230. 2-Vinylcyclobutanones by Cycloaddition of Vinylketenes to Simple Olefins

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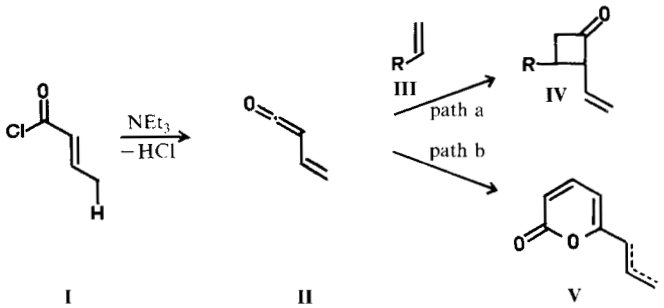
Summary

Selected [2 + 2]-cycloadditions of three alkylvinylketenes **2** to one mono- and seven dialkyl-olefins **3** yielded eleven 2-alkyl-2-vinylcyclobutanones **4** *(Tables 1* and *2)*. Three methods were compared, all involving *in situ* generation of the ketenes **2** by HCl-elimination from α,β-unsaturated acid chlorides **1**; the most effective employed a large excess of olefin **3** and a high reaction temperature. The [2 + 2]-cycloadditions were fully regio- and stereoselective with respect to the olefin **3**, but less so with respect to the ketene **2**, so that – where possible – two stereoisomers of **4** resulted, namely **A** and **B**, whose configurations were determined from their ^{1}H-NMR, spectra, mechanistic considerations and, in one case, **4f**, by chemical correlation with a previously known cycloadduct **8**.

1. Introduction. – 2-Vinylcyclobutanones **IV** are versatile intermediates for the synthesis of functionalized five-, six-, and eight-membered mono- as well as bi- and polycyclic systems [1–4]. The two methods for the preparation of **IV** are: *1)* rearrangement of 1-functionalized cyclopropyl-vinyl-carbinols [5] and *2)* the cycloaddition of vinylketenes **II** to olefins **III** *(Scheme 1)*. While *Method 2* is effective with activated olefins, such as conjugated dienes [1–3] [6] [7] fulvenes [1], enamines [8] and enolethers [9] [10], it has so far given only low yields with simple olefins **III** (*cf.* [3]).

Scheme 1

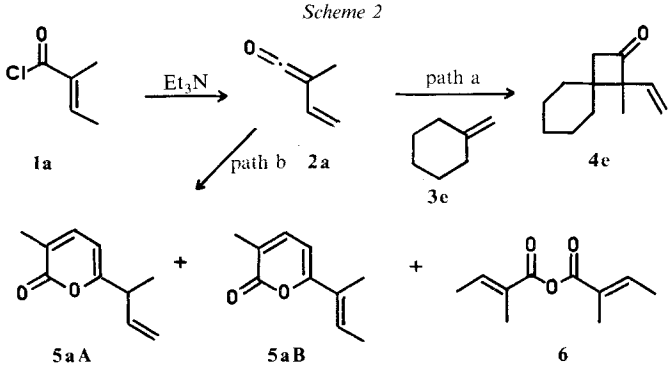


The vinylketenes **II** used in *Method 2* are usually prepared in the presence of the olefins **III** from α,β-unsaturated acid chlorides **I** by HCl-elimination with Et_3N. When **I** is subjected to this reaction in the absence of olefins, 2-pyrones **V** (two double-bond isomers) are formed [6]. Thus 2-vinylcyclobutanones **IV** can be expected from **I** and **III** only if the [2 + 2]-cycloaddition *(Scheme 1, path a)* competes successfully with 2-pyrone formation (path *b*). This is evidently the case with activated olefins but not with simple olefins under the conditions used up to now.

Because of the simplicity and the anticipated regioselectivity of the reaction and in view of the potential usefulness of the products **IV**, we undertook a study of the [2 + 2]-cycloaddition of alkylvinylketenes **II** to simple olefins **III.**

2. Conditions for the Cycloaddition of Methylvinylketene (2a) to Methylidencyclohexane (3e). – First we studied the effect of different conditions on the reaction of methylvinylketene (**2a**), generated *in situ* from the acid chloride **1a**, with methylidencyclohexane (**3e**). The major products were always the [2 + 2]-cycloadduct **4e**, the 2-pyrones **5aA** and **5aB** and the anhydride **6** *(Scheme 2)*. Their yields were determined by GC and, in the case of **4e**, also by isolation. Only 1–10% of unidentified products were found to be present. The results *(Table 3, Exper. Part)* may be summarized as follows: the reaction (**1a** → **2a**) + **3e** in refluxing $CHCl_3$ for 6 h *(Procedure B)* (*cf.* [1] [3]) or refluxing hexane for 48 h *(Procedure C)* (*cf.* [8]) afforded the cycloadduct **4e** in less than 17% yield, even when the concentration of the acid chloride **1a** was kept low by slow addition. Increasing the amount of **3e** from 1.2 to 6.0 mol-equiv. with respect to **1a**, however, improved this yield to 28%.

Scheme 2



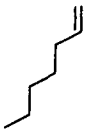
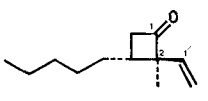
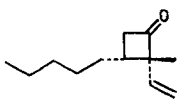
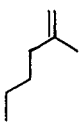
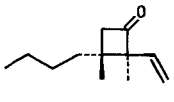
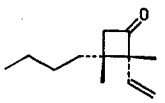
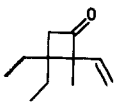
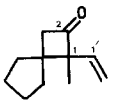
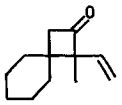
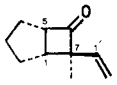
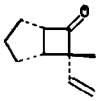
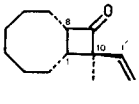
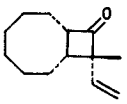
A further improvement resulted when the reaction was performed at 150° using the olefin **3e** as solvent, which required enclosure in a sealed tube *(Procedure A)*. The temperature was chosen as high as possible, but below the point at which cycloreversion or rearrangement of the product might be feared. Raising the excess of olefin **3e** over acid chloride **1a** from 1.2 to 3.0, 6.0 and 12.0 mol-equiv. under *Procedure A* increased the yield of **4e** from 19% to 34%, 51% and 63%, respectively.

3. Cycloadditions of Methylvinylketene (2a) to Different Olefins. – Having found *Procedure A* (sealed tube, 150°) to be the most successful one for the reaction of **1a** with **3e**, we examined the cycloaddition of methylvinylketene (**2a**) to six other simple olefins **3** listed in *Table 1*. We chose 6 mol-equiv. of the olefin **3** with respect to the acid

chloride **1a** as a standard since it gave reasonable yields still responsive to structural features of the olefin. *Table 1* also shows procedures, cycloadducts **4**[1]), yields and stereoisomer ratios of these cycloadducts.

The three procedures were also compared in the case of (*Z*)-cyclooctene (**3g**): *Procedure A* afforded a 60% yield of the cycloadduct **4g** (always a 3:1 mixture of the

Table 1. *[2 + 2]-Cycloadditions of Methylvinylketene* (**2a**) *to Different Olefins* **3**

Olefin **3**	Procedure	[2 + 2]-Cycloadduct(s) **4**	Yield [%]	Ratio of stereoisomers **A/B**
 **3a**	*A*	**4a**  **A**  **B**	40	7:3
 **3b**	*A*	**4b**  **A**  **B**	11	1:1
 **3c**	*A*	**4c** 	12	–
 **3d**	*A*	**4d** 	79	–
 **3e**	*A* *B* *C*	**4e** 	42 20 14	–
 **3f**	*A*	**4f**  **A**  **B**	28	7:3
 **3g**	*A* *B* *C*	**4g**  **A**  **B**	60 47 20	3:1 3:1 3:1

[1]) In the *Exper. Part* we specify the relative configurations of our racemic mixtures by the notation [11] which represents *R* R** by *'like'* as (*l*) and *R* S** by *'unlike'* as (*u*).

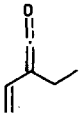
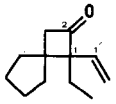
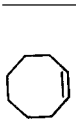
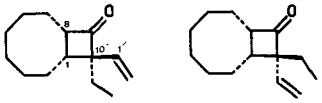
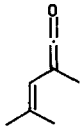
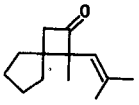
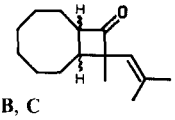
stereoisomers **4gA** and **4gB**), *Procedures B* and *C* 47% and 20% yields, respectively. With the other olefins (except for **3e**), only *Procedure A* was used. As expected, strain and lack of steric hinderance at the double bond of the olefin **3** appear to be positive factors for the [2 + 2]-cycloaddition.

In the case of the reaction of **3g** with **2a** a temperature of 140° could be reached without enclosing the reactants in a sealed tube. Since the yield of **4g** in an open vessel was about the same (60%) as in the sealed tube, we conclude that pressure is not responsible for the higher yields obtained with our *Procedure A* than with *Procedure B* or *C*.

When the 2-pyrone **5a** (1:1 mixture of **A** and **B**) was heated at 140° with Et_3N in **3g** (6.0 mol-equiv.) no cycloadduct **4g** was formed. Thus the higher yield of **4g** under *Procedure A* is not due to a reversible formation of **2a** from the 2-pyrone **5a** at the elevated temperature.

4. Cycloadditions of Two Other Alkylvinylketenes to Two Olefins. – Methylidencyclopentane (**3d**) and **3g** (the two best ketenophiles listed in *Table 1*) were reacted with ethylvinylketene (**2b**) and methyl(2-methyl-1-propenyl)ketene (**2c**), generated from the acid chlorides **1b** and **1c** (*cf.* [10]), respectively. *Procedure A* (150°, 4 h) was

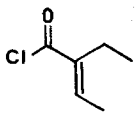
Table 2. *[2 + 2]-Cycloadditions of Ethylvinylketene* (**2b**) *and Methyl(2-methyl-1-propenyl)ketene* (**2c**) *to Methylidencyclopentane* (**3d**) *and (Z)-Cyclooctene* (**3g**)

Ketene **2**	Olefin **3**		Procedure	[2 + 2]-Cycloadduct(s) **4**	Yield [%]	Ratio of stereoisomers
 **2b**		**3d**	*A*	**4h** 	67	–
		**3g**	*A*	**4i**  **A** **B**	52[a])	**A/B** = 85:15
 **2c**		**3d**	*A*[b])	**4j** 	20	–
		**3g**	*A*[b])	**4k**  **A, B, C**	33	**A/B/C** = 20:7:3[c])

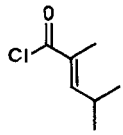
[a]) In addition the pyrone **5b** was isolated (34%).
[b]) Reaction at 165° for 44 h.
[c]) The configurations of the three isomers were not assigned.

adequate for the reactions with **1b**, but not for the ones with **1c**, since **1c** was recovered under these conditions. Thus the temperature and duration of the reactions with **1c** had to be increased to 165° and 44 h. This suggests that the tertiary proton at C(4) of **1c** is more resistant to abstraction than the corresponding primary protons of the acid chlorides **1a** and **1b**. *Table 2* shows the reactants **2** and **3**, procedures, the cycloadducts **4**[1]), yields and stereoisomer ratios of these four cycloadditions.

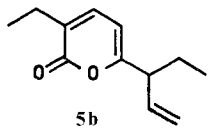
In the case of the reaction of (*Z*)-cyclooctene (**3g**) with the acid chloride **1b**, the 2-pyrone **5b** was also isolated (34%). No 2-pyrone is obtained from **1c**.



1b



1c

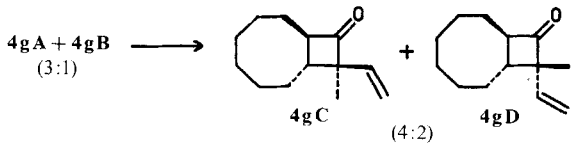


5b

5. Selectivities of the Cycloadditions. – The cycloadditions of alkylvinylketenes **2** to the 1,2-unequally substituted olefins appears to be fully regioselective *(Tables 1* and *2)*; only those products where the ketene carbonyl C-atom had become attached to the least substituted end of the olefin were formed, namely **4a–e**, **4h** and **4j**. All the bicyclic adducts, **4f**, **4g**, **4i** and **4k** (for the latter see also below), are *cis*-fused at the ring juncture, indicating that the reaction occurs suprafacially at the olefin. The major stereoisomer in the products, **4a**, **4f**, **4g** and **4i**, always has the larger ketene substituent (here the methyl or ethyl group) on the sterically more hindered side of the cyclobutanone ring, as expected from the 'orthogonal attack' model [12] [13]; the larger ratio of **4iA** to **4iB** *(Table 2)* than of **4gA** to **4gB** *(Table 1)* may be due to the slightly larger effective bulk of the ethyl group in **2b** than of the methyl group in **2a**.

In the case of the cycloaddition of **2c** to **3g**, three stereoisomers, **A**, **B** and **C**, of **4k** were isolated. One of them must be a *trans*-fused isomer formed by enolisation at C(8) due to the high temperature required for formation of the ketene **2c**. The spectral evidence does not suffice to assign configurations to **4kA–C**. An analogous stereoisomerization at C(8) could be effected with the cycloadduct **4g**: heating a mixture of the *cis*-isomers **4gA** and **4gB** at 165° for 44 h, resulted in their partial conversion to a mixture of the *trans*-isomers **4gC** and **4gD** *(Scheme 3)*.

Scheme 3

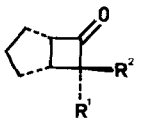


6. Structures of the Cycloadducts. – All the cycloadducts **4** have IR bands at 1770–1782 cm^{-1} (cyclobutanone); the nine **2a**- and **2b**-adducts show an IR band at 1632–

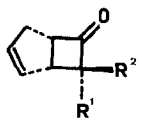
1638 cm^{-1} and a ^{1}H-NMR *ABM*-system at 6–5 ppm (vinyl group) while the two **2c**-adducts show IR bands at 1650–1670 cm^{-1} and a ^{1}H-NMR singlet at *ca.* 5.2 ppm (2,2-dimethylvinyl group).

Five of the cycloadducts, namely **4a**, **4b**, **4f**, **4g** and **4i**, were obtained as mixtures of two stereoisomers **A** and **B**, each of which was recognized in the mixture by some of its ^{1}H-NMR signals. In each pair, one stereoisomer (isomer **A**) is characterized by the fact that the ^{1}H-NMR signal of its α-methyl protons (except for **4i**) appears at a higher field (by 0.09–0.26 ppm) and the signal of *H*–C(1') at lower field (by 0.05–0.19 ppm) as compared to the corresponding signals of the other stereoisomer (isomer **B**). Assuming that the high-field shift of these protons is always associated with a vicinal alkyl group on the same side of the cyclobutanone ring, as has been observed in many related systems [1] [12] [13], we conclude that the isomers **A** and **B** have the configurations shown in *Tables 1* and *2*.

These assignments are supported by an unambiguous correlation of configurations of **4fA** and **4fB** to those of **8A** and **8B** of known configuration [12]: separate hydrogenation of **4f(A + B)** and of **8(A + B)**, both in a known isomer ratio **A/B**, gave the same saturated ketone **7(A + B)** in such isomer ratios **A/B** that showed **7A** to be derived from **8A** and from **4fA** (and **7B** from **8B** and from **4fB**). Thus **4fA** and **4fB** have the same configuration as the known **8A** and **8B**, respectively.



	R^1	R^2
4fA	CH_3	$CH{=}CH_2$
4fB	$CH{=}CH_2$	CH_3
7A	CH_3	CH_2CH_3
7B	CH_2CH_3	CH_3



	R^1	R^2
8A	CH_3	$CH{=}CH_2$
8B	$CH{=}CH_2$	CH_3

All our configurational assignments agree with the prediction made on the basis of the 'orthogonal approach' model of ketene additions [12] [13], namely that isomers **A** are the major and isomers **B** the minor stereoisomers. The configurations at C(10) of **4gC** and **4gD** *(Scheme 3)* are assigned on the assumption that the major C(10)-isomer in the *trans*-series (**4gC**) is derived from the major C(10)-isomer (**4gA**) in the *cis*-series.

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Experimental Part

1. General. – Melting points (m.p.) were determined on a *Mettler FP-52* apparatus with a microscope. The spectral data were recorded on the following instruments. UV: *Kontron Uvikon 810;* IR: *Perkin-Elmer 298*. GC/IR: on the fly with a *Digilab FTS-15 FT-IR* Spectrometer coupled through a *Digilab GC-C* interphase with a *Hewlett-Packard 5880 A* gas chromatograph, equipped with a *SE-54 WCOT* column (25 m × 0.3 mm) and

using H_2 as carrier gas. ^{1}H-NMR: *Varian EM-360* (60 MHz), *EM-390* (90 MHz) and *XL-200* (200 MHz); the 60-MHz-^{1}H-NMR δ-values are rounded to the nearest 0.05 ppm. For decoupling experiments, the chemical shift of the irradiated signal is given in square brackets [δ] followed by the multiplicity of the ensuing signal. MS: *Varian MAT 711* or *112S*. The notations and abbreviations used for the description of the spectral data are as in [14].

Chromatographic Methods: GC-A = anal. gas chromatography on *SE-54 WCOT* columns (12–25 m × 0.2–0.3 mm, film thickness *ca.* 0.2 μ), carrier gas H_2, FI-detector, split injection. GC-**B** = semiprep. gas chromatography on packed columns (4 m × 4 mm, 5–10% stationary phase on *Chromosorb W/AW-DMCS*, 80/100 mesh), carrier gas He (60–80 ml/min), TC-detector. The components of GC-analyzed mixtures are given in the order of increasing retention time. LC-A = low-pressure liquid chromatography on silica gel (40–63 μ) *'Merck LiChroprep Si 60'* at 2–6 bar.

2. Preparation of α,β-Unsaturated Acid Chlorides. – 2.1. *(E)-2-Ethyl-2-butenoyl Chloride* (**1b**). (*E*)-2-Ethyl-2-butenoic acid, m.p. 39–40°, obtained in 35% yield from α-bromobutyric acid and acetaldehyde following the general procedure of [15], was converted to **1b** (89%), b.p. 48–49°/12 Torr ([16]: 54–57°/14 Torr), by heating in $SOCl_2$. IR (film): 1755*s*, 1645*m*. ^{1}H-NMR (60 MHz), CCl_4): 7.15 (*q*, *J* = 7, 1 H, H–C(3)); 2.35 (*q*, *J* = 7, 2 H, 2H–C(1')); 1.95 (*d*, *J* = 7, 3 H, 3H–C(4)); 1.00 (*t*, *J* = 7, 3 H, 3H–C(2')).

2.2. (E)-*2,4-Dimethyl-2-pentenoyl Chloride* (**1c**). 2,4-Dimethyl-2-pentenoic acid, b.p. 96–99°/12 Torr, obtained as in [15], was converted to the acid chloride **1c** (55%), b.p. 57–59°/12 Torr, by heating in $SOCl_2$. The (*Z*)-isomer of **1c** was present to the extent of less than 5% (by ^{1}H-NMR). IR (film): 1760*s*, 1640*m*. ^{1}H-NMR (60 MHz, CCl_4): 6.85 (br. *d*, *J* = 9, 1 H, H–C(3)); 3.0–2.3 (*m*, 1 H, H–C(4)); 1.90 (br. *s*, 3 H, CH_3–C(2)); 1.10 (*d*, *J* = 7, 6 H, $2CH_3$–C(4)).

Table 3. *Yields of Products from the Reaction of (*E*)-2-Methyl-2-butenoyl Chloride* (**1a**) *with Et_3N in the Presence of Methylidencyclohexane* (**3e**) *under Different Conditions*

1	2	3	4	5	6	7	8
Molar ratio of **3e** to **1a**	Reaction conditions	Yield [%]					
		Cycloadduct **4e**		Pyrone **5aA**	Pyrone **5aB**	Anhydride **6**	Total
		GC[a])	Isol.[b])	GC	GC	GC	GC
	Procedure A						
1.2[c])	neat, sealed tube, 4 h at 150°[d])	19.2	16	20.8	20.2	5.6	65.8
3.0	ditto	34.2	19	19.0	13.4	4.4	71.0
6.0	ditto	50.8	42	17.4	5.4	5.1	78.7
12.0	ditto	62.6	64	10.2	0	6.4	79.2
	Procedure B						
	9 ml $CHCl_3$, 6 h at 65°						
1.2	addition of **1a** over 0.25 h	9.5	8	32.8	29.6	5.1	76.4
6.0	ditto	24.5	20	31.8	6.4	4.8	67.2
1.2	addition of **1a** over 5 h	13.3	10	25.6	18.0	4.4	61.4
6.0	ditto	27.9	26	24.4	3.8	6.0	62.1
1.2	addition of **1a** over 5 h[e])	16.6	13	24.8	14.8	4.8	61.0
1.2	addition of Et_3N to **1a** over 5 h	15.9	13	35.8	30.2	7.0	88.9
1.2	simultaneous addition of Et_3N and **1a** over 5 h	17.0	14	29.8	22.2	5.6	74.6
	Procedure C						
	9 ml hexane, 48 h at 70°						
6.0	addition of **1a** over 0.5 h	16.8	14	33.6	4.0	10.6	65.0

[a]) Yield determined by GC using an internal standard, see *Exper. 3.2.*

[b]) Yield determined by isolation, see *Exper. 3.3.*

[c]) Reactants washed into the reaction vessel with 1 ml of hexane.

[d]) Reactants mixed at 20°.

[e]) Reaction performed in 1 ml $CHCl_3$.

3. Study of the Cycloaddition of Methylvinylketene (2a) to Methylidencyclohexane (3e) under Various Conditions. – 3.1. *Reaction Procedures.* Different amounts (*Table 3*, column 1) of *methylidencyclohexane* (**3e**) and 1.18 g (10 mmol) of (E)-*methyl-2-butenoyl chloride* (**1a**) were reacted with 1.06 g (10.5 mmol) of Et_3N under different conditions (column 2). After the reaction was terminated, the cooled mixture was diluted with pentane and H_2O. The org. phase was separated and washed with 5% HCl- and sat. $NaHCO_3$-solution, dried ($MgSO_4$) and concentrated to leave an oily residue, which was dissolved in 25 ml toluene.

3.2. *GC-Analysis.* An aliquot of 2 ml was withdrawn from the toluene solution of *3.1* and combined with a known amount of undecane as internal standard for GC analysis by GC-A. The response factors were determined relative to undecane (1.00): 1.25 for **4e**, 2.14 for **5aA**, 2.01 for **5aB**, and 2.10 for **6**. The GC-analytical results are shown in *Table 3* as yields of **4e** (column 3), of **5aA** (column 5), of **5aB** (column 6) and of **6** (column 7). Column 8 shows the total yield of all four products.

3.3. *Isolation of the Cycloadduct* **4e**. The aliquot of *3.2* was recombined with the remainder of the toluene solution of *3.1* and the total solution concentrated. The residue was chromatographed with LC-A (pentane/Et_2O 12:1) to remove the internal standard and the more slowly moving by-products **5aA**, **5aB** and **6**, which usually were not collected. The eluate containing the cycloadduct **4e** was concentrated to yield **4e** (*Table 3*, column 4). According to GC-A and ^{1}H-NMR the product obtained in this way did not contain more than 5% impurities (including solvent). The properties of **4e** are given in *Exper. 5.5.*

3.4. *Identification of the By-products.* The by-products **5aA**, **5aB** and **6** from all experiments were characterized by their GC-retention times and by the identity of their GC/IR-spectra with those of authentic samples. The 2-pyrones **5aA** and **5aB** were prepared according to [6] and the anhydride **6** was obtained (80%) from (*E*)-2-methyl-2-butenoic acid and its chloride **1a** in the presence of pyridine [17], b.p. 130–132°/12 Torr. IR (film): 1775*s*, 1715*s*, 1650*m*. ^{1}H-NMR (60 MHz, CCl_4): 6.85 ($q \times q$, $J = 6$ and 2, 2 H, H–C(3) and H–C(3′)); 1.8–2.0 (*m*, 12 H, $4CH_3$).

4. Preparative Procedure for the Cycloadditions of Vinylketenes to Olefins. – 4.1. *Procedure A.* A mixture of 60 mmol of the olefin **3**, 1.06 g (10.5 mmol) of Et_3N and 10 mmol of α,β-unsaturated acid chloride **1** was heated in a sealed tube under N_2 (after degassing) at 150° (thermostated oven) for 4 h (except in *Exper. 10.1* and *10.2*), after which time the initially clear mixture contained a brown or yellow cake of $Et_3N \cdot HCl$. The cooled tube was opened, its contents diluted with H_2O and extracted with pentane. The extract was washed with 5% HCl- and sat. $NaHCO_3$-solution, dried over $MgSO_4$ and concentrated (distillation readily returned excess olefin). The residue was chromatographed with LC-A (pentane/Et_2O 12:1) to remove the slower moving by-products, namely the 2-pyrones **5aA** and **5aB** and the anhydride **6**, which were not collected. The eluate was concentrated to leave the oily cycloadduct(s) **4**, contaminated in all cases with not more than 5% impurities (by GC-A and ^{1}H-NMR). Its weight is the basis of the yield given (except in *Exper. 10.1*). Attempts to separate the stereoisomers of **4** during the chromatography were unsuccessful, except in *Exper. 10.2.* To obtain the spectroscopic properties of the cycloadduct(s) **4**, the residue was bulb-to-bulb distilled at the indicated reduced pressure. The ratio of stereoisomers (if present) in the crude product mixture before chromatography, in the product after chromatography and in the product after bulb-to-bulb distillation was found to be essentially the same (by GC-A and ^{1}H-NMR).

4.2. *Procedure B.* To a gently refluxing and stirred solution of 60 mmol of **3** and 1.06 g (10.5 mmol) of Et_3N in 5 ml of EtOH-free $CHCl_3$ was added a solution of 10 mmol α,β-unsaturated acid chloride **1** in 4 ml of the same solvent during 0.5 h. After a total reflux time of 6 h, the mixture was concentrated, the residue diluted with H_2O and extracted with pentane. The product was isolated by workup and chromatography, as described under *Procedure A.*

4.3. *Procedure C. Procedure B* was followed, but using hexane as solvent instead of $CHCl_3$. After 48 h at reflux, the mixture was diluted with H_2O and pentane and the product was isolated by workup and chromatography, as described unter *Procedure A.*

5. Cycloadditions of Methylvinylketene (2a) to Different Olefins. – 5.1. *To 1-Heptene* (**3a**). From 5.90 g (60 mmol) **3a** and 1.18 g (10 mmol) **1a**, using *Procedure A*, was obtained 0.71 g (40%) *2-methyl-3-pentyl-2-vinylcyclobutanone* (**4a**) as a colorless oil, b.p. 105–110°/14 Torr (bulb-to-bulb) containing the (*l*)- **4aB** and the (*u*)-isomer[1]) **4aA** in a 3:7 ratio (by GC-A and ^{1}H-NMR). IR (film): 1782*s*, 1637*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.88 (*dd*, $J = 17.5$ and 10.5, 0.7 H, H–C(1′) of **A**); 5.83 (*dd*, $J = 17.5$ and 10.5, 0.3 H, H–C(1′) of **B**); 5.16–5.02 (*m*, 2 H, H–C(2′)); 3.10 (*dd*, $J = 17.5$ and 9, 0.7 H, H–C(4) of **A**); 3.06 (*dd*, $J = 17.5$ and 9, 0.3 H, H–C(4) of **B**); 2.67 (*dd*, $J = 17.5$ and 8, 0.3 H, H–C(4) of **B**); 2.64 (*dd*, $J = 17.5$ and 8, 0.7 H, H–C(4) of **A**); 2.32 (br. *quint.*, $J = 8$, 0.7 H, H–C(3) of **A**); 2.05 (br. *quint.*, $J = 8$, 0.3 H, H–C(3) of **B**); 1.5–1.1 (*m*, 8 H,

$(CH_2)_4$); 1.29 (*s*, 0.9 H, CH_3–C(2) of **B**); 1.20 (*s*, 2.1 H, CH_3–C(2) of **A**); 0.95–0.80 (*m*, 3 H, CH_3 of pentyl). MS (70 eV): 138 (28, $M^+ - C_2H_2O$), 82 (75), 68 (100).

$C_{12}H_{20}O$ (180.29) Calc. C 79.94 H 11.18% Found C 79.83 H 10.99%

5.2. *To 2-Methyl-1-hexene* (**3b**). From 5.90 g (60 mmol) **3b** and 1.18 g (10 mmol) **1a**, using *Procedure A*, was obtained 0.20 g (11%) *3-butyl-2,3-dimethyl-2-vinylcyclobutanone* (**4b**) as a colorless oil, b.p. 120–130°/18 Torr (bulb-to-bulb), containing the (*u*)- **4bA** and the (*l*)-isomer[1]) **4bB** in a 1:1 ratio (by GC-A and ^{1}H-NMR). IR (film): 1780*s*, 1637*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.92 (*dd*, *J* = 17 and 10.5, 0.5 H, H–C(1′) of **A**); 5.82 (*dd*, *J* = 17 and 10.5, 0.5 H, H–C(1′) of **B**); 5.16 (*dd*, *J* = 17 and 1.5, 0.5 H, H–C(2′) of **B**); 5.11 (*dd*, *J* = 10.5 and 1.5, 0.5 H, H–C(2′) of **B**); 5.10 (*dd*, *J* = 10.5 and 1.5, 0.5 H, H–C(2′) of **A**); 5.07 (*dd*, *J* = 17 and 1.5, 0.5 H, H–C(2′) of **A**); 2.92, and 2.58 (2*d*, *J* = 17, 0.5 H each, 2H–C(4) of **A**); 2.88, and 2.60 (2*d*, *J* = 17, 0.5 H each, 2H–C(4) of **B**); 1.6–1.4 (*m*, 2 H, CH_2–C(3)); 1.4–1.2 and 0.95–0.80 (*m*, 7 H, $CH_3(CH_2)_2$); 1.25 (*s*, 1.5 H, CH_3 of **B**); 1.17 (*s*, 1.5 H, CH_3 of **A**); 1.14 (*s*, 3 H, CH_3). MS (70 eV): 138 (19, $M^+ - C_2H_2O$), 123 (22), 109 (49), 82 (100).

$C_{12}H_{20}O$ (180.29) Calc. C 79.94 H 11.18% Found C 79.69 H 10.88%

5.3. *To 2-Ethyl-1-butene* (**3c**). From 5.04 g (60 mmol) **3c** and 1.18 g (10 mmol) **1a**, using *Procedure A*, was obtained 0.19 g (12%) *3,3-diethyl-2-methyl-2-vinylcyclobutanone* (**4c**) as a colorless oil, b.p. 90–100°/14 Torr (bulb-to-bulb). IR (film): 1780*s*, 1635*w*. ^{1}H-NMR (60 MHz, CCl_4): 5.80 (*dd*, *J* = 18 and 10, 1 H, H–C(1′)); 5.00 (*dd*, *J* = 18 and 1.5, 1 H, H–C(2′)); 4.95 (*dd*, *J* = 10 and 1.5, 1 H, H–C(2′)); 2.60 (*s*, 2 H, 2H–C(4)); 2.0–1.2 (*m*, 4 H, 2 × CH_2–C(3)); 1.20 (*s*, 3 H, CH_3–C(2)); 0.85 (br. *t*, *J* = 7, 6 H, $2CH_3CH_2$). MS (70 eV): 137 (9, $M^+ - C_2H_5$), 124 (41), 109 (48), 95 (69), 82 (100).

$C_{11}H_{18}O$ (166.27) Calc. C 79.46 H 10.91% Found C 79.33 H 10.64%

5.4. *To Methylidencyclopentane* (**3d**). From 4.92 g (60 mmol) **3d** and 1.18 g (10 mmol) **1a**, using *Procedure A*, was obtained 1.30 g (79%) *1-methyl-1-vinylspiro[3.4]octan-2-one* (**4d**) as a colorless oil, b.p. 50–60°/0.1 Torr (bulb-to-bulb). IR (film): 1780*s*, 1636*w*. ^{1}H-NMR (60 MHz, $CDCl_3$): 5.85 (*dd*, *J* = 17 and 9, 1 H, H–C(1′)); 5.25–4.85 (*m*, 2 H, 2 H–C(2′)); 2.85 (*s*, 2 H, 2 H–C(3)); 2.1–1.4 (*m*, 8 H, $(CH_2)_4$); 1.25 (*s*, 3 H, CH_3). MS (70 eV): 164 (4, M^+), 122 (26), 107 (34), 82 (80), 67 (100).

$C_{11}H_{16}O$ (164.26) Calc. C 80.45 H 9.82% Found C 80.40 H 9.72%

5.5. *To Methylidencyclohexane* (**3e**). From 5.76 g (60 mmol) **3e** and 1.18 g (10 mmol) **1a**, using *Procedure A, B* and *C*, was obtained 0.75 g (42%), 0.36 g (20%) and 0.24 g (14%), respectively (*cf. Exper. 3, Table 3*, column 2 and 4) of *1-methyl-1-vinylspiro[3.5]nonan-2-one* (**4e**) as a colorless oil, b.p. 60–65°/0.08 Torr (bulb-to-bulb). IR (film): 1778*s*, 1635*w*. ^{1}H-NMR (60 MHz, CCl_4): 5.70 (*dd*, *J* = 17.5 and 9.5, 1 H, H–C(1′)); 5.15–4.75 (*m*, 2 H, H–C(2′)); 2.65 (*s*, 2 H, 2 H–C(3)); 1.0–1.9 (*m*, 10 H, $(CH_2)_5$); 1.15 (*s*, 3 H, CH_3). MS (70 eV): 178 (1, M^+), 137 (6), 136 (60), 82 (100).

$C_{12}H_{18}O$ (178.28) Calc. C 80.85 H 10.18% Found C 80.65 H 9.90%

5.6. *To Cyclopentene* (**3f**). From 4.08 g (60 mmol) **3f** and 1.18 g (10 mmol) **1a**, using *Procedure A*, was obtained 0.42 g (28%) *7-methyl-7-vinylbicyclo[3.2.0]heptan-6-one* (**4f**) as a colorless oil, b.p. 95–100°/18 Torr (bulb-to-bulb), containing the (*u,u*)- **4fB** and the (*u,l*)-isomer[1]) **4fA** in a 3:7 ratio (by GC-A und ^{1}H-NMR). IR (film): 1775*s*, 1633*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.90 (*dd*, *J* = 17 and 10, 0.7 H, H–(Cl′) of **A**); 5.71 (*dd*, *J* = 17.5 and 10.5, 0.3 H, H–C(1′) of **B**); 5.22 (*dd*, *J* = 17.5 and 1.5, 0.3 H, H–C(2′) of **B**); 5.11 (*dd*, *J* = 10.5 and 1.5, 0.3 H, H–C(2′) of **B**); 5.09 (*dd*, *J* = 17 and 0.5, 0.7 H, H–C(2′) of **A**); 5.06 (*dd*, *J* = 10 and 0.5, 0.7 H, H–C(2′) of **A**); 3.71 (*dd*, *J* = 7.5 and 7.5, 0.7 H, H–C(5) of **A**); 3.66 (*dd*, *J* = 7.5 and 7.5, 0.3 H, H–C(5) of **B**); 2.78 (*dd*, *J* = 7.5 and 7.5, 0.7 H, H–C(1) of **A**); 2.58 (*dd*, *J* = 7.5 and 7.5, 0.3 H, H–C(1) of **B**); 2.2–1.3 (*m*, 6 H, $(CH_2)_3$); 1.34 (*s*, 0.9 H, CH_3 of **B**); 1.06 (*s*, 2.1 H, CH_3 of **A**); MS (70 eV): 150 (3, M^+), 135 (6), 122 (13), 109 (18), 107 (48), 82 (83), 79 (100).

$C_{10}H_{14}O$ (150.22) Calc. C 79.96 H 9.39% Found C 79.73 H 9.36%

5.7. *To (Z)-Cyclooctene* (**3g**). From 6.60 g (60 mmol) **3g** and 1.18 g (10 mmol) **1a**, using *Procedures A, B* and *C*, was obtained 1.15 g (60%), 0.91 g (47%) and 0.40 g (21%), respectively, of *10-methyl-10-vinylbicyclo[6.2.0]decan-9-one* (**4g**) as a colorless oil, b.p. 70–75°/0.03 Torr (bulb-to-bulb), containing in all cases the (*u,u*)-isomer **4gB** and the (*u,l*)-isomer[1]) **4gA** in a 1:3 ratio (by GC-A and ^{1}H-NMR). IR (film): 1775*s*, 1632*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.91 (*dd*, *J* = 17.5 and 10.5, 0.75 H, H–C(1′) of **A**); 5.73 (*dd*, *J* = 17.5 and 10.5,

0.25 H, H–C(1') of **B**); 5.2–4.9 (*m*, 2 H, 2H–C(2')); 3.31 (*ddd*, *J* = 12, 11 and 2, 0.75 H, H–C(8) of **A**); 3.26 (*ddd*, *J* = 12, 11 and 2, 0.25 H, H–C(8) of **B**); 2.39 (split *dd*, *J* = 11 and 11, 0.75 H, H–C(1) of **A**); 2.23 (split, *dd*, *J* = 11 and 11, 0.25 H, H–C(1) of **B**); 1.9–1.1 (m, 12 H, $(CH_2)_6$); 1.35 (*s*, 0.75 H, CH_3 of **B**); 1.09 (*s*, 2.25 H, CH_3 of **A**). MS (70 eV): 192 (7, M^+), 109 (22), 94 (25), 93 (35), 82 (100).

$C_{13}H_{20}O$ (192.22) Calc. C 81.19 H 10.48% Found C 80.67 H 10.13%

6. Cycloaddition of Methylvinylketene (2a) to (*Z*)-Cyclooctene (3g) in an Open Vessel under Reflux. – A mixture of 6.60 g (60 mmol) **3g**, 1.06 g (10.5 mmol) of Et_3N and 1.18 g (10 mmol) of **1a** was heated under reflux in a N_2-atmosphere at 140° for 6 h. Workup according to *Procedure A* (see *Exper. 4.1*) gave 1.17 g (61%) **4g** containing the (*u,u*)-isomer **4gB** and the (*u,l*)-isomer[1]) **4gA** in a 1:3 ratio (by GC-A and ^{1}H-NMR, as in *Exper. 5.7*). Extending the duration of heating in this experiment to 24 h gave 1.18 g (62%) of **4g**.

7. Treatment of the 2-Pyrone 5a with Et_3N in (*Z*)-Cyclooctene (3g). – A solution of 0.82 g (5 mmol) **5a** (a mixture of **5aA** and **5aB**, ratio 1:1 by GC-A) [6], 1.06 g (10.5 mmol) Et_3N and 6.60 g (60 mmol) **3g** was heated under reflux at 140° for 5 h. The solution was cooled and **3g** removed by distillation at 33–34°/12 Torr. The residue was bulb-to-bulb distilled at 90–100°/0.1 Torr to give 0.45 g (55%) **5aB**, (by GC-A and ^{1}H-NMR) as the only product.

8. Isomerization of 4g. – Heating 40 mg (0.21 mmol) of a mixture of the (*u,u*)-isomer **4gB** and the (*u,l*)-isomer[1]) **4gA** (ratio 3:1) at 165° for 44 h in a sealed tube under N_2, yielded, after workup and CC (LC-A, pentane/Et_2O 12:1), 22 mg (55%) of a mixture of the (*l,l*)- **4gD**, the (*l,u*)- **4gC**, the (*u,u*)- **4gB** and the (*u,l*)-isomer[1]) **4gA** in a 2:4:1:3 ratio (by GC-A). GC/IR (gas phase, resolution 8 cm^{-1}): **D**: 3094*w*, 2974*m*, 2932*s*, 2862*m*, 1790*s*, 1632*w*, 1454*m*. **C**: 3094*w*, 2974*m*, 2932*s*, 2862*m*, 1790*s*, 1632*w*, 1454*m*. **B**: 3094*w*, 2970*m*, 2932*s*, 2862*m*, 1786*s*, 1632*w*, 1454*m*. **A**: 3094*w*, 2978*m*, 2932*s*, 2862*m*, 1786*s*, 1632*w*, 1454*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.1–5.4 (*m*, 1 H, H–C(1')); 5.2–4.9 (*m*, 2 H, 2H–C(2')); 3.4–3.1 (*m*, 1 H, H–C(8)); 2.40 (br. *t*, *J* ≈ 10, *ca.* 0.3 H, H–C(1) of **A**); 2.3–1.1 (*m*, *ca.* 13 H, H–C(1) of **B**, **C** and **D** and $(CH_2)_6$); 1.35, 1.23, 1.21 and 1.09 (all *s* in a 1:4:2:3 ratio, together 3 H, CH_3 of **B**, **C**, **D** and **A**, respectively). GC/MS: **D**: 192 (12, M^+), 160 (13), 135 (14), 121 (21), 109 (35), 107 (38), 94 (47), 93 (70), 82 (100), 41 (84). **C**: 192 (18, M^+), 135 (18), 121 (19), 109 (40), 107 (47), 94 (60), 93 (78), 82 (93), 81 (98), 41 (100). **B**: 192 (7, M^+), 135 (6), 121 (7), 109 (20), 107 (20), 94 (25), 93 (39), 82 (100), 41 (41). **A**: 192 (8, M^+), 135 (6), 121 (8), 109 (24), 107 (20), 94 (27), 93 (39), 82 (100), 41 (45).

9. Cycloadditions of Ethylvinylketene (2b) to Two Olefins. – 9.1. *To Methylidencyclopentane* (**3d**). From 4.92 g (60 mmol) **3d** and 1.32 g (10 mmol) **1b** *(Exper. 2.1)*, using *Procedure A*, was obtained 1.20 g (67%) *1-ethyl-1-vinylspiro[3.4]octan-2-one* (**4h**) as a colorless liquid, b.p. 70–75°/0.01 Torr (bulb-to-bulb). IR (film): 1772*s*, 1632*w*. ^{1}H-NMR (60 MHz, CCl_4): 5.60 (*dd*, *J* = 17.5 and 8.5, 1 H, H–C(1')); 5.05 (*dd*, *J* = 17.5 and 3, 1 H, H–C(2')); 5.00 (*dd*, *J* = 8.5 and 3, 1 H, H–C(2')); 2.70 (*s*, 2 H, 2H–C(3)); 2.0–1.2 (*m*, 10 H, $(CH_2)_4$ and CH_2–C(1)), 0.90 (*t*, *J* = 7, 3 H, CH_3). MS (70 eV): 178 (1, M^+), 149 (5), 137 (9), 136 (67), 107 (95), 96 (100).

$C_{12}H_{18}O$ (178.28) Calc. C 80.85 H 10.18% Found C 80.99 H 10.06%

9.2. *To (Z)-Cyclooctene* (**3g**). From 6.60 g (60 mmol) **3g** and 1.32 g (10 mmol) **1b**, using *Procedure A*, was obtained 1.07 g (52%) *10-ethyl-10-vinylbicyclo[6.2.0]decan-9-one* (**4i**) as a colorless oil, b.p. 85–90°/0.05 Torr (bulb-to-bulb), containing the (*u,u*)-isomer **4iB** and the (*u,l*)-isomer[1]) **4iA** in an 15:85 ratio (by GC-A and ^{1}H-NMR). IR (film): 1770*s*, 1632*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.83 (*dd*, *J* = 17 and 11, 0.85 H, H–C(1') of **A**); 5.63 (*dd*, *J* = 17 and 11, 0.15 H, H–C(1') of **B**); 5.2–5.0 (*m*, 2 H, 2H–C(2')); 3.20 (*ddd*, *J* = 12, 11 and 2.5, 0.85 H, H–C(8) of **A**); 3.09 (*ddd*, *J* = 12, 11 and 2.5, 0.15 H, H–C(8) of **B**); 2.35 (br. *dd*, *J* = 11 and 11, 0.85 H, H–C(1) of **A**); 2.18 (br. *dd*, *J* = 11 and 11, 0.15 H, H–C(1) of **B**); 1.9–1.1 (*m*, 14 H, $(CH_2)_6$ and CH_2–C(10)); 0.89 (*t*, *J* = 7.5, 0.15 H, CH_3 of **B**); 0.87 (*t*, *J* = 7.5, 0.85 H, CH_3 of **A**). MS (70 eV): 206 (7, M^+), 149 (12), 123 (28), 107 (29), 96 (100).

$C_{14}H_{22}O$ (206.33) Calc. C 81.50 H 10.75% Found C 81.75 H 10.54%

Upon further elution of LC-A was obtained 0.33 g (34%) *3-ethyl-6-(1-ethyl-2-propenyl)-2-pyrone* (**5 b**) as a pale yellow oil, b.p. 105–110°/0.02 Torr (bulb-to-bulb). UV (C_2H_5OH): 300 (9300), 222 (4400). IR (film): 1720*s*, 1646*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.05 (split *d*, *J* = 6.5, 1 H, H–C(4)); 5.95 (*d*, *J* = 6.5, 1 H, H–C(5)); 5.86 (*ddd*, *J* = 17.5, 10 and 7.5, 1 H, H–C(2')); 5.17 (split *d*, *J* = 10, 1 H, H–C(3')); 5.15 (split *d*, *J* = 17.5, 1 H, H–C(3')); 2.99 (*q*, *J* = 7.5, 1 H, H–C(1')); 2.47 (*q*, *J* = 7.5, 2 H, CH_2–C(3)); 1.85 and 1.63 (both *ddq*, *J* = 15,

7.5 and 7.5, 1 H each, CH_2–C(1')); 1.17 and 0.90 (2*t*, *J* = 7.5, 3 H each, 2 CH_3). MS (70 eV): 192 (29, M^+), 123 (92), 41 (100).

$C_{12}H_{16}O_2$ (192.26) Calc. C 74.97 H 8.39% Found C 74.68 H 8.21%

10. Cycloadditions of Methyl(2-methyl-1-propenyl)ketene (2c) to Two Olefins. – 10.1. *To Methylidencyclopentane* (**3d**). From 4.92 g (60 mmol) **3d** and 1.46 g (10 mmol) **1c**, using *Procedure A*, but heating at 165° for 44 h[2]), was obtained a crude product that was subjected to CC and bulb-to-bulb distillation at 60–65°/0.02 Torr to afford 0.39 g (20%) *1-methyl-1-(2-methyl-1-propenyl)spiro[3.4]octan-2-one* (**4j**) as a colorless oil of 90% purity (GC-A). A pure sample was obtained by semiprep. GC-B. IR (film): 1778*s*, 1665*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.28 (split *s*, 1 H, H–C(1')); 2.81 (*s*, 2 H, 2 H–C(3)); 1.9–1.5 (*m*, 8 H, $(CH_2)_4$); 1.72 and 1.66 (2*d*, *J* = 1, 3 H each, 2 CH_3–C(2')); 1.26 (*s*, 3 H, CH_3–C(1)). MS (70 eV): 192 (2, M^+), 151 (10), 150 (75), 135 (100).

$C_{13}H_{20}O$ (192.30) Calc. C 81.20 H 10.48% Found C 81.01 H 10.53%

10.2. *To* (Z)-*Cyclooctene* (**3g**). From 3.30 g (30 mmol) **3g**, 0.51 g (5.05 mmol) Et_3N and 0.73 g (5.0 mmol) **1c**, using *Procedure A* (note different weights), but heating at 165° for 44 h[3]) was obtained 0.36 g (33%) *10-methyl-10-(2-methyl-1-propenyl)bicyclo[6.2.0]decan-9-one* (**4k**) as a mixture of three stereoisomers **4kB**, **4kC** and **4kA** in a 7:3:20 ratio (by GC-A). Chromatography afforded two colorless oily fractions, 0.23 g fraction *a* and 0.13 g fraction *b*.

Fraction a contained only (by GC-A and ^{1}H-NMR) the major stereoisomer **4kA**, b.p. 95–100/0.03 Torr (bulb-to-bulb). IR (film): 1770*s*, 1662*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.32 (br. *s*, 1 H, H–C(1')); 3.34 (*ddd*, *J* = 11.5, 10 and 2, 1 H, H–C(8)); 2.34 (br. *dd*, *J* = 11.5 and 10, 1 H, H–C(1)); 1.70 and 1.75 (both br. *s*, 3 H each, 2 CH_3–C(2')); 2.0–1.1 (*m*, 12 H, $(CH_2)_6$); 1.10 (*s*, 3 H, CH_3–C(10)). MS (70 eV): 220 (16, M^+), 177 (21), 135 (22), 121 (44), 110 (48), 109 (53), 67 (100).

$C_{15}H_{24}O$ (220.36) Calc. C 81.76 H 10.98% Found C 81.56 H 10.98%

Fraction b, distilled at 120–130°/0.03 Torr (bulb-to-bulb), contained stereoisomers **4kB** and **4kC** in a 7:3 ratio (by GC-A).

$C_{15}H_{24}O$ (220.36) Calc. C 81.76 H 10.98% Found C 81.52 H 10.69%

Fraction b was subjected to semiprep. GC-B (*SP-2250*, 190°). The first GC-eluted component was stereoisomer **4kB**. IR (film): 1777*s*, 1670*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.22 (split *s*, 1 H, H–C(1')); 3.36 (*ddd*, *J* = 10.5, 10.5 and 2.5, 1 H, H–C(8)); 2.21 (split *dd*, *J* = 10.5 and 10.5, 1 H, H–C(1)); 1.9–1.2 (*m*, 12 H, $(CH_2)_6$); 1.71 and 1.62 (2*d*, *J* = 1, 3 H each, 2 CH_3–C(2')); 1.43 (*s*, 3 H, CH_3–C(10)). MS (70 eV): 220 (6, M^+), 177 (9), 135 (13), 121 (22), 110 (32), 107 (39), 81 (47), 67 (87), 41 (100).

The second GC-eluted component was the minor stereoisomer **4kC**. IR (film): 1777*s*, 1665 *w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.21 (br. *s*, 1 H, H–C(1')); 3.10 (*ddd*, *J* = 11, 9 and 4, 1 H, H–C(8)); 2.24–2.08 (*m*, 1 H, H–C(1)); 2.1–1.1 (*m*, 12 H, $(CH_2)_6$); 1.70 (*d*, *J* = 1, 3 H, CH_3–C(2')); 1.66 (br. *s*, 3 H, CH_3–C(2')); 1.22 (*s*, 3 H, CH_3–C(10)). MS (70 eV): 220 (9, M^+), 177 (17), 135 (20), 121 (41), 110 (15), 109 (39), 107 (60), 67 (81), 41 (100).

11. 7-Ethyl-7-methylbicyclo[3.2.0]heptan-6-one (**7**). – 11.1. *By Hydrogenation of 7-Methyl-7-vinylbicyclo[3.2.0]hept-2-en-6-one* (**8**). A solution of 0.16 g (1.1 mmol) of a mixture of the (*u,l*)-isomer **8A** and (*u,u*)-isomer[1]) **8B** (ratio 3:2, by ^{1}H-NMR), prepared as in [6][4]), in 1 ml EtOH was stirred with 20 mg 5%-Pd/C under an atmosphere of H_2 for 24 h. Filtration and evaporation left 0.16 g (98%) **7** as a mixture of the (*u,u*)-isomer **7B** and the (*u,l*)-isomer[1]) **7A** (ratio 2:3, by GC-A and ^{1}H-NMR) as a colorless oil. Bulb-to-bulb distillation at 90–100°/12 Torr afforded 50 mg (30%) **7** as a mixture of **7A** and **7B** in the same ratio (by GC-A and ^{1}H-NMR). IR (film): 1770*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.69 (br. *dd*, *J* = 7.5 and 7.5, 0.4 H, H–C(5) of **B**); 3.62 (br. *dd*, *J* = 7.5 and 7.5, 0.6 H, H–C(5) of **A**); 2.56 (br. *dd*, *J* = 7.5 and 7.5, 0.6 H, H–C(1) of **A**); 2.49 (br. *dd*, *J* = 7.5 and 7.5, 0.4 H, H–C(1) of **B**); 2.1–1.3 (*m*, 8 H, $(CH_2)_3$ and CH_2–C(7)); 1.22 (*s*, 1.8 H,

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[2]) These conditions were used here because of the experience mentioned in *Footnote 3*.

[3]) When these reactants were heated in the sealed tube at 150° for 4 h the precipitation of Et_3N was not noted and the acid chloride **1c** was recovered in high yield (by GC-A and ^{1}H-NMR).

[4]) Formed originally in a 2:1 ratio; the material used here was obtained from a middle cut of a CC purification.

CH_3–C(7) of **A**); 0.93 (*t*, *J* = 7, 1.8 H, CH_3CH_2 of **A**); 0.91 (*s*, 1.2 H, CH_3–C(7) of **B**); 0.89 (*t*, *J* = 7, 1.2 H, CH_3CH_2 of **B**). MS (70 eV): 152 (5, M^+), 109 (6), 96 (14), 95 (55), 84 (100).

$C_{10}H_{16}O$ (152.24) Calc. C 78.90 H 10.59% Found C 78.16 H 10.38%

11.2. *By Hydrogenation of* **4f**. A solution of 0.32 g (2.1 mmol) **4f** as a mixture of the (*u,u*)-isomer **4fB** and the (*u,l*)-isomer[1]) **4fA** (ratio 3:7, by GC-A and ^{1}H-NMR), as prepared in *Exper. 5.6* in 1 ml EtOH was hydrogenated in the presence of 40 mg 5%-Pd/C for 22 h. Filtration and bulb-to-bulb distillation at 90–100°/12 Torr afforded 0.22 g (69%) of **7** as a 3:7 mixture (by GC-A and ^{1}H-NMR) of the (*u,u*)-isomer **7B** and the (*u,l*)-isomer[1]) **7A**. The ^{1}H-NMR signals of the two isomers were exactly the same as the ones described in *Exper. 11.1*, except for a slight difference in their relative intensities.

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