63. Sigmatropic Reactions in Carbanions. I. The 5,6-Dihydro-2H-pyran-2-ide Cyclopropyl-enolate Rearrangement

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Summary. Lithiation of 5,6-dihydro-2*H*-pyran (**7**) gives a mixture of dihydropyranyllithiums **14** and **2**. **14** rearranges to **2**, and **2** in turn undergoes a [1,4] sigmatropic shift to give the lithium cyclopropyl-enolate **3**. Lithiation of nerol oxide **6** gives the lithio derivative **24**, which likewise undergoes [1,4] shifts to give cyclopropyl-enolates **28** and **29**.

1. Introduction. – Sigmatropic shifts [1] of alkyl or allyl groups ([1,2], [3,2], [1,4] shifts, etc.) in simple carbanionoids [2] have prohibitively high activation energies. Two factors contribute to this situation. There exists an inherent barrier — general molecular orbital theory indicates that sigmatropic reactivity is highest in a carbonium ion (π-acceptor), lower in a radical, and lowest in a carbanion (π-donor) [3][1] —, and a barrier which is due to the fact that dissociation of the carbon-metal bond is minimal in such systems [2]. These two factors are interrelated in that a favourable sigmatropic process may promote ionisation (neighbouring group participation).

The known anionic alkyl and allyl shifts occur in systems in which these barriers are drastically lowered by appropriate substitution [4]. The most general type of rearrangement occurs in carbanions which bear an electronegative α-substituent such as oxygen, nitrogen, or sulfur, which stabilizes the carbanion and to which the negative charge is transferred in the rearrangement [4]. These processes are highly exoenergetic and the activation barriers to rearrangement are therefore lowered (*Hammond* postulate).

A frontier orbital analysis of these rearrangements reveals the available concerted pathways [1]. In its simplest form, this analysis is carried out as follows: the bond to the migrating group is taken to be broken homolytically, but positive overlap between the highest occupied molecular orbitals ('HOMO's') of these fragments is maintained. The symmetries of these 'HOMO's' then determine the various concerted pathways.

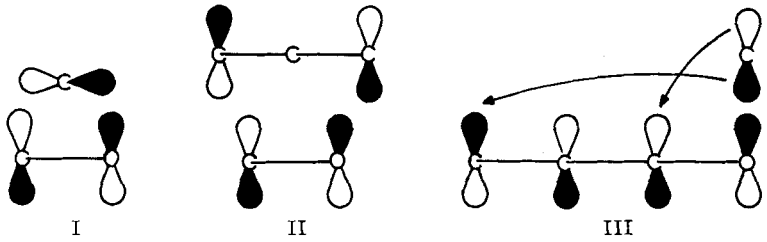
Alternative stepwise mechanisms very probably involve dissociation of these fragments into radical-radical anion pairs, and recombination [4]. These radical pairs may be stabilized by the hetero atom to such an extent that the stepwise and the concerted processes (whose transition states can be viewed as species in which these fragments interact) may have very similar activation barriers (this interaction leads to little further stabilization). The available concerted pathways are primarily determined by the geometry of the systems and may be sensitive to steric effects; both these factors have little, if any, influence on the stepwise pathways. If these factors are favourable, then concerted mechanisms may dominate; if they are not, then dissociation/recombination pathways of very similar activation energy may be available.

This mechanistic dichotomy is particularly evident in anionic alkyl (or allyl) shifts from oxygen to carbon. Three types of these have been studied in some detail.

1. In the classical *Wittig* rearrangement, the anionic [1,2] alkyl shift from oxygen to carbon, the dissociation/recombination mechanism is dominant [4]. This must be due to the fact that the concerted suprafacial pathway (transition state I) demands inversion at the migrating carbon

[1] This has only been shown in detail for the [1,2] shift with retention at the migrating carbon atom [3], which is not orbital-symmetry-allowed for the anion. The general principle should be valid for other geometries and migrating groups (with sp^2-hybridized carbon), and for other types of anionic shifts. The barrier is probably higher for 4π-(*Möbius*) systems (in [1,2] shifts) than for 6π-(*Hückel*) systems (in [3,2] or [1,4] shifts).

atom; this process may involve inefficient bonding between the two fragments and is unfavourable for steric reasons (on steric grounds, the concerted antarafacial [1,2] shift is excluded).



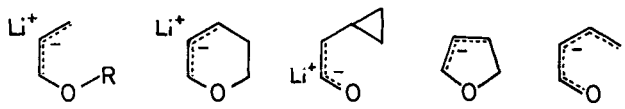
I II III

2. There is evidence [4] [5], that [3,2] anionic shifts from oxygen to carbon can occur in concert. A dissociation/recombination sequence of slightly higher activation energy can compete with this process [5]. The concerted [3,2] shift must be suprafacial (transition state II) or antarafacial with respect to both fragments; actually, the doubly suprafacial concerted process (II), which involves more efficient overlap and is geometrically more favourable, occurs [5].

3. Alkoxyallyllithiums of type **1** (R = Alkyl) have been found to undergo concurrent [1,2] and [1,4] shifts, which very probably occur via a dissociation/recombination process [6]. In this system, the concerted suprafacial [1,2] shift must again occur with inversion at the migrating carbon atom, while the concerted suprafacial [1,4] shift must occur with retention at the migrating carbon [transition state III, (arrows)]. Because of more efficient bonding and on steric grounds the concerted [1,4] shift should be favoured over the concerted [1,2] shift. In fact, both these pathways seem to have higher activation barriers than a dissociation/recombination sequence (on steric grounds, concerted antarafacial [1,2] and [1,4] shifts are again excluded).

In the more complex systems (2) and (3), the dissociation/recombination pathway characteristically leads to all possible recombination products; in the rearrangement of carbanions of type **1**, this process brings about concurrent [1,2] and [1,4] shifts.

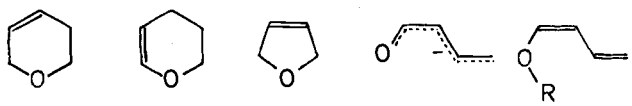
We report here on the rearrangement of dihydropyranyllithium **2**, the simplest cyclic system of type **1**, which gives the lithium cyclopropyl-enolate **3**, by an exclusive [1,4] anionic shift[2]) from oxygen to carbon, and the analogous rearrangement of the allylic lithium compound derived from nerol oxide (**6**).



1 **2** **3** **4** **5**

This type of [1,4] sigmatropic shift is related to the electrocyclic ring opening of dihydrofuranide anion **4** to give butadienolate **5** [8], in that, formally, one double bond in **5** is changed into a cyclopropane ring, whose ability to replace a π-bond is known. An analogous [1,4] anionic shift from sulfur to carbon has been recently described by *Biellmann & Ducep* [9].

The most direct way to **2** is by abstraction of an allylic proton next to oxygen in 5,6-dihydro-2*H*-pyran (**7**) [10]. We have studied the reaction of **7**, and in the context, that of the more accessible 3,4-dihydro-2*H*-pyran (**8**), with *n*-butyllithium.



7 **8** **9** **10** **11**

[2]) For a related [1,4] shift, see [7]; in this system, a [1,2] shift is not possible.

Products were trapped by reaction with acetic anhydride [11] or, more efficiently, with trimethylsilyl chloride [12]. The resulting enol acetates and trimethylsilyl derivatives could be distilled and subjected to gas chromatography (GLPC.).

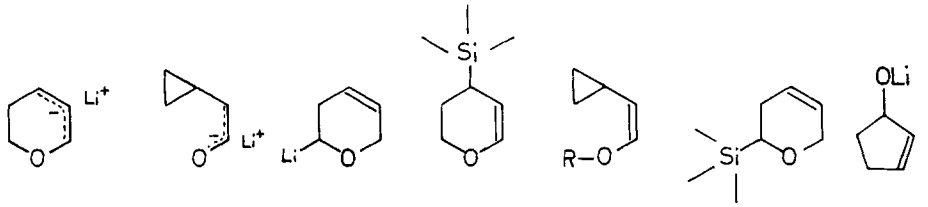
2. Model Studies in the Dihydrofuranyl System. – The analogous generation of dihydrofuranyllithium (**4**)[3] from 2,5-dihydrofuran (**9**) and the trapping of the products of its electrocyclic opening, lithium butadienolates **5** or **10**[3], served as models in elaborating lithiation and trapping methods.

Kloosterziel and coworkers [8] have observed the rapid formation of **10** on reaction of **9** with potassium amide in ammonia at $-60°$, by NMR. spectroscopy. We have found that **5** or **10**[3] is also readily formed by reaction of **9** with *n*-butyllithium at $-27°$ in tetrahydrofuran, or in ether in the presence of N,N,N',N'-tetramethylethylenediamine[4], and that **5** or **10** can then be trapped with acetic anhydride or trimethylsilyl chloride[4], to give the isomerically pure butadienes, *cis*-1-acetoxy-buta-1,3-diene (**11**, R = Ac)[5] (60%) and *cis*-1-trimethylsilyloxy-buta-1,3-diene (**11**, R = $SiMe_3$)[5] (70%). The opening of **4** is known [8] to be very fast at $-27°$ and no attempt was made to trap it. The rate of the conversion of **9** into **10** is determined by that of the lithiation step; the rate of this step was not studied in detail.

The enol acetate **11** (R = Ac) was identified by its IR. spectrum [13] and NMR. spectrum, which resembles that of **11** (R = $SiMe_3$). The structure of **11** (R = $SiMe_3$) was proved by converting it back to **10** (methyllithium in 1,2-dimethoxyethane [12]), which was then trapped to give **11** (R = Ac).

3. Lithiation of 5,6-Dihydro-2*H*-pyran (7) and Related Reactions. – When **7** was treated for 17 h with 1.6 equiv. of *n*-butyllithium in tetrahydrofuran at $-27°$, and the product then quenched with acetic anhydride, *cis*-acetoxyvinyl-cyclopropane (**12**, R = Ac)[5] was formed as the only detectable product, and could be isolated by GLPC., but the yield was low (ca. 10%).

Trapping of lithiated products with excess trimethylsilyl chloride after lithiation at $-27°$ with 1.5 equiv. of *n*-butyllithium in ether in the presence of tetramethylethylenediamine[4] was more effective and showed that lithiation and subsequent rearrangements were more complex than expected. Not only was enolate **3** efficiently O-silylated to give **12** (R = $SiMe_3$),[5] but in addition two unrearranged lithio derivatives of 5,6-dihydro-2*H*-pyran (**7**) were C-silylated in high yield. Acetic anhydride apparently did not trap these, and **7** or **8**, formed on hydrolysis, was lost during the work-up. Apart from the expected allylic dihydropyranyllithium **2**, which was tri-



2 **3** **14** **13** **12** **15** **16**

[3] The counter-ion is not drawn.

[4] Tetramethylethylenediamine was added because this amine facilitates not only lithiation but also trimethylsilylation [12].

methylsilylated to give **13**[5]), the homoallylic isomer **14**, trimethylsilylated to give **15**[5]) was formed. The products **12** (R = $SiMe_3$), **13**, and **15**, could be distilled, and pure samples were obtained by GLPC.

The structures of **13** and **15** were deduced from the NMR. spectra, by comparison with those of the unsubstituted dihydropyrans **7** and **8**, and had appropriate IR. and mass spectra. Enol acetate **12** (R = Ac) and enol ether **12** (R = $SiMe_3$) were likewise identified on the basis of their characteristic NMR. spectra and of the IR. and mass spectra.

Under the conditions (*n*-butyllithium/ether/tetramethylethylenediamine at $-27°$) lithiation of **7** to give **2** and **14** proved to be rapid, compared to the subsequent rearrangements of **2** and **14**, so that these rearrangements could be monitored by quenching individual runs with trimethylsilyl chloride after various reaction times at $-27°$, followed by work-up, distillation, and analysis by GLPC. The results are given in Table 1.

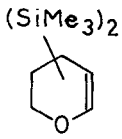
Table 1. *Trimethylsilylated Products from the Reaction of* **7** *with* n-*Butyllithium in Ether/Tetramethylethylenediamine at* $-27°$

time	yield[a])	ratio of products		
		15[a])	**13**	**12** (R = $SiMe_3$)
3 min	45	72	28	0
10 min	66	80	20	0
1 h	71	76	18	6
3.7 h	73	56	18	25
8 h	70	38	17	45
16 h	70	34	16	49
39 h	65	16	14	64
64 h	63	12	12	72
260 h	61	2	3	93

[a]) Corrected, see experimental section.

Lithiation of **7** is complete after ca. 30 min. At shorter reaction times, the yields reflect incomplete lithiation and after long reaction times, needed for complete rearrangement to **3**, some decomposition (presumably of all three lithio derivatives) occurs. During quenching and working-up, some of the lithio compounds and trimethylsilyl derivatives, in particular enol ether **12**, are probably lost and the real yields are probably higher.

In these reactions, a side-product was formed (see experimental section), which could be isolated by GLPC. and for which the NMR. and mass spectra indicate the general structure **17**[6]).



17

That **17** was not formed from a dilithiated precursor, but rather after quenching with trimethylsilyl chloride, by lithiation of **13** or **15** by surviving butyllithium and subsequent trimethylsilylation, was shown by treating a mixture of **13** and **15** with butyllithium and then immediately with

[5]) Systematic nomenclature is used in the experimental section.

[6]) Compound **17** is probably 3,4-dihydro-4,6-bis-trimethylsilyl-2*H*-pyran.

trimethylsilyl chloride, as in the usual lithiation and quenching procedure, which converted **15** almost completely into **17**, while **13** remained unchanged (Table 1 is corrected for this side reaction).

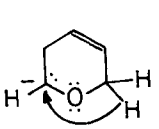
In these reactions, yellow-white precipitates are formed, which probably contain at least some of the lithiated species. Further kinetic analysis of these heterogenous systems is thus not feasible[7]).

The trimethylsilylated products **12** (R = $SiMe_3$), **13**, **15** and **17** were the only detectable products. In particular, the product of a [1,2] shift in **2**, lithium cyclopentenolate **16**, was not detected.

The product of the lithiation of **7** with *n*-butyllithium is a ca. 1:4 mixture of the dihydropyranyllithiums **2** and **14**. Both **2** and **14** rearrange completely to **3**. The mechanism of the [1,4] sigmatropic shift **2** → **3** will be discussed later, together with those of the analogous [1,4] shifts which have been found to occur on lithiation of nerol oxide (**6**) (*v. inf.*). Dihydropyranyllithium **14** cannot give **3** directly – a hydrogen shift and an alkyl shift must occur – and the simplest scheme which can account for this transformation is a rearrangement of **14** to **2**, followed by rearrangement of **2** to **3**. The mechanism of the postulated rearrangement **14** → **2** is not yet known. The following considerations are relevant to this problem.

The homoallyllithium compound **14** is the product of kinetically controlled lithiation, but could be in equilibrium with the allylic isomer **2**. At present we lack a method of generating **2** alone in order to see whether, apart from the rearrangement **2** → **3**, rearrangement back to **14** (**2** → **14**) occurs. The apparent stability of **14**, whether reflecting kinetic or thermodynamic acidity, must be due to homoallylic or to cyclic (6π) delocalisation[8]). For the proposed (possibly reversible) rearrangement **14** → **2**, various intermolecular mechanisms and an intramolecular one can be considered. An intermolecular mechanism could for instance involve reaction of **14** with unreacted**7**, which could be present in low concentration, to give **2** (and **7**). The intramolecular process is or a concerted [1,3] hydrogen shift in **14**, as indicated by the arrow in **18**[3]), allowed by orbital symmetry if an electron pair on the oxygen atom is assumed to complete the aromatic transition state. The alternative intramolecular pathway, the [1,3] hydrogen shift indicated by the arrow in **19**[3]), is not orbital-symmetry-allowed and therefore excluded.

A hydrogen shift across the heteroatom, analogous to the one formally depicted in **18** (a concerted [1,3] shift or a protonation-deprotonation sequence), but in reverse, has been observed in vinylsulfonium ylides [14]. This lends support to our hypothesis, and this type of hydrogen shift[9]) may prove to be general.



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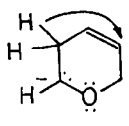

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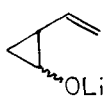


20

Another orbital-symmetry-allowed, concerted rearrangement which **14** could undergo, is a [2,3] sigmatropic shift to give lithium cyclopropanolates **20**, but this

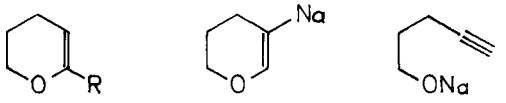
[7]) We hope to carry out a kinetic analysis, by direct NMR. spectroscopic observation of the anions in ammonia solution.

[8]) Note that **8** is lithiated in quite a different way (*v. inf.*).

[9]) It has also been envisaged in benzylthioallyl anions [15].

is not observed. In open-chain derivatives of **14**, this process occurs readily [5]. If the rearrangement **14** → **2** is an intermolecular process, then rearrangement **14** → **20** may take place under other conditions. (We assume that structure **20** is thermodynamically favoured over **14**, since **3** is favoured over **2** (*v. inf.*).)

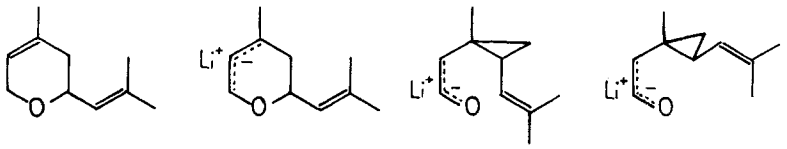
As another possible route to dihydropyranyllithium **2**, and in view of the abnormal lithiation of **7** (to give **14**), the lithiation of **8** under the conditions described for that of **7**, was briefly studied. It did not, however, lead to **2**; instead, in a slow reaction, **21** (R = Li) was formed as the only product and trapped as the trimethylsilyl derivative **21** (R = $SiMe_3$)[5]). This derivative was isolated by distillation and GLPC. Its structure was deduced on the basis of the NMR. and the mass spectra.



21 **22** **23**

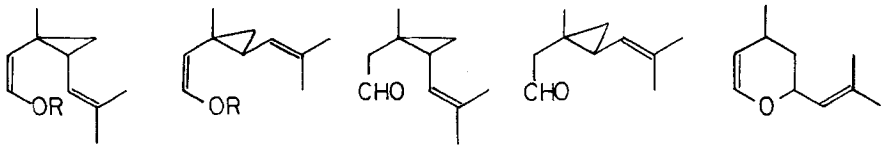
This type of metallation has been previously observed in the reaction of **8** and amylsodium giving **21** (R = Na) together with **22**, which then underwent ring opening to **23** [16]. The lithiations of ethyl vinyl ether [17] and of furan [18] are similar.

4. Lithiation of Nerol Oxide (6) and Related Reactions. – It was of interest to us to study the analogous lithiation of the terpenoid 5,6-dihydro-*2H*-pyran derivative, nerol oxide (**6**) [19]. We expected it to be lithiated at the less substituted allylic position next to oxygen to give allyllithium compound **24**, which could then undergo a [1,4] sigmatropic shift to lithium enolates **25** and **26**, with novel terpenoid structures not otherwise available. The presence of the allylic side chain might, however, permit other modes of rearrangement (see sections 5).



6 **24** **25** **26**

The only detectable products from reaction of **6** with *n*-butyllithium in tetrahydrofuran at –27°, or in ether in the presence of tetramethylethylenediamine, were the enolates **25** and **26**. These were trapped with acetic anhydride as enol acetates **27** (R = Ac) and **28** (R = Ac)[5]) (60%) or with trimethylsilyl chloride as enol ethers **27** (R = $SiMe_3$) and **28** (R = $SiMe_3$)[5]) (80%). Mixtures of these acetates and trimethylsilyl ethers could be obtained by distillation. Both mixtures could be subjected to GLPC., and pure samples of the isomeric acetates were thus isolated.



27 **28** **29** **30** **31**

On hydrolysis, the mixture of **25** and **26** gave a mixture of aldehydes **29** and **30**[5]) in ca. 40% yield. These were also formed on hydrolysis of the mixture of enol ethers **27** (R = $SiMe_3$) and **28** (R = $SiMe_3$). They were separated by GLPC.

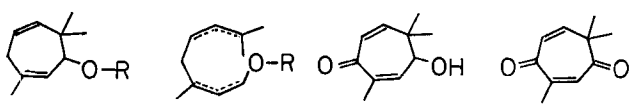
The structures and the stereochemistry of products **27**, **28** (R = Ac, $SiMe_3$), **29** and **30** were mainly assigned on the basis of the NMR. spectra (see experimental section). The chemical shifts of the geminal cyclopropane hydrogens differ more in the *cis*-divinylcyclopropane derivative **27** (R = Ac) (0.39 and 1.05 ppm) than in the *trans*-isomer **28** (R = Ac), because in **27** (R = Ac) the *endo*-hydrogen is shielded by the two double bonds; the coupling of the *endo*-hydrogen of **27** (R = Ac) is typically small ($J_2 = 3.7$, $J_3 = 5.7$ Hz). This shielding effect in *cis*-divinylcyclopropanes has been noted before [20] (see also the spectrum of bicyclo[6.1.0]nona-2,6-diene [21]). The mass spectra of **27** and **28** (R = Ac, $SiMe_3$) are identical and show signals corresponding to the molecular ions.

On quenching with trimethylsilyl chloride under conditions of incomplete conversion **6** → **25** + **26**, the presumed intermediate **24** was not trapped, only **6**, **27** and **28** (R = $SiMe_3$) being found. Similarly, hydrolysis at incomplete conversion gave only **6**, **29** and **30**, and no **31**, and hydrolysis with deuterium oxide did not lead to incorporation of deuterium into unreacted **6**. Formation of **24** must therefore be the rate-determining step of the reaction.

The acetates **27** and **28** (R = Ac) are thermally stable enough [while trimethylsilyl ethers **27** and **28** (R = $SiMe_3$) are not (*v. inf.*)], for their ratio, as determined by NMR. spectroscopy and GLPC. (**27**:**28** (R = Ac) = ca. 3:2, see experimental section) to represent the ratio in which enolates **25** and **26** are formed in the rearrangement. Hydrolysis of the mixture of **25** and **26** gave the aldehydes **29** and **30**, likewise in a 3:2 ratio, but in lower yield.

In connection with the determination of the ratio in which enolates **25** and **26** are formed, because the lithium alcoholate **32** (R = Li) is a potential product of the rearrangement of **24** (see section 5), and to arrive at further novel terpenoid structures, the thermal reactions of the *cis*- and *trans*-divinylcyclopropane derivatives **27** and **28** (R = Ac) and **27** and **28** (R = $SiMe_3$) were briefly studied.

High purity samples of the enol acetates **27** and **28** (R = Ac) could be isolated by GLPC., during which only some *cis-trans* isomerisation (with respect to the cyclopropane ring **27** ⇌ **28**), but no isomerisation to the cycloheptadiene derivative **32** (R = Ac) occurred. *cis-trans* Isomerisation (**27** ⇌ **28**) is facile in the case of the trimethylsilyl derivatives **27** and **28** (R = $SiMe_3$) and precluded the isolation of isomerically pure samples by GLPC. In both systems cyclisation to the isomeric cycloheptadienes **32** (R = Ac, $SiMe_3$) is much slower than *cis-trans* isomerisation (**27** ⇌ **28**). This must be due to the fact that interaction at the open ends of the π-systems of the *cis*-cyclopropane derivatives **27** (R = Ac, $SiMe_3$) and the diradical intermediates **33** (R = Ac, $SiMe_3$) is extremely hindered, and the latter are highly stabilized.



32 **33** **34** **35**

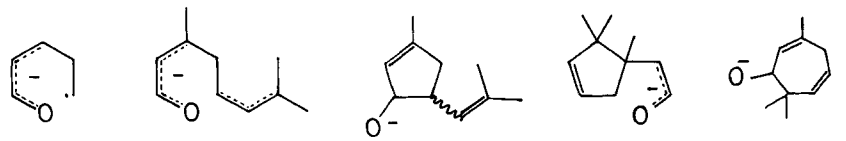
Thermolysis (210°, 3 h) of the mixture of acetates **27** and **28** (R = Ac) and of the mixture of trimethylsilyl ethers **27** and **28** (R = $SiMe_3$) gave the corresponding cycloheptadiene isomers **32** (R = Ac)[5]) and **32** (R = $SiMe_3$)[5]), respectively; preparatively the mixture of **27** and **28** (R = $SiMe_3$) gave **32** (R = $SiMe_3$) in ca. 50% yield, which was then hydrolysed to the alcohol **32** (R = H)[5]).

Oxidation of this alcohol **32** (R = H) with manganese dioxide in hexane proceeded abnormally to give the hydroxyketone **34**[5]) and the diketone **35**[5]) in low yields. Structures **32**, **34** and **35** were again deduced on the basis of NMR. spectra, and of the IR. and mass spectra.

Structures **29** and **30** represent variations of the neral/geranial skeleton[10]), and **32** (R = H) is similarly related to eucarvone and karahanaenone [23].

5. The Mechanism of the [1,4] Sigmatropic Shifts in 2 and 24. – Although the rearrangement of dihydropyranyllithium **2** to lithium cyclopropyl-enolate **3** is complicated by the presence of the isomeric dihydropyranyllithium **14** which likewise rearranges to **3**, and although the allylic dihydropyranyllithium **24** could not be trapped, the formation of **2** and **24** and their rearrangement by analogous [1,4] sigmatropic shifts is reasonably well established. At present we do not know whether these [1,4] anionic shifts are concerted or stepwise processes.

Both mechanisms can explain exclusive rearrangement via [1,4] shifts. Concerted [1,4] shifts with retention at the migrating carbon atom could well be favoured over concerted [1,2] shifts with inversion at the migrating carbon atom, as could be collapse of anion diradicals **36** and **37** to cyclopropanes rather than to isomer **16**, and isomers **38**, **39** and **40**, respectively[3]), although this high regioselectivity, particularly that of the rearrangement of **24**, may be better in accord with a concerted mechanism.



36 **37** **38** **39** **40**

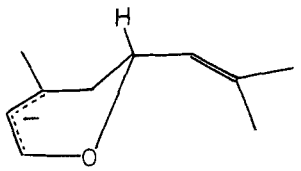
The stereochemical consequences of concerted and stepwise rearrangements of **24** are different, and will be briefly discussed, although we used racemic **6** and the available stereochemical evidence concerns only the formation of the diastereoisomers **25** and **26**. Two conformations of **24** can be envisaged: the side chain can be oriented quasi-equatorially as in **41** or quasi-axially, as in **42**[3]). Concerted rearrangements from these conformations could then occur via the corresponding transition states IV and V, which are again depicted with indication of the symmetries of the 'HOMO's'.

Formation of the three-membered rings with retention at the migrating carbon atom amounts to a conrotatory closure in one sense, as indicated by the dotted lines in IV and V, and which gives **43** from conformer **41**, via IV, and **44** from conformer **42**, via V. Enantiomer **41** should thus give enantiomer **43** and enantiomer **44** if concerted mechanisms operate.

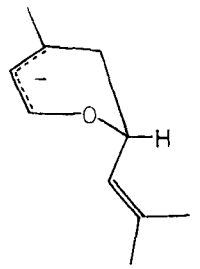
Intermediate **37**, as depicted, is achiral and should collapse to racemic products. Even if this intermediate is folded and in its geometry resembles transition states IV and/or V, conrotatory and disrotatory collapse in both senses would occur, so that more or less racemic products would result.

In the concerted mechanisms, transition state IV might be expected to be favoured over transition state V for steric reasons, so that **43** might be formed stereoselectively. No significant effect is observed (**43**:**44** = **25**:**26** = 3:2).

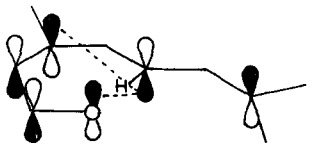
[10]) A derivative has been implicated in the biosynthesis of artemisia ketone [22].



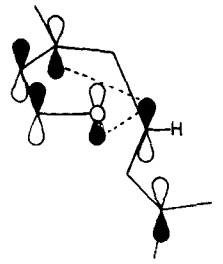
41



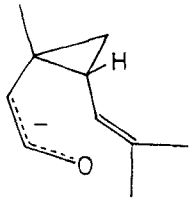
42



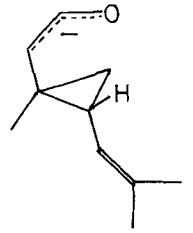
IV



V



43



44

The energy gained by transformation of the cyclic alkoxyal-lyllithiums **2** and **24** into lithium enolates compensates for the cyclopropane ring strain of ca. 27 kcal/mole[11]). In the case of the rearrangement **2** → **3** we have made sure that it is not reversible. Cleavage of enol ether **12** (R = $SiMe_3$) with methyllithium in 1,2-dimethoxyethane [12] gave lithium enolate **3**, which could be trapped with acetic anhydride to give **12** (R = Ac). When **3**, made in this way, was left for 12 h at – 27° and the product then trimethylsilylated again, only **12** (R = $SiMe_3$), and no **13**, resulted.

The rearrangement of **24**, in which the dimethylallyl group migrates, must be much faster than that of the unsubstituted **2**. Under comparable conditions, at – 27°, the lithiation step proved to be rate-determining and there occurred ca. 80% conversion of **6** in 10 min, while rearrangement of **2** is just detectable after 1 h (see Table 1).

I thank Dr. *Ohloff*, research director of *Firmenich & Cie* for his support and encouragement, Dr. *B. Willhalm* for his aid in obtaining and interpreting the spectra, and Miss *G. Keller* for technical assistance and for drawing the formulae.

[11]) This was not obvious from estimation of the pK's of **2** and **3**.

Experimental Section[12])

1. *Lithiation of 2,5-Dihydrofuran* (**9**) *and Quenching with Acetic Anhydride.* 420 mg of **9** (6.00 mMoles), in 6 ml of tetrahydrofuran, were treated with 4 ml of 1.7N *n*-butyllithium/hexane (6.80 mMoles) at $-65°$, with stirring, and the resulting yellow solution was then left at $-27°$ for 2.5 h. At $-65°$ 5.0 ml of acetic anhydride (5.40 g, 55 mMoles) were then added with stirring. The mixture was left at $-27°$ for 2 h, and then poured into a cooled ($+5°$), stirred mixture of 40 ml of pentane, 140 ml of aqueous sodium hydrogencarbonate solution and solid sodium hydrogencarbonate, and this mixture was stirred for 45 min at $+5°$. The pentane layer was then separated, and the aqueous layer was extracted with pentane. The combined pentane solutions were washed with water and dried over magnesium sulfate. The solvents were then distilled off and the residue was distilled: b.p. 50–51°/30 Torr; yield 416 mg (3.72 mMoles, 62%) of (Z)-*1-acetoxy-buta-1,3-diene* (**11**, $R = Ac$). According to GLPC. (5 m, 85°) this product was > 95% pure and contained none of the *trans* isomer. Spectral data: NMR.: 6.2–7.2 (2H, *m*), 4.8–5.6 (3H, *m*), 2.08 ppm (3H, *s*). IR.: 3110, 3100, 3060, 3000 (*w*), 1760, 1655 (*s*), 1430 (*m*), 1370, 1210, 1170, 1050 (*s*), 1000, 940, 910, 790, 670 (*m*), 620 (*w*), 590 cm^{-1} (*m*). MS.: $M^+ = 112$ (17), *m/e:* 70 (39), 69 (13), 43 (100).

The IR. spectrum was identical with the one reported in the literature [13].

(E)-*1-acetoxy-buta-1,3-diene*, prepared from (*E*)-crotonaldehyde, was different from **11** (R = Ac) in its spectral properties and behaviour on GLPC.

2. *Lithiation of* **9** *and Quenching with Trimethylsilyl Chloride.* 420 mg (6.00 mMoles) of **9** in 5 ml of ether and 1 ml of tetramethylethylenediamine were treated with 4 ml of 1.65N *n*-butyllithium/hexane (6.60 mMoles), at $-65°$, with stirring and the solution was kept at $-27°$ for 2.5 h. At $-65°$, 1.5 ml (1.3 g, 12 mMoles) of trimethylsilyl chloride were then added with stirring. The mixture was stirred, first for 15 min at $-65°$ and then for 1 h at $+5°$, and then taken up in 40 ml of pentane. This solution was washed with 2% sulfuric acid (twice) and then with 3% aqueous sodium hydrogencarbonate (twice) and dried over molecular sieves (*Linde*). The solvents were distilled off and the residue was distilled: b.p. 80–85°/740 Torr; yield 583 mg (4.11 mMoles, 69%) of (Z)-*1-trimethylsilyloxy-buta-1,3-diene* (**11**, $R = SiMe_3$). According to GLPC. (2.3 m, 60°) this product was > 95% pure. Spectral data: NMR.: 5.8–7.0 (2H, *m*), 4.5–5.3 (3H, *m*), 0.19 ppm (9H, *s*). IR.: 3090, 3040, 3020 (*w*), 2960, 1640, 1600, 1540, 1250, 1170, 1070, 930, 850 (*s*), 790, 750 (*m*), 690 (*w*), 650 cm^{-1} (*m*). MS.: $M^+ = 142$ (40), *m/e:* 127 (32), 101 (10), 99 (12), 75 (14), 73 (100), 59 (10), 45 (22).

3. *Reaction of* (Z)-*1-trimethylsilyloxy-buta-1,3-diene* (**11**, $R = SiMe_3$) *with Methyllithium and Quenching with Acetic Anhydride.* 519 mg (3.66 mMoles) of **11** (R = $SiMe_3$) in 4 ml of 1,2-dimethoxyethane were treated with 4 ml of 2N methyllithium/ether (8.00 mMoles) at $-65°$, with stirring. A thick white precipitate was immediately formed. The mixture was left at $-27°$ for 16 h. Then at $-65°$ 3 ml (3.2 g, 30 mMoles) of acetic anhydride were added with stirring. This mixture was kept at $-27°$ for 2 h and then worked up as described in Section 1. According to GLPC. (1.6 m, 90°) the crude product so obtained contained only **11** (R = Ac) and no trace of **11** (R = $SiMe_3$). It was then distilled: b.p. 50°/30 Torr and identified by its spectra; yield 280 mg of **11** (R = Ac) (2.50 mMoles, 68%).

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[12]) NMR. spectra: *Varian* A60 and *Hitachi Perkin-Elmer* R-20B, in CCl_4 solution, δ-scale (ppm), tetramethylsilane as internal standard, spherical micro-cells. IR. spectra: *Perkin-Elmer* 125, neat as films. Mass spectra: *Atlas* CH4, inlet temperature ca. 150°, ca. 70 eV electrons; the intensity of molecular ions and of fragment ions is given in % (the latter over 10%) relative to the most abundant one (100%). Gas chromatography (GLPC.): *F & M* 500 and *Carlo Erba* GT, glass columns with 5 mm internal diameter, length (and oven temperature) specified in the text, 15% Carbowax 20M15 on Chromosorb (acid washed, mesh 60/80), helium as carrier gas. Spectral data throughout are of samples purified by GLPC., of > 95% purity, unless otherwise specified.

Reactions with organolithium compounds were carried out in *Schlenck* tubes (joints) [2] under nitrogen, with magnetic stirring. Reagents [*n*-butyllithium/hexane (commercial *n*-butyllithium in hexane, diluted to ca. 1.70N) and quenching agents] were rapidly added at $-65°$ with a pipette. An 'Ultra Kryomat TK30D' (*Dr. R. Wobser KG*, Lauda/Tauber) was used (runs at $-27°$). In the working-up, solvents were distilled off on a water bath, through an efficient glass spiral column (length: 150 mm, internal diameter: 12 mm). A small short-path distillation apparatus was used for distillations.

4. *5,6-Dihydro-2H-pyran* (**7**) was prepared by the method of *Collonge & Poisde* [10]. Spectral data: NMR.: 5.72 (2H, *m*), 4.00 (2H, *m*), 3.67 (2H, *t*, J = 5 Hz), 2.09 ppm (2H, *m*). IR.: 3040, 2970, 2920, 2860, 2830 (*m*), 1460, 1450, 1430 (*w*), 1380 (*m*), 1330, 1280 (*w*), 1230, 1200 (*m*), 1180, 1090 (*s*), 1070, 1030, 1010, 980, 960, 920, 890, 840 (*m*), 650 cm^{-1} (*s*). MS.: M^+ = 84 (100), *m/e:* 83 (26), 69 (18), 56 (29), 55 (93), 54 (66), 53 (36), 50 (8), 41 (25), 39 (79).

5. *Lithiation of 5,6-Dihydro-2H-pyran* (**7**) *and Quenching with Acetic Anhydride.* 506 mg (6.03 mMoles) of **7** in 5 ml of tetrahydrofuran were treated with 5,4 ml of 1.65 N *n*-butyllithium/hexane (8.90 mMoles), at $-65°$, with stirring, and the resulting yellow solution was left at $-27°$ for 17 h. At $-65°$, 7 ml (7.6 g, 74 mMoles) of acetic anhydride were then added with stirring. This mixture was stirred first at $-65°$ for 15 min and then at $+5°$ for 25 min, and then poured into a cooled ($+5°$) mixture of 20 ml of pentane, 150 ml of aqueous sodium hydrogencarbonate solution, and solid sodium hydrogencarbonate. This mixture was stirred at $+5°$ for 35 min. The pentane layer was then separated and the aqueous layer extracted with pentane. The combined pentane solutions were washed with water and dried over magnesium sulfate. The solvents were distilled off. According to GLPC. (3 m, 150°) the crude product so obtained consisted of a mixture of **12** (R = Ac) and of 5-methyl-nonan-5-ol (**45**). The yield of **12** (R = Ac), as determined by GLPC., using added cyclopentenyl acetate (**16**) (Li = Ac) as a standard, was 61 mg (0.48 mMole, 8%). *(Z)-1-Acetoxy-2-cyclopropyl-ethylene* (**12**, *R = Ac*) was isolated by GLPC. (3 m, 150°). Spectral data: NMR.: 6.97 (1H, *d*, J_1 = 6.5 Hz), 4.23 (1H, *q*, J_1 = 6.5, J_2 = 9.5 Hz), 2.1 (3H, *s*), 1.3–2.0 (1H, *m*), 0.1–0.9 ppm (4H, *m*). IR.: 3110, 3100 (*m*), 3010, 1760, 1670 (*s*), 1430, 1400 (*m*), 1370, 1220, 1170, 1050, 940 (*s*), 880, 810 (*m*), 750 (*s*), 650, 600 cm^{-1} (*m*). MS.: M^+ = 126 (6), *m/e:* 84 (39), 83 (22), 55 (25), 43 (100).

The *alcohol* **45** is formed from unreacted *n*-butyllithium and acetic anhydride.

6. *Lithiation of* **7** *and Quenching with Trimethylsilyl Chloride.* 502 mg (5.97 mMoles) of **7** in 5 ml of ether and 1 ml of tetramethylethylenediamine were treated with 5.5 ml of 1.65 N *n*-butyllithium/hexane (9.08 mMoles), at $-65°$, with stirring. This mixture was kept at $-27°$ for 1 h. After 5–10 min, a thick yellow precipitate had formed. At $-65°$, 2 ml of trimethylsilyl chloride (1.7 g, 16 mMoles) were then added with stirring. The mixture was stirred for 15 min at $-65°$, then kept at $-27°$ for 15 min, finally stirred for 1 h at $+5°$, and then taken up in 40 ml of pentane. This pentane solution was washed with 2% sulfuric acid (twice) and then with 3% aqueous sodium hydrogencarbonate (twice), and dried over molecular sieves. The solvents were distilled off [spiral column, followed by a rotary evaporator (12 Torr, room temperature)] and the residue was distilled: b.p. 45–55°/12 Torr; yield 616 mg (≙ 3.95 mMoles of **15** and isomers, 66%). According to GLPC. (2.3 m, 60°), the crude (undistilled) product consisted of a mixture of **12** (R = $SiMe_3$), **13**, **15**, and **17**, in the ratios given in Table 2 (reaction time: 1 h), and the distillate [b.p. 45–55° (12 Torr)] consisted of a mixture of **12** (R = $SiMe_3$), **13**, and **15** in similar ratios, but contained only traces of **17**.

The reactions summarized in Tables 1 und 2 were carried out as the one described above (concentration, addition of reagents, work-up), except that the time in the bath at $-27°$ was varied.

Table 2. *Trimethylsiliated Products from the Reaction of 7 with* n-*butyllithium in Ether/Tetramethylendiamine at* $-27°$

time (at $-27°$)	yield (uncorrected)	yield (corrected)	**12** (R = $SiMe_3$)	**13**	**15** (uncorrected)	**17**	**15** (corrected)
3 min	34	45	0	28	52	20	72
10 min	59	66	0	19	68	12	80
1 h	66	71	6	18	68	8	77
3.7 h	70	73	25	18	51	5	56
8 h	67	70	45	17	34	4	38
16 h	67	70	50	16	29	5	24
39 h	64	65	70	14	15	1	16
64 h	62	63	76	12	11	1	12
260 h	61	61	93	3	2	0	2

In Table 2, the ratios of **12** (R = $SiMe_3$): **13**:**15** (uncorrected): **17** are given; these were determined by GLPC. (2.3 m, 60°) of the crude (undistilled) product and are not corrected for detector response. Compound **17** is formed from **15** by lithiation and trimethylsilylation during the quenching process (see section 7). The figures for **15** are therefore corrected: **15** (corrected) = **15** (uncorrected) + **17** (Table 2). The uncorrected yields are of distilled mixtures of **12** (R = $SiMe_3$), **13**, and **15** only, and they are corrected by adding the amount of **17** (≙**15**) in the undistilled product: corrected yield = uncorrected yield + % of **17** times uncorrected yield.

From the various distillates **12** (R = $SiMe_3$), **13**, and **15** were isolated by GLPC. [2.3 m, 60°, peaks in the order **12** (R = $SiMe_3$), **15**, **13**, (**17**)]. The distillation residues were collected and **17** was isolated by distillation (b.p. ca. 80°/12 Torr), followed by GLPC.

Spectral data of (Z)-*1-cyclopropyl-2-trimethylsilyloxy-ethylene* (**12**, *R* = *SiMe*$_3$): NMR.: 6.02 (1H, *d*, J_1 = 6.0 Hz), 3.91 (1H, *q*, J_1 = 6.0, J_2 = 9.0 Hz), 1.25–2.0 (1H, *m*), 0.1–1.0 (4H, *m*), 0.12 ppm (9H, *s*). IR.: 3080, 3020 (*m*), 3000, 2950 (*s*), 1720 (*w*), 1650, 1410 (*s*), 1310 (*w*), 1250, 1170, 1070 (*s*), 940 (*m*), 900, 840 (*s*), 800 (*m*), 750 (*s*), 630 cm^{-1} (*m*). MS.: M^+ = 156 (26), *m/e:* 155 (18), 75 (67), 73 (100), 45 (24).

*Spectral data of 3,4-dihydro-4-trimethylsilyl-2*H*-pyran* (**13**): NMR.: 6.24 (1H, apparent *d* of *d*, J_1 = 1.5, J_2 = 6.5 Hz), 4,46 (1H, *d* of *m*, J_2 = 6.5 Hz), 3.4–4.2 (2H, *m*), 1.2–2.0 (3H, *m*), 0.0 ppm (9H, *s*). IR.: 3060 (*w*), 2960 (*m*), 2880 (*w*), 1630 (*m*), 1250 (*s*), 1110, 1050, 1010, 910, 900, 860 (*m*), 770 cm^{-1} (*s*). MS.: M^+ = 156 (18), *m/e:* 155 (13), 113 (13), 75 (43), 73 (100), 45 (18), 43 (10).

*Spectral data of 5,6-dihydro-6-trimethylsilyl-2*H*-pyran* (**15**): NMR.: 5.57 (2H, *m*), 3.82 (2H, *m*), 3.35 (1H, *t* of *d*, J_1 = 3.9, J_2 = 10.0 Hz), 1.6–2.5 (2H, *m*), 0.0 ppm (9H, *s*). IR.: 3040 (*m*), 2980, 2920, 2860 (*s*), 2780 (*m*), 1640, 1610, 1460 (*w*), 1430 (*m*), 1390, 1360 (*w*), 1330 (*m*), 1290 (*w*), 1250 (*s*), 1210 (*m*), 1180 (*s*), 1160 (*m*), 1080, 1060 (*s*), 1040 (*w*), 990 (*m*), 960, 950 (*w*), 900, 850 (*s*), 780, 760, 750 (*m*), 710, 640 (*s*), 600 cm^{-1} (*w*). MS.: M^+ = 156 (13), *m/e:* 155 (20), 141 (13), 111 (13), 75 (55), 73 (100), 45 (23), 43 (14).

Spectral data of **17**: NMR.: 4.93 (1H, *m*), 3.4–4.4 (2H, *m*), 1.3–2.0 (3H, *m*), 0.06 (9H, *s*), 0.0 ppm (9H, *s*). IR.: 3040 (*w*), 2960 (*s*), 2920, 2880 (*m*), 2840 (*w*), 1740, 1725 (*m*), 1690, 1670 (*w*), 1610 (*m*), 1460, 1440 (*w*), 1410 (*m*), 1370, 1340, 1290 (*w*), 1250 (*s*), 1150 (*w*), 1120, 1090, 1060, 1020, 920, 850, 760 (*m*), 700 cm^{-1} (*w*). MS.: M^+ = 228 (1), *m/e:* 155 (70), 147 (26), 125 (27), 75 (49), 73 (100), 59 (12), 45 (23).

7. *Lithiation/Trimethylsilylation of 5,6-Dihydro-6-trimethylsilyl-2*H*-pyran* (**15**). By lithiation and subsequent trimethylsilylation of **7**, a mixture of **13** (31%) and **15** (66%), containing a trace of **17** (3%), (according to GLPC., 2.3 m, 60°) was prepared as described in Section 6.

322 mg (2.06 mMoles) of this mixture in 2 ml of ether and 0.33 ml of tetramethylethylenediamine were treated with 1.8 ml 1.75N butyllithium/hexane (3.10 mMoles) at −65°, with stirring, followed immediately by 0.68 ml of trimethylsilyl chloride (0.58 g, 5.40 mMoles). This mixture was then left at −65°, −27° and +5°, and worked up as described in Section 6. According to GLPC. (2.3 m, 60°), the crude product so obtained consisted of a mixture of **13** (28%), **15** (4%), and **17** (67%). Compounds **13** and **17** were isolated by GLPC. and identified by their spectra.

8. *Cleavage of* (Z)-*1-Cyclopropyl-2-trimethylsilyloxy-ethylene* (**12**, *R* = *SiMe*$_3$). 149 mg (0.95 mMole) of **12** (R = $SiMe_3$) in 1.1 ml of 1,2-dimethoxyethane were treated with 1 ml of 1.9N methyllithium/ether (1.90 mMoles), at −65°, with stirring. A white precipitate rapidly formed. The mixture was left at −27° for 12 h, and then at −65°, treated first with 0.4 ml of tetramethylethylenediamine and then with 0.7 ml (0.60 g, 5.5 mMoles) of trimethylsilyl chloride, with stirring. This mixture was left at −65°, −27°, and +5° and then worked up as described in Section 6. The crude product so obtained consisted only of **12** (R = $SiMe_3$), according to GLPC. (2.3 m, 65°). It was then again treated with methyllithium as described above and left at −27° for 12 h. Then 0.8 ml of acetic anhydride (0.85 g, 8.5 mMoles) was added at −65°, with stirring, the mixture stirred at +5° for 30 min and then worked up as described in section 5. According to GLPC. (2.3 m, 60° and 125°) the crude product so obtained contained only **12** (R = Ac) and no trace of compound **12** (R = $SiMe_3$). Compound **12** (R = Ac) was isolated by GLPC. (2.3 m, 125°) and identified by its spectra.

9. *Lithiation of 3,4-Dihydro-2*H*-pyran* (**8**). 500 mg (5.95 mMoles) of **8** in 5 ml of ether and 1 ml of tetramethylethylenediamine were treated with 5.5 ml of 1.65N *n*-butyllithium/hexane (9.09 mMoles), with stirring, at −65°, and the resulting yellow solution was kept at −27° for 16 h. At −65°, 2 ml (1.7 g, 16 mMoles) of trimethylsilyl chloride were then added with stirring, and the

mixture further stirred, and worked up as described in Section 5. The crude product so obtained was distilled: b.p. ca. 50°/12 Torr; yield 173 mg of *3,4-dihydro-6-trimethylsilyl-2*H*-pyran* (**21**, R = $SiMe_3$) (1.11 mMoles), 19%). According to GLPC. (2.3 m, 60°) this product contained no trace of **12** (R = $SiMe_3$), **13**, or **15**. Spectral data: NMR.: 4.95 (1H, *t*, (broad), *J* = ca. 4 Hz), 3.90 (1H, *t*, (broad), *J* = ca. 6 Hz), 1.5–2.3 (4 H, *m*), 0.03 ppm (9 H, *s*). IR.: 3050 (*m*), 2970 (*s*), 2940, 2900, 2870, 2850 (*m*), 1630 (*s*), 1480, 1460, 1450, 1420, 1390, 1350, 1340 (*w*), 1290, 1280, 1260, 1240, 1120, 1090, 1080, 1060, 970, 920, 890, 840 (*s*), 800 (*m*), 770 (*s*), 710, 650 cm^{-1} (*w*). MS.: M^+ = 156 (33), *m/e:* 155 (25), 141 (28), 111 (15), 83 (10), 75 (100), 73 (95), 59 (12), 45 (23), 43 (18).

10. *Lithiation of Nerol Oxide* (**6**) *and Quenching with Acetic Anhydride.* 1.06 g (6.97 mMoles) of **6** [19] in 10 ml of ether and 1 ml of tetramethylethylenediamine was treated with 7.0 ml 1.65 N *n*-butyllithium/hexane (11.5 mMoles), at –65°, with stirring. The resulting yellow solution was kept at –27° for 18 h, and then, at –65°, 5.6 ml of acetic anhydride (6.0 g, 56 mMoles) were added with stirring. The resulting mixture was kept at –27° for 2.5 h and then worked up as described in Section 5. The crude product so obtained was distilled: b.p. 115–125°/12 Torr; yield 845 mg (4.35 mMoles, 62%) of a mixture of enol-acetates **27** and **28** (R = Ac). According to GLPC. (1.6 m, 125°) this mixture contained none of **6**. Isomers **27** and **28** were separated by GLPC. (1.6 m, 125°, peaks in the order **28, 27**).

*Spectral data of 1-methyl-1-*r-((Z)*-2-acetoxy-ethen-1-yl-)-2-*c-(*2-methyl-prop-1-en-1-yl)-cyclopropane* (**27**, *R = Ac*): NMR.: 6.84 (1H, *d*, *J* = 6.9 Hz), 4.83 (1H, *d* (broad), *J* = 7.9 Hz), 4.59 (1H, *d*, *J* = 6.9 Hz), 2.05 (3H, *s*), 1.69 (6H, *s* (broad)), 1.54 (1H, *m*), 1.17 (3H, *s*), 1.05 (1H, *q* (?), J_1 = 8.5, J_2 = 3.7 Hz), 0.39 ppm (1H, *q*, J_2 = 3.7, J_3 = 5.7 Hz). IR.: 3100, 3060 (*w*), 2970, 2920, 2880, 1760 (*s*), 1660, 1440 (*m*), 1370, 1220 (*s*), 1150 (*m*), 1060 (*s*), 980 (*w*), 940, 910, 850 (*m*), 810 (*w*), 760 (*m*), 660, 600 cm^{-1} (*w*). MS.: M^+ = 194 (weak), *m/e:* 136 (10), 134 (22), 119 (31), 109 (36), 107 (10), 96 (12), 95 (20), 94 (14), 93 (10), 91 (14), 82 (16), 81 (29), 80 (66), 79 (12), 69 (52), 67 (19), 59 (19), 55 (15), 53 (10), 43 (100), 41 (49), 39 (20).

*Spectral data of 1-methyl-1-*r-((Z)*-2-acetoxy-ethen-1-yl-)-2-*t-(*2-methyl-prop-1-en-1-yl)-cyclopropane* (**28**, *R = Ac*): NMR.: 6.93 (1H, *d*, *J* = 6.6 Hz), 4.66 (1H, *d* (broad), *J* = ca. 8 Hz), 4.63 (1H, *d*, *J* = 6.6 Hz), 2.05 (3H, *s*), 1.67 (6H, *s* (broad)), 1.3–1.7 (1H, *m*), 1.25 (3H, *s*), 0.5–1.10 ppm (2H, *m*). IR.: identical with that of **27** except for intensity of some medium and weak bands. MS.: identical with that of **27**.

cis-trans *Isomerisation:* Both samples of **27** and **28** (R = Ac), separated by repeated GLPC., contained an essentially constant ca. 10% impurity of the other isomer, although the column was effective enough to ensure complete separation. We assume that these isomer impurities are due to *cis-trans* isomerisation during GLPC. (column 125°, injector and detector at ca. 220°). None of the cyclic isomer **32** (R = Ac) was formed on GLPC.

The ratio **27**:**28** (R = Ac) was determined from the NMR. spectra of the crude product (before distillation) and of the distillate, by measuring the signals of the cyclopropane-bound methyl groups (at 1.17 and 1.25 ppm), and also by GLPC. (during which some *cis-trans* isomerisation occurred). All three determinations gave **27**:**28** (R = Ac) = ca. 3:2. The ratio of **25**:**26**, as formed in the rearrangement, must therefore be ca. 3:2. This value is not very accurate, but the rearrangement is clearly not stereoselective.

11. *Lithiation of* **6** *and Quenching with Trimethylsilyl Chloride.* 916 mg (6.02 mMoles) of **6** in 5 ml of ether and 1 ml of tetramethylethylenediamine were treated with 5.5 ml of 1.65 N *n*-butyllithium/hexane (9.07 mMoles), at –65°, with stirring. The resulting yellow solution was left at –27° for 2.5 h, then treated with 2 ml (1.7 g, 16 mMoles) of trimethylsilyl chloride, at –65°, with stirring, then stirred at –65°, –28°, and +5°, and worked up as described in Section 6. The crude product so obtained was then distilled: b.p. 120–130°/12 Torr; yield 1.007 g (4.77 mMoles, 79%) of a mixture of **27** and **28** (R = $SiMe_3$). According to GLPC. (2.3 m, 105°) this mixture contained also a trace of **6**. On attempted separation of these isomers by GLPC. (peaks in the order **28**, **27**, **6**, 2.3 m, 90°, injector and detector at ca. 220°), samples somewhat enriched (*v. infr.*) in **27** and in **28** (R = $SiMe_3$) were isolated. Again the column was effective enough to ensure complete separation. This inefficient purification must be due to *cis-trans* isomerisation during GLPC.: these enriched samples gave identical chromatograms (ca. 1:1 ratio) on reinjection.

From the enriched mixtures (**27**:**28** (R = $SiMe_3$) = ca. 35:65 and = ca. 60:40 (ratios determined from the NMR. spectra) part of the NMR. spectra of **27** and **28** (R = $SiMe_3$), respectively, can be assigned. *Spectral data of 1-methyl-1-*r-((Z)*-2-trimethylsilyloxy-ethen-1-yl-)-2-*c-(*2-methyl-*

prop-1-en-1-yl)-cyclopropane (**27**, $R = SiMe_3$) *and of 1-methyl-1-*r-((Z)*-2-trimethylsilyloxy-ethen-1-yl-)-2-*t-(*2-methyl-prop-1-en-1-yl*)*-cyclopropane* (**28**, $R = SiMe_3$):

27 (R = $SiMe_3$): NMR.: 5.91 (1H, *d*, *J* = 6.0 Hz), 4.73 (1H, *t* (broad), *J* = ca. 7 Hz), 4.35 (1H, *d*, *J* = 6.0 Hz), 1.68 (6H, *m*), 1.10 (3H, *s*), 0.17 ppm (9H, *s*).

28 (R = $SiMe_3$): NMR.: 6.05 (1H, *d*, *J* = 6.0 Hz), 4.75 (1H, *t* (broad), *J* = ca. 7 Hz), 4.35 (1H, *d*, *J* = 6.0 Hz), 1.67 (6H, *m*), 1.19 (3H, *s*), 0.17 ppm (9H, *s*).

The assignment of stereochemistry is based on comparison of the NMR. spectra of **27** and **28** (R = $SiMe_3$) with those of **27** and **28** (R = Ac). In the spectrum of **28** (R = Ac) the low-field vinyl signal and the cyclopropane-bound methyl signal appear at lower field than in that of **27** (R = Ac). The spectra of **27** and **28** (R = $SiMe_3$), as identified, differ in the same way. Acetates **27** and **28** (R = OAc) had identical IR. and mass spectra within experimental error, and we assume that **27** and **28** (R = $SiMe_3$) likewise have very similar IR. and mass spectra.

27, **28** (R = $SiMe_3$): IR.: 3060, 3020 (*m*), 2960, 2920 (*s*), 2880 (*m*), 1650 (*s*), 1440, 1410, 1370 (*m*), 1250 (*s*), 1150 (*w*), 1100, 850 (*s*), 750 (*m*), 690 cm^{-1} (*w*). MS.: M^+ = 224 (2), *m/e:* 181 (12), 144 (35), 119 (22), 75 (30), 73 (100), 45 (19).

Reaction with incomplete conversion: Lithiation of **6** for 10 min at –27°, subsequent trimethylsilylation, and working-up as described above, gave a mixture of unreacted **6** (ca. 20%), **27** (R = $SiMe_3$), and **28** (R = $SiMe_3$) (together ca. 80%), according to GLPC. (2.3 m, 105°). In an analogous run, followed by hydrolysis with deuterium oxide, **6** was isolated and further identified (see Section 12).

12. *Lithiation of* **6** *and Hydrolysis.* 376 mg (2.47 mMoles) of **6** in 3.6 ml of ether and 0.4 ml of tetramethylethylenediamine, were treated with 2.4 ml 1.7 N *n*-butyllithium/hexane (4.1 mMoles) at –65°, with stirring. This solution was left at –27° for 17 h and then poured into water. The ether layer was separated and the water layer was extracted with ether. The combined ether solutions were washed with 2% sulfuric acid and with water, and dried over magnesium sulfate. The solvents were distilled off, and the residue was distilled: b.p. ca. 80°/12 Torr; yield 150 mg of a mixture of **29** and **30** (0.99 mMole, 40%). According to GLPC. (1.6 m, 120°) the ratio of **29**:**30** was ca. 3:2. Isomers **29** and **30** were separated by GLPC. (1.6 m, 105°, peaks in the order **30**, **29**).

*Spectral data of 1-methyl-1-*r*-formylmethyl-2-*c*-(2-methyl-prop-1-en-1-yl)-cyclopropane* (**29**): NMR.: 9.65 (1H, *t*, *J* = 2.5 Hz), 4.82 (1H, *d* (broad), *J* = ca. 7.5 Hz), 2.22 (2H, *d*, *J* = 2.5 Hz), 1.71 (3H, *s*), 1.67 (3H, *s*), 1.2–1.6 (1H, *m*), 1.09 (3H, *s*), 0.70–1.0 (1H, *m*), 0.30 ppm (1H, apparent *t*, *J* = ca. 5 Hz). IR.: 3060 (*m*), 2980, 2920, 2880 (*s*), 2820, 2720 (*m*), 1720 (*s*), 1680 (*m*), 1450, 1390 (*m*), 1340, 1310, 1270, 1240, 1200, 1180 (*w*), 1150, 1080, 1050 (*m*), 1010, 980, 940, 850 cm^{-1} (*w*). MS.: M^+ = 152 (6), *m/e:* 119 (12), 110 (21), 109 (75), 95 (31), 94 (56), 93 (22), 91 (21), 83 (13), 82 (62), 81 (67), 79 (32), 77 (18), 70 (12), 69 (40), 68 (13), 67 (100), 65 (10), 59 (10), 55 (55), 53 (32), 43 (67), 41 (100), 39 (55).

*Spectral data of 1-methyl-1-*r*-formylmethyl-2-*t*-(2-methyl-prop-1-en-1-yl)-cyclopropane* (**30**): NMR.: 9.65 (1H, *t*, *J* = 2.5 Hz), 4.82 (2H, *d* (broad), *J* = ca. 7.5 Hz), 2.23 (2H, *d*, *J* = 2.5 Hz), 1.70 (6H, apparent *s*), 1.05–1.40 (1H, *m*), 1.13 (3H, *s*), 0.55–0.90 (1H, *m*), 0.31 ppm (1H, apparent *t*, *J* = ca. 5 Hz). IR.: very similar to that of **29**, differences in the fingerprint region: 1750 (*w*), 1150, 1100, 1080, 1050 (*m*), 1010, 980 (*w*), 850 (*m*). MS.: identical with that of **29**.

Reaction with Incomplete Conversion and Hydrolysis with Deuterium Oxide: The lithiation of 903 mg (5.95 mMoles) of **6** was carried out as described in Section 11. (10 min at –27°). The mixture was then treated with 1 ml of deuterium oxide, stirred at +5° for 10 min, and worked up as described in Section 12. Distillation (12 Torr) gave 358 mg of a mixture of **29**, **30** (together ca. 40%), and **6** (ca. 60%), according to GLPC. (3 m, 150°). Starting material **6** was isolated by GLPC. and identified on the basis of the NMR., IR. and mass spectrum [19]. All three spectra showed this sample to be undeuterated.

13. *Hydrolysis of the Mixture of Trimethylsilyl Enol Ethers* **27** *and* **28** ($R = SiMe_3$). A solution of 995 mg of mixture of **27** and **28** (R = $SiMe_3$) (4.45 mMoles, ratio ca. 3:2) in 6 ml of dioxane and 1 ml of water was heated to reflux for 18 h. It was then diluted with water and extracted with ether. The combined ether solutions were washed with water and dried over magnesium sulfate. The solvents were distilled off and the residue was distilled: b.p. 79–81°/12 Torr; yield 348 mg of a mixture of aldehydes **29** and **30** (2.30 mMoles, 52%). This mixture was identified by its NMR. spectrum.

14. *Thermolysis of the Mixture of Enol-Acetates* **27** *and* **28** (*R = Ac*). 200 mg of a mixture of **27** and **28** (R = Ac) (1.03 mMoles, ratio ca. 3:2) was introduced into a 500 ml glass bulb and cooled with liquid nitrogen. The glass bulb was then sealed at 0.1 Torr. The sealed bulb was heated in an oil bath of ca. 210° for 2 h. Its contents were taken up in ether and the ether was distilled off. According to GLPC. (1.6 m, 130°), the crude pyrolysate so obtained consisted of **32** (R = Ac), and of traces of **27** and **28** (R = Ac). *7-Acetoxy-2,6,6-trimethyl-cyclohepta-1,4-diene* (**32**, R = Ac) was isolated by GLPC. (1.6 m, 130°). Spectral data: NMR.: 5.55 (4H, *m*), 3.00 (1H, *d* (broad), J_1 = ca. 20 Hz), 2.45 (1H, *d* of *d*, J_1 = ca. 20, J_2 = ca. 3.5 Hz), 1.98 (3H, *s*), 1.75 (3H, *s* (broad)), 1.00 (3H, *s*), 0.97 ppm (3H, *s*). IR.: 3000 (*m*), 2960, 2920 (*s*), 2860 (*m*), 1630 (*s*), 1460, 1430 (*m*), 1360, 1230 (*s*), 1160, 1130, 1100 (*w*), 1020 (*s*), 970 (*m*), 900, 870, 860, 820 (*w*), 710 cm^{-1} (*m*). MS.: M^+ = 194 (weak), *m/e:* 134 (33), 119 (63), 109 (36), 96 (11), 95 (12), 94 (10), 93 (18), 91 (36), 82 (10), 81 (18), 80 (100), 79 (10), 77 (14), 69 (28), 59 (16), 43 (81).

15. *Thermolysis of the Mixture of* **27** *and* **28** (*R = SiMe$_3$*). – a) *In the gas phase:* 200 mg of a mixture of **27** and **28** (R = $SiMe_3$) (0.89 mMole) was thermolysed as described in Section 14 for 2 h at 210°. According to GLPC. (2.3 m, 105°) the pyrolysate consisted of a mixture of **32** (R = $SiMe_3$) (ca. 72%) and of both **27** (R = $SiMe_3$) (ca. 13%) and **28** (R = $SiMe_3$) (ca. 15%). Compounds **27**, **28**, and **32** (R = $SiMe_3$) were isolated by GLPC. (2.3 m, 105°); **27** and **28** were further identified by the NMR. spectra.

Spectral data of 2,6,6-trimethyl-7-trimethylsilyloxy-cyclohepta-1,4-diene (**32**, *R = SiMe$_3$*): NMR.: 5.27 (3H, *m*), 4.32 (1H, *d* (broad), *J* = ca. 4 Hz), 2.91 (1H, *d* (broad), *J* = ca. 18 Hz), 2.22 (1H, *d* of *m*, *J* = ca. 18 Hz), 1.69 (3H, *s* (broad)), 0.94 (3H, *s*), 0.91 (3H, *s*), 0.09 ppm (9H, *s*). IR.: 3010 (*m*), 2960, 2930 (*s*), 2880 (*m*), 1680, 1640 (*w*), 1470, 1430, 1400, 1370, 1350 (*m*), 1260, 1250 (*s*), 1190, 1160, 1130 (*w*), 1110, 1060 (*s*), 1000, 960 (*w*), 890, 840 (*s*), 740, 710 (*m*), 680 cm^{-1} (*w*). MS.: M^+ = 224 (0.4), *m/e:* 219 (24), 181 (18), 144 (65), 143 (11), 134 (10), 119 (40), 93 (10), 91 (12), 75 (41), 73 (100), 45 (20), 39 (16).

b) *Neat:* In a preparative run, 925 mg of a neat mixture of **27** and **28** (R = $SiMe_3$) were heated to 205° for 3 h. The thermolysate was then distilled: b.p. ca. 110°/12 Torr; yield 487 mg (53%) of **32** (R = $SiMe_3$). According to GLPC. (2.3 m, 105°) this product was > 95% pure.

16. *Hydrolysis of 2,6,6-trimethyl-7-trimethylsilyloxy-cyclohepta-1,4-diene* (**32**, *R = SiMe$_3$*). A solution of 487 mg (2.18 mMoles) of **32** (R = $SiMe_3$) in a mixture of 1 ml of water and 4 ml of methanol, containing 100 mg of potassium carbonate, was heated to reflux for 2 h. The solution was then diluted with water and extracted with ether. The combined ether solutions were washed with water, dried over magnesium sulfate, and the ether was distilled off. According to GLPC. (2.3 m, 105 and 150°) the crude product so obtained consisted of **32** (R = H) and contained no trace of **32** (R = $SiMe_3$). The crude product was distilled: b.p. ca. 85°/12 Torr; yield 164 mg (1.08 mMoles, 50%) of *3,7,7-trimethyl-cyclohepta-2,5-dien-1-ol* (**32**, R = H). According to GLPC. (2.3 m, 150°) this product was > 95% pure. Spectral data: NMR.: 5.25–5.70 (3H, *m*), 4.27 (1H, *d* (broad), *J* = ca. 4 Hz), 3.85 (OH), 2.93 (1H, *d* of *m*, *J* = ca. 20 Hz), 2.65 (1H, *d* of *m*, *J* = ca. 20 Hz), 1.73 (3H, *s* (broad)), 1.06 (3H, *s*), 0.97 ppm (3H, *s*). IR.: 3420, 3010, 2960, 2940, 2880 (*s*), 1690, 1680, 1660, 1650, 1640 (*w*), 1470, 1440, 1380, 1360 (*m*), 1250, 1190, 1160, 1130, 1100 (*w*), 1030 (*s*), 960, 910 (*w*), 880, 870, 830, 720, 700 cm^{-1} (*m*). MS.: M^+ = 152 (weak), *m/e:* 137 (12), 119 (40), 109 (62), 107 (17), 96 (16), 95 (43), 94 (70), 93 (19), 91 (38), 85 (29), 84 (17), 83 (31), 82 (44), 81 (20), 80 (30), 78 (27), 69 (75), 67 (50), 65 (14), 59 (58), 55 (38), 53 (27), 51 (14), 43 (55), 41 (100), 38 (62).

17. *Oxidation of 3,7,7-trimethyl-cyclohepta-2,5-dien-1-ol* (**32**, *R = H*). – a) *With stirring at room temperature:* 164 mg (1.08 mMoles) of **32** (R = H) in 5 ml of hexane were stirred with 848 mg (9.75 mMoles) of manganese dioxide at room temperature for 45 h. The suspension was then filtered and the inorganic solid was washed with dichloromethane. The combined organic solutions were dried over magnesium sulfate and the solvents were distilled off. According to GLPC. (2.3 m, 150° and 200°) the residue consisted of a mixture of **34** (main product) and of a small amount of **35** (*v. infr.*). *4-Hydroxy-2,5,5-trimethyl-cyclohepta-2,6-dien-1-one* (**34**) was isolated by GLPC. (2.3 m, 200°). Spectral data: NMR.: 6.37 (1H, *m*), 6.25 (1H, *d*, *J* = 12.5 Hz), 5.82 (1H, *d*, *J* = 12.5 Hz), 4.47 (1H, *m*), 3.7 (OH), 1.86 (3H, *s* (broad)), 1.23 (3H, *s*), 1.11 ppm (3H, *s*). IR.: 3460 (*s*), 3040 (*w*), 2980, 2940, 2880, 1650, 1630, 1610 (*s*), 1470, 1450, 1430, 1410, 1380, 1360 (*m*), 1330 (*w*), 1290, 1230, 1200 (*m*), 1130 (*w*), 1110, 1080, 1040, 1000 (*m*), 960 (*w*), 900, 870, 820 (*m*), 760, 720 cm^{-1} (*w*). MS.: M^+ = 166 (26), *m/e:* 152 (10), 151 (100), 137 (14), 123 (44), 122 (14), 121 (28), 111 (26), 109 (24),

108 (12), 107 (24), 105 (38), 96 (12), 95 (32), 93 (15), 91 (28), 82 (12), 81 (18), 79 (27), 77 (25), 69 (48), 67 (34), 65 (11), 55 (28), 53 (30), 51 (15), 44 (16), 43 (95), 42 (11), 41 (79), 40 (13), 39 (56).

b) *With a high-speed shaker:* 557 mg of **32** (R = H) (3.65 mMoles) in 15 ml of hexane were shaken with 2.88 g of manganese dioxide (33.1 mMoles), for 48 h, with a high-speed shaker (BTL Flask Shaker, *Baird & Tatlock*, London), friction causing the temperature of the mixture to reach 40–50°, and then worked up as described above. According to GLPC. (1.6 m, 145° and 200°) the crude product so obtained consisted of **35**, as the main product and of some **34**, and contained no **32** (R = H). *2,5,5-trimethyl-cyclohepta-2,6-dien-1,4-dione* (**35**) was isolated by GLPC. (1.6 m, 175°). Spectral data: NMR.: 6.51 (1H, *m*), 6,36 (1H, *d*, J = 13.0 Hz), 6.0 (1H, *d*, J = 13.0 Hz), 2.02 (3H, apparent *d*, J = ca. 1.5 Hz), 1.38 ppm (6H, *s*). IR.: 3040 (*w*), 2990, 2940 (*s*), 2880 (*m*), 1680, 1650, 1630 (*s*), 1470, 1460, 1450, 1400 (*m*), 1380 (*s*), 1360 (*m*), 1260 (*s*), 1230 (*w*), 1200 (*m*), 1150 (*w*), 1130, 1090 (*m*), 1040 (*w*), 1010 (*m*), 960, 930 (*w*), 880, 820 cm^{-1} (*m*). MS.: M^+ = 164 (49), *m/e:* 150 (10), 149 (100), 136 (37), 135 (16), 121 (54), 107 (12), 96 (29), 95 (17), 93 (14), 91 (33), 81 (28), 79 (16), 77 (37), 69 (14), 68 (33), 67 (38), 65 (12), 55 (17), 53 (35), 51 (15), 44 (29), 43 (39), 41 (46), 40 (39), 41 (46), 40 (31), 39 (66). UV.: λ_{max} (ethanol) = 237 nm (ε = 10,500), shoulder at 275 nm (ε = 1200).

In both runs, the yields were not determined, but we estimate them to be very low.

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