e.* formation of an ate-complex [21] [22] and collapse of this oriented pair *via* a cyclic (perhaps aromatic) transition state, C–C bond formation occuring at the 'free', uncomplexed positions in the ate-complex, as shown for the main reaction between benzaldehyde (**4**) and **1** (*Scheme 1*).

Scheme 1



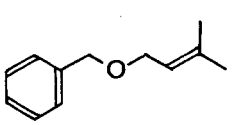
[4]) As usually discussed for the related *Grignard* additions.

Another possibility is a mechanism analogous to the one proposed by *Felkin et al.* for the related *Grignard* additions [23]. It involves S_E2-like, antarafacial attack by the carbonyl C-atom, at the 'unoccupied' side of the allyllithium.

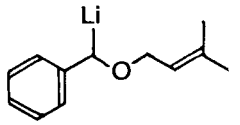
Apart from these ionic mechanisms, a number of mechanisms which proceed by initial one-electron transfer, to give a caged radical-radical anion pair and collapse of the pair to give products are also possible [9] [24–27].

The relation to the anionic rearrangements referred to in the beginning is the following. On lithiation of – for instance – benzyl prenyl ether (**41**), with *n*-butyllithium, the lithio derivative **42** is formed and undergoes rapid intramolecular rearrangements to give a mixture of the alcoholates of **16** and **17** [5] [6] which are also formed in the reaction of benzaldehyde and prenyllithium (**1**) (see the Table). Lithio derivative **42** would be the product of a hypothetical addition of **1** to benzaldehyde, in the 'wrong' sense, at the oxygen atom, and the question arises whether the pathways of addition and rearrangement are perhaps related[5]).

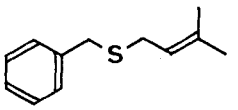
Interestingly, *n*-butyllithium and phenyllithium have been shown to react with thioketones – for instance with thiobenzophenone – by thiophilic addition to give an organolithium compound rather than a thiolate[6]) [28–33], but – for instance – lithio derivative **44** made by lithiation of the corresponding sulfide **43** with *n*-butyllithium – a hypothetical product of a thiophilic addition of **1** to thiobenzaldehyde – undergoes a very clean and rapid [2,3] – rearrangement to give the thiolate **45** [7] [8] which is analogous to the corresponding ether rearrangement (of **42** to give the alcoholate of **16**). Taken together, these findings imply that, contrary to the reaction of alkyllithiums and phenyllithium, the end result of the reaction between allyllithiums and thioketones should be the formation of a C–C rather than a C–S bond. This was indeed observed when adamantanethione (**12**) [34] was treated with prenyllithium (**1**) in tetrahydrofuran solution (see the Table). After methylation of the resulting thiolates with methyl iodide[7]) a *ca.* 1:3 mixture of 2-adamantyl methyl sulfide (**46**) and of the (S-methylated) adduct **26** was obtained (combined



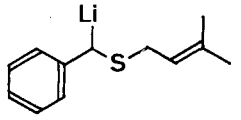
41



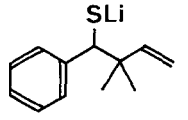
42



43



44



45

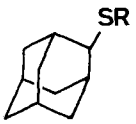
[5]) This will be discussed in the full paper on the rearrangements.

[6]) This is of course in accord with the fact that few [1,2]-anionic shifts from sulfur to carbon (*Wittig* rearrangements) are known.

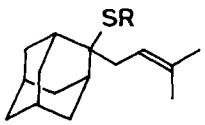
[7]) The thiolates formed were methylated in order to avoid separation of the corresponding thiols from phenol during work-up and because the methyl sulfides are more stable and easier to handle than the thiols.

yield *ca.* 73%). This thioketone was chosen because it is aliphatic and yet non-enolizable, relatively unhindered and stable. That the side chain in **26** is indeed linked to C(2) of the adamantane nucleus by a C–C bond was shown by the spectra and by chemical means. Reaction of **26** with lithium in ammonia gave the hydrocarbon **47**; this reduction seems to be very slow since the corresponding thiol **48** was isolated as the main product (after work-up with aqueous acid).

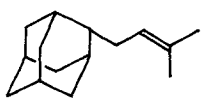
By contrast, reaction of adamantanethione (**12**) with *n*-butyllithium in tetrahydrofuran and work-up with aqueous acid gave mainly adamantane-2-thiol (**49**) but also a small amount of 2-adamantyl *n*-butyl sulfide (**50**) (**49**/**50** *ca.* 95:5, combined yield *ca.* 50%)[8]).



46 R = Me
49 R = H
50 R = Bu



26 R = Me
48 R = H



47

The reaction of prenyllithium (**1**) with adamantanethione (**12**) brings about reduction (*ca.* 25%) and addition (*ca.* 75%) with a bond being formed between the unsubstituted end of the allyl system and the C-atom of the C=S group. Compared with the addition of **1** to adamantanone (**11**) (Table), the orientation of these additions is thus the same with respect to the C=O and C=S groups, but different with respect to the allyl group, **11** giving mainly the branched adduct (**24**) and **12** giving the unbranched one (**26**, after S-methylation) – and this seems to fit the idea of an 'inverse' addition.

The mechanism of this reaction is unclear. Some of the speculation concerning the mechanism of the reaction between carbonyl compounds and allyllithiums is also relevant in this case. The higher polarizability of the C=S bond, its enhanced tendency to react by one-electron transfer processes [30a] [33], as compared to those of the C=O bond, may be important factors.

The reactions of the terpenoid, 'classical' thioketones, thiocamphor (**51**) and thiofenchone (**52**), were also examined but turned out to be less straightforward. Thiocamphor (**51**) reacted exclusively by thioenolization [31], while thiofenchone (**52**), unenolizable but very hindered, underwent mainly reduction [31] along with addition to give the unbranched thiolates.

Experimental Part

Reactions with organolithium compounds were carried out in *Schlenck* tubes (joints) [35] under nitrogen, with magnetic stirring. Solvents were distilled off through an efficient glass spiral column. A small short-path distillation apparatus was used for distillations. NMR. spectra: *Hitachi Perkin-Elmer* R-20 B (60 MHz), in CCl_4 solution, and *Bruker* HF X90, in $DCCl_3$ solution, δ-scale (ppm). IR. spectra: *Perkin-Elmer* 125 (films) max (cm^{-1}). Mass spectra (MS.): *Atlas* CH4,

[8]) In this case the product was not methylated since addition of methyl iodide to the reaction mixture might have led to halogen-metal exchange with excess butyllithium giving butyl iodide, which, in turn, could react with the thiolate of **49** to give **50**; sulfide **50** is indeed formed by thiophilic attack of butyllithium on **12**.

inlet temperature *ca.* 150°; *ca.* 70 eV; M^+ and up to ten fragment ions (down to 10%) are given as *m/e* in % of the most abundant ion. Gas chromatography (GC.): *F & M* 500 and *Carlo Erba* GT, glass columns, 15% Carbowax 20 M on Chromosorb. M. p. were determined on a *Büchi* apparatus (Dr. *Tottoli*) and are not corrected. Abbreviations: tetrahydrofuran, THF; tris (1,1,1,2,2,3,3-heptafluor-7,7-dimethyl-4,6-octadionato)Eu^{III}, $Eu(FOD)_3$ (*Sievers'* reagent).

1. *Prenyllithium* (**1**) [1] [2] [4]. A solution of 8.0 g of phenyl 3-methylbut-2-en-1-yl ether (**53**) [4] (50 mmol) in 170 ml of THF containing 120 mg of biphenyl was treated with 1.6 g (230 mmol) of finely cut lithium (99.8%, max. 0.02% Na; *ca.* 5×5×1 mm pieces, cut in pentane). After stirring for 10–20 min at 25°, the solution turned reddish-brown, the surface of the lithium pieces became shiny, and the temperature rose (to *ca.* 30°). The flask was cooled (water, 25°) and stirring was continued at 25° for *ca.* 24 h. After *ca.* 30 min, the solution turned dark green and after 2–3 h it again turned reddish-brown. The resulting turbid solution of **1**, still containing the excess lithium, was used rapidly; aliquots were taken out with a pipette. The excess lithium was used in the next run. The concentration of **1** in the resulting solution was not determined accurately, but estimated from reactions with adamantanone (**11**) ('titration' with **11**) as *ca.* 0.25 N (*ca.* 65% yield). GC. analysis of the product obtained from reaction of this solution with carbonyl compounds showed the absence of **53**.

2. *Reaction of prenyllithium* (**1**) *with carbonyl compounds. – General procedure.* 3–6 mmol of **1** in THF solution (section 1) were cooled to −60° to −70°, 2.5–5 mmol of the carbonyl compound (as a liquid or in THF solution) were added rapidly with stirring and stirring at −60° to −70° was continued for 25 min. The cold mixture was then poured into water. Extraction with ether, drying ($MgSO_4$), concentration and distillation furnished the products. The yield of distilled product (for simplicity reported incorrectly as 100% adduct[s]) and the b.p. are given in sections 2a to 2k. The distilled products were analyzed by GC. and usually contained 5–15% (35% in the reaction between **1** and **7**) of other minor unidentified components. GC. conditions are reported in sections 2a to 2e. Samples for spectral characterization were isolated by preparative GC. Spectral data are listed in sections 2a to 2e. The structures, product ratios and working temperatures are given in the Table.

a) *Reaction of* **1** *with benzaldehyde* (**4**). B.p. of the distilled product 110–115°/12 Torr. Yield 70%. In the runs at −79° and −25° the distillate was reasonably pure; in the run at 25°, *ca.* 50% of the product consisted of benzyl alcohol. GC. 1.6 m 180° (peaks in the order **16**, **17**). *2,2-Dimethyl-1-phenylbut-3-en-1-ol* (**16**) [5] [6]. – NMR. (60 MHz): 7.13 (5H, *s*); 5.82 (1H, '*d*×*d*', J_1 = 11.5, J_2 = 16.5 Hz); 4.65–5.05 (2H, *m*); 4.18 (1H, *s*); 0.92, 0.90 (2×3H, *s*). – IR. 3450 s, 3090, 3070, 3040 m, 2970, 2930, 2870 s, 1600, 1585 w, 1490, 1470 m, 1450 s, 1410, 1375, 1360, 1200, 1180, 1080 m, 1050, 1020, 910 s, 880, 825 w, 775 m, 725, 700 s. – MS. 107 (100), 105 (16), 79 (73), 77 (41), 70 (70), 56 (11), 55 (19), 51 (16), 41 (20), 39 (18). *4-Methyl-1-phenylpent-3-en-1-ol* (**17**) [5] [6]. – NMR. (60 MHz): 7.12 (5H, *s*); 5.01 (1H, '*t*' (further fine structure), J_1 = 7 Hz); 4.40 (1H, *t*, J_2 = 6.5 Hz); 2.27 (1H, *t* (broad), J_1 = 7 Hz); 1.65, 1.49 (2×3 H, '*s*' [broad]). – IR.: 3400 s, 3090, 3070 w, 3030 m, 2970, 2910 s, 1600 w, 1495 m, 1455 s, 1375 m, 1050, 1030 s, 910, 880 w, 750, 700 s. – MS.: 176 (M^+, weak), 107 (100), 79 (67), 77 (30), 70 (86), 55 (17), 41 (17).

b) *With phenylacetaldehyde* (**5**). B.p. 115–125°/12 Torr. Yield 50%. GC. 2.3 m, 175°. *3,3-Dimethyl-1-phenylpent-4-en-2-ol* (**18**). – NMR. (60 MHz): 7.08 (5 H, *s*); 5.87 (1H, '*d*×*d*', J_1 = 9.5, J_2 = 18 Hz); 4.80–5.20 (2 H, *m*); 3.33 (1H, *d*×*d*, J_3 = 2, J_4 = 10 Hz); 2.78 (1H, *d*×*d*, J_3 = 2, J_5 = 13.5 Hz); 2.29 (1H, *d*×*d*, J_4 = 10, J_5 = 13.5 Hz); 1.02 (6 H, *s*). – IR.: 3570, 3460, 3080, 3060, 3030 m, 2960, 2930 s, 2870, 1635, 1605 m, 1495 s, 1465, 1445, 1415 m, 1285, 1180 w, 1080, 1070, 1030, 1010, 910 s, 855 w, 760 m, 730, 700 s. – MS.: 121 (32), 103 (24), 92 (30), 91 (40), 70 (100), 55 (25), 43 (28).

c) *With hexanal* (**6**). B.p. 87–92°/12 Torr. Yield 80%. GC. 2.3 m, 130°. *3,3-Dimethylnon-1-en-4-ol* (**19**). – NMR. (60 MHz): 5.70 (1H, '*d*×*d*', J_1 = 9.5, J_2 = 18 Hz); 4.7–5.2 (2 H, *m*); 3.16 (1H, *d*, (broad), J_3 = 8.5 Hz); 1.1–1.5 (8 H, *m*); 0.95 (6 H, *s*); 0.95 (3 H, *m*). – IR.: 3400 m, 3080 w, 2960, 2920, 2880, 2860 s, 1635, 1465, 1415, 1375, 1110, 1070, 1000 m, 910 s. – MS.: 83 (15), 70 (100), 55 (58), 43 (25), 42 (12), 41 (25).

d) *With 3-methylbut-2-en-1-al* ('senecia aldehyde') (**7**). B.p. 75–85°/12 Torr. 'Yield' 50% (actual yield of **20** *ca.* 33%). GC. 5 m, 140°. Six minor products (together *ca.* 35% of the distilled

product) were isolated and none of them was the isomeric alcohol or either of the corresponding aldehydes (see the Table). These products were not studied further. *3,3,6-Trimethylhepta-1,5-dien-4-ol* ('artemisia alcohol, [36] **20**). – NMR. (60 MHz): 5.85 (1H, *p*, × *d*', $J_1 = 10$, $J_2 = 18.5$ Hz); 4.70–5.30 (3 H, *m*); 3.88 (1 H, *d*, $J_3 = 9.5$ Hz); 1.71, 1.64, (2 × 3 H, '*s*' [further fine structure]); 0.95, 0.93 (2 × 3 H, *s*). – IR.: 3400 s, 3080 m, 2960, 2920, 2870 s, 1670, 1635 m, 1440, 1410, 1370 s, 1260, 1180 w, 1045, 1000, 905 s, 875, 840 m. – MS.: 85 (100), 55 (13), 43 (12), 41 (28).

e) *With cyclohexanone* (**8**). B.p. 90–95°/12 Torr. Yield 85%. GC. 2.3 m, 130°. *1-(2-Methylbut-3-en-2-yl)cyclohexan-1-ol* (**21**) [37]. – NMR. (60 MHz): 5.70–6.25 (1H [A of an ABC-system[9])]); 4.70–5.15 (2 H, BC); 1.15–1.90 (10 H, *m*); 0.98 (6 H, *s*). – IR.: 3500 m, 3080 w, 2940, 2860 s, 1630 *m*, 1605, 1592 w, 1470, 1450, 1415, 1380, 1340, 1260, 1140 m, 1050, 1030 w, 1005 m, 960, 910 s, 850 m, 840, 750 w. – MS.: 99 (100), 81 (89), 70 (62), 69 (16), 55 (49), 43 (29), 41 (35).

f) *With 2-methylcyclohexanone* (**9**). B.p. 100–110°/12 Torr. Yield 90%. GC. 2.3 m, 130°. According to NMR. spectroscopy using $Eu(FOD)_3$, only one diastereoisomer of **22** was present. Its relative configuration is unknown. *1-(2-methylbut-3-en-2-yl)-2-methylcyclohexan-1-ol* (**22**). – NMR. (90 MHz): 6.23 (1H, '*d* × *d*', $J_1 = 10$, $J_2 = 18$ Hz); 4.8–5.2 (2 H, *m*); 1.15–1.90 (9 H, *m*); 1.10, 1.06 (2 × 3 H, *s*). – IR.: 3550, 3080 w, 2960, 2930, 2850 s, 1630 w, 1550, 1510, 1475 m, 1290, 1250, 1140 w, 1010, 980, 950, 900 m. – MS.: 182 (M^+ (weak)), 113 (100), 95 (85), 70 (34), 69 (37), 55 (44), 45 (25), 43 (49), 39 (42).

g) *With 2,2,6-trimethylcyclohexanone* (**10**). B.p. 125–128°/12 Torr. Yield 80%. A mixture of diastereoisomers **23** was formed and GC. (2.3 m, 150°) did not separate the isomers, which were collected as a mixture. *1-(3-Methylbut-2-en-1-yl)-2,2,6-trimethylcyclohexan-1-ols* (**23**). – NMR. (60 MHz): 5.22 (1H, '*t*' (further fine structure), $J = 7.5$ Hz); 2.24 (d (broad), $J = 7.5$ Hz); 1.68 (2 × 3 H, '*s*' [further fine structure]); 1.1–1.8 (7 H, *m*); 0.75–1.05 (9 H, *m*). – IR.: 3550 m, 2930, 2860 s, 1610, 1595 w, 1460 m, 1385, 1375, 1360 m, 1270, 1220, 1070, 1060, 1040, 980, 950, 925, 860 w. – MS.: 210 (M^+, weak), 141 (77), 123 (100), 94 (57), 83 (63), 71 (34), 69 (52), 59 (84), 55 (52), 43 (71), 41 (68).

h) *With adamantanone* (**11**). **11** was added in THF solution to the solution of **1**. B.p. 128–138°/12 Torr. Yield 80% (oil + crystals). GC. 3 m, 190° (peaks in the order **24**, **25**). M.p. of **24** after sublimation 41–44°. **25** was isolated as an oil. *2-(2-Methylbut-3-en-2-yl)adamantan-2-ol* (**24**). – NMR. (90 MHz): 6.20 (1H, '*d* × *d*', $J_1 = 10$, $J_2 = 18$ Hz); 4.9–5.25 (2 H, *m*); 1.3–2.5 (14 H, *m*[10])); 1.60 (1H(OH)[11]), *s*, did not shift on dilution, but disappeared on shaking with D_2O); 1.21 (6 H, *s*). – IR. (CCl_4): 3620, 3560, 3080 w, 2960, 2900, 2860 s, 1630, 1470, 1460, 1430, 1380, 1360, 1330, 1295, 1160 w, 1100 m, 1060, 1040 w, 1000 m, 970, 935, 925 w, 910 m. – MS.: 151 (100), 107 (12), 91 (21), 81 (22), 79 (21), 70 (12), 67 (14), 55 (54), 55 (54), 44 (16), 41 (29). *2-(3-Methylbut-2-en-1-yl)adamantane-2-ol* (**25**). – NMR. (90 MHz): 5.27 (1H, '*t*' (further fine structure), $J_1 = 8$ Hz); 2.39 (2 H, *d* (broad), $J_1 = 8$ Hz); 1.3–2.5 (14 H, *m*[10])); 1.78, 1.69 (2 × 3 H, *s* [broad]). – IR.: 3560, 3490 m, 2900, 2850 s, 1470 w, 1450 m, 1370, 1350, 1330, 1280, 1155 w, 1100, 1060, 1040, 1020, 1000, 980, 930 m, 900 w, 870 m, 850, 830 w. – MS.: 151 (100), 91 (15), 55 (10), 43 (22), 41 (15).

i) *With cyclopentanone* (**13**). B.p. 82–87°/12 Torr. Yield 85%. GC. 5 m 150°. *2-(2-Methylbut-3-en-2-yl)cyclopentan-1-ol* (**27**). – NMR. (60 MHz): 5.92 (1H, '*d* × *d*', $J_1 = 10$, $J_2 = 18$ Hz); 4.75–5.20 (2 H, *m*); 1.20–1.90 (8 H, *m*); 1.00 (6 H, *s*). – IR.: 3480 s, 3080 m, 2960, 2870 s, 1635, 1465, 1410, 1375, 1360 m, 1280 w, 1180, 1160, 1090, 1050 m, 1000, 980, 910 s. – MS.: 85 (100), 70 (92), 69 (10), 67 (63), 57 (30), 55 (57), 43 (35), 42 (12), 41 (50), 39 (14).

j) *With camphor* (**14**). B.p. 125–135°/12 Torr. Yield 50%. GC. (2.3 m, 160°) separated **28** and **29** on an analytical scale but these isomers were collected together. *2-(2-Methylbut-3-en-2-yl)isoborneol* (**28**)[12]) and *2-(3-methylbut-2-en-1-yl)*isoborneol (**29**)[12]). – Partial NMR. of **28** (60 MHz): 6.19 (1H, '*d* × *d*'); 4.75–5.25 (2 H, *m*); 1.02 (6 H, *s*). – Partial NMR. of **29**: 5.22 (1H, '*t*' [further fine structure]); 2.20 (2 H, *m*); 1.73, 1.62 (2 × 3 H, *s*, [broad]). – IR.: 3560 m, 1630 w. – MS.: 222 (M^+, weak).

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[9]) The other spectra of the corresponding series are reported as *AMX* spectra (sometimes an oversimplification).

[10]) Showing the typical pattern of a 2-substituted adamantane [38].

[11]) The OH signal is not listed in the other reported spectra.

k) *With fenchone* (**15**). B.p. 125–135°/12 Torr. Yield 50%. GC. 2.3 m, 170°. *1,3,3-Trimethyl-2-(3-methylbut-2-en-1-yl)-endo-norborneol* (**30**)[12]. – NMR. (90 MHz): 5.34 (1H, *'t'* (further fine structure), J = 7 Hz); 2.26 (2 H, *d* (broad), J = 7 Hz); 1.76, 1.65 (2×3 H, *s* [broad]); 1.07, 1.04, 0.95 (3×3 H, *s*). – IR.: 3550 m, 2940, 2860 s, 1450, 1380, 1370, 1360 m, 1330, 1300, 1280, 1260, 1245, 1235, 1200, 1105 w, 1060 s, 1040 w, 1000 s, 965, 915, 900, 885, 845, 810, 800 w. – MS.: 222 (M^+, 18), 153 (84), 139 (41), 125 (19), 109 (22), 97 (28), 81 (64), 69 (100), 55 (23), 43 (57), 41 (65).

1) *With adamantanethione* (**12**). This reaction is described in more detail: 30 ml of *ca.* 0.25N solution of **1** (*ca.* 7.5 mmol) (section 1) was cooled to –75° and a solution of 781 mg of **12** (4.40 mmol) in 3 ml of THF was added rapidly with stirring. Stirring at –75° was continued until the red color of **12** has disappeared (15 min) and 1 ml of methyl iodide (2.28 g, 16 mmol) was then added. After stirring for 20 min at –75° and for another 5 min at 25°, water was added. The usual work-up and distillation (b.p. 125–150°/12 Torr) furnished 728 mg of a mixture which consisted (GC. 3 m, 190°, peaks in the order **46**, **26**) of *ca.* 25% of **46** (*ca.* 1.00 mmol, *ca.* 23% yield) and *ca.* 75% of **26** (*ca.* 2.18 mmol, *ca.* 50% yield). GC. also showed several minor unidentified components. **26** and **46** were isolated by GC. *2-(Methylthio)adamantane* (**46**). – NMR. (90 MHz): 3.00 (1H, *'s'*, [broad]); 2.10 (3 H, *s*); 1.3–2.4 (14 H, m[10]). – MS.: 182 (M^+, 33), 136 (12), 135 (100), 94 (40), 93 (32), 92 (16), 81 (14), 79 (31), 77 (13), 67 (30).

2-(3-Methylbut-2-en-1-yl)-2-(methylthio)adamantane (**26**).

$C_{16}H_{26}S$ (250.4) Calc. C 76.75 H 10.47 S 12.78% Found C 76.81 H 10.56 S 12.56%

NMR. (90 MHz): 5.40 (1H, *'t'* (further fine structure), J = 7 Hz); 2.3–2.8 (4 H, m); 1.86 (3 H, *s*); 1.76, 1.69 (2×3 H, *'s'* [further fine structure]); 1.3–2.3 (12 H, m[10]). – IR.: 2970, 2900, 2860 s, 1470 m, 1450, 1440 s, 1370 m, 1350, 1280, 1240, 1115, 1105 w, 1100 m, 1055, 1035, 950, 920, 885, 875, 845, 820, 800 w.

3. *Reduction of the mixture of* **26** *and* **46**. 423 mg of the mixture **26**+**46** obtained as described (section 2 l) in 7 ml of THF were added at –75° with stirring to 25 ml of ammonia. 133 mg of lithium cut into small pieces were added and the mixture was stirred and kept at reflux for 30 min. Excess lithium was then decomposed by addition of methanol/ether and the ammonia was allowed to evaporate. The usual hydrolytic work-up gave *ca.* 400 mg of crude product. GC.-analysis (3 m, 190°) showed two major products, **48**, and adamantane-2-thiol (**49**) [34], and a minor component, **47** (peaks in the order **47**, **49**, **48**). Compounds **47**, **48** and **49** were isolated by GC. Thiol **49** was identified by comparison (GC., spectra, m.p.) with an authentic sample [34]. *2-(3-Methylbut-2-en-1-yl)adamantane* (**47**). – NMR. (90 MHz): 5.12 (1H, *'t'* (further fine structure), J = 7 Hz); 1.35–2.30 (17 H, m, in part m[10]); 1.71, 1.65 (2×3 H, *'s'* [further fine structure]). – MS.: 204 (M^+, 4), 148 (59), 136 (12), 135 (100), 93 (29), 91 (12), 81 (16), 79 (28), 69 (10), 67 (35), 41 (25). *2-(3-Methylbut-2-en-1-yl)adamantane-2-thiol* (**48**). – NMR. (90 MHz): 5.32 (1H, *'t'* (further fine structure), J = 7 Hz); 2.64 (2 H, *d* (broad), J = 7 Hz); 1.4–2.6 (14 H, m[10]); 1.93 (1H, *s*); 1.79, 1.70 (2×3 H, *'s'* [further fine structure]). – IR.: 2900, 2860 *s*, 1470, 1450, 1375 m, 1350, 1305, 1280, 1240, 1215, 1115 w, 1100 m, 1050, 1030, 970, 920, 890, 880, 840, 800 w. – MS.: 236 (M^+, weak), 202 (26), 168 (13), 167 (100), 166 (18), 133 (23), 105 (13), 91 (46), 88 (15), 79 (42), 69 (14).

4. *Reaction of adamantanethione* (**12**) *with* n-*butyllithium*. A stirred solution of 401 mg of **12** (containing an impurity of *ca.* 9% of **11** according to GC.) (2.40 mmol) in 3 ml of THF was treated at –75° with 1.85 ml of 1.63N *n*-butyllithium/hexane (3.0 mmol). The orange colour of **12** disappeared when *ca.* 1.65 mmol of *n*-butyllithium had been added. The resulting yellow solution was stirred for 10 min at –75° and then poured into 2% aqueous H_2SO_4. The usual work-up and distillation (b.p. 112–117°/12 Torr) gave 228 mg of a crystalline mixture. GC. (3 m, 175°) indicated that it consisted of *ca.* 85% of **49** (*ca.* 1.15 mmol, *ca.* 48% yield), *ca.* 10% of 2-butyladamantan-2-ol (**54**), *ca.* 5% of **50** (*ca.* 0.05 mmol, *ca.* 2% yield), and of a trace of **12** (peaks in the order **49**, **12**, **50**, **54**). Thiol **49** was isolated by GC., further purified by sublimation and identified by comparison with an authentic sample (GC., spectra, m.p.) [34]. Compounds **50** and **54** could be separated by analytical GC. but were collected as a mixture. The components were identified by comparison

[12] The geometry was not proven, the assignment is based only on analogy to related addition reactions.

(GC., spectra) of the collected mixture with authentic samples of **50** and **54** (section 5 and 6). *2-Butyladamantan-2-ol* (**54**) is formed from butyllithium and *ca.* 9% adamantanone (**11**) which was present in the sample of **12** used.

5. *2-(Butylthio)adamantane* (**50**). A stirred solution of 440 mg of **49** [34] (2.62 mmol) in 5 ml of THF was treated at −75° with 1.95 ml of 1.63N *n*-butyllithium/hexane (320 mmol). The mixture was first warmed to 23°, then cooled to −75°, 0.45 ml of butyl iodide (725 mg, 3.95 mmol) were added, and stirring was continued for 10 min at −75° and 1 h at 23°. Addition of water, the usual work-up and distillation (b.p. 120–130°/12 Torr) afforded 335 mg of **50** (1.50 mmol, 57%), which was purified by GC. (3 m, 175°). **50** (oil). – NMR. (90 MHz): 3.05 (1H, '*s*' [broad]); 2.52 (2 H, '*t*' (broad), $J = 6$ Hz); 1.1–2.4 (18 H, *m*, in part *m*[10])); 0.8–1.1 (3H, *m*). – IR.: 2960, 2900, 2850 s, 2650 w, 1475, 1450 s, 1375 w, 1350 m, 1340, 1310, 1300 w, 1290 m, 1270, 1240 w, 1220 m, 1200 w, 1100 s, 1060, 1040 w, 960 m. – MS.: 224 (M^+, 30), 135 (100), 93 (22), 79 (20), 67 (24).

6. *2-Butyladamantan-2-ol* (**54**). A stirred solution of 50 mg of **11** (3.34 mmol) in 4 ml of THF was treated at −75° with 2.65 ml of 1.63N *n*-butyllithium/hexane (4.30 mmol). After warming up and stirring at 23° for 5 min water was added. The usual work-up and distillation (b.p. 120–130°/12 Torr) gave 547 mg (2.65 mmol, 79%) of **54**, which was purified by GC. (3 m, 175°), followed by sublimation: m.p. 77–78°. **54**. – NMR. (90 MHz): 1.1–2.4 (20 H, *m*, in part *m*[10])); 1.37 (1H (OH), *s*[11])); 0.8–1.1 (3 H, *m*). – IR. (CCl_4): 3600, 3500 w, 2960, 2900, 2860 s, 1450 m, 1375, 1350, 1280 w, 1140 m, 1095, 1040, 1030 w, 990 m, 980 m, 925. – MS.: 151 (100).

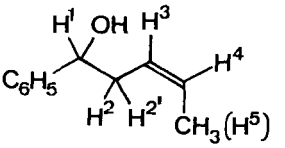
7. *A mixture of but-3-en-2-yl phenyl ether* (**55**) and (E)-*but-2-en-1-yl ether* (**56**) was prepared from phenol and *E*-crotyl bromide (**57**) according to [4]. This mixture was used as such for the preparation of **2** (section 8) [2].

8. *Crotyllithium* (**2**) was obtained exactly as described for the preparation of **1** (section 1) in similar yield.

9. *Reactions of crotyllithium* (**2**) *with carbonyl compounds* were carried out as described for those of **1** (section 2). B.p. of distilled product, yields (as specified in section 2), GC. conditions, and spectral data are given in sections 9a to 9g. The structures, product ratios and working temperatures are given in the Table.

a) *Reaction of* **2** *with benzaldehyde*. B.p. 90–100°/12 Torr. Yield 80%. GC. 3 m, 180° (peaks in the order *erythro*-**31**, *threo*-**31**, **32**). Diastereoisomers **31** were just separable by analytical GC. but collected as a mixture. A *ca.* 55:45 mixture of *threo*-**31**[13]) and *erythro*-**31**[13]) was obtained. Threo- *and* erythro-*2-methyl-1-phenyl-but-3-en-1-ols* (**31**) (mixture) [5] [39]. – NMR. (90 MHz): The following signals of *threo*-**34** and *erythro*-**34** coincide: 7.32 (5H, *s*); 5.55–6.10 (1H, *m*); 4.85–5.35 (2H, *m*); 2.30–2.80 (1H, *m*). *Threo*-**34**: 4.63 (1H, *d*, $J_1 = 6$ Hz); 1.02 (3H, *d*, $J_2 = 7$ Hz). *Erythro*-**34**: 4.38 (1H, *d*, $J_1 = 8$ Hz); 0.88 (3H, *d*, $J_2 = 7$ Hz). – IR. (CCl_4): 3450, 3080, 3060, 3030, 2970, 2930, 2870 s, 1635, 1490 m, 1450 s, 1410, 1370 m, 1220, 1190, 1100, 1070 w, 1000, 910, 700 s. – MS.: 107 (100), 79 (75), 77 (41), 51 (10).

(Z)-*1-Phenylpent-3-en-1-ol* (**32**). – NMR. (90 MHz): 7.2–7.5 (5H, *m*); 5.2–5.9 (H^3, H^4, *m*); 4.72 (H^1, '*t*' (broad), $J_{12} \approx J_{12'} = 7$ Hz); 2.3–2.7 (H^3, H^4, *m*); 1.62 (3H[5], *d*, $J_{45} = 5.5$ Hz). Complexation with $Eu(FOD)_3$ gave a spectrum in which the signals of H^3 and H^4 were resolved and on irradiation of H^5, H^4 appeared as a doublet ($J_{34} = 10.8$ Hz).



32

b) *With phenylacetaldehyde* (**5**). B.p. 100–110°/12 Torr. Yield 50%. Very probably a mixture of diastereoisomers **33** is formed and GC. (2.3 m, 175°) did not separate the isomers which were collected as a mixture. *3-Methyl-1-phenylpent-4-en-2-ols* (**33**) (mixture). – NMR (60 MHz): 7.05

[13]) As defined in [5].

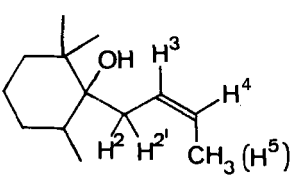
(5H, *s*); 5.4–6.1 (1H, *m*); 4.7–5.2 (2H, *m*); 3.3–3.7 (1H, *m*); 2.3–2.8 (3H, *m*); 1.01 (3H, *d*, J = 6.5 Hz). – IR.: 3570 m, 3450 s, 3090, 3070 m, 3030, 2980, 2930, 2880 s, 1640, 1605 m, 1495, 1455 s, 1420, 1390, 1370, 1105 w, 1075 m, 1030, 1000 s, 965 m, 915 s, 960 w, 745, 700 s. – MS.: 176 (M^+, weak), 121 (72), 120 (30), 103 (48), 92 (100), 91 (88), **77** (17), 65 (20), 56 (16), 44 (16), 43 (38.

c) *With hexanal* (**6**). B.p. 87–91°/12 Torr. Yield 70%. A mixture of diasteroisomers **34a**, **34b** was formed (ratio 45:55) and GC. (5 m, 135°, peaks in the order **34a**, **34b**, **35**) did just separate isomers **34** on an analytical scale. These isomers (**34**) were collected together. *3-Methylnon-1-en-4-ols* (**34a** + **34b**) (mixture). – NMR. (60 MHz): 5.4–6.1 (1H, *m*); 4.7–5.3 (2H, *m*); 3.1–3.6 (1H, *m*); 1.8–2.5 (1H, *m*); 1.1–1.7 (8H, *m*); 0.96 (3H, *d*, J = 6.5 Hz); 0.75–1.0 (3H, *m*). – IR.: 3400 s, 3070 m, 2900, 2850 s, 1635 m, 1450 s, 1410, 1370, 990 m, 905 s. – MS.: 156 (M^+, weak), 101 (12), 83 (63), 57 (17), 56 (100), 55 (93), 43 (36), 41 (44).

d) *With cyclohexanone* (**8**). B.p. 82–86°/12 Torr. Yield 90%. GC. 5 m, 150°. *1-(But-3-en-2-yl)-cyclohexan-1-ol* (**36**). – NMR. (60 MHz): 5.4–6.2 (1H, *m*); 4.7–5.2 (2 H, *m*); 1.8–2.4 (1H, *m*); 1.3–1.6 (10 H, *m*); 0.96 (3 H, *d*, J = 7 Hz). – IR.: 3460 s, 3080 m, 2980, 2940, 2860 s, 1635 m, 1450 s, 1415, 1370, 1260, 1250, 1160, 1135 m, 1050, 1035 w, 1020, 1000 m, 950, 910 s, 750 w. – MS.: 99 (100), 81 (90), 57 (11), 55 (51), 43 (21), 41 (21).

e) *With 2-methylcyclohexanone* (**9**). B.p. 90–94°/12 Torr. Yield 85%. GC. (5 m, 135°) showed that all four possible diastereoisomers **37a–c** were present. Two of these were collected in pure form. The remaining two were difficult to separate, and were collected as a mixture. The relative configurations of these isomers are unknown. *1-(But-3-en-2-yl)-2-methyl-cyclohexan-1-ols* (**37a–c**). **37a**. – NMR. (60 MHz): 5.5–6.15 (1H, *m*); 4.8–5.3 (2 H, *m*); 2.1–2.7 (1H, *m* [5 lines]); 1.2–1.9 (9 H, *m*); 0.92 (3 H, *d*, J_1 = 7 Hz); 0.84 (3 H, *d* (broad), J_2 = 5 Hz). – IR.: 3590, 3500, 3080 m, 2970, 2940, 2860 s, 1630 m, 1500 w, 1460 s, 1415 w, 1380 s, 1360 m, 1300 w, 1250, 1200, 1160, 1145 m, 1080, 1060 w, 1005, 990, 960, 920 s, 890 m, 800, 750 w, 725 m. – MS.: 168 (M^+, weak), 113 (100), 95 (92), 69 (35), 68 (12), 67 (16), 57 (13), 55 (56), 45 (31), 43 (39). **37b**. – NMR. very similar to that of **37a** differing in: 2.15–2.80 (1H, *m*); 0.95 (3 H, *d*, J_1 = 7 Hz); 0.92 (3 H, *d* (broad), J_2 = 5 Hz). – IR. differing from that of **37a** in 1370 m, 1270, 1250 w, 1130 m, 1080, 1070, 1030 w, 1000, 970, 950, 920 s, 890 m, 870, 815, 800, 750 w, 725 m. – MS. identical with that of **37a**. **37c**+**37d**. – Spectra very similar to those of **37a** and **37b**.

f) *With 2,2,6-trimethylcyclohexanone* (**10**). B.p. 115–120°/12 Torr. Yield 90%. A mixture of diastereoisomers **38** was formed and GC. (5 m, 170°) did not separate the isomers, which were collected as a mixture. *1-((Z)-but-2-en-1-yl)-2,2,6-trimethylcyclohexan-1-ols* (**38a–b**) (mixture). – NMR. (90 MHz): 5.35–5.90 (H^3, H^4, *m*); 2.25–2.50 (H^2, $H^{2'}$, *m*); 1.2–2.0 (10 H, *m*); 0.8–1.1 (9 H, *m*). Complexation with $Eu(FOD)_3$ gave a spectrum in which the signals of H^3 and H^4 of both isomers **38a** and **38b** were resolved.



38a,b

Irradiation at the multiplet corresponding to H^2, $H^{2'}$ of **38a** and **38b** (Eu $(FOD)_3$ complexes) gave partial spectra: **38a**. – H^3 (*d* (broad), J_{34} = 11 Hz), H^4 (*d* × *q*, J_{34} = 11, J_{45} = 5.5 Hz). **38b** similar but differing in the chemical shifts. Integration (of the OH-signals) gave **38a**/**38b** 65:35. The relative configurations of these isomers are not known. – IR.: 3530, 3030 w, 2980, 2960, 2930, 2880, 2860 s, 1475, 1460 m, 1385, 1370, 1270, 1210, 1070, 1060, 1040 w. – MS.: 196 (M^+, weak), 141 (80), 123 (100), 83 (79), 71 (47), 69 (80), 59 (86), 57 (37), 55 (88), 43 (96), 41 (75).

g) *With cyclopentanone* (**13**). B.p. 74–76°/12 Torr. Yield 65%. GC. 5 m, 140°. *1-(But-3-en-2-yl)-cyclopentan-1-ol* (**39**). – NMR. (60 MHz): 5.5–6.2 (1H, *m*); 4.8–5.3 (2 H, *m*); 1.3–2.5 (9 H, *m*); 1.02 (3 H, *d*, J = 6.5 Hz). – IR.: 3520 s, 3070 m, 2960, 2880 s, 1635, 1450 m, 1430, 1410 w, 1360 m, 1330 w, 1270, 1190 m, 1120 w, 980, 960, 910 m. – MS.: 85 (100), 67 (63), 57 (38), 55 (51), 43 (23), 41 (34).

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