44. Vinylketenes as Synthons for Bicyclo[4.2.1]nonadienones[1])

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Zusammenfassung

Sechs Vinylketene (**9a–9f**), wovon fünf Chlor-vinylketene (**9a–e**) (s. *Schema 2*), *in situ* durch 1,4-Eliminierung von HCl aus den entsprechenden α,β-ungesättigten Säurechloriden hergestellt, wurden mit Cyclopentadien (**2**) bzw. 6,6-Dimethylfulven (**3**) umgesetzt. Durch [2+2]-Cycloaddition entstanden fünf 7-vinylsubstituierte Bicyclo[3.2.0]-2-hepten-6-one (**10/11**) bzw. drei 4-Isopropylidenbicyclo[3.2.0]-2-hepten-6-one (**12/13**), wobei das Stereoisomerenverhältnis **10:11** bzw. **12:13** von der Grösse der Ketensubstituenten beeinflusst wurde. Die Vinylketen-Cycloaddukte **10/11** und **12/13** enthalten ein *Cope*-System, das entweder in einer syn- (**10** und **12**) oder in einer anti-Konfiguration (**11** und **13**) vorliegt. Beim Erwärmen auf 140–190° ergaben **10/11** bzw. **12/13** durch *Cope*-Umlagerung die entsprechend substituierten Bicyclo[4.2.1]-3,7-nonadien-2-one (**14**) bzw. 9-Isopropylidenbicyclo[4.2.1]-3,7-nonadien-2-one (**15**). Mittels der beschriebenen Reaktionen werden die Ringsysteme von **14** und **15** in einer zweistufigen Synthese leicht zugänglich.

1. Introduction. – Vinylketenes (**1**) have been generated by several reactions, for instance: *a*) by elimination of hydrogen chloride from α,β-unsaturated acid chlorides [1–7] or of nitrogen from acyl pyrazolenines [8]; *b*) by ring opening of cyclobutenones [9] [10], of bicyclo[3.1.0]hexenones [11] and their 6-aza-derivatives [12], of cyclohexadienones [13]; *c*) by other methods (*e. g.* [7] [14–16]). Vinylketene itself (**1**, R = H) and some of its substituted derivatives were observed spectroscopically [7] [13–15] and some substituted vinylketenes have even been isolated [4] [6] [14]. In most cases, the presence of the relatively unstable vinylketenes could be demonstrated by allowing them to cyclize [9–12] [15], dimerize [2] [3], react with nucleophiles [1] [8] [9] [11] or with olefins [2] [3] [5] [6] [10] and in other ways [4] [10] [15] [17]. Of interest, in connection with the present work, are the cycloadditions of vinylketenes (**1**) to cyclopentadiene (**2**) [3] [5]. We report here several new cycloadditions of vinylketenes (**1**), especially chloro-vinylketenes, to cyclopentadiene (**2**) and to 6,6-dimethylfulvene (**3**), as well as the thermal rearrangement of the cycloadducts to bicyclo[4.2.1]nonadienones.

[1]) From the planned dissertation of *R. H.* Presented by *R. H.* at the meeting of the Swiss Chemical Society in October 1979.

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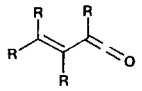

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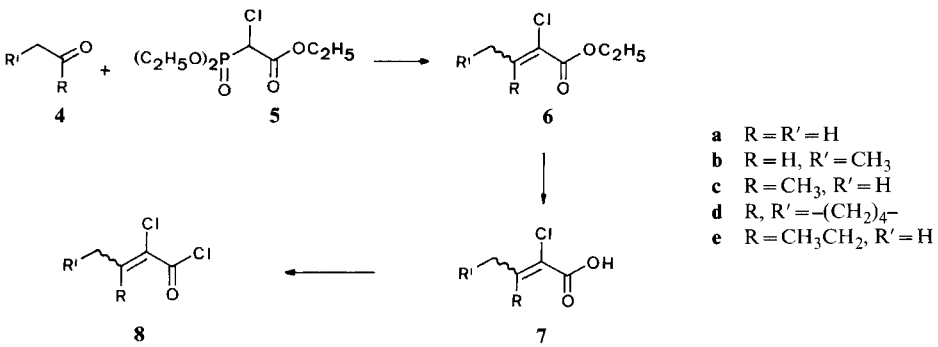
2. Preparation of 7-Vinylbicyclo[3.2.0]-2-hepten-6-ones. The α-chloro-α,β-unsaturated acid chlorides **8**, required as chloro-vinylketene precursors, were prepared as follows (see *Scheme 1*): *Wittig-Horner* condensation of the carbonyl compounds **4** with diethyl 1-chloro-1-ethoxycarbonylmethanephosphonate (**5**) [18] afforded the α-chloro-α,β-unsaturated esters **6**, which were saponified in crude form to give the α-chloro-α,β-unsaturated acids **7**, previously available [19–23] from other methods. Conversion of **7** to the corresponding α-chloro-acid chlorides **8** was accomplished with $SOCl_2$; the overall yields of **8** from **5** were 31–54%. No effort was made to control the stereospecificity of the condensations **4** + **5** → **6** since the stereogenic double bond was destined to be moved away in the formation of the chloro-vinylketenes from **8**.

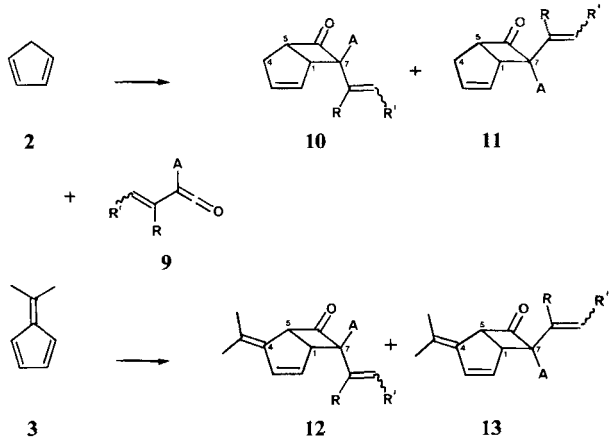
Scheme 1



The vinylketenes **9**, generated *in situ* from the α-chloro-acid chlorides **8a** to **8d** and from *(E)*-2-methyl-2-butenoyl chloride with triethylamine, were added to cyclopentadiene (**2**) to give the stereoisomeric 7-vinyl-substituted bicyclo[3.2.0]-2-hepten-6-ones **10** and **11**. In the same way, the vinylketenes **9**, generated from the α-chloro-acid chlorides **8a** and **8e** and from *(E)*-2-methyl-2-butenoyl chloride reacted with 6,6-dimethylfulvene (**3**) to give the stereoisomeric 7-vinyl-substituted 4-isopropylidenebicyclo[3.2.0]-2-hepten-6-ones **12** and **13** (see *Scheme 2*). The yields of formation of **10/11** and of **12/13** (57–84%) are presented in *Table 1*.

[2 + 2]-Cycloadditions of this kind are fully regiospecific, so that two C,C-double bonds in the products always turn out to form a *Cope*-system. However, two stereoisomers may be formed, one with the vinyl group in the *endo*- (**10** and **12**) and the other with the vinyl group in the *exo*-position (**11** and **13**) (see *Scheme 2*). The ratio of these stereoisomers (as shown in *Table 1*) depends on the relative size of the two

Scheme 2



	R	R'	A
a	H	H	Cl
b	H	CH_3	Cl
c	CH_3	H	Cl
d	$-(CH_2)_4-$		Cl
e	CH_2CH_3	H	Cl
f	H	H	CH_3

substituents on the ketene function: increasing the size difference between these two substituents leads to a greater preponderance of the cycloadduct with the larger substituent in the 7*endo*-position, an effect which has been observed [24] [25] in other ketene/cyclopentadiene cycloadditions. The two stereoisomers of the cycloadducts **10** to **13** were not separated; the vinyl-*endo*-/vinyl-*exo*- (**10/11** and **12/13**) isomer distribution was determined by gas-liquid chromatography and verified by the relative intensities of the characteristic ^{1}H-NMR. signals, as follows:

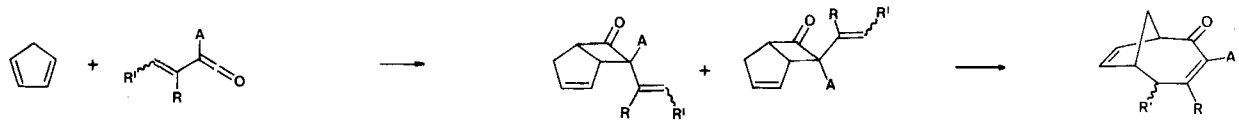
In the chloro-vinylketene/cyclopentadiene cycloadducts **10/11** (A = Cl), the configuration at C(7) was assigned on the basis of the ^{1}H-NMR. signal for H–C(5), which always occurs at lower field when the Cl-atom at C(7) is in the *exo*- (4.08–4.27 ppm) rather than in the *endo*-position (3.88–3.90 ppm) [25]. The same effect can be used with the chlorovinylketene/fulvene cycloadducts **12/13** (A = Cl), even though their H–C(5) signals occur further downfield (by about 0.5 ppm) due to the additional exocyclic double bond at C(4). In the cycloadducts **12f/13f** (A = CH_3), the configuration at C(7) was derived from the larger chemical shift difference of the *exo*-methyl group in CCl_4- and in C_6D_6-solution as compared to the *endo*-methyl group, a criterion previously employed for a series of 7,7-dialkyl substituted bicycloheptenones [24] including **10f/11f.** Thus $\Delta\delta_{CCl_4-C_6D_6}$ is 0.19 ppm for **12f** (*exo*-methyl) and 0.03 ppm for **13f** (*endo*-methyl).

A further stereogenic center is the double bond of the side chain of **10b** and **11b**. These compounds were not separated from each other and it is not possible, at present, to say whether their propenyl groups have the *(E)*- or *(Z)*-configuration or whether they are mixtures of double bond isomers.

3. Thermal rearrangement of the cycloadducts. – The cycloadducts **10** to **13** contain a *Cope*-system, the C-atoms C(3), C(2), C(1), C(7), C(α) and C(β) (see *Scheme 3*). In the vinyl-*endo*-isomers **10** and **12**, this system is fixed in a *syn*-conformation at C(1), C(7); in the vinyl-*exo*-isomers **11** and **13**, however, in an *anti*-conformation. Heating these cycloadducts **10** to **13** either in xylene (~ 140°) or neat (160° or 190°) yielded the substituted bicyclo[4.2.1]-3,7-nonadienones **14** and **15** (see *Scheme 3*) in

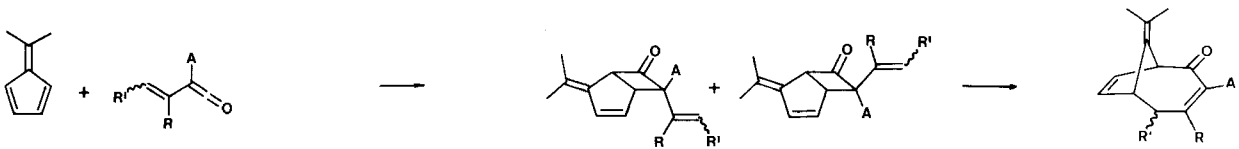
Table 1. *Summary of results on the vinylketene-cycloadditions and on the thermal rearrangements of the resulting 7-vinylbicyclo[3.2.0]-2-hepten-6-ones* **10–13** *to bicyclo[4.2.1]-3,7-nonadien-2-ones* **14** *and* **15**

Vinylketenes | Cycloadducts | Rearrangement products



2 **9** **10** (vinyl-*endo*) **11** (vinyl-*exo*) **14**

	R	R′	A	Isomer ratio **10:11**	Yield	Rearrangement conditions	Yield
a	H	H	Cl	50:50	84%	190° neat, 1 h	48%
b	H	CH_3	Cl	50:50	80%	145° xylene, 12 h	6%
c	CH_3	H	Cl	100: 0	73%	160° neat, 1 h	81%
d	$-(CH_2)_4-$		Cl	100: 0	76%	145° xylene, 4 h	70%
f	H	H	CH_3	30:70	77% [3]	160° neat, 4 h	83%

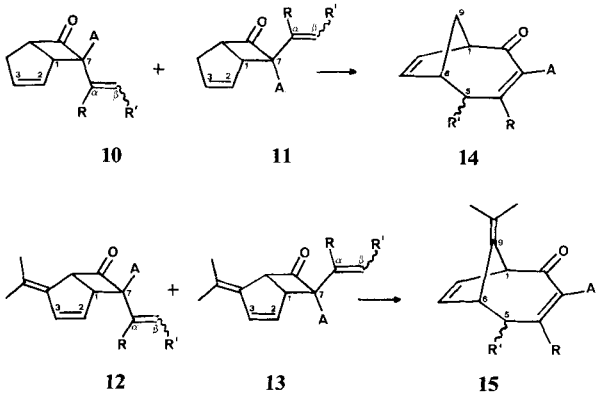


3 **9** **12** (vinyl-*endo*) **13** (vinyl-*exo*) **15**

	R	R′	A	Isomer ratio **12:13**	Yield	Rearrangement conditions	Yield
a	H	H	Cl	50:50	57%	145° xylene, 4 h	50%
e	CH_2CH_3	H	Cl	100: 0	66%	145° xylene, 1.5 h	45%
f	H	H	CH_3	30:70	69%	145° xylene, 3 h	54%

48–83% yields (excepting **14b**), as shown in *Table 1.* Their structures will be discussed in *Section 4.* The low yield of **14b** (6%) is due to the formation of by products, which will be treated in another paper [26].

Scheme 3

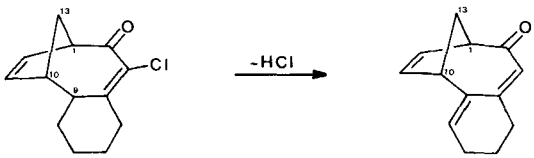


	R	R′	A
a	H	H	Cl
b	H	CH_3	Cl
c	CH_3	H	Cl
d	$-(CH_2)_4-$		Cl
e	CH_2CH_3	H	Cl
f	H	H	CH_3

A comparison of the yields of **14f** and **15f** with the stereoisomer ratios of the starting materials **10f**:**11f** and **12f**:**13f**, respectively, shows that the products of the *Cope*-rearrangement are obtained not only from the vinyl-*endo*- (**10** and **12**) but also from the vinyl-*exo*-isomers (**11** and **13**). Gas-chromatographic monitoring of the thermolysis mixture in the case of **10f**/**11f** showed that the vinyl-*endo*-isomer disappeared about three times as fast as the vinyl-*exo*-isomer.

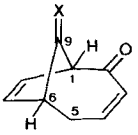
Two of the rearrangement products of this series, namely **14b** and **14d**, carry a substituent at C(5), making C(5) a stereogenic center. We note that in both of these cases only one stereoisomer was found and that at least **14d** was formed from a precursor (**10d**) with an *E*-configurated double bond (fixed by the six-membered ring) in the vinyl substituent.

The rearrangement products **14** and **15** were found to be reasonably stable with the exception of the tricyclic example **14d**, which – on standing at RT. – lost HCl to form the trienone **16**. The detailed course of the latter transformation was not examined.



4. Structure of the rearrangement products. –The following arguments support the structure of the rearrangement products **14** and **15** as shown in *Scheme 3*: from the UV.-maxima (230–265 nm) and the IR.-bands (1660–1690 cm^{-1}), both due to the

conjugated enone system, it is evident that all eight products (see *Table 1*) contain either the bicyclo[4.2.1]nonadienone (**17**) or the bicyclo[4.3.0]nonadienone skeleton (**18**), *i. e.* that they were formed by either a [3,3]- or a [1,3]-rearrangement of the cycloadducts **10–13**.



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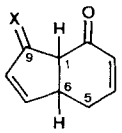

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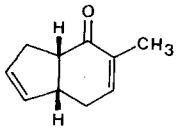

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Further evidence may be adduced first for the five rearrangement products **14**, the series without the isopropylidene group. Their ^{1}H-NMR.-spectra all contain four characteristic signals, namely two due to a CH_2-group (near 1.8–2.3 ppm) and two due to two CH-groups (near 3.5–3.7 and 3.0–3.3 ppm). These four signals are produced by 2 H–C(9), H–C(1) and H–C(6) in either **17** or **18** (X = H,H). An analysis of their coupling pattern in the 360-MHz-^{1}H-NMR.-spectrum of **14f** confirms the presence of a CH_2-bridge attached on both sides to two bridgehead CH-groups, a system present in **17** but not in **18** (X = H,H), as follows: *1)* the geminal coupling of 12–13 Hz between the two H–C(9) is in better agreement with non-allylic (as found in **17**, X = H,H) than with an allylic CH_2-group (as in **18**, X = H,H); *2)* one of the two H–C(9) shows almost equal coupling (J = 6–7.5 Hz), and the other no coupling, with two H-atoms, a feature not expected for the substructure –CH_2–CH–CH– in **18**, but in good agreement with the substructure –CH–CH_2–CH– in **17**, X = H,H; *3)* a coupling between H–C(1) and H–C(6), which would clearly be expected if these H-atoms were vicinal (*cis* or *trans*) neighbors as in **18**, is not observed. Furthermore, a compound with the skeleton of **18** (X = H,H), namely its 3-methyl-derivative **19**, was available from other work in our laboratory [26]; its 360-MHz.-^{1}H-NMR.-spectrum confirmed that the features discussed above (along with further ones) are indeed characteristic for the difference between **17** and **18** (X = H,H).

Concerning the three rearrangement products **15** with the isopropylidene group, their well-separated ^{1}H-NMR. signals for H–C(6) (4.30–3.96 ppm) and H–C(1) (3.75–3.45 ppm) exhibit only very small or no couplings. This eliminates the skeleton **18** (X = $C(CH_3)_2$) and thus establishes **17** (X = $C(CH_3)_2$) for the rearrangement products **15**.

A simple [3s,3s]-sigmatropic rearrangement cannot be postulated for all the observed thermal transformations, since a pericyclic transition state from the vinyl-*exo*-isomers (**11** and **13**) would be energetically disfavored. Of interest in this connection would be the configuration at C(5) of **14b** and **14d**: without the other diastereoisomer being available in both cases, we refrain from drawing a conclusion at present. In another paper we expect to present the work on stereochemical and mechanistic aspects of this reaction. The results of the present paper show that compounds containing the bicyclo[4.2.1]nonadienone system without or with an isopropylidene group at position 9 are readily available in a two step process from vinylketenes and cyclopentadiene or 6,6-dimethylfulvene.

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Experimental Part

1. General. – Chromatographic methods. LC.-A = Column chromatography on silicagel (40–63 μm) *"Merck LiChroprep Si 60"* at 2–6 bar pressure. – TLC.-A = Thin- (analytical) or thick- (preparative) layer chromatography on silicagel plates. GC.-A = Gas chromatography on *WCOT* columns (12–25 m × 0.2–0.3 mm) with H_2 as carrier gas. The abbreviations and notations used have been described in [27].

2. Preparation of α-chloro-α,β-unsaturated acids. – *General procedure.* To a stirred suspension of 100 mmol NaH (55–60% dispersion in mineral oil) in 150 ml dry dimethoxyethane was added 100 mmol of diethyl 1-chloro-1-ethoxycarbonylmethanephosphonate (**5**) [18] during 20 min at 0°. The mixture was stirred at RT. for 30 min, treated with 100 mmol of the carbonyl compound (**4**) at once, refluxed for 1 to 4 h, cooled, diluted with water and extracted with ether. The combined ethereal extracts were dried over Na_2SO_4 and evaporated. The residual ester (**6**) was heated for 15 h in a refluxing mixture of 60 ml 2N KOH and 20 ml dioxane. After cooling, the mixture was washed twice with ether, acidified with 5% hydrochloric acid and extracted three times with ether. The combined ethereal extracts were dried over Na_2SO_4, concentrated and the residual acid (**7**) was either distilled in a *Kugelrohr* or recrystallized.

2.1. *(Z)-2-Chloro-2-butenoic acid* (**7a**). From 2.2 ml (39 mmol) acetaldehyde, after recrystallization from hexane, 3.39 g (72%) of *(Z)*-**7a** were obtained as colorless crystals, m.p. 98.5° ([19]: 99.5°). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 9.45 (*s*, 1 H, OH); 7.31 (*qa*, J=7, 1 H, H–C(3)); 1.98 (*d*, J=7, 3 H, CH_3).

2.2. *2-Chloro-2-pentenoic acid* (**7b**). From 4.3 ml (59 mmol) propionaldehyde, after distillation at 120°/12 Torr, 4.32 g (54%) of a (7:3)-mixture of *(Z)*- and *(E)*-**7b** were obtained as a colorless oil ([20]: m.p. 48.5–49.5° for the *(Z)*-acid). – ^{1}H-NMR. (60 MHz, CCl_4): 11.70 (*s*, 1 H, OH); 7.16 and 6.54 (*2 t*, both J=7, together 1 H, H–C(3)); 2.40 and 2.63 (*2qi*, both J=7, together 2 H, 2 H–C(4)); 1.15 and 1.13 (*2 t* both J=7, together 3 H, H_3C–C(4)).

2.3. *2-Chloro-3-methyl-2-butenoic acid* (**7c**). From 4.3 ml (58 mmol) acetone, after recrystallization from hexane, 3.4 g (43%) **7c** were obtained as pale-yellow crystals, m.p. 85–87° ([21]: 85–86°). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 10.80 (*s*, 1 H, OH); 2.23 and 2.06 (*2s*, each 3 H, 2 H_3C–C(3)).

2.4. *2-Chloro-2-cyclohexylideneacetic acid* (**7d**). From 7.1 ml (69 mmol) cyclohexanone, after recrystallization from hexane, 7.7 g (64%) **7d** were obtained as colorless crystals, m.p. 100–101° ([22]: 101–102°). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 11.75 (*s*, 1 H, OH); 2.96–2.34 (*m*, 4 H, 2 H–C(2') and 2 H–C(6')); 1.66 (br. *s*, 6 H, 2 H–C(3'), 2 H–C(4') and 2 H–C(5')).

2.5. *2-Chloro-3-methyl-2-pentenoic acid* (**7e**). From 13.4 ml (150 mmol) ethyl methyl ketone, after distillation at 140–150°/12 Torr, 11.3 g (51%) of a mixture consisting of *(Z)*- and *(E)*-**7e** in a (1:1)-ratio and about 10% of what might be the β,γ-unsaturated isomer of **7e** were obtained as a pale-yellow oil ([23]: 73–76°/0.05 Torr). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 10.86 (*s*, 1 H, OH); 2.65 and 2.45 (*2qa*, both J=7, together 2 H, 2 H–C(4)); 2.23 and 2.05 (*2s*, together 3 H, H_3C–C(3)); 1.10 (*t*, J=7, 3 H, H_3C–C(4)). The β,γ-unsaturated isomer manifested itself by the signals of its vinyl protons.

3. Preparation of α-chloro-α,β-unsaturated acid chlorides. – *General procedure.* The α-chloro-α,β-unsaturated acid was heated for 4 h, under reflux with an 100% excess of thionyl chloride. After removing the excess reagent under reduced pressure, the residual acid chloride was distilled in a *Kugelrohr*. The acid chlorides prepared in this way were pure by their ^{1}H-NMR. spectra.

3.1. *(Z)-2-Chloro-2-butenoyl chloride* (**8a**). From 8.0 g (66 mmol) *(Z)*-2-chloro-2-butenoic acid (**7a**) was obtained 5.70 g (62%) *(Z)*-**8a** as a colorless liquid, distilled at 70–100°/12 Torr. – ^{1}H-NMR. (60 MHz, CCl_4): 7.37 (*qa*, J=7, 1 H, H–C(3)); 1.9 (*d*, J=7, 3 H, H_3C–C(3)).

3.2. *2-Chloro-2-pentenoyl chloride* (**8b**). From 2.44 g (18 mmol) 2-chloro-2-pentenoic acid (**7b**) was obtained 1.59 g (57%) of an (8:2)-mixture of *(Z)*- and *(E)*-**8b** as a colorless oil, distilled at 85°/12 Torr. – ^{1}H-NMR. (60 MHz, CCl_4): 7.46 and 6.49 (*2 t*, both J=7, together 1 H, H–C(3)); 2.48 (*qi*, J=7, 2 H, 2 H–C(4)); 1.18 and 1.06 (*2t*, both J=7, together 3 H, H_3C–C(4)).

3.3. *2-Chloro-3-methyl-2-butenoyl chloride* (**8c**). From 3.1 g (23 mmol) 2-chloro-3-methyl-2-butenoic acid (**7c**) was obtained 2.43 g (69%) **8c** as a pale-yellow oil, distilled at 100°/25 Torr. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 2.1 and 2.15 (*2s*, each 3 H, 2 H_3C–C(2)).

3.4. *2-Chloro-2-cyclohexylideneacetyl chloride* (**8d**). From 3.5 g (20 mmol) 2-chloro-2-cyclohexylideneacetic acid (**7d**) was obtained 3.5 g (90%) **8d** as a colorless oil, distilled at 70°/0.03 Torr. – ^{1}H-NMR. (60 MHz, CCl_4): 2.53 (br. *s*, 4 H, 2 H–C(2′) and 2 H–C(6′)); 1.68 (br. *s*, 6 H, 2 H–C(3′), 2 H–C(4′) and 2 H–C(5′)).

3.5. *2-Chloro-3-methyl-2-pentenoyl chloride* (**8e**). From 11.2 g (75 mmol) 2-chloro-3-methyl-2-pentenoic acid (**7e**) was obtained 7.4 g (59%) of a (6:4)-mixture of *(Z)*- and *(E)*-**8e** as a colorless oil, distilled at 95°/12 Torr. – ^{1}H-NMR. (60 MHz, CCl_4): 2.46 (*qa*, J=7, 2 H, 2 H–C(4)); 2.12 and 2.05 (2 *s*, together 3 H, H_3C–C(3)); 1.13 (*t*, J=7, 3 H, H_3C–C(4)).

4. Preparation of the ketene-adducts. – *General Procedure.* To a stirred, ice-cooled solution of 100 mmol α,β-unsaturated acid chloride (**8**) and 300 mmol of cyclopentadiene (**2**) or 120 mmol of 6,6-dimethylfulvene (**3**) in 45 ml of ethanol-free chloroform was added slowly a solution of 105 mmol of triethylamine in 5 ml of the same solvent. After stirring for 15 h at RT., the mixture was washed three times with water, dried (Na_2SO_4) and evaporated. The residual ketene-adduct (**10/11** or **12/13**) was distilled in a *Kugelrohr.*

4.1. *7-Chloro-7-vinylbicyclo[3.2.0]-2-hepten-6-one* (**10a/11a**). From 2.34 g (16.9 mmol) 2-chloro-2-butenoyl chloride (**8a**) and 6 ml (54 mmol) cyclopentadiene (**2**) was obtained 2.40 g (84%) of a colorless oil, after distillation at 115–125°/12 Torr. The product consisted (GC.-A, SE-52, 90° and ^{1}H-NMR.) of a (1:1)-mixture of **10a** and **11a**. – IR. (CCl_4): 1795*s* (C=O). – ^{1}H-NMR. (90 MHz, CCl_4): 6.3–5.2 (*m*, 5 H, H–C(2), H–C(3), H–C(1′) and 2 H–C(2′)); 4.25 (*d*×*d*×*d*, J=8, 8 and 2.5, H–C(5) of **10a**) and 3.90 (*d*×*d*×*d*, J=8, 8 and 2.5, H–C(5) of **11a**), intensity ratio=1:1, together 1 H; 3.9–3.6 (*m*, 1 H, H–C(1)); 3.0–2.3 (*m*, 2 H, 2 H–C(4)). – MS. (168): 168 (3, M^+); 133 (45, M^+–Cl); 105 (98); 104 (20); 102 (50, M^+–C_5H_6); 79 (40); 77 (41); 66 (100, C_5H_6); 65 (20); 38 (61).

C_9H_9ClO (168.62) Calc. C 64.11 H 5.38% Found C 64.70 H 6.00%

4.2. *7-Chloro-7-propenylbicyclo[3.2.0]-2-hepten-6-one* (**10b/11b**). From 1.6 g (10.5 mmol) 2-chloro-2-pentenoyl chloride (**8b**) and 3.5 ml (32 mmol) cyclopentadiene (**2**) was obtained 1.54 g (80%) of a colorless oil, after distillation at 125°/12 Torr. The product consisted (GC.-A, SE-52, 96° and ^{1}H-NMR.) of a (1:1)-mixture of **10b** and **11b**. – IR. (CCl_4): 1795*s* (C=O). – ^{1}H-NMR. (90 MHz, CCl_4): 6.2–5.4 (*m*, 4 H, H–C(2), H–C(3), H–C(1′) and H–C(2′)); 4.27 (*d*×*d*×*d*, J=8, 8 and 2.5, H–C(5) of **10b**) and 3.88 (*d*×*d*×*d*, J=8, 8 and 2.5, H–C(5) of **11b**), intensity ratio=1:1, together 1 H; 3.8–3.6 (*m*, 1 H, H–C(1)); 2.96–2.30 (*m*, 2 H, 2 H–C(4)); 1.77 and 1.73 (2*d*, both J=6.5, 3 H, H_3C–C(2′)). – MS. (182): 182 (3, M^+); 147 (17, M^+–Cl); 91 (100); 66 (53, C_5H_6).

$C_{10}H_{11}ClO$ (182.65) Calc. C 65.76 H 6.07% Found C 66.00 H 6.09%

4.3. *7*exo*-Chloro-7*endo*-isopropenylbicyclo[3.2.0]-2-hepten-6-one* (**10c**). From 2.43 g (16 mmol) 2-chloro-3-methyl-2-butenoyl chloride (**8c**) and 5.3 ml (48 mmol) cyclopentadiene (**2**) was obtained 2.12 g (73%) **10c** as a pale-yellow oil, after distillation at 125°/12 Torr, 98% pure (GC.-A, SE-52, 94°). – IR. (CCl_4): 1793*s* (C=O). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 6.06–5.90, 5.76–5.56 (2*m*, each 1 H, H–C(2) and H–C(3)); 5.23 and 5.0 (2 split *s*, each 1 H, 2 H–C(1′)); 4.23 (*d*×*d*×*d*, J=8, 8 and 2.5, 1 H, H–C(5)); 3.90–3.63 (*m*, 1 H, H–C(1)); 2.9–2.0 (*m*, 2 H, 2 H–C(4)); 1.85 (*d*×*d*, J=2 and 1, 3 H, H_3C–C(2′)). – MS. (182): 182 (6, M^+); 147 (97, M^+–Cl); 91 (100); 66 (79, C_5H_6); 53 (55).

$C_{10}H_{11}ClO$ (182.65) Calc. C 65.76 H 6.07% Found C 66.64 H 6.44%

4.4. *7*exo*-Chloro-7*endo*-cyclohex-1′-enylbicyclo[3.2.0]-2-hepten-6-one* (**10d**). From 4.10 g (21 mmol) 2-chloro-2-cyclohexylideneacetyl chloride (**8d**) and 6.5 ml (59 mmol) cyclopentadiene (**2**) was obtained 3.60 g (76%) **10d** as a colorless oil, after distillation at 110°/0.001 Torr, 98% pure (GC.-A, OV-1, 126°). – IR. (CCl_4): 1795*s* (C=O). – ^{1}H-NMR. (60 MHz, CCl_4): 6.10–5.76 (*m*, 2 H, H–C(2) and H–C(3)); 5.66–5.43 (*m*, 1 H, H–C(2′)); 4.08 (*d*×*d*×*d*, J=8, 8 and 2.5, 1 H, H–C(5)); 3.86–3.50 (*m*, 1 H, H–C(1)); 3.0–2.36 (*m*, 2 H, 2 H–C(4)); 2.36–1.86 (*m*, 4 H, 2 H–C(3′) and 2 H–C(6′)); 1.86–1.43 (*m*, 4 H, 2 H–C(4′) and 2 H–C(5′)). – MS. (222): 222 (4, M^+); 187 (21, M^+–Cl); 159 (24); 156 (39, M^+–C_5H_6); 130 (43); 129 (42); 128 (100, C_7H_9Cl); 117 (20); 93 (31); 91 (57); 77 (30); 66 (27, C_5H_6).

$C_{13}H_{15}ClO$ (222.71) Calc. C 70.11 H 6.79 Cl 15.92% Found C 69.31 H 6.71 Cl 15.25%

4.5. *7-Chloro-4-isopropylidene-7-vinylbicyclo[3.2.0]-2-hepten-6-one* (**12a/13a**). From 3.0 g (21.6 mmol) 2-chloro-2-butenoyl chloride (**8a**) and 3.0 g (28.5 mmol) 6,6-dimethylfulvene (**3**) was obtained 2.8 g (62%) of an orange oil, after distillation at 120°/0.03 Torr. The product consisted of a (1:1)-mixture

of **12a** and **13a**. – IR (CCl_4): 1795*s* (C=O), 1630*w* (C=C). – ^{1}H-NMR. (60 MHz, CCl_4): 6.50 (br. *d*, *J*=6, 1 H, H–C(3)); 6.3–5.0 (*m*, 4 H, H–C(2), H–C(1′) and 2 H–C(2′)); 4.63 (br. *d*, H–C(5) of **12a**) and 4.36 (br. *d*, H–C(5) of **13a**), both *J*=8, intensity ratio 1:1, together 1 H; 3.74 (br. *d*, *J*=8, 1 H, H–C(1)); 1.80 (*s*, 6 H, $(CH_3)_2C=C(4)$).

$C_{12}H_{13}ClO$ (208.69) Calc. C 69.07 H 6.28% Found C 68.89 H 6.23%

4.6. *7*endo*-1′-Buten-2′-yl-7*exo*-chloro-4-isopropylidenebicyclo[3.2.0]-2-hepten-6-one* (**12e**). From 3.4 g (20 mmol) 2-chloro-3-methyl-2-pentenoyl chloride (**8e**) and 3.7 g (35 mmol) 6,6-dimethylfulvene (**3**) was obtained, after distillation at 125°/0.02 Torr, 3.2 g of a (7:3)-mixture (GC.-A, SE-52, 114°) of **12e** and **15e** (see *Exper. Part, Sect. 5*), which was purified by chromatography (LC.-A, hexane/ether 47:3) to give 1.95 g (41%) of **12e**. – IR (CCl_4): 1790*s* (C=O). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 6.55 (*d*×*d*, *J*=6 and 1, 1 H, H–C(3)); 5.77 (*d*×*d*, *J*=6 and 2.5, 1 H, H–C(2)); 5.17 (br. *s*, 1 H, H–C(1′)); 5.02 (br. *s*, 1 H, H–C(1′)); 4.72 (br. *d*, *J*=7.5, 1 H, H–C(5)); 3.88 (br. *d*, *J*=7.5, 1 H, H–C(1)); 2.31 (*d*×*qa*, *J*=16 and 8, 1 H, H–C(3′)); 2.11 (*d*×*qa*, *J*=16 and 8, 1 H, H–C(3′)); 1.88 and 1.80 (2*s*, each 3 H, $(CH_3)_2C=C(4)$); 1.11 (*t*, *J*=8, 3 H, H_3C–C(3′)). – MS. (236): 236 (5, M^+); 106 (100, C_8H_{10}); 91 (60).

$C_{14}H_{17}ClO$ (236.74) Calc. C 71.03 H 7.24% Found C 70.13 H 7.03%

4.7. *4-Isopropylidene-7-methyl-7-vinylbicyclo[3.2.0]-2-hepten-6-one* (**12f/13f**). From 5.53 g (47 mmol) *(E)*-2-methyl-2-butenoyl chloride [3] and 6.37 g (60 mmol) 6,6-dimethylfulvene (**3**) was obtained 6.05 g (69%) of a yellow oil, after distillation at 95°/0.001 Torr. It consisted of a (3:7)-mixture of **12f** and **13f**. – IR. (CCl_4): 1775*s* (C=O), 1632*w* (C=C). – ^{1}H-NMR. (90 MHz, CCl_4): 6.50 (*d*×*d*, *J*= 5 and 1.5, H–C(3) of **13f**) and 6.38 (*d*×*d*, *J*=5 and 1.5, H–C(3) of **12f**), intensity ratio=7:3, together 1 H; 6.1–5.5 (*m*, 2 H, H–C(2) and H–C(1′)); 5.3–4.9 (*m*, 2 H, 2 H–C(2′)); 4.36 (*d*×*m*, *J*=7, 1 H, H–C(5)); 3.50 (br. *d*, H–C(1) of **13f**) and 3.28 (br. *d*, H–C(1) of **12f**), both *J*=7, intensity ratio=7:3, together 1 H; 1.83 (*s*, 6 H, $(CH_3)_2C=C(4)$); 1.38 (*s*, H_3C–C(7) of **12f**) and 1.08 (*s*, H_3C–C(7) of **13f**), intensity ratio=3:7, together 3 H. – ^{1}H-NMR. (60 MHz, C_6D_6): 6.40 (*d*×*d*, *J*=5 and 1.5, 1 H, H–C(3)); 6.10–5.45 (*m*, 2 H, H–C(2) and H–C(1′)); 5.3–4.8 (*m*, 2 H, 2 H–C(2′)); 4.20 (*d*×*m*, *J*=7, 1 H, H–C(5)); 3.25 (br. *d*, H–C(1) of **13f**) and 2.96 (br. *d*, H–C(1) of **12f**), both *J*=7, intensity ratio 7:3, together 1 H; 1.82 and 1.62 (2*s*, each 3 H, $(CH_3)_2C=C(4)$); 1.19 (*s*, H_3C–C(7) of **12f**) and 1.05 (*s*, H_3C–C(7) of **13f**), intensity ratio 3:7, together 3 H. – MS. (188): 188 (14, M^+); 173 (12, M^+-CH_3); 106 (100, C_8H_{10}); 91 (99, C_7H_7); 82 (17).

$C_{13}H_{16}O$ (188.27) Calc. C 82.94 H 8.57% Found C 82.34 H 7.89%

5. Thermal rearrangements. – *General procedure.* The 7-vinylbicyclo[3.2.0]-2-hepten-6-ones (**10/11** or **12/13**) were heated without solvent or in refluxing xylene under N_2 for 2 to 4 h and the crude products purified by *Kugelrohr*-distillation, recrystallization or chromatography.

5.1. *3-Chlorobicyclo[4.2.1]-3,7-nonadien-2-one* (**14a**). Thermolysis of 99 mg (0.6 mmol) of a mixture of 50% 7*exo*-chloro-7*endo*-vinyl- (**10a**) and 7*endo*-chloro-7*exo*-vinylbicyclo[3.2.0]-2-hepten-6-one (**11a**) at 190° for 1 h yielded, after chromatography (TLC.-A, diisopropyl ether, Rf 0.35), 48 mg (48%) **14a** as a yellow oil. – UV. (C_2H_5OH): 245 (4200), 211 (2000). – IR. (CCl_4): 1690*s* (C=O). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 6.59 (*d*×*d*, *J*=6 and 4, 1 H, H–C(4)); 6.07–5.75 (*m*, 2 H, H–C(7) and H–C(8)); 3.68 (*d*×*m*, *J*=6, 1 H, H–C(1)); 3.27–2.93 (*m*, 1 H, H–C(6)); 2.8–2.5 (*m*, 2 H, 2 H–C(5)); 2.23 (*d*×*d*×*d*, *J*=13, 6 and 6, 1 H, H_{anti}–C(9)); 1.93 (*d*, *J*=13, 1 H, H_{syn}–C(9)).

C_9H_9ClO (168.62) Calc. C 64.11 H 5.38% Found C 63.84 H 5.57%

5.2. *3-Chloro-5-methylbicyclo[4.2.1]-3,7-nonadien-2-one* (**14b**). From 1.2 g (6.6 mmol) of a mixture of 50% 7*exo*-chloro-7*endo*-(1′-propenyl- (**10b**) and 50% 7*endo*-chloro-7-*exo*-(1′-propenyl)bicyclo[3.2.0]-2-hepten-6-one (**11b**), after refluxing in 30 ml xylene for 12 h, multiple chromatography of the residue (TLC.-A, ethyl acetate/pentane 1:4, Rf=0.30) and *Kugelrohr*-distillation at 140–150°/0.1 Torr was obtained 70 mg (6%) of **14b** as a colorless liquid (99% pure, GC.-A, SE-52, 108°). – UV. (C_2H_5OH): 245.5 (2090). – IR. (CCl_4): 1690*s* (C=O); 1595*m* (C=C). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 6.46 (*d*×*d*, *J*=3.5 and 1, 1 H, H–C(4)); 6.03 (br. *s*, 2 H, H–C(7) and H–C(8)); 3.68 (*d*×*d*, *J*=7 and 2, 1 H, H–C(1)); 3.22–2.84 (*m*, 2 H, H–C(5) and H–C(6)); 2.31 (*d*×*d*×*d*, *J*=13, 7 and 7, 1 H, H_{anti}–C(9)); 2.11 (*d*, *J*=13, 1 H, H_{syn}–C(9)); 1.22 (*d*, *J*=6, 3 H, H_3C–C(5)).

$C_{10}H_{11}ClO$ (182.65) Calc. C 65.76 H 6.07% Found C 65.74 H 6.28%

5.3. *3-Chloro-4-methylbicyclo[4.2.1]-3,7-nonadien-2-one* (**14c**). Thermolysis of 119 mg (0.7 mmol) 7*exo*-chloro-7*endo*-isopropenylbicyclo[3.2.0]-2-hepten-6-one (**10c**) at 160° for 1 h afforded, after distilla-

tion at 180°/12 Torr, 96 mg (81%) **14c** as a pale-yellow oil. – UV. (C_2H_5OH): 257 (5300), 207 (3150). – IR. (CCl_4): 1680*s* (C=O). – ^{1}H-NMR. (90 MHz, CCl_4): 6.0–5.75 (*m*, 2 H, H–C(7) and H–C(8)); 3.57 (*d*×*d*×*d*, *J*=6, 2 and 2, 1 H, H–C(1)); 3.2–3.0 (*m*, 1 H, H–C(6)); 3.0–2.4 (*m*, 2 H, 2 H–C(5)); 2.04 (*s*, 3 H, H_3C–C(4)); 2.3–1.8 (*m*, 2 H, 2 H–C(9)). – MS. (182): 182 (15, M^+); 147 (38, M^+–Cl); 116 (100, C_5H_5ClO); 66 (44, C_5H_6).

$C_{10}H_{11}ClO$ (182.65) Calc. C 65.76 H 6.07 Cl 19.41% Found C 65.99 H 6.03 Cl 19.30%

5.4. *3-Chlorotricyclo[8.2.1.0^{4,9}]-3,11-tridecadien-2-one* (**14d**). Thermolysis of 212 mg (0.95 mmol) 7*exo*-chloro-7*endo*-cyclohex-1′-enylbicyclo[3.2.0]-2-hepten-6-one (**10d**) in 5 ml refluxing xylene for 4 h yielded, after distillation at 130–140°/0.03 Torr and recrystallization from petroleum ether/ethanol, 150 mg (71%) **14d** as colorless crystals, m.p. 73.5–75.5°. – UV. (C_2H_5OH): 265 (5900), 245 (6100). – IR. ($CHCl_3$): 1666*s* (C=O). – ^{1}H-NMR. (400 MHz, $CDCl_3$): 5.98 and 5.94 (each *d*×*d*, each *J*=6 and 3, each 1 H, H–C(11) and H–C(12)); 3.67 (*d*×*d*, *J*=7.2 and 3, 1 H, H–C(1)); 3.55 (*d*×*m*, *J*=13.3, 1 H, H_{eq}–C(5)); 2.96 (*d*×*d*×*d*, *J*=7.2, 6.3 and 3, 1 H, H–C(10)); 2.78 (*d*×*d*×*d*, *J*=11.7, 6.3 and 3, 1 H, H–C(9)); 2.15 (*d*×*d*×*d*, *J*=12.6, 7.2 and 7.2, 1 H, H_{anti}–C(13)); 2.08 (*d*, *J*=12.6, 1 H, H_{syn}–C(13)); 1.97 (*d*×*d*×*d*, *J*=13.3, 13 and 4.2, 1 H, H_{ax}–C(5)); 1.95–1.8 and 1.6–1.35 (2*m*, each 3 H, 2 H–C(6), 2 H–C(7) and 2 H–C(8)).

$C_{13}H_{15}ClO$ (222.71) Calc. C 70.11 H 6.79% Found C 70.44 H 7.14%

On brief heating to 170–190°, or on standing in $CHCl_3$ solution at RT. for several weeks, **14d** was smoothly transformed into an oil which, after crystallization from hexane, yielded *tricyclo[8.2.1.0^{4,9}]-3,8,11-tridecatrien-2-one* (**16**), m.p. 64–66°. – UV. (C_2H_5OH): 295 (12000), 207 (5300). – IR. (KBr): 1640*s* (C=O). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 6.14 (m, 1 H, H–C(8)); 5.81 (*m*, 2 H, H–C(11) and H–C(12)); 5.56 (br. *s*, 1 H, H–C(3)); 3.54 (*m*, 1 H, H–C(1)); 3.41 (*m*, 1 H, H–C(10)); 2.5–2.3 and 2.3–2.15 (2*m*, each 2 H, 2 H–C(5) and 2 H–C(7)); 2.15–2.05 (*m*, 2 H, 2 H–C(6)); 1.75–1.6 (*m*, 2 H, 2 H–C(13)). – ^{13}C-NMR. ($CDCl_3$): 203.5 (*s*, C=O); 144.0 and 140.1 (2*s*, C(4) and C(9)); 136.4, 135.0, 131.1 and 123.8 (4*d*, C(3), C(8), C(11) and C(12)); 57.8 and 52.4 (2*d*, C(1) and C(10)); 35.6, 33.2, 26.6 and 22.9 (4*t*, C(5), C(6), C(7) and C(13)).

$C_{13}H_{14}O$ (186.25) Calc. C 83.83 H 7.58% Found C 83.71 H 7.56%

5.5 *3-Methylbicyclo[4.2.1]-3,7-nonadien-2-one* (**14f**). Thermolysis of 1.05 g (7 mmol) of a mixture of 30% 7*exo*-methyl-7*endo*-vinyl- (**10f**) and 70% 7*endo*-methyl-7*exo*-vinylbicyclo[3.2.0]-2-hepten-6-one (**11f**) [3] at 160° for 4 h under N_2 yielded, after distillation at 130°/12 Torr, 0.87 g (83%) **14f** as a yellow oil (97% pure, GC.-A, SE-52, 82°). – UV. (C_2H_5OH): 233 (4800). – IR. (CCl_4): 1662*s* (C=O). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 6.06 (*d*×*d*×*qa*, *J*=5.5, 3.5 and ≈1, 1 H, H–C(4)); 5.86 (*m*, 2 H, H–C(7) and H–C(8)); 3.50 (*d*×*d*, *J*=7.5 and 2.3, 1 H, H–C(1)); 3.04 (*m*, 1 H, H–C(6)); 2.75 (*d*×*d*×*d*×*qa*, *J*=20.5, ≈6, 3.5 and 2, 1 H, H–C(5)); 2.46 (br. *d*×*d*, *J*=20.5 and 5, 1 H, H–C(5)); 2.12 (*d*×*d*×*d*, *J*=12.7, 7.5 and 7.5, 1 H, H_{anti}–C(9)); 1.96 (*d*, *J*=12.7, 1 H, H_{syn}–C(9)); 1.82 (br. *s*, 3 H, H_3C–C(3)). – ^{13}C-NMR. ($CDCl_3$): 205.0 (*s*, C=O); 136.2, 135.5 and 132.0 (3*d*, C(4), C(7) and C(8)); 131.1 (*s*, C(3)); 58.1 and 41.1 (2 *d*, C(1) and C(6)); 38.7 (*t*, C(5)); 30.0 (*t*, C(9)), 21.5 (*qa*, CH_3).

$C_{10}H_{12}O$ (148.21) Calc. C 81.04 H 8.16% Found C 79.76 H 8.24%

5.6. *3-Chloro-9-isopropylidenebicyclo[4.2.1]-3,7-nonadien-2-one* (**15a**). Refluxing 145 mg (0.7 mmol) of a mixture of 50% 7*exo*-chloro-7*endo*-vinyl- (**12a**) and 50% 7*exo*-vinyl-7*endo*-chloro-4-isopropylidenebicyclo[3.2.0]-2-hepten-6-one (**13a**) in 5 ml xylene for 4 h afforded, after recrystallization, 72 mg (50%) of **15a** as colorless crystals, m.p. 80–82°. – UV. (C_2H_5OH): 240 (3900), 211 (5900). – IR. ($CHCl_3$): 1677*s* (C=O). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 6.50 (*d*×*d*, *J*=5.5 and 4, 1 H, H–C(4)); 6.1–5.85 (*m*, 2 H, H–C(7) and H–C(8)); 4.23 (br. *s*, 1 H, H–C(1)); 3.75–3.5 (*m*, 1 H, H–C(6)); 2.87 (*d*×*d*, *J*=19 and 4, 1 H, H–C(5)); 2.42 (*d*×*d*×*d*, *J*=19. 5.5 and 4, 1 H, H–C(5)); 1.70 and 1.60 (2 *s*, each 3 H, $(CH_3)_2C$=C(9)). – MS. (208): 208 (28, M^+); 106 (100, C_8H_{10}); 91 (69).

$C_{12}H_{13}ClO$ (208.69) Calc. C 69.07 H 6.28% Found C 70.00 H 5.69%

5.7. *3-Chloro-4-ethyl-9-isopropylidenebicyclo[4.2.1]-3,7-nonadien-2-one* (**15e**). Refluxing a solution of 205 mg (0.87 mmol) 7*endo*-(1′-buten-2′-yl)-7*exo*-chloro-4-isopropylidenebicyclo[3.2.0]-2-hepten-6-one (**12e**) in 1 ml xylene for 1.5 h gave, after recrystallization from hexane, 91 mg (45%) of **15e** as colorless crystals, m.p. 87–89°. – UV. (C_2H_5OH): 261 (4760), 236 (4280). – IR. ($CHCl_3$): 1668*s* (C=O). – ^{1}H-NMR. (200 MHz, $CDCl_3$): 6.04 (br. *d*, *J*=1.5, 2 H, H–C(7) and H–C(8)); 4.30 (br. *s*, 1 H, H–C(1));

3.72–3.62 (*m*, 1 H, H–C(6)); 2.86 (*d*×*d*, *J*=19 and 5, 1 H, H–C(5)); 2.61 (*d*×*d*, *J*=19 and 2.5, 1 H, H–C(5)); 2.56 (*d*×*qa*, *J*=20 and 7, 1 H, H–C(1')); 2.20 (*d*×*qa*, *J*=20 and 7, 1 H, H–C(1')); 1.66 and 1.74 (2 *s*, each 3 H, $(CH_3)_2C=C(9)$); 1.06 (*t*, *J*=7, 3 H, H_3C–C(1')). – MS. (236): 236 (8, M^+); 106 (100, C_8H_{10}); 91 (31).

$C_{14}H_{17}ClO$ (236.75) Calc. C 71.03 H 7.24% Found C 71.30 H 7.10%

5.8. *9-Isopropylidene-3-methylbicyclo[4.2.1]-3,7-nonadien-2-one* (**15f**). Refluxing 6.24 g (33 mmol) of a mixture of 30% 7*exo*-methyl-7*endo*-vinyl-(**12f**) and 70% 7*endo*-methyl-7*exo*-vinylbicyclo[3.2.0]-2-hepten-6-one (**13f**) in 15 ml xylene for 3 h yielded, after distillation at 160°/0.05 Torr, 3.35 g (54%) of **15f** as a yellow oil. – UV. (C_2H_5OH): 230 (5700), 208 (8300). – IR. (CCl_4): 1662*s* (C=O). – ^{1}H-NMR. (60 MHz, CCl_4): 6.0–5.7 (*m*, 3 H, H–C(4), H–C(7) and H–C(8)); 3.96 (br. *s*, 1 H, H–C(1)); 3.65–3.45 (*m*, 1 H, H–C(6)); 3.0–2.0 (*m*, 2 H, 2 H–C(5)); 1.74 and 1.63 (2 *s*, 6 H and 3 H resp., $(CH_3)_2C=C(9)$ and H_3C–C(3)). – MS. (188): 188 (13, M^+); 106 (100, C_8H_{10}); 91 (42); 81 (11).

$C_{13}H_{16}O$ (188.27) Calc. C 82.94 H 8.57% Found C 82.88 H 8.34%

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