154. Acid-Catalyzed Rearrangements of Vinylketene/Cyclopentadiene Adducts

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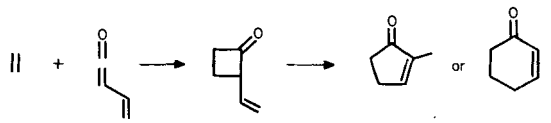
Säurekatalysierte Umlagerungen von Vinylketen/Cyclopentadien-Addukten

Zusammenfassung

Vier Alkyl-vinylketene (**7b–e**), *in situ* durch 1,4-Eliminierung von HCl aus den entsprechenden α,β-ungesättigten Acylchloriden hergestellt, wurden mit Cyclopentadien umgesetzt. Durch [2+2]-Cycloaddition entstanden 7-alkyl-7-vinylsubstituierte Bicyclo[3.2.0]hept-2-en-6-one **8/9**. Das Stereoisomerenverhältnis **8**:**9** hängt von der relativen Grösse der Ketensubstituenten ab. Die Vinylketen/Cyclopentadien-Addukte **8/9** enthalten ein α-Vinylcyclobutanon-, ein *Cope*- und (bei **8f**) ein Allylchlorid-System. Unter dem Einfluss von Säuren (meistens BF_3-Ätherat) wurden bei **8/9** vier verschiedene Typen von Umlagerungsreaktionen beobachtet, nämlich, je nach dem Substitutionsmuster: [1,3]-Alkyl-Wanderung zu Bicyclo[4.3.0]-nonadienonen **12**, [1,2]-Acyl-Wanderung zu Bicyclo[3.3.0]octenonen **13**, [3,3]-*Cope*-Umlagerung zu Bicyclo[4.2.1]nonadienonen **14** oder [1,3]-Halogen-Wanderung zu 7-Alkylidenbicyclo[3.2.0]heptenonen **15**. Die [1,3]-Alkyl- und [1,2]-Acyl-Wanderungen konkurrieren mit der *Cope*-Umlagerung, wobei auch die Konfiguration an C(7) der Vinylketen/Cyclopentadien-Addukte (**8** bzw. **9**) und das Lösungsmittel eine Rolle spielen können.

1. Introduction. – Vinylcyclobutanones **C**, readily available from the [2+2]-cycloaddition of vinylketenes **B** and certain olefines **A**, are strained intermediates, prone to further reactions by thermal [1] and catalyzed rearrangements [2] [3]. Under acid catalysis they have been found [2] to lead to cyclopentenones **D** or to cyclohexenones **E**.



A **B** **C** **D** **E**

[1]) Part of the planned dissertation of *R. H.*

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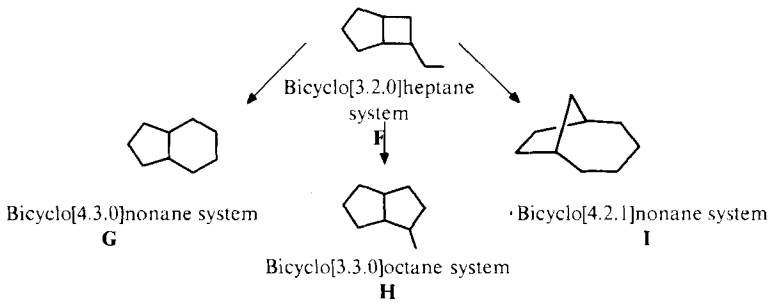
To further investigate the synthetic potential of vinylketene-cycloadducts **C** (*cf.* [4] [5]), we subjected some of them to acid catalysis. In this paper we report our experience with six vinylketene/cyclopentadiene adducts (= 7-vinylbicyclo-[3.2.0]hept-2-en-6-ones), which shows that their bicyclo[3.2.0]heptane skeleton **F** can be converted to at least three other bicyclic systems, namely **G**, **H** and **I**.



2. Cycloadditions. – Two of the 7-vinylbicyclo[3.2.0]hept-2-en-6-ones **8/9** used in the present study were available from previous work (**8a/9a** and **8f**) [4][6], while the other four (**8b/9b**, **8c**, **8d/9d** and **8e**) were prepared here by the addition of the vinylketenes **7b–e** to cyclopentadiene (see *Scheme 1*).

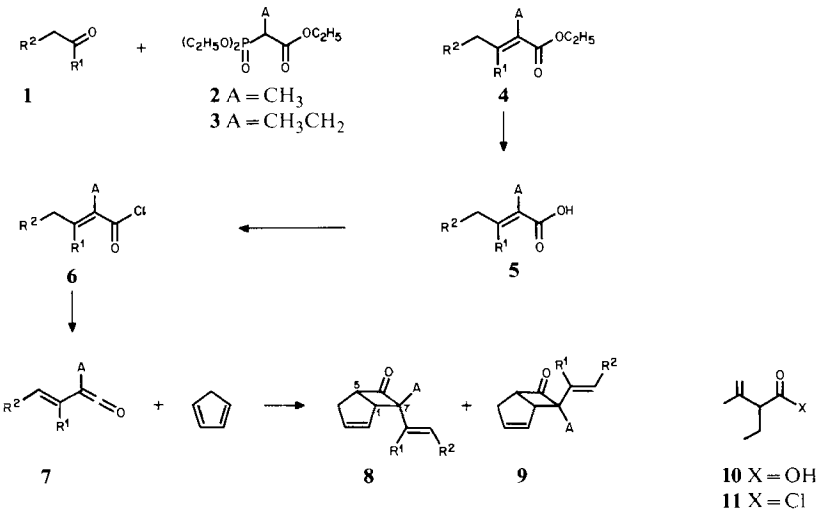
The vinylketenes were generated *in situ* from the α,β-unsaturated acyl chlorides **6b–e**, which were available from the *Wittig-Horner* condensation of the appropriate carbonyl compounds **1** with alkyl-phosphonates **2** or **3** [7], followed by saponification of the resulting esters **4b–e** to the corresponding α-alkyl-α,β-unsaturated acids **5b–e** and treatment of the latter with thionyl chloride (see *Scheme 1*). The acid **5b** and its chloride **6b** were obtained as the pure *(E)*-isomer (H–C(3) at 6.93 and 7.19 ppm, respectively, *cf.* [8]), and the acid **5d** and its chloride **6d** were accompanied by an about equal amount of their β,γ-double bond isomers **10** and **11**, respectively.

In all cycloadditions of **7** to cyclopentadiene, the [2 + 2]-cycloadduct **8/9** was the only one formed, except in the case of **7c** where the [2 + 2]-cycloadduct **8c** (only one stereoisomer) was accompanied by about ⅓ *(cf. Scheme 1)* of the total amount of 3,4-dimethylbicyclo[4.2.1]nona-3,7-dien-2-one (**14c**), probably due to a secondary rearrangement (*cf.* chapt. 3). As expected, the [2 + 2]-cycloaddition of alkylvinylketenes **7** (A = alkyl) to cyclopentadiene sometimes gave mixtures of the two C(7)-stereoisomers **8** and **9** of the 7-alkyl-7-vinylbicyclo[3.2.0]hept-2-en-6-ones. In accordance with the well documented effect in ketene cycloadditions to cyclopentadiene [4] [9] [10], the stereoisomer with the larger substituent in the *endo*-position (here **9b**, **8c**, **8d** and **8e**) was formed in preference. *Scheme 1* shows the isomer ratio **8/9** and the yields of the cycloadducts **8 + 9**. The ratios **8/9** were determined by GC. and verified, in the case of **8b/9b**, by the intensity ratio of the ^{1}H-NMR. signals for the H_3C–C(7) group (1.41 and 1.06 ppm signal in the ratio 2:3). Attempts to improve the yields of **8c** and **8d/9d** by varying the conditions of the cycloaddition (see *Exper. Part*) were without avail, for a reason not immediately evident.

The configuration at C(7) of the cycloadducts **8** and **9** was assigned on the basis of the $\Delta\delta(CDCl_3, C_6D_6)$-value of the ^{1}H-NMR. signals due to H_3C–C(7) in the me-

thyl-*exo*-isomers **8a–8c** and **8e** (0.22–0.25 ppm) as compared to that of the methyl-*endo*-isomers **9a** and **9b** (0.01–0.07 ppm), as it had been done previously [4] [9] for similar compounds. In the case of **8d/9d**, which carry an ethyl instead of a methyl group at C(7), the $\Delta\delta(CDCl_3, C_6D_6)$-values for the (diastereotopic) H_2C–C(7) protons exhibited a similar difference: 0.42 and 0.31 ppm in **8d** and 0 and 0.1 ppm for **9d**. Furthermore, the ^{1}H-NMR. signals (in $CDCl_3$) due to H_3C–C(7) or H_2C–C(7) occurred at lower field by more than 0.3 ppm in **8a–8d** than in **9a–9d**. After separating **8b** and **9b**, both stereoisomers could be shown to contain *(E)*-configurated propenyl side chains by the *trans* coupling constant (15.5 Hz) between H–C(1′) and H–C(2′) in the ^{1}H-NMR. spectrum.

Scheme 1



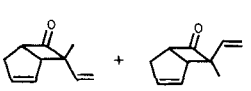
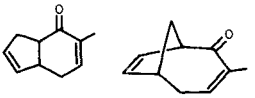
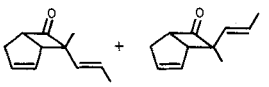
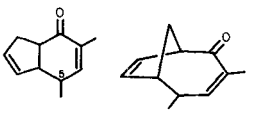
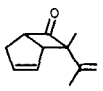
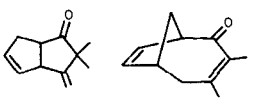
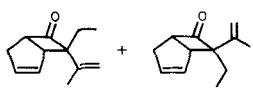
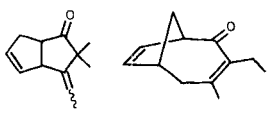
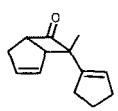
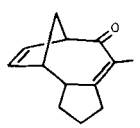
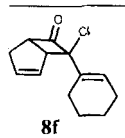
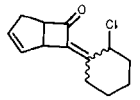
1 + **2** A = CH_3, **3** A = CH_3CH_2 → **4** → **5** → **6** → **7** + → **8** + **9**; **10** X = OH, **11** X = Cl

	A	R^1	R^2		Yield **8+9**	Ratio **8/9**
a	CH_3	H	H	**a**	77% [6]	3:7
b	CH_3	H	CH_3	**b**	33%	2:3
c	CH_3	CH_3	H	**c**	28%[a])	10:0
d	CH_3CH_2	CH_3	H	**d**	10%	10:1
e	CH_3	$(CH_2)_3$		**e**	74%	10:0
f	Cl	$(CH_2)_4$		**f**	76% [4]	10:0

[a]) In addition, 12% of **14c** was isolated.

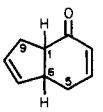
3. Acid-catalyzed rearrangements of the vinylketene/cyclopentadiene adducts. – The vinylketene/cyclopentadiene adducts **8a/9a**, **8b/9b**, **8c**, **8d/9d**, **8e** and **8f** were subjected to reaction under acid catalysis. For **8a/9a** and **8b/9b**, neat BF_3-etherate was chosen because the reaction was too slow in diluted solutions; with CF_3COOH, complex mixtures resulted. For the rearrangements of **8c** and **8d/9d**, BF_3-etherate diluted with dimethoxyethane (DME) sufficed; in other solvents more by-products were formed . The cycloadducts **8e** and **8f** were rearranged under the influence of both BF_3-etherate and CF_3COOH, yielding in each case the same product. Starting materials, conditions and results of these reactions are shown in *Table 1*.

Table 1. *Summary of results on the acid-catalyzed rearrangement of vinylketene/cyclopentadiene adducts* **8/9**

Cycloadducts ratio	Conditions	Observed products ratio(s)[a]	Isolated product(s) yield(s)
			
8a **9a**		**12a** **14a**	**12a**
30:70	BF_3-etherate	80:20	51%
			
8b **9b**		**12b1 + 12b2** **14b**	**12b**
40:60	BF_3-etherate	(28 + 49):23	54%
98:2	BF_3-etherate	(21 + 37):42	
2:98	BF_3-etherate	(30 + 60):10	
			
8c		**13c** **14c**	**13c** **14c**
	BF_3-etherate in DME	80:20	36% 10%
			
8d **9d**		**13d** **14d**	**13d** **14d**
90:10	BF_3-etherate in DME	80:20	35% 7%
			
8e		**14e**	**14e**
	a) BF_3-etherate		45%
	b) CF_3COOH		62%
	c) thermolysis		90%
			
8f		**15f**	**15f**
	a) BF_3-etherate		50%
	b) CF_3COOH		90%

[a] Observed in the crude rearrangement product by GC.

From the treatment of the cycloadducts **8a/9a** and **8b/9b** with BF_3-etherate the bicyclo[4.3.0]nonadienones **12a** and **12b** were isolated in moderate yields. Gas chromatographic examination of the crude product mixture showed that in both cases some of the bicyclo[4.2.1]nonadienones **14a** and **14b** (which had been prepared previously [4] [11]) were also formed. The spectra of **12a** and of **12b** showed these products to contain a conjugated α-methyl-enone system (UV.: 236 nm (ε = 6500–8000); IR. 1668–1670 cm^{-1}; ^{1}H-NMR.: 1.75–1.78 ppm), which could either correspond to a bicyclo[4.3.0]- (**16**) or a bicyclo[4.2.1]nonadienone (**17**) skeleton. The latter was excluded by three ^{1}H-NMR.-signals in both **12a** and **12b**, namely one for a methylene-group (2.55–2.7 ppm) which does not correspond to a non-allylic position ($H_2C(9)$ in **17**) and two for methine-protons (2.87–2.94 and 2.86–3.28 ppm) with a mutual coupling of 7.6–8 Hz, which excludes their non-vicinal position (H–C(1) and H–C(6) in **17**) (*cf.* [4]). The latter coupling establishes the (expected) *cis*-ring fusion in **12a** and **12b**. The product **12b** consisted of a (4:7)-mixture of two diastereoisomers **12b1** and **12b2**; although they were separated from each other, it has so far not been possible to determine their configuration at C(5).



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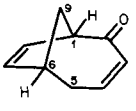

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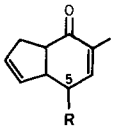
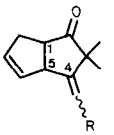
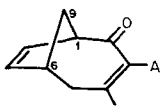


12a R = H
12b R = CH_3

From the treatment of the cycloadducts **8c** and **8d/9d** with BF_3-etherate in dimethoxyethane the 4-alkylidenebicyclo[3.3.0]octenones **13c** and **13d** were isolated in moderate yields, accompanied in both cases by lesser amounts of the bicyclo[4.2.1]nonadienones **14c** and **14d**. The properties of **14c** and **14d** clearly showed them to possess the skeleton **17** (see *Exper. Part*), the characteristics of which have been discussed elsewhere [4]. With respect to **13c** and **13d**, their UV. (no maxima in the range of 220–240 nm) and IR. (1743 cm^{-1}) spectra characterize them as five-membered ring ketones without conjugation. Their ^{1}H-NMR. signals for two vinyl H (in **13c**) or for one vinyl H (in **13d**) point to an exocyclic double bond and the signals for a doubly allylic proton (at 4.00 and 4.14 ppm) and for two diastereotopic geminal methyl groups confirm structure **13**. The coupling constant of 8 Hz between H–C(1) and H–C(5) corresponds to a *cis*-ring fusion between the two five-membered rings. In the case of **8c**, the ratio **13/14** was found to be solvent dependent; using eight solvents (see *Exper. Part*), the two extremes were 0:100 in acetonitrile and 80:20 in dimethoxyethane or diglyme. This solvent effect does not appear to correlate either with the polarity or the dielectric constant of the solvent. The ratio **13c/14c** was 90:10 and 7:93 when $TiCl_4$ was used as catalyst in dimethoxyethane and in $CHCl_3$, respectively.

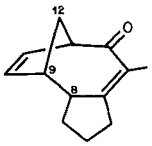


13c R = H
13d R = CH_3

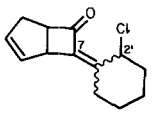


14c A = CH_3
14d A = CH_2CH_3

When the cycloadduct **8e** was exposed either to BF_3-etherate or to CF_3COOH and when it was heated in refluxing xylene, only the bicyclo[4.2.1]nonadienone **14e** was observed, and this as a single diastereoisomer. That the product **14e** belongs to the structure type **17** is evident from the similarity of its spectral features to those of **14c** and **14d** (see also [4]). The configuration at C(8) could not be established so far.



14e



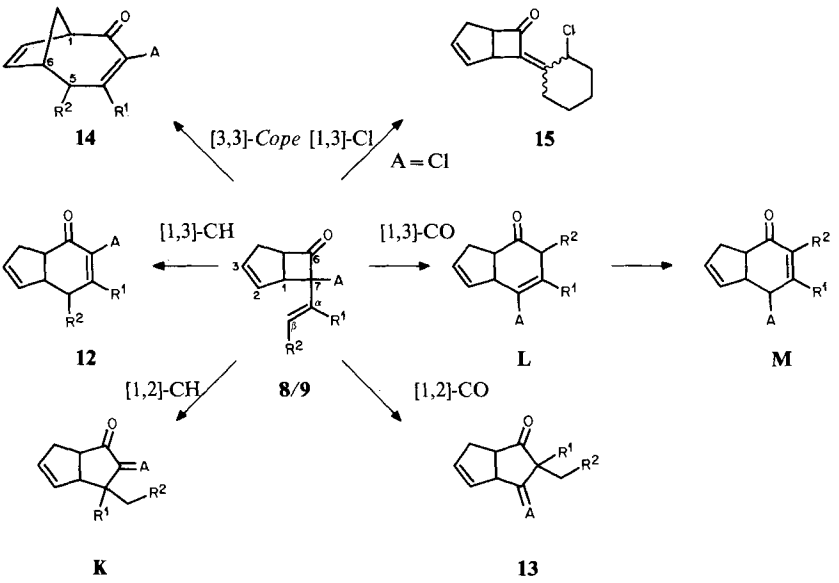
15f

The rearrangement of **8f** in presence of both BF_3-etherate and CF_3COOH proceeded without rearrangement of the C-skeleton to yield the 7-alkylidenebicyclo[3.2.0]heptenone **15f**. The product was only one of the four possible diastereoisomers. The spectral features of known [6] [12] 7-alkylidenebicyclo[3.2.0]heptenones without a Cl-atom are similar to those of **15f** [UV.: 249 nm ($\varepsilon = 10600$); IR.: 1750 and 1670 cm^{-1}; ^{1}H-NMR.: signals for H–C(1) and H–C(5) near 4.2–3.4 ppm]. The configuration of **15f** at the double bond and at C(Cl) could not be determined.

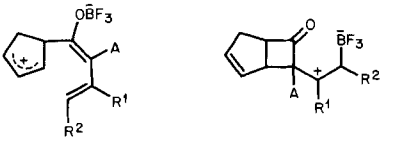
4. Reaction paths of the acid-catalyzed rearrangements. – The vinylketene/cyclopentadiene adducts **8/9** contain the following functional structures potentially sensitive to acid catalysis: an α-vinylcyclobutanone, two allylic, one *Cope* and (in the case of **8f**) an allyl chloride system. The isolated products show that, of the numerous rearrangements conceivable for **8/9** under these circumstances, the following four actually occurred (in parenthesis the transformation of bonds, i, j → k, l): [3,3]-*Cope* (1,7 → 3,β), [1,3]-CH (1,7 → 1,β), [1,2]-CO (6,7 → 6,α), and [1,3]-Cl rearangement (7,A → β,A). *Scheme 2* shows the observed rearrangements (four) together with (two) others conceivable as the most reasonable alternatives (the products which were not observed are designated with letters). The following arguments show that **K**, **L** (and **M**) are not among the isolated products: None of the products contained a conjugated exocyclic enone, which would have been expected for the bicyclo[3.3.0]octane system **K**, and none of them a non-conjugated cyclohexenone, as expected for **L**; moreover, **L** would most likely be converted to **M** under the conditions of isolation. While **M** is not distinguishable from product **12** for our example **8/9** with $A = R^2 = CH_3$ and $R^1 = H$ (→ **12b**), our other example with $A = CH_3$ and $R^2 = R^1 = H$ (→ **12a**), however, excludes **M** by the absence in **12a** of ^{1}H-NMR. signals for two vicinal enone protons and for a methyl group attached to a CH.

The [1,3]-Cl rearrangement **8f** → **15f** (allylic rearrangement) appears to be strongly preferred over other reactions when A = Cl; the driving force being the migration of the double bond into conjugation. The functionalities in, and the ready availability of **15** may confer some synthetic interest to compounds of this type.

Scheme 2



The driving force for the three C-skeleton rearrangements is probably the strain relief due to the expansion of the cyclobutanone ring. The difference in activation energy between the [1,3]-CH, the [1,2]-CO and the [3,3]-*Cope* rearrangement under acid catalysis in this system must be small, since relatively minor variations of R^1 and R^2 already cause a change of reaction preference. For this reason we cannot, at present, propose a working hypothesis for further experiments. It appears likely that a species with the B-atom complexed on the O-atom (such as **18**) is involved in the [1,3]-CH rearrangement, whereas a species with the B-atom complexed at C(β) (such as **19**) may be passed through in the [1,2]-CO rearrangement. The [3,3]-*Cope* rearrangement which is known [4] to occur thermally, is evidently also catalyzed by acids (BF_3, $TiCl_4$ and CF_3COOH).



A difference in the behavior of the two stereoisomers, the vinyl-*endo* (**8**) and the vinyl-*exo* (**9**) isomers, was observed in the case of **8b**/**9b** when the product distribution was monitored by GC. Thus the ratio **12b**/**14b** was 60:40 from pure **8b** but 90:10 from pure **9b**. No information is available on the nature of the transition states of the various rearrangements; two diastereomeric ones are available, one with the C(α),C(β)-double bond pointing over and the other away from the four-membered

ring. While the configuration of the side chain double bond of **8b**, **9b** und **8e** is known, it was not possible to establish the configuration of the rearrangement products **12b** at C(5) and **14e** at C(8). The result of the [1,3]-CH rearrangement is retention of configuration at C(1).

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Experimental Part

1. General. – The chromatographic methods have been described in [4] whith the exception of semi-preparative gas chromatography (GC.-B): packed glass columns, 1–4 m × 4 mm iD, 5–10% stationary phase on *Chromosorb W/AW-DMCS*, 80/100 mesh, carrier gas He, TC-detector. For ^{1}H-NMR. decoupling experiments, the chemical shift of the irradiated signal is given in square brackets [δ], followed by the multiplicity of the ensuing signal.

2. Preparation of α,β-unsaturated α-alkylcarboxylic acids *5*. – 2.1. *General procedure.* To a stirred suspension of 110–120 mmol of NaH (55–60% dispersion in mineral oil) in 150 ml of dry dimethoxyethane was added 105 mmol of ethyl 2-(diethoxyphosphoryl)propionate (**2**) or ethyl 2-(diethoxyphosphoryl)butyrate (**3**) [7] during 20 min at 0°. The mixture was stirred at r.t. for 30 min, treated with the carbonyl compound **1** at once, refluxed for 4 to 8 h, cooled, diluted with water and extracted with ether. The combined ethereal extracts were dried over Na_2SO_4 and evaporated. The residual ester **4** was saponified by heating it for 15 h in a refluxing mixture of 200 mmol of NaOH, 40 ml of water and 30 ml of ethanol. After cooling and removing the ethanol, the mixture was washed twice with ether, acidified with 10% HCl-solution and extracted 3 times with ether. The combined ethereal extracts were dried (Na_2SO_4), concentrated and the residual unsaturated acid (**5**, in case **d** mixed with **10**) was either bulb-to-bulb distilled at reduced pressure or recrystallized.

2.2. (E)-*2-Methyl-2-pentenoic acid* (**5b**). From 7.8 ml (105 mmol) of propionaldehyde and 25 g (105 mmol) of **2**, after recrystallization from hexane at 0°, was obtained 8.0 g (67%) of **5b**, m.p. 15–20° ([13]: b.p. 123–125°/30 Torr). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 11.76 (*s*, 1 H, HO); 6.93 (br. *t*, *J* = 7, 1 H, H–C(3)); 2.23 (*qi*, *J* = 7, 2 H, 2 H–C(4)); 1.83 (*s*, 3 H, H_3C–C(2)); 1.07 (*t*, *J* = 7, 3 H, H_3C–C(4)).

2.3. *2,3-Dimethyl-2-butenoic acid* (**5c**). From 7 ml (95 mmol) of acetone and 24 g (101 mmol) of **2**, after recrystallization from pentane, was obtained 9.5 g (88%) of **5c** as colorless needles, m.p. 69–70° ([14]: m.p. 68–68.5°). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 11.64 (*s*, 1 H, HO); 2.10 and 1.86 (2 *s*, 3 and 6 H, resp., H_3C–C(2) and 2 H_3C–C(3)).

2.4. *2-Ethyl-3-methyl-2-* (**5d**) *and 2-ethyl-3-methyl-3-butenoic acid* (**10**). From 9.1 ml (124 mmol) of acetone and 33 g (131 mmol) of **3**, after distillation at 140–150°/12 Torr, was obtained 11.0 g (70%) of a yellow oil consisting of a 55:45 mixture of **5d** ([15]: m.p. 47–48°) and **10**. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 10.80 (*s*, 2 H, HO of **5d** and HO of **10**); 5.00 (split *s*, 2 H, 2 H–C(4) of **10**); 3.00 (*t*, *J* = 7, 1 H, H–C(2) of **10**); 2.20 (*qa*, *J* = 7, 2 H, 2 H–C(1′) of **5d**); 2.12 and 1.92 (2 *s*, 6 H, 2 H_3C–C(3) of **5d**); 2.0–1.57 (*m*, 2 H, 2 H–C(1′) of **10**); 1.82 (split *s*, 3 H, H_3C–C(3) of **10**); 0.91 and 1.02 (2 *t*, both *J* = 7, 6 H, H_3C–C(1′) of **5d** and H_3C–C(1′) of **10**).

2.5. *2-Cyclopentylidenepropionic acid* (**5e**). From 8.9 ml (100 mmol) of cyclopentanone and 24.6 g (103 mmol) of **2**, after crystallization from pentane, was obtained 6.9 g (49%) of **5e** as colorless needles, m.p. 106–108°. – IR. ($CHCl_3$): 1670*s* (C=O), 1620*m* (C=C). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 11.0 (*s*, 1 H, HO); 2.93–2.63 and 2.46–2.23 (2 *m*, each 2 H, 2 H–C(2′) and 2 H–C(5′)); 1.86 (split *s*, 3 H, H_3C–C(2)); 1.8–1.56 (*m*, 4 H, 2 H–C(3′) and 2 H–C(4′)).

$C_8H_{12}O_2$ (140.18) Calc. C 68.54 H 8.63% Found C 68.40 H 8.54%

3. Preparation of α,β-unsaturated α-alkyl acyl chloride *6*. – 3.1. *General procedure.* A mixture of 1 mol-equiv. of acid **5** (in case **d** mixed with **10**) and 2 mol-equiv. of $SOCl_2$ was heated at reflux for 4 h, cooled, the excess $SOCl_2$ removed and the residue bulb-to-bulb distilled at reduced pressure to yield **6** (in case **d** mixed with **11**). Due to instability, the acyl chlorides were not subjected to elemental analysis.

3.2. (E)-*2-Methyl-2-pentenoyl chloride* (**6b**). From 8.0 g (70 mmol) of **5b** and 16.7 g (140 mmol) of $SOCl_2$ was obtained 8.1 g (87%) of **6b** as a colorless liquid, b.p. 90–100°/12 Torr. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 7.19 (split *t*, *J*=7, 1 H, H–C(3)); 2.32 (split *qi*, *J*=7, 2 H, 2 H–C(4)); 1.92 (split *s*, 3 H, H_3C–C(2)); 1.12 (*t*, *J*=7, 3 H, H_3C–C(3)).

3.3. *2,3-Dimethyl-2-butenoyl chloride* (**6c**). From 9.5 g (83 mmol) of **5c** and 19.5 g (164 mmol) of $SOCl_2$ was obtained 7.3 g (66%) of **6c** as a colorless liquid, b.p. 80–100°/12 Torr. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 2.06 and 1.92 (2 *s*, 6 and 3 H, resp. 2 H_3C–C(3) and H_3C–C(2)).

3.4. *2-Ethyl-3-methyl-2-* (**6d**) *and 2-ethyl-3-methyl-3-butenoyl chloride* (**11**). From 11.0 g (86 mmol) of the (55:45)-mixture **5d**/**10** and 20.5 g (172 mmol) of $SOCl_2$ was obtained 10.4 g (83%) of a (1:1)-mixture (^{1}H-NMR.) **6d**/**11** as a colorless liquid, b.p. 90–100°/12 Torr. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 5.08 (*t*, *J*=2, 1 H, H–C(4) of **11**); 5.00 (br. *s*, 1 H, H–C(4) of **11**); 3.30 (*t*, *J*=7, 1 H, H–C(2) of **11**); 2.50 (*qa*, *J*=7, 2 H, 2 H–C(1′) of **6d**); 1.96 and 1.90 (2 *s*, 6 H, H_3C–C(3) of **6d**); 1.76 (split *s*, 3 H, H_3C–C(3) of **11**); 2.1–1.6 (*m*, 2 H, 2 H–C(1′) of **11**); 1.10 and 0.93 (2 *t*, both *J*=7, each 3 H, H_3C–C(1′) of **6d** and H_3C–C(1′) of **11**).

3.5. *2-Cyclopentylidenepropionyl chloride* (**6e**). From 5.8 g (41 mmol) of **5e** and 9.8 g (82 mmol) of $SOCl_2$ was obtained 5.5 g (84%) of **6e** as a pale-yellow oil, b.p. 70–80°/0.01 Torr. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 2.83–2.30 (*m*, 4 H, 2 H–C(2′) and 2 H–C(5′)); 2.03 (split *s*, 3 H, H_3C–C(2)); 1.96–1.60 (*m*, 4 H, 2 H–C(3′) and 2 H–C(4′)).

4. Preparation of the vinylketene/cyclopentadiene adducts *8/9*. – 4.1. *General procedure.* To a stirred solution of 1 mol-equiv. of chloride **6** (in case **d** mixed with **11**) and 3–6 mol-equiv. of cyclopentadiene in dry CH_2Cl_2 or $CHCl_3$ was added slowly a solution of 1.05 mol.-equiv. of NEt_3 in the same solvent. After stirring for 15–48 h at r.t. the mixture was washed 3 times with water, dried (Na_2SO_4) and concentrated. The residual vinylketene/cyclopentadiene adduct **8/9** was bulb-to-bulb distilled at reduced pressure and/or purified by chromatography.

4.2. 7endo-*Methyl-7*exo-((E)-*1-propenyl)-* (**9b**) *and* 7exo-*methyl-7*endo-((E)-*1-propenyl)bicyclo[3.2.0]-hept-2-en-6-one* (**8b**). From 4.0 g (30 mmol) of **6b**, 12 ml (146 mmol) of cyclopentadiene and 3.18 g (31.5 mmol) of NEt_3 in 30 ml of CH_2Cl_2, after stirring the mixture for 16 h at r.t. was obtained 3.1 g of a crude oil, 1.0 g of which was chromatographed (LC.-A, hexane/ethyl acetate 97:3) to give 0.52 g (33%) of a (6:4)-mixture **9b**/**8b**. The two stereoisomers **9b** and **8b** were separated in this order by chromatography (LC.-A, hexane/ethyl acetate 95:5). Data of **9b** (98% pure, GC.-A, *SE 52*, 88°). – IR. (CCl_4): 1788*s* (C=O). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 5.94–5.84 and 5.82–5.72 (2 *m*, each 1 H, H–C(2) and H–C(3)); 5.65–5.45 (*m*, 2 H, H–C(1′) and H–C(2′)); 3.96 (*d*×*d*×*d*, *J*=9, 7.5 and 2, 1 H, H–C(5)); 3.48–3.36 (*m*, 1 H, H–C(1)); 2.66 (*d*×*qi*, *J*=17 and 2, 1 H, H_{endo}–C(4)); 2.40 (*d*×*d*×*qa*, *J*=17, 9 and 2, 1 H, H_{exo}–C(4)); 1.60 (*d*×*d*, *J*=6 and 1.5, 3 H, H_3C–C(2′)); 1.06 (*s*, 3 H, H_3C–C(7)). The olefinic protons H–C(1′) and H–C(2′) were shifted by the addition of Eu(fod)$_3$ to give a splitting pattern at 6.42 (br. *d*, *J*=15.5, 1 H, H–C(1′)) and 6.60 (*d*×*qa*, *J*=15.5 and 6, 1 H, H–C(2′)). – ^{1}H-NMR. (200 MHz, C_6D_6): 5.6–5.3 (*m*, 4 H, H–C(2), H–C(3), H–C(1′) and H–C(2′)); 3.58 (*d*×*d*×*d*, *J*=9, 7.5 and 1.5, 1 H, H–C(5)); 3.10–3.00 (*m*, 1 H, H–C(1)); 2.59 (br. *d*, *J*=17, 1 H, H_{endo}–C(4)); 2.02 (*d*×*d*×*qa*, *J*=17, 9 and 2, 1 H, H_{exo}–C(4)); 1.50 (*d*, *J*=5, 3 H, H_3C–C(2′)); 1.05 (*s*, 3 H, H_3C-C(7)).

$C_{11}H_{14}O$ (162.23) Calc. C 81.44 H 8.70% Found C 81.08 H 8.98%

Data of **8b** (99% pure, GC.-A, *SE 52*, 88°). – IR. (CCl_4): 1787*s* (C=O). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 5.94–5.84 and 5.80–5.70 (2 *m*, each 1 H, H–C(2) and H–C(3)); 5.60 (*d*×*qa*, *J*=15.5 and 6, 1 H, H–C(2′)); 5.50 (*d*×*qa*, *J*=15.5 and 1.5, 1 H, H–C(1′)); 3.96 (*d*×*d*×*d*, *J*=9, 7.5 and 2, 1 H, H–C(5)); 3.36–3.22 (*m*, 1 H, H–C(1)); 2.68 (*d*×*qi*, *J*=17 and 2, 1 H, H_{endo}–C(4)); 2.45 (*d*×*d*×*qa*, *J*=17, 9 and 2, 1 H, H_{exo}–C(4)); 1.68 (*d*×*d*, *J*=6 and 1.5, 3 H, H_3C–C(2′)); 1.41 (*s*, 3 H, H_3C–C(7)). – ^{1}H-NMR. (200 MHz, C_6D_6): 5.61 (*d*×*qa*, *J*=15.5 and 6.5, 1 H, H–C(2′)); 5.58–5.47 (*m*, 2 H, H–C(2) and H–C(3)); 5.36 (*d*×*qa*, *J*=15.5 and 1.5, 1 H, H–C(1′)); 3.45 (*d*×*d*×*d*, *J*=9, 7.5 and 2, 1 H, H–C(5)); 2.87–2.76 (*m*, 1 H, H–C(1)); 2.57 (*d*×*m*, *J*=17, 1 H, H_{endo}–C(4)); 2.09 (*d*×*d*×*qa*, *J*=17, 9 and 1.5, 1 H, H_{exo}–C(4)); 1.54 (*d*×*d*, *J*=6.5 and 1.5, 3 H, H_3C–C(2′)); 1.16 (*s*, 3 H, H_3C–C(7)). – MS.: 162 (6, M^+), 134 (18), 96 (100), 91 (37), 66 (18), 41 (51).

$C_{11}H_{14}O$ (162.23) Calc. C 81.44 H 8.70% Found C 81.31 H 8.70%

4.3. 7endo-*Isopropenyl-7*exo-*methylcicyclo[3.2.0]hept-2-en-6-one* (**8c**). From 4.6 g (39 mmol) of **6c**, 20 ml (242 mmol) of cyclopentadiene and 4.1 g (41 mmol) of NEt_3 in 50 ml of $CHCl_3$, after 26 h at r.t., was obtained 4.6 g of a crude oil, which was separated into two components by chromatography (LC.-B, hexane/ether 9:1) to yield 1.8 g (28%) of **8c** and 0.8 g (12%) of *3,4-dimethylbicyclo[4.2.1]nona-3,7-dien-2-one* (**14c**), both as colorless oils.

Data of **8c**. – IR. (CCl_4): 1775*s* (C=O). – ^{1}H-NMR. (60 MHz, CCl_4): 5.9–5.5 (*m*, 2 H, H–C(2) and H–C(3)); 4.86 (br. *s*, 1 H, H–C(2′)); 4.64 (split *s*, 1 H, H–C(2′)); 3.76 (*d*×*d*×*d*, *J*=8, 8 and 2, 1 H, H–C(5)); 3.4–3.1 (*m*, 1 H, H–C(1)); 2.9–2.0 (*m*, 2 H, 2 H–C(4)); 1.67 (br. *s*, 3 H, H_3C–C(1′)); 1.40 (*s*, 3 H, H_3C–C(7)). – ^{1}H-NMR. (200 MHz, C_6D_6): 5.58–5.45 (*m*, 2 H, H–C(2) and H–C(3)); 5.26 (*qa*×*d*, *J*=1 and 1.5, 1 H, H–C(2′)); 4.76 (*qa*×*d*, *J*=1.5 and 1.5, 1 H, H–C(2′)); 3.38 (*d*×*d*×*d*, *J*=8.5, 7 and 1.5, 1 H, H–C(5)); 2.90–2.80 (*m*, 1 H, H–C(1)); 2.54 (*d*×*m*, *J*=17, 1 H, H_{endo}–C(4)); 2.08 (*d*×*d*×*qa*, *J*=17, 9 and 2, 1 H, H_{exo}–C(4)); 1.50 (*d*×*d*, *J*=1.5 and 1, 3 H, H_3C–C(1′)); 1.16 (*s*, 3 H, H_3C–C(7)). – MS.: 162 (13, M^+), 147 (10), 96 (100), 68 (46), 67 (42), 66 (9), 41 (12).

$C_{11}H_{14}O$ (162.23) Calc. C 81.44 H 8.70% Found C 80.39% H 9.00%

Data of **14c** (99% pure, GC.-A, *SE 52*, 88°). – IR. (CCl_4): 1650*s* (C=O), 1605*w* (C=C). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 6.00–5.84 (*m*, 2 H, H–C(7) and H–C(8)); 3.54 (*d*×*d*, *J*=7 and 2.5, 1 H, H–C(1)); 3.06–2.95 (*m*, 1 H, H–C(6)); 2.85 (br. *d*, *J*=20, 1 H, H–C(5)); 2.52 (br. *d*, *J*=20, 1 H, H–C(5)); 2.13 (*d*×*d*×*d*, *J*=12.7, 7.7 and 7.7, 1 H, H_{anti}–C(9)[2]); 1.96 (*d*, *J*=12.7, 1 H, H_{syn}–C(9)[2]); 1.82 and 1.80 (2 *s*, each 3 H, H_3C–C(3) and H_3C–C(4)). – MS.: 162 (14, M^+), 147 (10), 96 (100), 68 (46), 67 (38), 53 (11), 41 (14).

$C_{11}H_{14}O$ (162.23) Calc. C 81.44 H 8.70% Found C 81.24 H 8.39%

In another experiment the reaction mixture was stirred for 6 h under otherwise identical conditions to yield 20% of **8c** and 4% of **14c**. In refluxing benzene for 16 h, this reaction gave a (3:2)-mixture of **8c** and **14c**; the yield of **8c** was 10%.

4.4. *7exo-Ethyl-7endo-isopropenyl-* (**8d**) *and 7endo-ethyl-7exo-isopropenylbicyclo[3.2.0]hept-2-en-6-one* (**9d**). From 5.0 g (34 mmol) of **6d**/**11** ((6:4)-mixture), 19 ml (230 mmol) of cyclopentadiene and 3.6 g (34 mmol) of NEt_3 in 40 ml of $CHCl_3$ was obtained, after stirring for 16 h at r.t. and chromatography (LC.-A, pentane/ether 95:5), 0.63 g (10%) of a (10:1)-mixture **8d**/**9d**. – IR. (CCl_4): 1770*s* (C=O). – MS.: 176 (10, M^+), 110 (100), 82 (51), 66 (24), 41 (23).

$C_{12}H_{16}O$ (176.26) Calc. C 81.77 H 9.15% Found C 81.63 H 9.40%

The mixture **8d**/**9d** was separated by chromatography (LC.-A, hexane/ethyl acetate 95:5).

Data of **8d** (95% pure, GC.-A, *SE 52*, 90°). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 5.90–5.80 and 5.74–5.64 (2 *m*, each 1 H, H–C(2) and H–C(3)); 5.02 (split *s*, 1 H, H–C(2′)); 4.88 (split *s*, 1 H, 1 H–C(2′)); 3.83 (*d*×*d*×*d*, *J*=9, 7 and 2, 1 H, H–C(5)); 3.36–3.24 (*m*, 1 H, H–C(1)); 2.64 (*d*×*qi*, *J*=17 and 2, 1 H, H_{endo}–C(4)); 2.44 (*d*×*d*×*qa*, *J*=17, 9 and 2, 1 H, H_{exo}–C(4)); 1.95 (d×*qa*, *J*=14 and 7, 1 H, *H*–$CHCH_3$); 1.84 (*d*×*qa*, *J*=14 and 7, 1 H, H–$CHCH_3$); 1.64 (split *s*, 3 H, H_3C–C(1′)); 0,88 (*t*, *J*=7, 3 H, CH_2CH_3). – ^{1}H-NMR. (200 MHz, C_6D_6): 5.57–5.46 (*m*, 2 H, H–C(2) and H–C(3)); 5.40 (*qi*, *J*=1, 1 H, H–C(2′)); 4.91 (*qi*, *J*=1, 1 H, H–C(2′)); 3.38 (br. *d*×*d*, *J*=8 and 8, 1 H, H–C(5)); 2.88–2.78 (*m*, 1 H, H–C(1)); 2.55 (*d*×*m*, *J*=17, 1 H, H_{endo}–C(4)); 2.08 (*d*×*d*×*qa*, *J*=17, 9 and 2, 1 H, H_{exo}–C(4)); 1.53 (*qa*, *J*=7, 2 H, CH_2CH_3); 1.44 (split *s*, 3 H, H_3C–C(1′)); 0.87 (*t*, *J*=7, 3 H, CH_2CH_3). – For elemental analysis, see mixture **8d**/**9d** above.

Data of **9d** (86% pure, GC.-A, *SE 52*, 90°). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 5.98–5.85 and 5.85–5.60 (2 *m*, each 1 H, H–C(2) and H–C(3)); 5.01 (split *s*, 1 H, H–C(2′)); 4.97 (split *s*, 1 H, H–C(2′)); 3.86 (*d*×*d*×*d*, *J*=9, 8 and 2, 1 H, H–C(5)); 3.64–3.52 (m, 1 H, H–C(1)); 2.65 (*d*×*qi*, *J*=17 and 2, 1 H, H_{endo}–C(4)); 2.37 (*d*×*d*×*qa*, *J*=17, 9 and 2, 1 H, H_{exo}–C(4)); 1.76 (split *s*, 3 H, H_3C–C(1′)); 1.68 (*d*×*qa*, *J*=14 and 7, 1 H, *H*–$CHCH_3$); 1.46 (*d*×*qa*, *J*=14 and 7, 1 H, H–$CHCH_3$; 0.80 (*t*, *J*=7, 3 H, CH_2CH_3). – ^{1}H-NMR. (200 MHz, C_6D_6): 5.63–5.56 and 5.52–5.45 (2 *m*, each 1 H, H–C(2) and H–C(3)); 4.99 (br. *s*, 1 H, H–C(2′)); 4.89 (*qi*, *J*=1, 1 H, H–C(2′)); 3.53 (*d*×*d*×*d*, *J*=9, 7 and 1.5, 1 H, H–C(5)); 3.30–3.20 (*m*, 1 H, H–C(1)); 2.56 (*d*×*m*, *J*=17, 1 H, H_{endo}–C(4)); 1.98 (*d*×*d*×*qa*, *J*=17, 8 and 2, 1 H, H_{exo}–C(4)); 1.68 (*d*×*qa*, *J*=14 and 7, 1 H, $HCHCH_3$); 1.58 (split *s*, 3 H, H_3C–C(1′)); 1.36 (*d*×*qa*, *J*=14 and 7, 1 H, $HCHCH_3$); 0.79 (*t*, *J*=7, 3 H, CH_2CH_3). – For elemental analysis, see mixture **8d**/**9d** above.

The yield of this cycloaddition did not improve when $CHCl_3$ was used as solvent and when the reaction time was increased to 16 and 26 h. When benzene was used as a solvent and the reaction time prolonged to 48 h at r.t., only 5% of **8d**/**9d** was obtained.

4.5. *7endo-Cyclopent-1′-enyl-7exo-methylbicyclo[3.2.0]hept-2-en-6-one* (**8e**). From 5.5 g (35 mmol) of **6e**, 19 ml (230 mmol) of cyclopentadiene and 3.7 g (37 mmol) of NEt_3 in 30 ml of CH_2Cl_2, after stirring

[2]) The terms *syn* and *anti* refer to the relative position of the H-atoms at C(9) with respect to the C_4-branch of the main ring.

the mixture for 16 h at r.t. and bulb-to-bulb distillation at 120–130°/0.01 Torr, was obtained 4.8 g (74%) of **8e** as a colorless oil (95% pure, GC.-A, *SE 52*, 107°). – IR. (CCl_4): 1780*s* (C=O). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 5.84–5.76 and 5.65–5.57 (2 *m*, each 1 H, H–C(2) and H–C(3)); 5.53 (*qi*, *J*=2, 1 H, H–C(2′)); 3.88 (*d*×*d*×*d*, *J*=9, 7.5 and 2, 1 H, H–C(5)); 3.35–3.25 (*m*, 1 H, H–C(1)); 2.64 (*d*×*m*, *J*=17, 1 H, H_{endo}–C(4)); 2.43 (*d*×*d*×*qa*, *J*=17, 9 and 2, 1 H, H_{exo}–C(4)); 2.4–2.0 (*m*, 4 H, 2 H–C(3′) and 2 H–C(5′)); 2.0–1.7 (*m*, 2 H, 2 H–C(4′)); 1.42 (*s*, 3 H, H_3C–C(7)). – ^{1}H-NMR. (200 MHz, C_6D_6): 5.77 (*qi*, *J*=2, 1 H, H–C(2′)); 5.57–5.42 (*m*, 2 H, H–C(2) and H–C(3)); 3.44 (*d*×*d*×*d*, *J*=9, 7 and 1, 1 H, H–C(5)); 2.94–2.84 (*m*, 1 H, H–C(1)); 2.59 (*d*×*m*, *J*=17, 1 H, H_{endo}–C(4)); 2.3–1.9 (*m*, 5 H, H_{exo}–C(4), 2 H–C(3′) and 2 H–C(5′)); 1.8–1.6 (*m*, 2 H, 2 H–C(4′)); 1.20 (*s*, 3 H, H_3C–C(7)). – MS.: 188 (11, M^+), 122 (100), 94 (14), 79 (51), 66 (37).

$C_{13}H_{16}O$ (188.27) Calc. C 82.94 H 8.57% Found C 82.73 H 8.66%

5. Acid-catalyzed rearrangements of vinylketene/cyclopentadiene adducts *8/9*. – 5.1. *Rearrangement of* **9a/8a**. A solution of 0.53 g (3.6 mmol) of a (7:3)-mixture **9a/8a** [4] in 4 ml of BF_3-etherate was allowed to stand at r.t. for 10 min with occasional stirring. Sat. $NaHCO_3$-solution was added cautiously and the mixture extracted with ether; the ether extracts were dried (Na_2SO_4) and concentrated. Bulb-to-bulb distillation of the orange oily residue at 150–160°/12 Torr and chromatography (LC.-A, hexane/ether 9:1) gave 0.27 g (51%) of *3-methyl-cis-bicyclo[4.3.0]nona-3,7-dien-2-one* (**12a**), as a colorless oil (95% pure, GC.-A, *SE 52*, 86°). GC.-A (*SE 52*, 86°) of the crude rearrangement product showed that it contained, in addition to **12a**, 20% of **14a** [4]. – UV. (C_2H_5OH): 236 (6450). – IR. (CCl_4): 1668*s* (C=O). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 6.57 (*d*×*d*×*qa*, *J*=4.8, 4.3 and 2, 1 H, H–C(4)); 5.77 (*d*×*qa*, *J*=5.5 and 2.4, 1 H) and 5.64 (*d*×*qa*, *J*=5.5 and 2.2, 1 H, H–C(7) and H–C(8)); 3.23 (*d*×*d*×*d*×*t*, *J*=7.6, 7.3, 4.8 and 1.8, 1 H, H–C(6)); 2.88 (*t*×*d*, *J*=7.6 and 5.4, 1 H, H–C(1)); 2.7–2.6 (*m*, 2 H, 2 H–C(9)); 2.56 (*d*×*d*×*d*×*qa*, *J*=18.3, 7.3, 4.3 and 2, 1 H, H–C(5)); 2.30 (*d*×*t*×*qa*, *J*=18.3, 4.8 and 2, 1 H, H–C(5)); 1.78 (*qa*, *J*=2, 3 H, H_3C–C(3)). – ^{13}C-NMR. ($CDCl_3$): 201.1 (s, C=O); 142.5 (*d*, C(4)); 135.7 (*s*, C(3)); 134.8 and 130.7 (each *d*, (C(7) and C(8)); 47.7 and 42.4 (each *d*, C(1) and C(6)); 36.7 and 27.3 (each *t*, C(5) and C(9)); 16.4 (*qa*, H_3C–C(3)).

$C_{10}H_{12}O$ (148.21) Calc. C 81.04 H 8.16% Found C 80.81 H 8.21%

5.2. *Rearrangement of* **9b/8b**. A solution of 300 mg (1.9 mmol) of (3:2)-mixture **9b/8b** in 0.5 ml of BF_3-etherate was allowed to stand at r.t. for 15 min, treated with sat. $NaHCO_3$-solution and extracted with ether. The ethereal extracts, after drying (Na_2SO_4) and evaporating, yielded 189 mg of an orange oil, which was chromatographed (LC.-A, hexane/ethyl acetate 96:4) to give 162 mg (54%) of *3,5-dimethyl-cis-bicyclo[4.3.0]nona-3,7-dien-2-one* (**12b**) as a colorless oil consisting to 77% of a (4:7)-mixture (GC.-A, *SE 52*, 86°) of the two diastereomers **12b1** and **12b2** (GC. and ^{1}H-NMR.); the other 23% being **14b** [11]. – UV. (C_2H_5OH): 236 (8000). – IR. (CCl_4): 1670*s* (C=O). – MS.: 162 (3, M^+), 96 (100), 68 (29).

$C_{11}H_{14}O$ (162.23) Calc. C 81.44 H 8.70% Found C 80.44 H 8.35%

The two diastereoisomers were separated by prep. GC. (GC.-B, 115°).

The rearrangement of the pure isomers **8b** and **9b** (10 mg, 0.06 mmol of the cycloadduct and 10 drops of BF_3-etherate at r.t. for 15 min, hydrolysis with sat. $NaHCO_3$-solution and extraction with ether) gave (GC.-A, *SE 52*, 86°) **12b/14b** in a ratio of 9:1 from **9b** and 58:42 from **8b**.

Data of **12b1** (99% pure, GC.-A, *SE 52*, 90°). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 6.50–6.46 (*m*, 1 H, H–C(4); [1.77] *d*, *J*=4; [2.38] br. *s*); 5.85–5.74 (*m*, 2 H, H–C(7) and H–C(8)); 2.94 (*d*×*d*×*d*, *J*=8, 8 and 6, 1 H, H–C(1)); 2.86 (split *d*×*d*, *J*=8 and 7, 1 H, H–C(6); [2.38] br. *d*, *J*=8); 2.69 (*d*×*d*×*d*, *J*=17, 8 and 2, 1 H, H–C(9)); 2.55 (*d*×*d*×*d*, *J*=17, 6 and 2, 1 H, H–C(9)); 2.43–2.33 (*m*, 1 H, H–C(5); [1.77] *qi*×*d*, *J*=7 and 4); 1.77 (split *s*, 3 H, H_3C–C(3)); 1.18 (*d*, *J*=7, 3 H, H_3C–C(5)). – For elemental analysis see mixture **12b1/12b2** above.

Data of **12b2** (95% pure, GC.-A, *SE 52*, 90°). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 6.38 (br. *d*×*d*, *J*=3 and 1.5, 1 H, H–C(4); [1.75] *d*×*d*, *J*=3 and 1.5); 5.87–5.77 and 5.76–5.66 (2 *m*, each 1 H, H–C(7) and H–C(8)); 3.28–3.18 (*m*, 1 H, H–C(6)); 2.87 (*d*×*d*×*d*, *J*=8, 8 and 2, 1 H, H–C(1)); 2.8 (hidden, H–C(5)); 2.78 (br. *d*, *J*=16.5, 1 H, H–C(9)); 2.65–2.55 (*m*, 1 H, H–C(9); [5.87–5.66] *d*×*d*×*d*, *J*=16.5, 8 and 4); 1.75 (split *s*, 3 H, H_3C–C(3)); 1.23 (*d*, *J*=7, 3 H, H_3C–C(5)). – For elemental analysis see mixture **12b1/12b2** above.

5.3. *Rearrangement of* **8c**. A solution of 200 mg (1.23 mmol) of **8c** (purified by chromatography and not containing any **14c**) and 0.5 ml of BF_3-etherate in 5 ml of dimethoxyethane was allowed to stand for 10 days at r.t. After treatment with sat. $NaHCO_3$-solution, the mixture was extracted with ether, dried

(Na_2SO_4) and concentrated to yield 130 mg (65%) of an oil consisting of a (4:1)-mixture (GC.-A, *SE 52*, 86°) of *3,3-dimethyl-4-methylidene*-cis-*bicyclo[3.3.0]octa-6-en-2-one* (**13c**) and *3,4-dimethylbicyclo[4.2.1]nona-3,7-dien-2-one* (**14c**). Chromatography of the residue (LC.-A, hexane/ether 97:3) afforded 73 mg (36%) of **13c** and 20 mg (10%) of **14c**. The latter (99% pure, GC.-A, *SE 52*, 86°) was characterized by its ^{1}H-NMR., which was identical to the one described in exp. 4.3.

Data of **13c** (98% pure, GC.-A, *SE 52*, 86°). – IR. (CCl_4): 1745*s* (C=O). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 5.72–5.58 (*m*, 2 H, H–C(6) and H–C(7)); 5.13 and 5.00 (2 *d*, both J=2, each 1 H, H_2C=C(4)); 4.00 (*d*×*m*, J=8, 1 H, H–C(5)); 3.07 (*d*×*d*×*d*, J=8, 8 and 4, 1 H, H–C(1)); 2.8–2.6 (*m*, 2 H, 2 H–C(8)); 1.16 and 1.07 (2 *s*, each 3 H, 2 H_3C–C(3)). – MS.: 162 (29, M^+), 147 (24), 134 (67), 120 (14), 91 (100), 66 (80), 41 (54).

$C_{11}H_{14}O$ (162.23) Calc. C 81.44 H 8.70% Found 81.12 H 8.54%

The BF_3-etherate catalyzed rearrangement of **8c** was performed in 8 solvents under otherwise the same conditions. In each experiment 30 mg of **8c** was dissolved in 0.7 ml of solvent and 0.1 ml of BF_3-etherate and the mixture kept for 1–26 days at r.t. The product distribution was monitored by GC. The results are given as follows: solvent/time in days/dielectric constant in E [16] /dipole moment $\mu \times 10^{30}$ in coulombmeter/% **13c**/% **14c**; CH_3CN/3/11.48/37.5/0/100; CH_2Cl_2/1/5.70/8.9/23/69; $CHCl_3$/1/3.84/4.7/21/71; CCl_4/2/0/2.2/19/69; diethylether/8/4.34/4.2/69/31; diisopropylether/18/4.20/3.9/29/67; dimethoxyethane/10/5.70/7.20/80/15; diglyme/26/6.57/7.3/76/16.

In two other qualitative (GC.-A, *SE 52*, 86°) experiments, $TiCl_4$ was used as acid catalyst in dimethoxyethane for 20 min and in $CHCl_3$ for 80 min. The ratios of **13c**/**14c** in the product were 90:10 and 7:93, respectively.

5.4. *Rearrangement of* **8d**/**9d**. A solution of 200 mg (1.1 mmol) of a (10:1)-mixture **8d**/**9d** (purified by chromatography and not containing any **14d**) in 1 ml of BF_3-etherate and 7 ml of dimethoxyethane was allowed to stand for 17 days at r.t., cautiously treated with sat. $NaHCO_3$-solution and extracted with ether. The combined ethereal extracts were dried (Na_2SO_4) and evaporated to give 129 mg of a (4:1)-mixture of *3,3-dimethyl-4-ethylidene*-cis-*bicyclo[3.3.0]octa-6-en-2-one* (**13d**, probably only one double bond isomer) and *3-ethyl-4-methylbicyclo[4.2.1]nona-3,7-dien-2-one* (**14d**). The two products were separated by chromatography (LC.-A, pentane/ether 97:3) to give 70 mg (35%) of **13d** and 13 mg (7%) of **14d** both as colorless oils.

Data of **13d** (99% pure, GC.-A, *SE 52*, 86°). – IR. (CCl_4): 1743*s* (C=O). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 5.60 (br. *s*, 2 H, H–C(6) and H–C(7)); 5.46 (*qa*×*d*, J=7 and 2, 1 H, H–C(1')); 4.14 (*d*×*m*, J=8, 1 H, H–C(5)); 3.03 (*d*×*d*×*d*, J=8, 8 and 3, 1 H, H–C(1)); 2.84–2.56 (*m*, 2 H, 2 H–C(8)); 1.80 (*d*×*d*, J=7 and 2, 3 H, H_3C–C(1')); 1.09 and 1.01 (2 *s*, 6 H, 2 H_3C–C(3)); the signal at 5.46 shows that **13d** is probably only one isomer. – MS.: 176 (67, M^+), 161 (31), 148 (33), 106 (32), 105 (80), 91 (90), 67 (100), 66 (34).

$C_{12}H_{16}O$ (176.26) Calc. C 81.77 H 9.15% Found C 80.58 H 8.90%

Data of **14d** (94% pure, GC.-A, *SE 52*, 90°). – UV. (C_2H_5OH): 253 (5700). – IR. (CCl_4): 1650 (C=O), 1600 (C=C). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 5.98–5.84 (*m*, 2 H, H–C(7) and H–C(8)); 3.52 (*d*×*d*, J=7 and 2.5, 1 H, H–C(1)); 3.06–2.94 (*m*, 1 H, H–C(6)); 2.83 (*d*×*d*, J=19 and 5.5, 1 H, H–C(5)); 2.48 (br. *d*, J=19, 1 H, H–C(5)); 2.40–2.25 (*m*, 2 H, 2 H–C(1')); 2.12 (*d*×*d*×*d*, J=11.5, 7 and 7, 1 H, H_{anti}–C(9)^2)); 1.97 (*d*, J=11.5, 1 H, H_{syn}–C(9)^2)); 1.85 (*s*, 3 H, H_3C–C(4)); 0.90 (*t*, J=7.5, 3 H, H_3C–C(1')). – ^{13}C-NMR. ($CDCl_3$): 204.8 (*s*, C=O); 143.4, 136, 134.5 and 132.4 (C(3), C(4), C(7), C(8)); 58.7 and 46.5 C(1), C(6)); 41.8, 34.0, 24.1, 23.7 and 13.6 (C(5), C(1'), C(9), CH_3–C(4), CH_3–C(1')).

$C_{12}H_{16}O$ (176.26) Calc. C 81.77 H 9.15% Found C 81.57 H 9.40%

5.5. *Rearrangement of* **8e**. A mixture of 110 mg (0.6 mmol) of **8e** and 0.5 ml of BF_3-etherate was kept at r.t. for 1 h, treated with sat. $NaHCO_3$-solution and extracted with ether. The ethereal extracts were dried (Na_2SO_4), concentrated and the residue chromatographed (LC.-A, hexane/ethyl acetate 96:4) to yield 58 mg (52%) of *3-methyltricyclo[7.2.1.0^{4,8}]dodeca-3,10-dien-2-one* (**14e**) as a colorless oil (95% pure, GC.-A, *SE 52*, 107°). – UV. (C_2H_5OH): 260 (7500). – IR. (CCl_4): 1657*s* (C=O), 1617*m* (C=C). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 6.00 (br. *s*, 2 H, H–C(10) and H–C(11)); 3.43 (*d*×*d*, J=8 and 1.5, 1 H, H–C(1)); 3.14 (*d*×*d*×*d*, J=8, 4 and 1.5, 1 H, H–C(9)); 2.98–2.78 (*m*, 1 H, H–C(8)); 2.72–2.18 (*m*, 3 H, 2 H–C(5) and H_{anti}–C(12)^2)); 2.02 (*d*, J=12, 1 H, H_{syn}–C(12)^2)); 2.0–1.3 (*m*, 4 H, 2 H–C(6) and 2 H–C(7)); 1.71 (split *s*, 3 H, H_3C–C(3)). – MS.: 188 (12, M^+), 122 (100), 79 (41), 66 (12).

$C_{13}H_{16}O$ (188.27) Calc. C 82.54 H 8.57% Found C 82.81 H 8.50%

Treatment of **8e** with CF_3COOH for 1 h at r.t. or heating **8e** in refluxing xylene for 3 h yielded, after purification by chromatography, **14e** in 62 and 90% yield, respectively.

5.6. *Rearrangement of* **8f**. A solution of 258 mg (1.2 mmol) of **8f** [4] in 1 ml of CF_3COOH and 2 ml of $CHCl_3$ was kept for 2 h at r.t., whereupon $NaHCO_3$-solution was added, the mixture extracted with $CHCl_3$ and the organic phase dried (Na_2SO_4) and concentrated. Bulb-to-bulb distillation of the residue at 130–140°/0.01 Torr gave 234 mg (91%) of *7-(2'-chlorocyclohexylidene)bicyclo[3.2.0]hept-2-en-6-one* (**15f**) as a pale yellow oil. – UV. (C_2H_5OH): 249 (10600). – IR. (CCl_4): 1752*s* (C=O), 1672*m* (C=C). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 6.1–5.6 (*m*, 3 H, H–C(2), H–C(2') and H–C(3)); 4.2–3.4 (*m*, 2 H, H–C(1) and H–C(5)); 3.0–2.4 (*m*, 2 H, 2 H–C(4)); 2.4–1.0 (*m*, 8 H, 2 H–C(3'), 2 H–C(4'), 2 H–C(5') and 2 H–C(6')).

$C_{13}H_{15}ClO$ (222.47) Calc. C 70.11 H 6.79 Cl 15.92% Found C 71.40 H 7.27 Cl 15.40%

Treatment of **8f** with BF_3-etherate for 1 h at r.t. gave, after hydrolytic workup with sat. $NaHCO_3$-solution, **15f** in 68% yield.

REFERENCES

[1] *M. Bertrand, G. Gil & A. Junino,* Tetrahedron Lett. *1977,* 1779.

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

[3] *V. P. Abegg, A. C. Hopkinson & E. Lee-Ruff,* Can. J. Chem. *56,* 99 (1978); *Le H. Dao, A. C. Hopkinson & E. Lee-Ruff,* Tetrahedron Lett. *1978,* 1413; *E. Lee-Ruff, A. C. Hopkinson & Le H. Dao,* Can. J. Chem. *59,* 1675 (1981); *R. L. Danheiser, C. Martinez-Davila & H. Sard,* Tetrahedron *37,* 3943 (1981).

[4] *R. Huston, M. Rey & A. S. Dreiding,* Helv. Chim. Acta *65,* 451 (1982).

[5] *J. Berge, M. Rey & A. S. Dreiding,* in preparation.

[6] *M. Rey, E. Dunkelblum, R. Allain & A. S. Dreiding,* Helv. Chim. Acta *53,* 2159 (1970).

[7] *G. Gallagher & R. L. Webb,* Synthesis *1974,* 122.

[8] *U. E. Matter, C. Pascual, E. Pretsch, A. Pross & W. Simon,* Tetrahedron *25,* 691 (1969).

[9] *M. Rey, S. Roberts, A. Dieffenbacher & A. S. Dreiding,* Helv. Chim. Acta *53,* 414 (1970).

[10] *W. T. Brady & R. Roe,* J. Am. Chem. Soc. *92,* 4618 (1970); *iidem,* ibid. *93,* 1662 (1971).

[11] *R. Huston, M. Rey & A. S. Dreiding,* in preparation.

[12] *R. W. Holder, H. S. Freiman & M. F. Stefanchik,* J. Org. Chem. *41,* 3303 (1976).

[13] *J. Cason & M. J. Kahn.* J. Org. Chem. *19,* 1947 (1954).

[14] *L. B. Bos & J. F. Arens,* Recl. Trav. Chim. Pays-Bas *82,* 339 (1963); *C. R. Hauser & W. H. Puterbaugh,* J. Am. Chem. Soc. *75,* 1068 (1953).

[15] *R. C. Huston, G. L. Goerner & H. H. Gyorgy,* J. Am. Chem. Soc. *70,* 389 (1948).

[16] *C. Reichardt,* «Lösungsmittel Effekte in der organischen Chemie», Verlag Chemie, Weinheim 1973, p. 163.