49. Acid-Catalysed Rearrangements of α-Vinylcyclobutanones

by **David A. Jackson**[1]), **Max Rey**, and **André S. Dreiding***

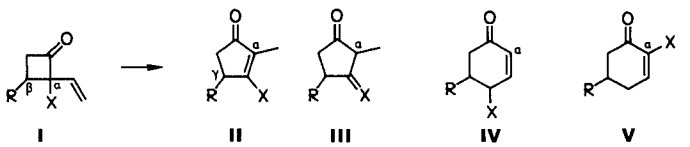
Organisch-Chemisches Institut der Universität Zürich-Irchel, Winterthurerstr. 190, 8057 Zürich

(5.XII.84)

The $BF_3 \cdot Et_2O$- and the CH_3SO_3H-catalysed rearrangements of 10 α-vinylcyclobutanones have been examined. With little acid, the β,β-dialkyl derivatives **1** were transformed into linear dienones **2** and **3**; with more acid, they were converted into cyclopentenones **4** by *Nazarov* cyclisation of initially formed **2**/**3**. The β-monoalkyl (including the β,γ-dialkyl) derivatives **7** rearranged only with a high acid concentration to afford the cyclopentenones **8** by 1,2-acyl migration. In the case of **7a**, the cyclopentenone **8a** was accompanied by the unexpected constitutional isomer **9a**, which is explained by a reversible interconversion of the cyclobutanone **7a** with its isomer **19** *via* a cyclopropane intermediate like **18**. In the case of the β,β-dialkyl derivative **5**, which contains an α-isobutenyl (instead of an α-vinyl) group, the acid-catalysed rearrangement product was the bicyclo[3.1.0]hexanone derivative **6**.

1. Introduction. – α-Vinylcyclobutanones **I** are strained compounds prone to thermal [1] or catalysed rearrangements. Under acid catalysis, three types of skeletal rearrangements have been observed: *i*) [1,2]-CO migration to give α-cyclopentenones **II** [2] or β-alkylidenecyclopentanones **III** [3], *ii*) [1,3]-CO migration to give α-cyclohexenones **IV** [2], and *iii*) [1,3]-C(β) migration to give α-cyclohexenones **V** [3] *(Scheme 1)*.

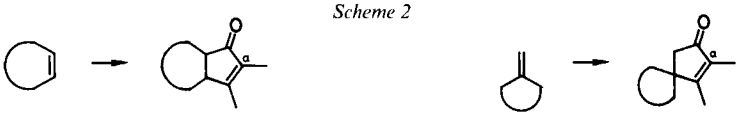
Scheme 1



I **II** **III** **IV** **V**

Recently, we have described [4] a convenient method for obtaining a number of α-vinylcyclobutanones **I** by the direct cycloaddition of vinylketenes to simple olefins. In this paper, we report the acid-catalysed rearrangement of **I** to linear dienones and to cyclopentenones. Our work provides a two-step access to certain substituted α-cyclopentenones, including bicyclic (**VI**) and spirocyclic (**VII**) systems *(Scheme 2)*.

Scheme 2

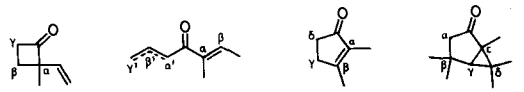


VI **VII**

[1]) Post-doctoral fellow, University of Zürich, 1981–1983.

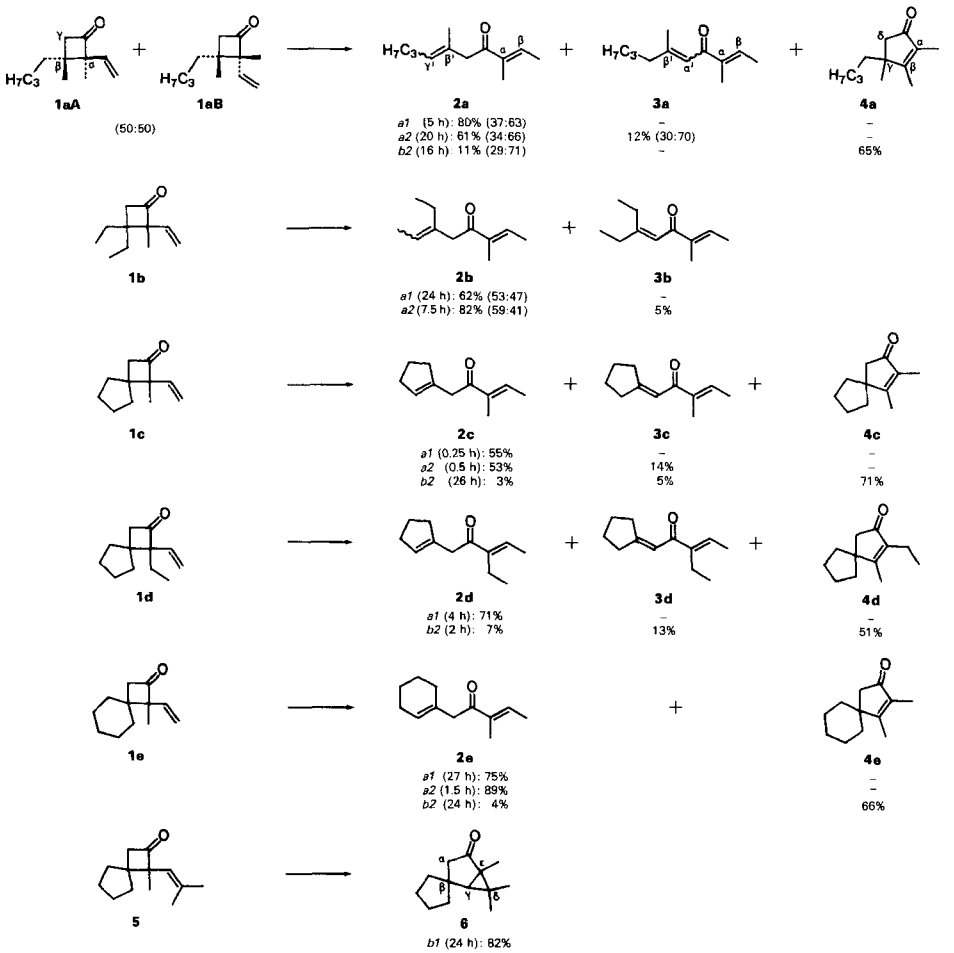
2. Acid-Catalysed Rearrangements of α-Vinylcyclobutanones. – The 10 α-vinylcyclobutanones used in the present study, all available from our previous work [4], are shown in *Schemes 3* and *4*, together with the reaction conditions and the products.

Since corresponding atoms of identical substructures may receive different numbers depending on the systematic name of the compound they belong to (s. *Exper. Part*), we identify the atoms of substructures relevant to this work with Greek letters as shown below and also in *Schemes 3* and *4*.

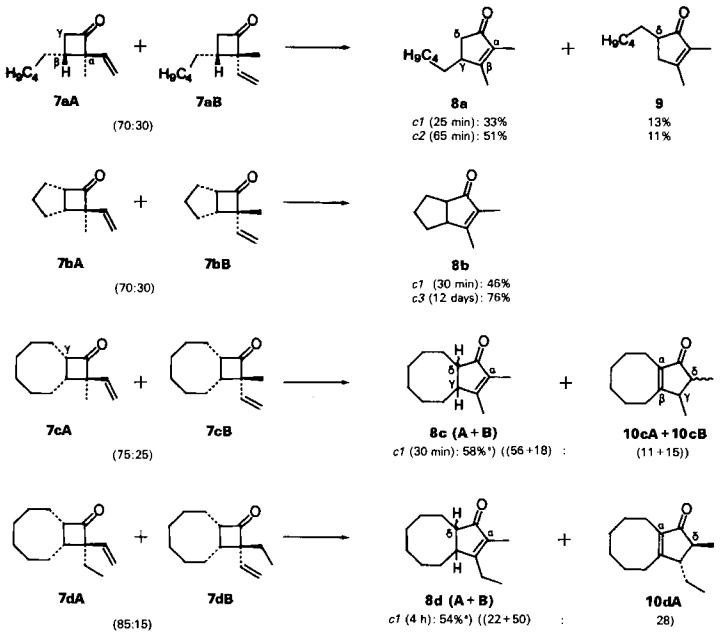


The following structural features should be noted in the starting materials since they will be found to influence reactivity: The variants of **1** all carry 2 alkyl groups at C(β), as does also **5** *(Scheme 3)*. The variants of **7** all carry only 1 alkyl group at C(β); three of them (**7b**–**7d**) carry a 2nd alkyl group at C(γ) *(Scheme 4)*. The vinyl group at C(α) in all

Scheme 3. *Acid-Catalysed Rearrangement of β,β-Dialkyl-α-vinylcyclobutanones* **1**



Scheme 4. *Acid-Catalysed Rearrangement of the β-Monoalkyl- and the β,γ-Dialkyl-α-vinylcyclobutanones* **7**



a) Yield of **8** + **10**.

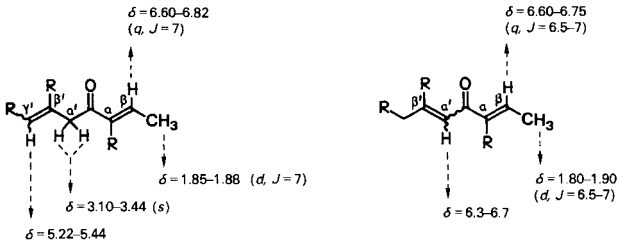
variants of **1** and **7** is unsubstituted; in **5**, however, it carries 2 geminal CH_3-groups. The second substituent at C(α) is a CH_3-group, except in **1d** and **7d** where it is ethyl. The substituents at C(β) and C(γ) are equal to each other in all the examples of *Scheme 4*, except in **7a**.

The different acid conditions used for the rearrangements include: *a*) two mild conditions *(Scheme 3), i.e.* 0.2 mol-equiv. of $BF_3 \cdot Et_2O$ in CH_2Cl_2 at r.t. (condition *a1*) and 0.2 mol-equiv. of CH_3SO_3H in CH_2Cl_2 at r.t. (condition *a2*), *b*) two intermediate conditions *(Scheme 3), i.e.* 1 mol-equiv. of $BF_3 \cdot Et_2O$ in CH_2Cl_2 at r.t. (condition *b1*) or 1 mol-equiv. of CH_3SO_3H in CH_2Cl_2 at r.t. (condition *b2*) and *c*) three severe conditions *(Scheme 4), i.e.* 15 mol-equiv. of CH_3SO_3H neat at r.t. (condition *c1*) or 28 mol-equiv. of CH_3SO_3H in CH_2Cl_2 at r.t. (condition *c2*) or 1 mol-equiv. of CH_3SO_3H in $CDCl_3$ at 60° (condition *c3*).

The products obtained under each of these conditions are dienones (**2** and **3**, *Scheme 3*), cyclopentenones (**4**, **8**, **9**, and **10**, *Scheme 3* and *4*), and a bicyclo[3.1.0]hexanone (**6**, *Scheme 3*). Note the position of the alkyl group at C(γ) or C(δ) in **4a**, **8a**, and **9**, as well as the position of the ethyl group at C(α) or C(β) in **4d**, **8d**, and **10d**.

2.1. *Two Alkyl Groups at C(β).* Under mild acid catalysis (conditions *a*), the β,β-dialkyl-α-vinylcyclobutanones **1a–e** *(Scheme 3)* underwent opening of the four-membered ring between C(α) and C(β) to give linear dienones: Condition *a1* afforded the allyl vinyl ketones **2a–e** as the sole products (55–80%), while with condition *a2* these same products **2a–d** (53–85%) were accompanied by 5–14% of the corresponding divinyl ketones **3a–d**.

Some characteristic spectral properties of **2** and **3** are summarised in *Fig. 1*.



2

IR: 1667–1675, 1642–1650 cm^{-1}
UV: 228–229 (5300–15100) nm (ϵ)

3

IR: 1650–1658, 1605–1615 cm^{-1}
UV: 253–262 (8600–13400) nm (ϵ)

Fig. 1. *Characteristic Spectral Data of the Ally Vinyl and the Divinyl Ketones* **2** *and* **3**. ^{1}H-NMR: δ in ppm, J in Hz.

The low-field ^{1}H-NMR δ-value for H–C(β) observed for **2a–e** and **3a–d** shows the C(α),C(β)-double bond in all of them to be (*E*)-configurated (*cf.*[5]). With respect to the second double bond (at C(β'),C(γ') or at C(α'),C(β')), the dienones **2a**, **2b**, and **3a** are mixtures of (*E*)- and (*Z*)-stereoisomers; although these isomers were separated in the case of **2a** and **2b**, their configurations could not be determined.

Under the intermediate acid condition *b2*, the β,β-dialkylcyclobutanones **1a**, and **1c–e** afforded the cyclopentenones **4a**, and **4c–e** (51–71%), respectively, along with 4–20% of the dienones **2** and **3** *(Scheme 3)*. On monitoring this rearrangement of **1e** by ^{1}H-NMR under condition *b2* using $CDCl_3$ instead of CH_2Cl_2 as solvent (s. *Exper. Part*), it was noted that **1e** was first cleanly converted into the dienone **2e** (4 h) and the latter much more slowly (21 h) into the cyclopentenone **4e**. The α-vinylcyclobutanone **1d** with an ethyl group at C(α) was transformed into the cyclopentenone **4d** which carries the ethyl group at C(α) (and not at C(β)). The evidence for and the mechanistic implication of this will be given further below and in *Section 3*.

2.2. *One Alkyl Group at C(β).* The β-monoalkyl-(**7a**) and β,γ-dialkyl-α-vinylcyclobutanones **7b–d** *(Scheme 4)* did not rearrange at all under the mild or intermediate acid conditions *a* and *b*. Under the severe acid conditions *c1*, *c2*, and *c3*, however, **7a–d** were converted into the cyclopentenones **8a–d**. No effect was noted on these results which might have been attributed to the fact that **7a–d** were all mixtures of two stereoisomers **A** and **B** differing in the relative configuration at C(α)/C(β). In the case of the β-monoalkyl-α-vinylcyclobutanone **7a**, the expected cyclopentenone **8a** with its pentyl group at C(γ) was accompanied by an unexpected constitutional isomer **9** which carries the pentyl group at C(δ). The cyclopentenones **8c** and **8d** obtained from the bicyclo[6.2.0]decanones **7c** and **7d**, respectively, consisted of (non-separated) mixtures of the two (configurationally unassigned) ring-juncture stereoisomers **A** and **B** and were accompanied by the double bond isomers **10c** and **10d**, respectively, the former as a mixture of the *cis*- and *trans*-isomer **10cA** and **10cB**, the latter just as the *trans*-isomer **10dA**. The α-vinylcyclobutanone **7d** with an ethyl group at C(α) was transformed into the cyclopentenones **8d** and **10d**, the former carrying the ethyl group at C(β) (and not at C(α)) and the latter at C(γ) (and not at C(δ)). Structural evidence for these products will be given below, and the mechanistic consequences will be discussed in *Section 3*.

Scheme 5

7cA **7cB** **7cC** **7cD**

A stereoisomerisation was observed within the α-vinylcyclobutanone **7c** under intermediate acid conditions *b2* in $CDCl_3$ for 44 h (^{1}H-NMR monitoring): A 3:1 mixture **7cA/7cB** with *cis*-ring juncture was partially converted into **7cC/7cD** with *trans*-ring juncture, presumably by enolisation at C(γ) *(Scheme 5)*. The resulting 30:15:30:25 ratio of **7cA/B/C/D** did not change significantly any more for 5 days (for the configurations of **7cA–D**, see [4]). The above-mentioned formation of *cis*- and *trans*-isomers **8cA/8cB** as well as **8dA/8dB** in the **7**→**8** conversion under condition *c1* may well be due to this stereoisomerisation at the level of the α-vinylcyclobutanone **7** prior to the ring expanding rearrangement.

Some characteristic spectral properties of **4a**, **4c–e**, **8a–d**, **9**, **10c**, and **10d** are summarised in *Fig. 2*.

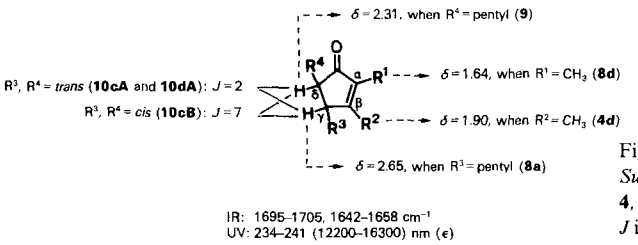
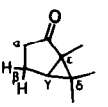


Fig. 2. *Characteristic Spectral Data of the Substituted Conjugated Cyclopentenones* **4**, **8**, **9**, *and* **10**. ^{1}H-NMR: δ in ppm, *J* in Hz.

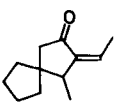
They manifest the presence of a conjugated cyclopentenone moiety (UV and IR) bearing substituents at C(α) and C(β) (by ^{1}H-NMR: no olefinic H-atoms). The β-position of the CH_3-group in **4d** follows from its lower-field and the α-position of the CH_3-group in **8d** from its higher-field ^{1}H-NMR signal (for similar cases, see [6] [7]). These positions of the CH_3-groups imply, of course, the correspondingly other positions (α in **4d** and β in **8d**) of the ethyl groups. The γ-position of the pentyl group in **8a** and its δ-position in **9** was derived from the lower-field ^{1}H-NMR signal of the methine-H in **8a** as compared to that of the methine-H in **9** (for similar cases, see [7] [8]). In the bicyclo[6.3.0]nonenones **10c** and **10d** with shifted double bonds, the relative configuration of the 2 alkyl groups at C(γ) and C(δ) of the cyclopentenone moiety was assigned from the larger coupling between the 2 vicinal methine-H's in the *trans*-isomers **10cA** and **10dA** than in the *cis*-isomer **10cB** (for similar cases, see [7] [8]). The relative configuration of **8c** and **8d** could not be established in an analogous manner because the signals of H–C(γ) and H–C(δ) – here the ring-juncture H-atoms – were not sufficiently resolved to determine the coupling constants.

2.3. *Two Geminal CH_3-Groups at the Vinyl Group.* When the cyclobutanone **5**, which carries two CH_3-groups at the end of its α-vinyl group, was exposed to the intermediate acid condition *b1*, the produt was not a cyclopentenone, but rather the bicyclo[3.1.0]hexanone spiro derivative **6** (82%). A mechanism will be considered in *Section 3*.

The structure of **6** was evident from the similarity of its pertinent spectral properties with those of the known [9] 1,6,6-trimethylbicyclo[3.1.0]hexane-2-one (**11**). A comparison of the ^{13}C-NMR spectra of **6** and **11** is especially informative since the only differences are the 4 CH_2 signals of the spiro-cyclopentane ring in **6** and the expected [10] deshielding Δδ of C(α), C(β), and C(γ) (Δδ = 13.7, 26.6, and 11.0 ppm, resp.) in **6** as compared to **11**, which is due to the atoms of the spiro-cyclopentane ring attached at C(β) in **6**. This deshielding effect on the C(γ) *d* is the evidence for the position of the angular CH_3-group at C(ε) and not at C(γ) of **6**.

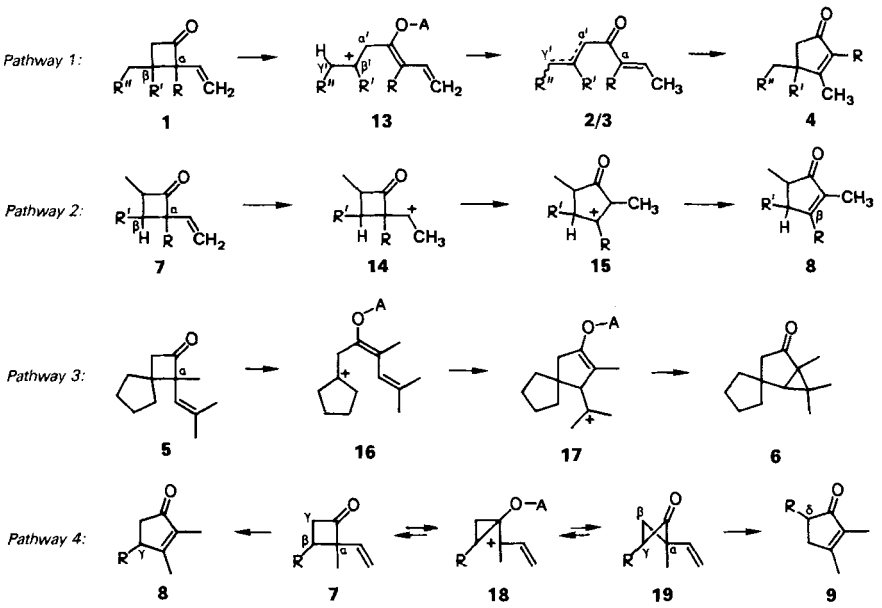


11



12

Scheme 6



3. Reaction Paths of the Acid-Catalysed Rearrangements. – The processes by which our α-vinylcyclobutanones are thought to be converted into products are shown in *Scheme 6*. The following differences in substitution patterns appear to play a role: The difference in the number of alkyl substituents at C(β) (comparison of *Pathways 1* and *2*), the absence or presence of alkyl substituents at the vinyl group (comparison of *Pathways 1* and *3*), and the equality or difference of the substituents at C(β) and C(γ) (*Pathway 4* as an elaboration of *Pathway 2*).

Pathway 1 is followed by the β,β-dialkyl derivatives **1**, which undergo C(α),C(β)-bond cleavage to **13** under the mild acid conditions *a*, because in this way the original C(β) can become a tertiary carbenium ion. Deprotonation produces the dienones **2**/**3** with the unconjugated **2** being kinetically preferred over **3**, possibly because H–C(γ') can be captured by the O-atom *via* a six-membered cyclic transition state (*c.f.* [11]) within **13**. The dienones **2**/**3** are isolable when they are formed under the mild acid catalysis. Their subsequent cyclisation to cyclopentenones **4**, which requires intermediate acid conditions *b2*, is thought to occur by a *Nazarov*-type mechanism [12].

In agreement with this postulated pathway, the dienone **2d** was found to be converted into a mixture of the cyclopentenone **4d** (36%) and the ethylidenecyclopentanone **12** (8%; see above) on treatment with the intermediate acid conditions *b2*, and the dienones **2** were observed (^{1}H-NMR or GC) to be formed transiently during the conversion of all cases of **1** into **4**. Furthermore, as is expected from the *Nazarov* mechanism of the last step of *Pathway 1*, the α-vinylcyclobutanone **1d** with the ethyl group at C(α) is transformed into the cyclopentenone **4d** with its ethyl group (R = Et) at C(α).

Pathway 2 is followed by the β-monoalkyl-cyclobutanones **7**. It involves the formation of the intermediate **14** and its transformation into **15** by a [1,2]-acyl shift. This mechanism follows from the example **7d** with an ethyl group at C(α), which is trans-

formed into the cyclopentenone **8d** carrying its ethyl group (R = Et) at C(β). This path has been suggested previously [2] [3] for acid-catalysed rearrangements of other α-vinylcyclobutanones and occurs when *Pathway 1* would produce a secondary carbenium ion (R' = H in **13**) instead of a tertiary one. This also makes it reasonable that the formation of cyclopentenones requires more severe acid conditions from **7** than from **1**. The difference between the *Pathways 1* and *2* would not have been noticed without the two examples **1d** and **7d** which carry an ethyl group at C(α).

Pathway 3 is followed in the special case of the β,β-dialkyl-cyclobutanone **5** which carries a 2,2-dimethylvinyl group at C(α). It proceeds by the intermediate **16** which is of the same type as **13** (tertiary carbenium ion), but – instead of loosing a proton – cyclises to another tertiary carbenium ion **17**. The latter stabilises itself by closing to a highly substituted cyclopropane, *i.e.* **6**.

Pathway 4 explains the formation of the two constitutionally different cyclopentenones **8a** and **9** from the constitutionally uniform **7a**. It proceeds by a preliminary (possibly reversible) rearrangement of the α-vinylcyclobutanone **7** (R at C(β)) *via* the three-membered ring intermediate **18** to the constitutionally isomeric α-vinylcyclobutanone **19** (R at C(γ)). Similar rearrangements have been observed previously [13]. The two ketones **7** and **19** subsequently rearrange (presumably by *Pathway 2*) to the observed cyclopentenones **8a** and **9**. In accord with this pathway is our observation, that **8a** is not interconvertible with **9** (67% of **8a** recovered unchanged) under condition *c1*. *Pathway 4* probably also occurs prior to *Pathway 2* with the bicyclic examples **7b–d**. However, since in these cases the two substituents at C(β) and C(γ) (of **7** or **19**) are the same, the effect of *Pathway 4* could not be noticed.

This work was supported by the *Swiss National Science Foundation* and by *Sandoz AG*, Basel.

Experimental Part

1. General. – The instruments, abbreviations, and chromatographic methods have been described in [4]. Here (in contrast to the preceding text), compounds in mixtures (products or educts) are always listed in the order of their elution in the chromatographic method used for the analysis. In order to remain consistent with our previous publication in this field [4], we have specified the relative configurations of racemic compounds by the notation [14] which represents (*nR,xR*) or (*nS,xS*) by like as (*l*), (*nR,xS*) or (*nS,xR*) by unlike as (*u*), (*nR,xR,yR*) or (*nS,xS,yS*) as (*l,l*), (*nR,xS,yR*) or (*nS,xR,yS*) as (*u,u*), (*nR,xR,yS*) or (*nS,xS,yR*) as (*l,u*), and (*nR,xS,yS*) or (*nS,xR,yR*) as (*u,l*), whereby *n,x,y* represent the numbers of the chiral C-atoms in the systematic name in increasing order ($n < x < y$). Not all examples given in [14] follow this rule.

2. Rearrangements of β,β-Dialkyl-α-vinylcyclobutanones 1 to Linear Dienones 2/3. – 2.1. *General Procedure.* A soln. of the distilled vinylcyclobutanone in CH_2Cl_2 (*ca.* 0.3–0.6 mol·l^{-1}) was treated at r.t. with 0.2 mol-equiv. of $BF_3 \cdot Et_2O$ or CH_3SO_3H. After the time indicated, the mixture was diluted with pentane and washed with sat. $NaHCO_3$ soln., dried over $MgSO_4$, and evaporated. The residue was subjected to LC-A (pentane/Et_2O 12:1, unless otherwise noted) or to bulb-to-bulb distillation (in *Exper. 2.4*) affording the product(s), which contained less than 5% of unidentified impurities (by GC-A and ^{1}H-NMR). This material was weighed to determine the yield and bulb-to-bulb distilled to obtain the spectroscopic properties.

2.2. *Rearrangement of 3-Butyl-2,3-dimethyl-2-vinylcyclobutanone* (**1a**). 2.2.1. *By $BF_3 \cdot Et_2O$.* From **1a** (50 mg, 0.28 mmol, 1:1 mixture (GC-A) of (*u*)- (**1aA**) and (*l*)-isomer **1aB**) [4] in CH_2Cl_2 (1 ml) with $BF_3 \cdot Et_2O$ (8.6 mg, 0.06 mmol), after 5 h, was obtained *(2E)-3,6-dimethyl-2,6-decadien-4-one* (**2a**; 40 mg, 80%) as a 37:63 mixture (GC-A) of (6*E*/*Z*)-isomers **A** and **B** (configuration unassigned), colourless liquid, b.p. 65–70°/0.1 Torr. Anal. calc. for $C_{12}H_{20}O$ (180.29): C 79.94, H 11.18; found: C 79.66, H 10.89.

The 2 isomers were separated by semiprep. GC-B (*SP-2250*, 150°). **2aA** (1st fraction): UV (C_2H_5OH): 228 (8600). IR (film): 1675*s*, 1650*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.78 (*qq*, *J* = 1.5, 7, H–C(2)); 5.35 (br. *t*, *J* = 7,

H–C(7)); 3.39 (br. *s*, 2H–C(5)); 1.96 (br. *q*, *J* = 7, 2H–C(8)); 1.87 (*dq*, *J* = 7, 1, 3H–C(1)); 1.78 (*dq*, *J* = 1.5, 1, CH_3–C(3)); 1.67 (br. *d*, *J* = 1, CH_3–C(6)); 1.35 (*sext.*, *J* = 7, 2H–C(9)); 0.89 (*t*, *J* = 7, 3H–C(10)). MS (70 eV): 180 (11, M^+), 83 (91), 55 (100).

2aB (2nd fraction): UV (C_2H_5OH): 228 (5300). IR (film): 1675*s*, 1650*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.82 (br. *q*, *J* = 7, H–C(2)); 5.19 (br. *t*, *J* = 7, H–C(7)); 3.33 (br. *s*, 2H–C(5)); 2.00 (br. *q*, *J* = 7, 2H–C(8)); 1.84 (br. *d*, *J* = 7, 3H–C(1)); 1.77 (br. *s*, CH_3–(3)); 1.61 (br. *s*, CH_3–(6)); 1.37 (br. *sext.*, *J* = 7, 2H–C(9)); 0.89 (*t*, *J* = 7, 3H–C(10)). MS (70 eV): 180 (11, M^+), 83 (89), 55 (100).

2.2.2. *By CH_3SO_3H.* As in *2.2.1*, from **1a** (150 mg, 0.83 mmol) in CH_2Cl_2 (3 ml) with CH_3SO_3H (16 mg, 0.17 mmol), after 20 h, was obtained a 28:55:17 mixture (GC-A, ^{1}H-NMR) of **2aA**, **2aB**, and *(2E)-3,6-dimethyl-2,5-decadien-4-one* (**3a**) (110 mg) which corresponds to a yield of 61% of **2a** and 12% of **3a**. Semiprep. GC-B (*SP-2250*, 150°) gave, in addition to **2a**, a sample of **3a** which consisted of a 3:7 mixture (^{1}H-NMR) of (5*E*/*Z*)-isomers **A** and **B**. UV (C_2H_5OH): 254 (13400). IR (film): 1658*s*, 1614*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.77–6.59 (*m*, H–C(2)); 6.41–6.32 (*m*, H–C(5)); 2.42 (br. *t*, *J* = 7, 0.6 H, 2H–C(7) of **A**); 2.15 (br. *t*, *J* = 7, 1.4 H, 2H–C(7) of **B**); 2.01 (*d*, *J* = 1, *ca.* 2 H, CH_3–C(6) of **B**); 1.95–1.80 (*m*, *ca.* 7 H, CH_3–C(6) of **A**, CH_3–C(3), 3H–C(1)); 1.6–1.2 (*m*, *ca.* 4 H, $(CH_2)_2$); 1.00–0.85 (*m*, 3H–C(10)). MS (70 eV): 180 (2, M^+), 165 (9), 123 (9), 83 (100).

2.3 *Rearrangement of 3,3-Diethyl-2-methyl-2-vinylcyclobutanone* (**1b**). 2.3.1. *By $BF_3 \cdot Et_2O$.* From **1b** (25 mg, 0.15 mmol) [4] in CH_2Cl_2 (0.5 ml) with $BF_3 \cdot Et_2O$ (4.3 mg, 0.03 mmol), after 24 h, was obtained *(2E)-6-ethyl-3-methyl-2,6-octadien-4-one* (**2b**). The 1st fraction of LC-A yielded one C(6) double bond isomer **2bA** (8.2 mg, 33%; configuration unassigned) as colourless oil, b.p. 100–110°/12 Torr. UV (C_2H_5OH): 228 (14100). IR (film): 1675*s*, 1648*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.81 (*qq*, *J* = 7, 1, H–C(2)); 5.44 (br. *q*, *J* = 7, H–C(7)); 3.42 (br. *s*, 2H–C(5)); 1.99 (br. *q*, *J* = 7.5, 2H–C(1′)); 1.86 (*dq*, *J* = 7, 1, 3H–C(1)); 1.78 (br. *s*, CH_3–C(3)); 1.58 (br. *d*, *J* = 7, 3H–C(8)); 0.96 (*t*, *J* = 7.5, 3H–C(2′)). MS (70 eV): 166 (5, M^+), 83 (100).

The 2nd fraction contained 7.2 mg (29%) of the other C(6) double bond isomer **2bB** as a colourless oil, b.p. 100–110°/12 Torr. UV (C_2H_5OH): 228 (12600). IR (film): 1670*s*, 1648*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.81 (br. *q*, *J* = 7, H–C(2)); 5.22 (br. *q*, *J* = 7, H–C(7)); 3.34 (br. *s*, 2H–C(5)); 2.07 (br. *q*, *J* = 7.5, 2H–C(1′)); 1.85 (br. *d*, *J* = 7, 3H–C(1)); 1.78 (br. *s*, CH_3–C(3)); 1.62 (br. *d*, *J* = 7, 3H–C(8)); 0.94 (*t*, *J* = 7.5, 3H–C(2′)). MS (70 eV): 166 (5, M^+), 83 (100). Anal. calc. for $C_{11}H_{18}O$ (166.27; **2bA**/**2bB** 1:1 by GC-A and ^{1}H-NMR): C 79.46, H 10.91; found: C 79.32, H 10.63.

2.3.2. *By CH_3SO_3H.* From **1b** (100 mg, 0.6 mmol) in CH_2Cl_2 (2 ml) with CH_3SO_3H (11.5 mg, 0.12 mmol), after 7.5 h, was obtained in the 1st fraction of LC-A *(2E)-6-ethyl-3-methyl-2,5-octadien-4-one* (**3b**; 5 mg, 5%) as a colourless liquid, b.p. 100–110°/12 Torr. UV (C_2H_5OH): 253 (11100). IR (film): 1655*s*, 1615*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.73 (br. *q*, *J* = 6.5, H–C(2)); 6.28 (br. *s*, H–C(5)); 2.41, 2.20 (*q* and br. *q*, both *J* = 7.5, 2H–C(7), 2H–C(1′)); 1.84 (br. *d*, *J* = 6.5, 3H–C(1)); 1.82 (*s*, CH_3–C(3)); 1.09, 1.06 (2 *t*, *J* = 7.5, 3H–C(8), 3H–C(2′)). MS (70 eV): 166 (3, M^+), 83 (100). The 2nd and 3rd fractions contained 48 mg (48%) of **2bA** and 34 mg (34%) of **2bB** (by GC-A and ^{1}H-NMR, see *2.3.1*), resp.

2.4. *Rearrangment of 1-Methyl-1-vinylspiro[3.4]octan-2-one* (**1c**). 2.4.1. *By $BF_3 \cdot Et_2O$.* From **1c** (630 mg, 3.8 mmol) [4] in CH_2Cl_2 (6 ml) with $BF_3 \cdot Et_2O$ (110 mg, 0.77 mmol), after 15 min and bulb-to-bulb distillation of the crude product at 140–150°/12 Torr, was obtained *(3E)-1-(cyclopent-1-enyl)-3-methyl-3-penten-2-one* (**2c**; 350 mg, 55%) as a colourless liquid. UV (C_2H_5OH): 229 (8400). IR (film): 1670*s*, 1648*m*. ^{1}H-NMR (60 MHz, CCl_4): 6.65 (br. *q*, *J* = 7, H–C(4)); 5.30 (br. *s*, H–C(2′)); 3.30 (br. *s*, 2H–C(1)); 2.4–2.0 (*m*, 2H–C(3′), 2H–C(5′)); 2.0–1.8 (*m*, CH_3–C(3), 3H–C(5), 2H–C(4′)). MS (70 eV): 164 (7, M^+), 149 (13), 83 (100). Anal. calc. for $C_{11}H_{16}O$ (164.25): C 80.45, H 9.82; found: C 80.22, H 9.68.

2.4.2. *By CH_3SO_3H.* From **1c** (90 mg, 0.55 mmol) in CH_2Cl_2 (1 ml) with CH_3SO_3H (10.6 mg, 0.11 mmol), after 30 min, was obtained 60 mg (67%) of a 79:21 mixture of **2c** and *(3E)-1-cyclopentyliden-3-methyl-3-penten-2-one* (**3c**) as a colourless oil, which was subjected to semiprep. GC-B (*SP-2250*, 160°). The 1st (major) fraction consisted of **2c** (by ^{1}H-NMR, see *2.4.1*) and the 2nd of **3c**. UV (C_2H_5OH): 262 (8600). IR (film): 1650*s*, 1605*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.75–6.61 (*m*, H–C(1), H–C(4)); 2.85–2.70 (*m*, 2H–C(2′)); 2.55–2.40 (*m*, 2H–C(5′)); 1.82 (br. *d*, *J* = 7, 3H–C(5)); 1.80 (br. *s*, CH_3–C(3)); 1.90–1.60 (*m*, 2H–C(3′), 2H–C(4′)). ^{1}H-NMR (200 MHz, C_6D_6): 6.15 (br. *s*, H–C(1)); 5.95 (br. *q*, *J* = 7, H–C(4)); 2.60–2.45 (*m*, 2H–C(2′)); 1.80–1.65 (*m*, 2H–C(5′)); 1.42 (br. *s*, CH_3–C(3)); 0.98 (br. *d*, *J* = 7, 3H–C(5)); 1.10–0.80 (*m*, 2H–C(3′), 2H–C(4′)). MS (70 eV): 164 (19, M^+), 149 (100).

2.5. *Rearrangment of 1-Ethyl-1-vinylspiro[3.4]octan-2-one* (**1d**) *by $BF_3 \cdot Et_2O$.* From **1d** (400 mg, 2.25 mmol) [4] in CH_2Cl_2 (7.5 ml) with $BF_3 \cdot Et_2O$ (64.5 mg, 0.45 mmol), after 4 h, was obtained *(3E)-1-(cyclopent-1-enyl)-3-ethyl-3-penten-2-one* (**2d**; 284 mg, 71%) as a colourless liquid, b.p. 70–75°/0.01 Torr. UV (C_2H_5OH): 229 (13400). IR (film): 1667*s*, 1642*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.75 (*q*, *J* = 7, H–C(4)); 5.44 (br. *s*, H–C(2′)); 3.44 (br. *s*, 2H–C(1)); 2.40–2.20 (*m*, 2H–C(3′), 2H–C(5′), CH_3CH_2); 1.95–1.80 (*m*, 2H–C(4′)); 1.88 (*d*, *J* = 7, 3H–C(5));

0.94 (*t*, *J* = 7.5, CH_3CH_2). MS (70 eV): 178 (7, M^+), 97 (100). Anal. calc. for $C_{12}H_{18}O$ (178.28): C 80.85, H 10.18; found: C 81.01, H 10.01.

2.6. *Rearrangment of 1-Methyl-1-vinylspiro[3.5]nonan-2-one* (**1e**). 2.6.1. *By* $BF_3 \cdot Et_2O$. From **1e** (270 mg, 1.5 mmol) [4] in CH_2Cl_2 (5 ml) with $BF_3 \cdot Et_2O$ (43 mg, 0.3 mmol), after 27 h, was obtained *(3E)-1-(cyclohex-1-enyl)-3-methyl-3-penten-2-one* (**2e**; 202 mg, 75%) as a colourless liquid, b.p. 60–65°/0.05 Torr. UV (C_2H_5OH): 228 (15100). IR (film): 1672*s*, 1660*s*, 1645*m*. ^{1}H-NMR (60 MHz, CCl_4): 6.60 (br. *q*, *J* = 7, H–C(4)); 5.4–5.2 (*m*, H–C(2')); 3.10 (br. *s*, 2H–C(1)); 2.2–1.4 (*m*, $(CH_2)_4$, CH_3–C(3), 3H–C(5)). MS (70 eV): 178 (8, M^+), 83 (100). Anal. calc. for $C_{12}H_{18}O$ (178.28): C 80.85, H 10.18; found: C 80.77, H 9.89.

2.6.2. *By* CH_3SO_3H. From **1e** (90 mg, 0.51 mmol) in CH_2Cl_2 (1 ml) with CH_3SO_3H (9.6 mg, 0.1 mmol), after 1.5 h, was obtained **2e** (80 mg, 89%; by GC-A and ^{1}H-NMR, see *2.6.1*) as a colourless liquid.

3. Rearrangements of 1 to Cyclopentenones 4. – 3.1. *General Procedure.* A soln. of the distilled **1** in CH_2Cl_2 (*ca.* 0.3 mol·l^{-1}) was treated at r.t. with 1 mol.-equiv. of CH_3SO_3H. The rapid formation and slow disappearance of the ring-opened products **2** and **3** was followed by GC-A and the final *Nazarov*-cyclisation products **4** were isolated as in *Exper. 2.1.*

3.2. *Rearrangement of* **1a**. From **1a** (150 mg, 0.83 mmol; see *2.2.1*) in CH_2Cl_2 (2.8 ml) with CH_3SO_3H (80 mg, 0.83 mmol), after 16 h, was obtained in the 1st fraction of LC-A 16 mg (11%) of **2a** as a 29:71 mixture (GC-A, ^{1}H-NMR) of **2aA** and **2aB** (see *2.2.1*). The 2nd fraction contained *4-butyl-2,3,4-trimethyl-2-cyclopenten-1-one* (**4a**; 97 mg, 65%) as a colourless liquid, b.p. 65°/0.1 Torr. UV (C_2H_5OH): 236 (13500). IR (film): 1705*s*, 1650*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.35, 2.09 (2 *d*, *J* = 18 each, 2H–C(5)); 1.89 (br. *s*, CH_3–C(3)); 1.67 (br. *s*, CH_3–C(2)); 1.15 (*s*, CH_3–C(4)); 1.5–1.0 (*m*, $(CH_2)_3$); 0.86 (*t*, *J* = 7, $CH_3(CH_2)_3$). MS (70 eV): 180 (17 M^+), 124 (27), 123 (100). Anal. calc for $C_{12}H_{20}O$ (180.29): C 79.94, H 11.18; found: C 79.67, H 10,89.

3.3. *Rearrangement of* **1c**. From **1c** (400 mg, 2.4 mmol) in CH_2Cl_2 (8.1 ml) with CH_3SO_3H (230 mg, 2.4 mmol), after 26 h, was obtained in the 1st fraction of LC-A (pentane/Et_2O 4:1) 30 mg (8%) of a 37:63 mixture (GC-A) of **2c** and **3c** (see *2.4*). The 2nd fraction contained *3,4-dimethylspiro[4.4]non-3-en-2-one* (**4c**; 285 mg, 71%) as a pale yellow oil. Bulb-to-bulb distillation at 45–50°/0.015 Torr gave a pure sample of **4c** as a colourless oil. UV (C_2H_5OH): 239 (16000). IR (film): 1703*s*, 1645*m*. ^{1}H-NMR (60 MHz, CCl_4): 2.10 (*s*, 2H–C(1)); 1.90 (br. *s*, CH_3–C(4)); 1.60 (br. *s*, CH_3–C(3)); 2.0–1.0 (*m*, $(CH_2)_4$). MS (70 eV): 164 (73, M^+), 123 (79), 122 (100). Anal. calc. for $C_{11}H_{16}O$ (164.25): C 80.44, H 9,82; found: C 80.66, H 10.06.

3.4. *Rearrangement of* **1d**. From **1d** (370 mg, 2.1 mmol) in CH_2Cl_2 (7 ml) with CH_3SO_3H (202 mg, 2.1 mmol), after 2 h, was obtained in the 1st fraction of LC-A 74 mg (20%) of a 1:2 mixture (^{1}H-NMR) of **2d** (see *2.5*) and an uncharacterised compound, assumed (on the basis of ^{1}H-NMR) to be *(3E)-1-cyclopentyliden-3-ethyl-3-penten-2-one* (**3d**). The 2nd fraction contained *3-ethyl-4-methylspiro[4.4]non-3-en-2-one* (**4d**; 190 mg, 51%) as a colourless oil, b.p. 80–85°/0.03 Torr. UV (C_2H_5OH): 240 (16300). IR (film): 1700*s*, 1642*m*. ^{1}H-NMR (60 MHz, CCl_4): 2.10 (*q*, *J* = 7, CH_3CH_2); 2.10 (*s*, 2H–C(1)); 1.90 (*s*, CH_3–C(4)); 2.0–1.2 (*m*, $(CH_2)_4$); 1.0 (*t*, *J* = 7.5, CH_3CH_2). MS (70 eV): 178 (31, M^+), 137 (100). Anal. calc. for $C_{12}H_{18}O$ (178.28): C 80.85, H 10.18; found: C 80.63, H 10.31.

3.5. *Rearrangement of* **1e**. From **1e** (200 mg, 1.12 mmol) in CH_2Cl_2 (4 ml) with CH_3SO_3H (108 mg, 1.12 mmol), after 24 h, was obtained in the 1st fraction of LC-A (pentane/Et_2O 4:1) **2e** (8 mg, 4%; by GC-A and ^{1}H-NMR, see *2.6.1*). The 2nd fraction contained *3,4-dimethylspiro[4.5]dec-3-en-2-one* (**4e**; 132 mg, 66%) as a colourless liquid, b.p. 80–85°/0.07 Torr. UV (C_2H_5OH): 238 (15300). IR (film): 1700*s*, 1650*m*. ^{1}H-NMR (60 MHz, CCl_4): 2.10 (*s*, 2H–C(1)); 1,90 (br. *s*, CH_3–C(4)); 1.60 (br. *s*, CH_3–C(3)); 2.0–0.9 (*m*, $(CH_2)_5$). MS (70 eV): 178 (36, M^+), 122 (100). Anal. calc. for $C_{12}H_{18}O$ (178.28): C 80.85, H 10.18; found: C 80.53, H 9.91.

3.6. *Cyclisation of* **2d**. From **2d** (220 mg, 1.23 mmol; from *Exper. 2.5*) in CH_2Cl_2 (4 ml) with CH_3SO_3H (118 mg, 1.23 mmol), after 28 h, was obtained in the 1st fraction of LC-A 20 mg of a yellow oil that was bulb-to-bulb distilled at 80–85°/0.07 Torr to give *(Z)-3-ethyliden-4-methylspiro[4.4]nonan-2-one* (**12**; 18 mg, 8%) as a colourless oil. UV (C_2H_5OH): 241 (7200). IR (film): 1722*s*, 1650*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.59 (*dq*, *J* = 1.5, 7, H–C(1')); 2.78–2.60 (*m*, H–C(4)) [1.06, br. *s*]; 2.36, 2.13 (2 *d*, *J* = 17.5 each, 2H–C(1)); 1.82 (*d*, *J* = 7, 3H–C(2')); 1.8–1.2 (*m*, $(CH_2)_4$); 1.06 (*d*, *J* = 7, CH_3–C(4)) [2.7, br. *s*]. MS (70 eV): 178 (63, M^+), 136 (100).

The 2nd fraction contained 85 mg of a yellow oil that was bulb-to-bulb distilled at 80–85°/0.07 Torr to give **4d** (80 mg, 36%; by ^{1}H-NMR; see *3.4*) as a colourless oil.

4. Rearrangements of β-Monoalkyl-α-vinylcyclobutanones 7 to Cyclopentenones 8. – 4.1. *General Procedure.* The indicated amount of CH_3SO_3H was added in a steady stream from a pipette to the stirred distilled vinylcyclobutanone **7** without solv. (except for **7a** where CH_2Cl_2 was used (see *4.2.2*) and **7b** where $CDCl_3$ was used (see *4.3.2*)) at r.t. After the time indicated, when no starting material remained (by GC-A), the mixture was diluted with pentane and washed with H_2O and sat. $NaHCO_3$ soln., dried over $MgSO_4$, and evaporated. The residue was subjected to LC-A to afford the products (containing less than 5% of impurities by GC-A and ^{1}H-NMR) which were weighed to determine their yields and bulb-to-bulb distilled to obtain their spectroscopic properties.

4.2. *Rearrangement of 2-Methyl-3-pentyl-2-vinylcyclobutanone* (**7a**). 4.2.1. *Reaction without Solv.* From **7a** (0.27 g, 1.5 mmol; 3:7 mixture (GC-A) of (*l*)- (**7aB**) and (*u*)-isomer **7aA**) [4] and CH_3SO_3H (2.2 g, 23 mmol), after 25 min, was obtained in the 1st fraction of LC-A (pentane/Et_2O 12:1) 40 mg of a yellow oil that was distilled at 55–60°/0.005 Torr to give *2,3-dimethyl-5-pentylcyclopent-2-enone* (**9**; 35 mg, 13%) as a colourless liquid. UV (C_2H_5OH): 234 (12200). IR (film): 1700*s*, 1658*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.66 (br. *dd*, *J* = 18, 6, H–C(4)); 2.38–2.24 (*m*, H–C(5)); 2.15 (br. *d*, *J* = 18, H–C(4)); 2.05 (*s*, CH_3–C(3)); 1.69 (br. *s*, CH_3–C(2)); 1.5–1.1 (*m*, $(CH_2)_4$); 1.0–0.8 (*m*, $CH_3(CH_2)_4$). MS (70 eV): 180 (2, M^+), 124 (4), 123 (26), 110 (100). Anal. calc. for $C_{12}H_{20}O$ (180.29): C 79.94, H 11.18; found: C 80.06, H 10.93.

The 2nd fraction contained 108 mg of a yellow oil that was distilled at 55–60°/0.005 Torr to give *2,3-dimethyl-4-pentylcyclopent-2-enone* (**8a**; 89 mg, 33%) as a colourless liquid. UV (C_2H_5OH): 235 (13600). IR (film): 1705*s*, 1652*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.73–2.58 (*m*, H–C(4)); 2.51 (*dd*, *J* = 18, 6.5, H–C(5)); 2.06 (br. *d*, *J* = 18, H–C(5)); 2.00 (*s*, CH_3–C(3)); 1.68 (br. *s*, CH_3–C(2)); 1.4–1.0 (*m*, $(CH_2)_4$); 0.95–0.80 (*m*, $CH_3(CH_2)_4$). MS (70 eV): 180 (20, M^+), 123 (33), 110 (100). Anal. calc. for $C_{12}H_{20}O$ (180.29): C 79.94, H 11.18; found: C 80.18, H 11.02.

4.2.2. *Reaction with Solv.* To **7a** (90 mg, 0.50 mmol; see *4.2.1*) in CH_2Cl_2 (0.9 ml) at 0° was added CH_3SO_3H (1.3 g, 14 mmol). After 65 min, the mixture was worked up according to *4.1*. The 1st fraction of LC-A (pentane/Et_2O 12:1) contained **9** (10 mg, 11%) and the 2nd **8a** (46 mg, 51%, by GC-A and ^{1}H-NMR) as colourless liquids.

4.3. *Rearrangement of 7-Methyl-7-vinylbicyclo[3.2.0]heptan-6-one* (**7b**). 4.3.1. *Without Solv.* From **7b** (390 mg, 2.6 mmol; 3:7 mixture (GC-A and ^{1}H-NMR), of (*u,u*)- (**7bB**) and (*u,l*)-isomer **7bA**) [4] in CH_3SO_3H (3.7 g, 39 mmol), after 30 min, was obtained from LC-A (pentane/Et_2O 12:1) *(u)-3,4-dimethylbicyclo[3.3.0]oct-3-en-2-one* (**8b**; 180 mg, 46%) as a colourless liquid, b.p. 125–130°/12 Torr. UV (C_2H_5OH): 237 (12200). IR (film): 1695*s*, 1650*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.15–3.00 (*m*, H–C(5)); 2.80–2.65 (*m*, H–C(1)); 2.00 (br. *s*, CH_3–C(4)); 1.65 (br. *s*, CH_3–C(3)); 1.95–1.50 (*m*, $(CH_2)_3$). MS (70 eV): 150 (47, M^+), 122 (100). Anal. calc. for $C_{10}H_{14}O$ (150.22): C 79.96, H 9.39; found: C 78.41, H 9.62%.

4.3.2. *With Solv.* From **7b** (50 mg, 0.33 mmol; see *4.3.1*) in $CDCl_3$ (0.5 ml) with CH_3SO_3H (32 mg, 0.33 mmol), heated at 60° for 12 days, was obtained from LC-A (pentane/Et_2O 12:1) **8b** (38 mg, 76%; by ^{1}H-NMR, see *4.3.1*) as a colourless liquid.

4.4. *Rearrangement of 10-Methyl-10-vinylbicyclo[6.2.0]decan-9-one* (**7c**). From **7c** (1.0 g, 5.2 mmol; 1:3 mixture (GC-A) of (*u,u*)- (**7cB**) and (*u,l*)-isomer **7cA**) [4] and CH_3SO_3H (7.4 g, 77 mmol), after 30 min, was obtained in a single fraction of LC-A (pentane/Et_2O 4:1) 0.58 g (58%) of a 11:15:56:18 mixture (GC-A) containing *(l)*- (**10cA**) and *(u)-10,11-dimethylbicyclo[6.3.0]undec-1(8)-en-9-one* (**10cB**) as well as the two ring-juncture isomers **8cA** and **8cB** of *10,11-dimethylbicyclo[6.3.0]undec-10-en-9-one* (**8c**) as a colourless liquid, b.p. 95–100°/0.025 Torr. Anal. calc. for $C_{13}H_{20}O$ (192.30): C 81.20, H 10.50; found: C 80.97, H 10.27.

The isomers were separated by semiprep. GC-B (*SP-2250*, 180°). The 1st fraction consisted of **10cA**. UV (C_2H_5OH): 241 (14400). IR (film): 1700*s*, 1645*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.58–2.46 (*m*, 2H–C(2)); 2.40–2.22 (*m*, 2H–C(7), H–C(11)); 1.94 (*dq*, *J* = 2, 7, H–C(10)); 1.85–1.40 (*m*, $(CH_2)_4$); 1.20, 1.16 (2 *d*, *J* = 7, CH_3–C(10), CH_3C(11)). GC/MS (70 eV): 192 (86, M^+), 177 (100). The 2nd fraction consisted of **10cB**. UV (C_2H_5OH): 240 (13900). IR (film): 1700*s*, 1648*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.88 (br. *quint.*, *J* = 7, H–C(11)); 2.60–2.46 (*m*, 2H–C(2), H–C(10)); 2.44–2.30 (*m*, 2H–C(7)); 1.9–1.4 (*m*, $(CH_2)_4$); 1.08, 1.06 (2 *d*, *J* = 7.5, CH_3–C(10), CH_3–C(11)). GC/MS (70 eV): 192 (85, M^+), 177 (100).

The 3rd (major) fraction consisted of **8cA/8cB** (unassigned) in a 3:1 ratio (by GC-A and ^{1}H-NMR). UV (C_2H_5OH): 236 (14700). IR (film): 1700*s*, 1655*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.70–2.56 (*m*, 0.7 H, H–C(1) of **A**); 2.60–2.45 (*m*, 0.3 H, H–C(1) of **B**); 2.25–2.00 (*m*, H–C(8)); 2.02 (br. *s*, 2.3 H, CH_3–C(11) of **A**); 1.98 (br. *s*, 0.7 H, CH_3–C(11) of **B**); 1.68 (br. *s*, CH_3–C(10)); 1.9–1.0 (*m*, $(CH_2)_6$). MS (70 eV): 192 (43, M^+), 177 (43), 123 (100).

4.5. *Rearrangement of 10-Ethyl-10-vinylbicyclo[6.2.0]decan-9-one* (**7d**). From **7d** (0.52 g, 2.5 mmol; 15:85 mixture (GC-A) of (*u,u*)- (**7dB**) and (*u,l*)-isomer **7dA**) [4] with CH_3SO_3H (3.7 g, 39 mmol), after 4 h, was obtained 0.40 g of a brown oil containing *(l)-11-ethyl-10-methylbicyclo[6.3.0]undec-1(8)-en-9-one* (**10dA**) and the two ring-juncture isomers **8dA** and **8dB** of *11-ethyl-10-methylbicyclo[6.3.0]undec-10-en-9-one* (**8d**) in a 28:22:50 ratio (GC-A). Twice repeated LC-A (pentane/Et_2O 12:1) gave 0.28 g (54%) of a 31:25:44 mixture (GC-A) of **10dA**, **8dA**, and **8dB** as a colourless liquid, b.p. 90–95°/0.01 Torr. Anal. calc. for $C_{14}H_{22}O$ (206.33): C 81.50, H 10.75; found: C 81.75, H 10.96.

A sample of this mixture was partially resolved by semiprep. GC-B (*SP-2250*, 210°). The 1st fraction consisted of **10dA**. UV (C_2H_5OH): 240 (12600). IR (film): 1700*s*, 1647*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.55–2.43 (*m*, 2H–C(2)); 2.36–2.24 (*m*, 2H–C(7)); 2.23–2.10 (*m*, H–C(11)); 2.02 (*dq*, *J* = 2, 7.5, H–C(10)) [1.15, br. *s*]; 1.9–1.2 (*m*, $(CH_2)_4$, CH_3CH_2); 1.15 (*d*, *J* = 7.5, CH_3–C(10)); 0.93 (*t*, *J* = 7, CH_3CH_2). MS (70 eV): 206 (94, M^+), 178 (95), 41 (100).

The 2nd fraction consisted of a 35:65 mixture (GC-A, ^{1}H-NMR) **8dA/8dB** (unassigned). UV (C_2H_5OH): 237

(14200). IR (film): 1702*s*, 1648*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.83–1.92 (*m*, H–C(8), H–C(1), H–C(7), CH_3CH_2); 1.92–1.68 (*m*, 2H–C(2), H–C(7)); 1.64 (br. *s*, CH_3–C(10)); 1.62–1.15 (*m*, $(CH_2)_4$); 1.10, 1.09 (2 *t*, J = 7.5, intensity ratio 0.65:0.35, together 3 H, CH_3CH_2). MS (70 eV): 206 (65, M^+), 149 (73), 137 (77), 41 (95), 40 (100).

5. Rearrangement of 1-Methyl-1-(2-methyl-1-propenyl)spiro[3.4]octan-2-one (5). – From **5** (*ca.* 90% pure; 0.12 g, 0.63 mmol) [4] in CH_2Cl_2 (2 ml) with $BF_3 \cdot Et_2O$ (84 mg, 0.59 mmol), after 24 h and workup as in *2.1* including LC-A (pentane/Et_2O 4:1), was obtained *5,6,6-trimethylspiro[bicyclo[3.1.0]hexan-2,1'-cyclopentan]-4-one* (**6**; 89 mg, 82%) as a colourless oil that was bulb-to-bulb distilled at 135–140°/12 Torr. UV (C_2H_5OH): 218 (4300). IR (film): 1720*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.23, 2.11 (2*d*, J = 20, 2H–C(3)); 1.8–1.5 (*m*, $(CH_2)_4$); 1.40 (*s*, H–C(1)); 1.23, 1.24 (2 *s*, $2CH_3$–C(6)); 1.12 (*s*, CH_3–C(5)). ^{13}C-NMR ($CDCl_3$): 216.7 (*s*, C(4)); 52.0 (*t*, C(3)); 51.2 (*d*, C(1)); 45.2 (*s*, C(2)); 43.6, 36.4, 24.5, 23.2 (4 *t*, C(2'), C(3'), C(4'), C(5')); 43.0 (*s*, C(5)); 28.2 (*s*, C(6)); 25.0, 19.0, 11.0 (3 *q*, 3 CH_3). MS (70 eV): 192 (10, M^+), 110 (100). Anal. calc. for $C_{13}H_{20}O$ (192.30): C 81.20, H 10.48; found: C 81.29, H 10.70.

6. Treatment of 8a with CH_3SO_3H. – Following the general procedure of *Exper. 4.1*, from **8a** (30 mg, 0.17 mmol) and CH_3SO_3H (0.25 g, 2.6 mmol) was recovered, after 25 min, workup, and distillation at 50–55°/0.04 Torr of the crude product, **8a** (20 mg, 67%; by GC-A and ^{1}H-NMR) as the only product.

7. Acid-Catalysed Reaction of 1e and 7c. – 7.1. *General Procedure.* To a soln. of **1e** or **7c** (0.23 mmol) [4] in $CDCl_3$ (0.5 ml) was added at r.t. CH_3SO_3H (22 mg, 0.23 mmol). The reaction (followed by ^{1}H-NMR (60 MHz)) was allowed to proceed for the given time and worked up as in *2.1*. The crude material was purified by LC-A (pentane/Et_2O 4:1) to yield the product.

7.2. *Reaction of* **1e**. In the soln. of **1e** (41 mg, 0.23 mmol), after 4 h, ^{1}H-NMR showed (in addition to CH_3SO_3H) only signals of **2e** (for properties, see *2.6*). After 25 h, these signals had disappeared and were replaced by those of **4e**. Isolation yielded **4e** (30 mg, 73%) as a colourless oil (by ^{1}H-NMR, see *3.5*).

7.3. *Reaction of* **7c**. In the soln. of **7c** (44 mg, 0.23 mmol, see *4.4*), after 44 h, ^{1}H-NMR showed (in addition to those of CH_3SO_3H) signals of **7c** as a 25:30:15:30 mixture (GC-A) of the *trans*-isomers **7cD** ((*l*,*l*)) and **7cC** ((*l*,*u*)) and the *cis*-isomers **7cB** ((*u*,*u*)) and **7cA** ((*u*,*l*)). The ^{1}H-NMR did not change significantly over 5 days. Isolation yielded 35 mg (80%) of a colourless oil composed of **7cD**, **7cC**, **7cB**, and **7cA** in the same ratio, identical with material previously reported [4] (by GC/IR and GC/MS). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.91 (*dd*, J = 17.5, 10.5, 0.30 H, H–C(1') of **A**); 5,73 (*dd*, J = 17.5, 10.5, 0.15 H, H–C(1') of **B**); 6.0–5.8 (*m*, 0.55 H, H–C(1') of **C** and **D**); 5.2–4.9 (*m*, 2H–C(2')); 3.4–3.1 (*m*, H–C(8)); 2.5–2.0 (*m*, H–C(1)); 2.0–1.0 (*m*, *ca.* 12 H, $(CH_2)_6$); 1.35 (*s*, 0.15 H, CH_3 of **B**); 1.23 (*s*, 0.30 H, CH_3 of **C**); 1.22 (*s*, 0.25 H, CH_3 of **D**); 1.09 (*s*, 0.30 H, CH_3 of **A**).

REFERENCES

[1] R. Huston, M. Rey, A.S. Dreiding, *Helv. Chim. Acta* **1982,** *65,* 451; R.L. Danheiser, S.K. Gee, H. Sard, *J. Am. Chem. Soc.* **1982** *104,* 7670; M. Bertrauch, G. Gil, A. Junino, R. Maurin, *J. Chem. Res. M* **1980,** 1551.

[2] J.R. Matz, T. Cohen, *Tetrahedron Lett.* **1981,** 2459.

[3] R. Huston, M. Rey, A.S. Dreiding, *Helv. Chim. Acta* **1982,** *65,* 1563; unpublished results from this laboratory.

[4] D.A. Jackson, M. Rey, A.S. Dreiding, *Helv. Chim. Acta* **1983,** *66,* 2330.

[5] A. Löffler, R.J. Pratt, H.P. Rüesch, A.S. Dreiding, *Helv. Chim. Acta* **1970,** *53,* 383.

[6] H.N.A. Al-Jallo, E.S. Waight, *J. Chem. Soc. B* **1966,** *73,* 75.

[7] Y. Hayakawa, K. Yokoyama, R. Noyori, *J. Am. Chem. Soc.* **1978,** *100,* 1799.

[8] M. Karpf, J. Huguet, A.S. Dreiding, *Helv. Chim. Acta* **1982,** *65,* 13.

[9] D.I. Schuster, J.M. Rao, *J. Org. Chem.* **1981,** *46,* 1515.

[10] H. Kalinowski, S. Berger, S. Braun, ^{13}C-NMR-Spektroskopie, G. Thieme Verlag, Stuttgart, 1984.

[11] J.K. Groves, *J. Chem. Soc., Chem. Rev.* **1972,** *1,* 73; B.B. Snider, A.C. Jackson, *J. Org. Chem.* **1982,** *47,* 5393.

[12] C. Santelli-Rouvier, M. Santelli, *Synthesis* **1983,** 429.

[13] T.J. Katz, R. Dessau, *J. Am. Chem. Soc.* **1963,** *85,* 2172; W.F. Erman, R.S. Treptow, P. Bakuzis, E. Wenkert, *ibid.* **1971,** *93,* 657; Y. Tsuda, T. Tanno, A. Ukai, K. Isobe, *Tetrahedron Lett.* **1971,** 2009; F. Bourelle-Wargnier, *ibid.* **1974,** 1589; F. Bourelle-Wargnier, R. Jeanne-Carlier, *Tetrahedron* **1976,** *32,* 2725; K.E. Hine, R.F. Childs, *Can. J. Chem.* **1976,** *54,* 12.

[14] D. Seebach, V. Prelog, *Angew. Chem.* **1982,** *94,* 696; *ibid. Int. Ed.* **1982,** *21,* 654.