218. Addition of Vinylketenes to Enamines. A Method for the Preparation of 6,6-Dialkylcyclohexa-2,4-dienones and 4,4-Dialkyl-2-vinylcyclobutenones

by **John M. Berge**[1]), **Max Rey** and **André S. Dreiding**

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

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Addition von Vinylketenen an Enamine. Eine Methode zur Herstellung von 6,6-Dialkylcyclohexa-2,4-dienonen und 4,4-Dialkyl-2-vinylcyclobutenonen

Zusammenfassung

Drei Enamine (**1**–**3**) wurden mit fünf Vinylketenen (**5a**–**5e**) (s. *Schema 2*) zur Reaktion gebracht. Die Vinylketene wurden *in situ* durch HCl-Eliminierung aus α,β-ungesättigten Säurechloriden mit Triäthylamin hergestellt. Die Cycloadditionen von **1**–**3** an **5a**–**5e** führten zu 6,6-Dialkyl-5-dialkylaminocyclohex-2-enonen (kurz: Cyclohexenone) bzw. zu 3-Dialkylamino-4,4-dimethyl-2-vinylcyclobutanonen (kurz: Vinylcyclobutanone) oder zu einem Gemisch der beiden, je nach Natur der Partner bzw. des Lösungsmittels (s. *Tab. 1*). Durch oxydative Amin-Eliminierung wurden die Cyclohexenone in 6,6-Dialkylcyclohexa-2,4-dienone und die Vinylcyclobutanone in 4,4-Dialkyl-2-vinylcyclobutenone übergeführt.

Diese Reaktion stellt eine einfache Synthese von verschieden substituierten 6,6-Dialkylcyclohexa-2,4-dienonen bzw. 4,4-Dialkyl-2-vinylcyclobutenonen (siehe *Schema 1*) dar.

1. Introduction. – In connection with our interest in synthetic applications of vinylketenes [1] we studied their reaction with enamines. A previous observation in this field was made by *Hickmott et al.* [2], who found that the product (22%) of the reaction between methylvinylketene and 2-methyl-1-morpholinopropene was a mixture of the [2+2]-adduct and the [2+4]-adduct. Our goal was to investigate the usefulness of the reaction of β,β-dialkyl-enamines **I** with vinylketenes **II** for the synthesis of the cyclohexa-2,4-dienones **IV** and of the 2-vinylcyclobutenones **VI** through the 5-amino-cyclohex-2-enones **III** and the 3-amino-2-vinylcyclobutanones **V** [2].

2. Cycloadditions. – We used three β,β-dialkylenamines, namely 2-methyl-1-pyrrolidinopropene (**1**), 4-pyrrolidinomethylidene-cyclohexene (**2**) and 2-methyl-1-morpholinopropene (**3**), and three types of vinylketenes (alkyl-vinyl-, halo-vinyl-

[1]) Post-doctoral fellow, 1978–1980.

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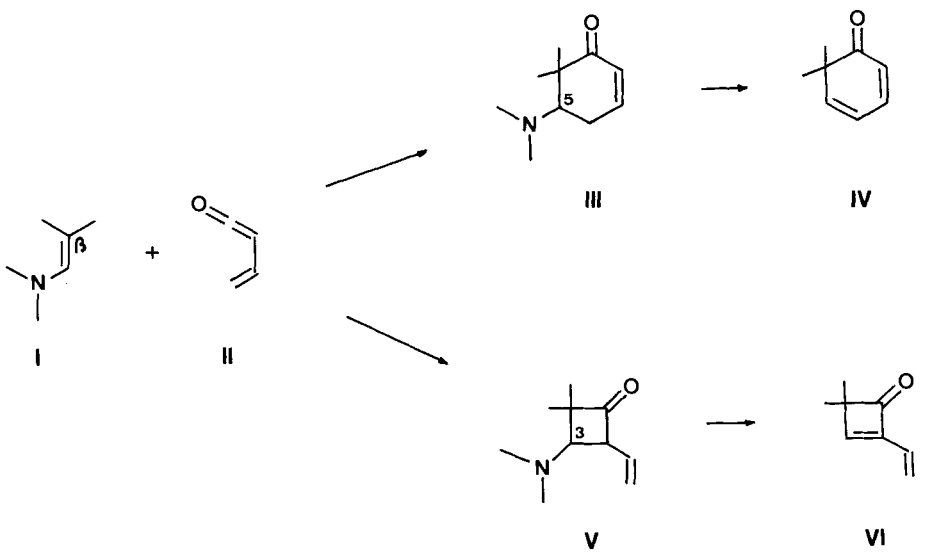
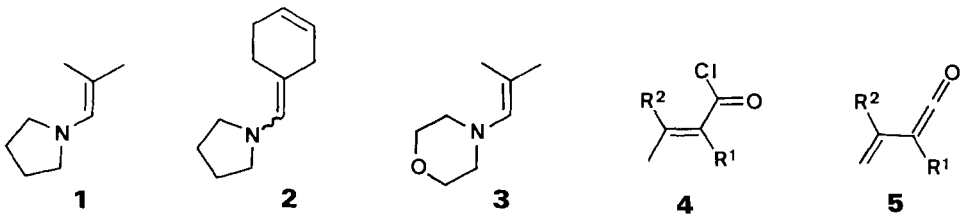
Scheme 1



and aldo-vinylketenes), namely methyl-vinylketene (**5a**), bromo-vinylketene (**5b**), bromo-isopropenylketene (**5c**), vinylketene (**5d**) and isopropenylketene (**5e**). The vinylketenes were generated *in situ*, by the elimination of hydrogen chloride with triethylamine from the corresponding α,β-unsaturated acid chlorides. *Scheme 2* contains the formulae of the starting materials and of the ketene intermediates.

Scheme 2

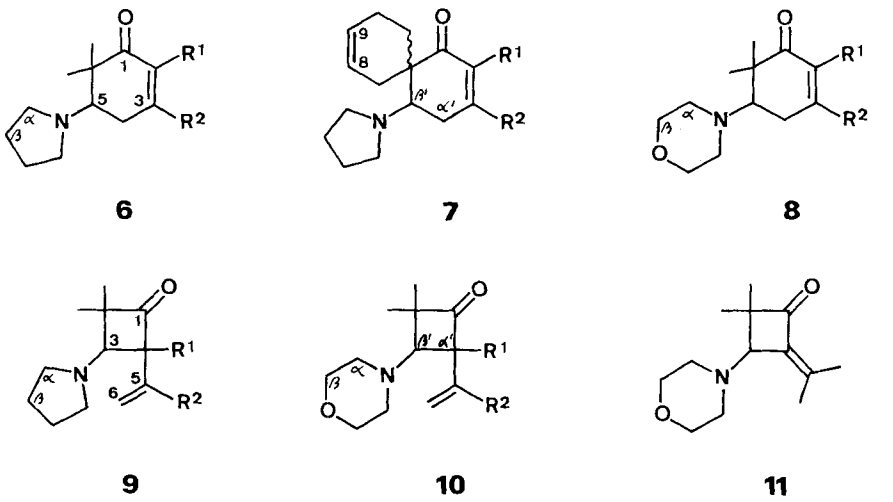


	a	b	c	d	e
R^1	CH_3	Br	Br	H	H
R^2	H	H	CH_3	H	CH_3

Some reactions were performed in a polar (CH_2Cl_2) and some in a non-polar solvent (hexane). The overall process was sufficiently fast in CH_2Cl_2 that the reactions could be carried out at room temperature; comparable reactions in hexane, however, were slower so that a higher temperature ($\approx 70°$) was needed. The reaction times ranged from 6 to 48 hours, depending on the solvent and the acid chloride. Yields were not optimized.

The cycloaddition reaction mixtures were worked up by procedures which included their being taken-up in an aqueous acid solution. Thus our products contained the organic amines, which include the true cycloadducts, the 5-dialkylamino-6,6-dialkylcyclohex-2-enones **6** to **8** (short: the cyclohexenones) and the 3-dialkylamino-4,4-dialkyl-2-vinylcyclobutanones **9** and **10** (short: the vinylcyclobutanones), freed from any neutral by-products. The products were not purified further in order to be certain that the spectral analysis reflected the ratio of cyclohexenone to vinylcyclobutanone as formed in the reaction. The cyclohexenones and the vinylcyclobutanones were identified by their characteristic IR. and ^{1}H-NMR.-spectral features and the composition of the mixtures was estimated from the relative intensities of separately visible ^{1}H-NMR.-signals, as will be described in *Chapter 3*. The ^{1}H-NMR. spectra also indicated that the products were not contaminated in appreciable amounts. *Scheme 3* contains the formulae of the cycloadducts.

Scheme 3



6 **7** **8**

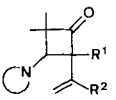
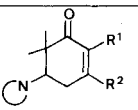
9 **10** **11**

	a	b	c	d	e
R^1	CH_3	Br	Br	H	H
R^2	H	H	CH_3	H	CH_3

Table 1 summarizes starting materials, conditions and products of the cycloadditions studied in this work. We note that the cycloadditions **1**+**5a**, **1**+**5b**, **2**+**5a**, **3**+**5b** and **3**+**5c**, all in CH_2Cl_2, yielded only cyclohexenones (**6a**, **6b**, **7a**, **8b** and **8c**), whereas the cycloadditions **3**+**5d** in hexane and **3**+**5e** in CH_2Cl_2 afforded only vinylcyclobutanones (**10d** and **10e**)[2]). The cycloadditions **1**+**5a** in hexane and **3**+**5a** in hexane or CH_2Cl_2, on the other hand, gave mixtures of cyclohexenones and vinylcyclobutanones (**6a**+**9a** and **8a**+**10a**).

[2]) We thank Dr. *D.A. Jackson* for improving the method to prepare **10d** and **10e** and for obtaining the high-field ^{1}H-NMR. data of **10d**.

Table 1. *Starting materials, reaction conditions and products of the cycloadditions of enamines with vinylketenes*

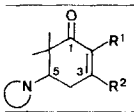
Enamine + vinylketene	Solvent (temp.)	Products R^1	R^2		Ratio		Total yield (%)
1+**5a**	CH_2Cl_2 (RT.)	CH_3	H	**6a**	1:0	–	53[a])
1+**5a**	Hexane (70°)	CH_3	H	**6a**	1:1	**9a** (4:1[b])	56[c])
1+**5b**	CH_2Cl_2 (RT.)	Br	H	**6b**	1:0	–	92[c])
2+**5a**	CH_2Cl_2 (RT.)	CH_3	H	**7a** (2:1[b])	1:0	–	83[c])
3+**5a**	CH_2Cl_2 (RT.)	CH_3	H	**8a**	9:5	**10a** (3:2[b])	26[c])[d])
3+**5a**	Hexane (70°)	CH_3	H	**8a**	1:10	**10a** (3:7[b])	26[c])
3+**5b**	CH_2Cl_2 (RT.)	Br	H	**8b**	1:0	–	69[c])
3+**5c**	CH_2Cl_2 (RT.)	Br	CH_3	**8c**	1:0	–	63[c])
3+**5d**	Hexane (RT.)	H	H	–	1:0	**10d**	46[d])[e])
3+**5e**	CH_2Cl_2 (RT.)	H	CH_3	–	1:0	**10e**[f])	67[c])

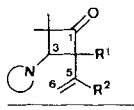
[a]) Product purified by distillation. [b]) Ratio of diastereoisomers: **A**/**B**. [c]) Crude product, but essentially free of impurities by ^{1}H-NMR. [d]) Compare [2] for the same reaction under other conditions. [e]) Crude product, containing by ^{1}H-NMR. about 50% of impurities. [f]) Isomerizes to the conjugated ketone **11**.

The cyclohexenone **7a** was formed as a mixture of diastereoisomers **A** and **B** (2:1). The same is true for the vinylcyclobutanones **9a** (**A**/**B** = 4:1) and **10a** (**A**/**B** = 3:2 when formed in CH_2Cl_2, 3:7 when formed in hexane). The vinylcyclobutanones **10d** and **10e** were found as one diastereoisomer only. The vinylcyclobutanone **10e** isomerized slowly on standing, the only product being 2-isopropylidene-4,4-dimethyl-3-morpholino-cyclobutanone (**11**). This presumably protolytic reaction is driven by the tendency of the β,γ-double bond to move into conjugation with the carbonyl group.

The results shown in *Table 1* suggest the following general conclusions: 1) The overall yields of cycloadducts in otherwise comparable cases are higher *a)* with pyrrolidino-enamines (than with morpholino-enamines) and *b)* with halo-vinylketenes (than with other vinylketenes); 2) cyclohexenone formation is favored over vinylcyclobutanone formation in the cycloadditions *a)* with alkyl- and halo-vinylketenes (as compared to those with aldo-vinylketenes); *b)* with halo-vinylketenes (as compared to those with the other vinylketenes) and *c)* with pyrrolidino-enamines (as compared to those with morpholino-enamines) and *d)* using CH_2Cl_2 (as compared to using hexane) as a solvent.

Table 2. *Some spectral properties of the cyclohexenones and the vinylcyclobutanones, obtained by cycloaddition of enamines with vinylketenes*

	IR. (C=O)	UV. (Max.)	^{1}H-NMR.[a])[b]) R^1	R^2	2 H–C(4)	H–C(5)
6a	1665	232	CH_3: 1.77	H: 6.60	under 2.8–2.3	3.05
6b	1680	247	Br: –	H: 7.28	under 2.7–1.4	3.15
7a[c])	1660	232	CH_3: 1.72	H: 6.6–6.4	under 2.7–1.1	**A** 3.5–3.4 **B** 3.36
8a[d])	1668	–	CH_3: 1.72	H: 6.60	under 2.7–2.2	2.75
8b	1680	249	Br: –	H: 7.29	under 2.7–2.2	2.82
8c	1680	257	Br: –	CH_3: 2.18	under 2.8–2.2	under 2.8–2.2

			R^1	R^2	2 H–C(6)	H–C(3)
9a[c])[e])	1770	–	CH_3: under 1.5–0.8	H: **A** 6.35 **B** 5.83	5.3–4.9	under 3.2–2.3
10a[c])	1775	–	CH_3: under 1.4–1.1	H: **A** 6.38 **B** 5.82	5.3–4.9	**A** under 2.6–2.2 **B** 2.62
10d	1780	–	H: 3.85	H: 5.78	5.22 + 5.18	2.52
10e	1780	–	H: 3.76	CH_3: 1.78	4.82 + 4.75	2.69

[a]) Signals in the two subtables are ordered so that substituents from equivalent positions in the starting materials occur in the same columns. [b]) Signals for which chemical shifts are not given as a range possess the correct multiplicity and, when not in mixtures, the correct value of integration; these signals were used to estimate purity or composition of mixtures. [c]) Mixture of diastereoisomers **A** and **B**. [d]) From the spectra of a mixture of **8a** and **10a**. [e]) From the spectra of a mixture of **9a** and **6a**.

3. Structure of the cycloadducts and estimation of the components in mixtures. – The spectral features which characterize the structure of each cyclohexenone and vinylcyclobutanone are summarized in *Table 2* and will now be discussed.

All the cyclohexenones exhibit an IR. carbonyl-band between 1665 and 1680 cm^{-1}, a UV. maximum between 230 and 250 nm and a ^{1}H-NMR.-signal for 2 H–C(4) in the aliphatic range. In contrast, the vinylcyclobutanones show an IR. band between 1770 and 1780 cm^{-1} and ^{1}H-NMR. signals for 2 H–C(6) (s. numbering in *Table 2*) in the olefinic range, but no UV. maximum. In addition, the ^{1}H-NMR. spectra of all the cycloadducts are characterized by the signals of their pyrrolidino- or morpholino-substituents and all, except **7a**, by those of the diastereotopic gem.-dimethyl groups.

Within the cyclohexenones, those with a methyl group at C(2) (**6a**, **7a** and **8a**) have an IR. band between 1660 and 1668 cm^{-1}, a UV. maximum at $\approx$232 nm and

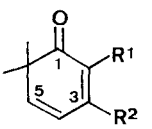
a ^{1}H-NMR.-signal for H–C(3) at $\delta = 6.6$ ppm, whereas those with a Br-atom at C(2) (**6b**, **8b** and **8c**) present the corresponding features at ≈ 1680 cm^{-1}, at 247–257 nm and at $\delta = 7.3$ ppm. The ^{1}H-NMR. signal for H–C(5) of the pyrrolidino-derivatives (**6a**, **6b** and **7a**) is found between $\delta = 3.0$ and 3.5 ppm, that of the morpholino-derivatives (**8a**, **8b** and **8c**) between $\delta = 2.75$ and 2.85 ppm. Other ^{1}H-NMR. signals characterize structural aspects of individual cycloadducts.

The spectral features of the cyclohexenone **8a** and the vinylcyclobutanone **9a** were obtained from mixtures (**8a** with **10a** and **9a** with **6a**). In both cases, the spectrum of one of the pure components (**10a** and **6a**) was available from another experiment. The differentiation of **6a** from **9a**, and also of **8a** from **10a**, is possible using the signal for H–C(3) ($\delta = 6.60$ ppm) in **6a** and **8a** and the signals for H–C(5) (δ near 6.4 and near 5.8 ppm) in **9a** and **10a**.

In the three cycloadducts, where two diastereoisomers, **A** and **B**, were observed (**7a**, **9a** and **10a**), the differentiation was possible since at least one ^{1}H-NMR. signal was separately visible for both diastereoisomers, namely the signal for H–C(5) in the cyclohexenone **7a** ($\delta = 3.5$–3.4 and 3.36 ppm), the signal for H–C(5) in the vinylcyclobutanone **9a** ($\delta = 6.35$ and 5.83 ppm) and the signals for H–C(3) and H–C(5) in the vinylcyclobutanone **10a** ($\delta = 2.6$–2.2 and 2.62 ppm and $\delta = 6.38$ and 5.82 ppm, respectively). These observations make it highly probable that **10d** and **10e** with their single signals for R^1, R^2 and H–C(3) consist of only one diastereoisomer. A configurational assignement to the two diastereoisomers on the basis of the above mentioned ^{1}H-NMR. signals is not immediately evident.

4. Preparation of 6,6-dialkylcyclohexa-2,4-dienones and 4,4-dialkyl-2-vinylcyclobutenones by oxidative elimination from the cycloadducts. – All the cycloadducts obtained in this work from vinylketenes and enamines contain a dialkylamino-group in the β-position (the vinylcyclobutanones) or in the vinylogous β'-position (the cyclohexenones). When these cycloadducts carry a H-atom in the corresponding α- or α'-position (some vinylcyclobutanones and all cyclohexenones) they are susceptible to an elimination reaction which introduces a conjugated double bond. This was accomplished by mild oxidation of the N-atom in the appropriate cycloadduct with *m*-chloroperbenzoic acid, whereupon a spontaneous *Cope*-type elimination [3] took place from the intermediate amine-oxide to yield the unsaturated

Scheme 4



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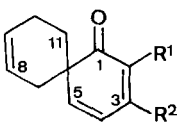

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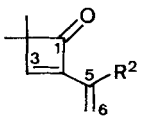


14

	a	b	c	d	e
R^1	CH_3	Br	Br	–	–
R^2	H	H	CH_3	H	CH_3

ketone. Thus the cyclohexenones **6a**, **6b** (or **8b**), **8c** and **7a** were transformed to the corresponding 6,6-dialkylcyclohexa-2,4-dienones **12a**, **12b**, **12c** and **13a** (short: cyclohexadienones), and from the vinylcyclobutanones **10d** and **10e** resulted the corresponding 4,4-dialkyl-2-vinylcyclobutenones **14d** and **14e** (short: vinylcyclobutenones). The formulae of these elimination products are shown in *Scheme 4;* the starting materials, yields and some spectral properties of the products of the elimination are summarized in *Table 3.*

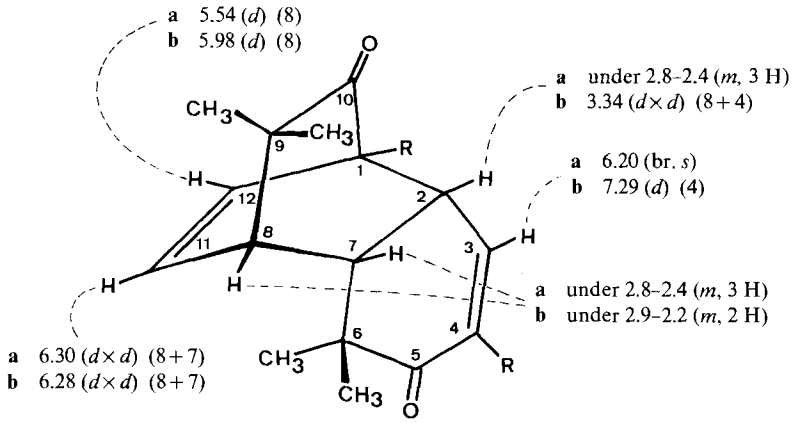
Table 3. *Starting materials, products and some spectral properties of the cyclohexadienones and the vinylcyclobutenones, obtained by the elimination reaction from some of the cycloadducts*

Starting material	Product	Yield (%)	IR. (C=O)	UV. (Max.)	^{1}H-NMR. R^1	R^2	H–C(4)	H–C(5)
6a	**12a**	82	1655 1640	308	CH_3: 1.87	H: 6.9–6.7	6.3–5.9	
6b or **8b**	**12b**	62	1666 1620		Br: –	H: 7.42	6.05	6.37
8c	**12c**	63	1660	314	Br: –	CH_3: 2.27	6.05	6.25
7a	**13a**	68	1660 1635	308	CH_3: 1.89	H: 6.80	6.15	6.51
						R^2	2 H–C(6)	H–C(3)
10d	**14d**	30	1760		–	H: 6.15	5.88 5.38	7.70
10e	**14e**	74	1760		–	CH_3: 1.80	5.65 5.09	7.71

The cyclohexadienone **12a** has been described before [4]. The characteristic properties of the others (**12b**, **12c** and **13a**) correspond in the expected manner to those of **12a**, namely two IR. bands, one between 1655 and 1660 and the other between 1620 and 1640 cm^{-1}, a UV. maximum between 308 and 314 nm and ^{1}H-NMR. signals for H–C(4) between $\delta = 6.2$ and 5.9 and for H–C(5) between $\delta = 6.5$ and 6.1 ppm. The signal for H–C(3) depends on R–C(2): $\delta \approx 6.9$ for $R = CH_3$, $\delta \approx 7.4$ ppm for R = Br.

The cyclohexadienones **12a** and **12b** show a strong tendency to dimerization by a [4+2]-cycloaddition. When they were allowed to stand, their dimers **15a** and **15b** were obtained. In *Scheme 5* we summarize some of the ^{1}H-NMR. properties of these dimers. The dimer **15a** has been isolated previously and its structure derived from its dipole moment [4]. The ^{1}H-NMR. data, particularly when comparing **15a** and **15b** with respect to the signals of H–C(2) and H–C(3), are not in contradiction with this structure type, which is, in fact, the one proven for the dimers of a number of other 6,6-disubstituted cyclohexa-2,4-dienones [5] [6]. Its formation can be rationalized by the modern concepts on the regiospecificity (bond formation be-

Scheme 5



15a R = CH_3
15b R = Br

tween the C(5)'s of the two cyclohexadienones) and the stereospecificity *(endo)* of the *Diels-Alder* reaction [6] [7].

The 2-vinylcyclobutenones (**14d** and **14e**) exhibit an IR. band at 1760 cm^{-1} and an ^{1}H-NMR. signal at $\delta \approx 7.7$ ppm for H–C(3) aside from the olefinic-H signals of the vinyl-substituent. The single ^{1}H-NMR. signal for the gem-dimethyl groups in **12** and **14** corresponds to their enantiotopicity.

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Experimental Part

1. General. – For apparatus and abbreviations see [8]. Thin layer chromatography was performed on silica plates. – The enamines 2-methyl-1-pyrrolidino-propene (**1**), 4-pyrrolidinomethylidene-cyclohexene (**2**) and 2-methyl-1-morpholinopropene (**3**) were freshly prepared by condensing the corresponding aldehydes and amines according to the method of *Benzing* [9]. 2-Bromo-crotonic acid [10], m.p. 99–100°, was converted (89%) to 2-bromocrotonyl chloride (**4b**), b.p. 80–85°/16 Torr, by heating in $SOCl_2$ [IR. (Film: 1775*s*, 1615*m*; ^{1}H-NMR. (60 MHz, $CDCl_3$): 7.85 (*qa*, *J* = 7, 1 H, H–C(3)); 2.05 (*d*, *J* = 7, 3 H, H_3C–C(3))]. – The yield of a number of products in this work refer to material not purified by chromatography, destillation or crystallization. However, in each case, except in *Exper. 3.1*, the ^{1}H-NMR. spectrum of the crude material showed no significant signals other than the ones reported in the individual experiments. – Salts of the amines **6b**, **7a** and **8c** were prepared by the following procedures: *a)* Hydrochlorides: To a saturated solution of the amine in ether/C_2H_5OH 9:1 was added excess HCl-gas; the precipitated salt was filtered off and recrystallized from ether/C_2H_5OH; *b)* Perchlorates: To a saturated solution of the amine in ether/C_2H_5OH 9:1 at 0° was added carefully a 3-fold excess of 70% $HClO_4$-solution; after 2 h at 0° the precipitate was filtered off and recrystallized from C_2H_5OH.

2. Cycloadditions leading to 6,6-dialkyl-5-dialkylamino-cyclohex-2-enones (6a, 6b, 7a, 8b and 8c). – 2.1. *General procedure.* To a solution of 10–12 mmol of the enamine and 1.4 ml (10 mmol) of triethylamine in 20 ml of CH_2Cl_2 at RT. was added a solution of 10 mmol of the acid chloride in 10 ml of CH_2Cl_2 over a period of 1 h. The mixture was allowed to stand at RT. for 6–36 h, after which time

it was washed with 20 ml of water and then with saturated $NaHCO_3$-solution. The amines were extracted from the organic phase with 2×20 ml of 5% HCl-solution and the aqueous phase was washed with 2× 10 ml of ether, basified by addition of excess solid K_2CO_3 and the product extracted with CH_2Cl_2. Drying and evaporation of the organic layer afforded the crude amino-cyclohexenones.

2.2. *2,6,6-Trimethyl-5-pyrrolidino-cyclohex-2-enone* (**6a**). From 1.18 g (10 mmol) of 2-methyl-butanoyl chloride (**4a**) and 1.25 g (10 mmol) of 2-methyl-1-pyrrolidinopropene (**1**) was obtained, after 10 h and upon Kugelrohr-distillation at 65–75°/0.01 Torr, 1.10 g (53%) of **6a** as a colorless oil. – UV. (C_2H_5OH): 232 (9000). – IR. (film): 1665*s*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 6.60 (split *t*, J=4, 1 H, H–C(3)); 3.03 (*t*, J=5, 1 H, H–C(5)); 2.8–2.3 (*m*, 6 H, 2 H–C(4) and 2 H–C(α,α')); 2.2–1.5 (*m* together with 1.77, split *s*, 7 H, 2 H–C(β,β') and H_3C–C(2)); 1.20 (*s*, 3 H, H_3C–C(6)); 1.10 (*s*, 3 H, H_3C–C(6)). – MS. (70 eV): 207 (30, *M*)), 164 (61), 125 (17), 83 (51), 54 (100).

$C_{13}H_{21}NO$ (207.32) Calc. C 75.32 H 10.21 N 6.75% Found C 74.91 H 10.06 N 7.18%

2.3. *2-Bromo-6,6-dimethyl-5-pyrrolidino-cyclohex-2-enone* (**6b**). From 1.83 g (10 mmol) of 2-bromo-2-butenoyl chloride (**4b**) and 1.25 g (10 mmol) of 2-methyl-1-pyrrolidinopropene (**1**) was obtained, after 6 h, 2.50 g (92%) of **6b** as a dark oil. – UV. (C_2H_5OH): 247 (4200). – IR. (film): 1680*s*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.28 (*t*, J=4.5, 1 H, H–C(3)); 3.15 (*t*, J=5, 1 H, H–C(5)); 2.7–1.4 (*m*, 10 H, 2 H–C(α,α'), 2 H–C(4) and 2 H–C(β,β')); 1.23 (*s*, 3 H, H_3C–C(6)); 1.17 (*s*, 3 H, H_3C–C(6)). – MS. (70 eV): 273 (32), 271 (32, *M*), 230 (22), 228 (22), 192 (52), 125 (56), 39 (100).

Hydrochloride, m.p. 186–188°.

$C_{12}H_{19}BrClNO$ (308.65) Calc. C 46.70 H 6.21 N 4.54% Found C 47.28 H 5.89 N 4.56%

2.4. *2-Methyl-5-pyrrolidino-spiro[5.5]undeca-2,8-dienone* (**7a**). From 1.18 g (10 mmol) of (*E*)-2-methyl-2-butenoyl chloride (**4a**) and 1.63 g (10 mmol) of 4-pyrrolidinomethylidene-cyclohexene (**2**) was obtained, after 12 h, 2.02 g (83%) crude **7a** as a mixture of diastereoisomers **A** and **B** in the ratio of 2:1 as a yellow oil, which solidified on standing at −20°. – UV. (C_2H_5OH): 232 (5200). – IR. (film): 1660*s*. – ^{1}H-NMR. (200 MHz, $CDCl_3$, 50°): 6.6–6.4 (*m*, 1 H, H–C(3)); 5.74 and 5.60 (2 br. *d*, J=8 each, 1 H each, H–C(8) and H–C(9)); 3.5–3.4 (*m*, 0.66 H, H–C(5) of **A**); 3.36 (*d*, J=4, 0.33 H, H–C(5) of **B**); 2.7–1.1 (*m*, 16 H, 2 H–C(α,α'), 2 H–C(4), 2 H–C(β,β'), 2 H–C(7), 2 H–C(10) and 2 H–C(11)); 1.72 (*s*, 3 H, H_3C–C(2)). – MS. (70 eV): 245 (12, *M*), 138 (29), 83 (60), 55 (96), 38 (100).

Perchlorate, m.p. 188–191°.

$C_{16}H_{24}ClNO_5$ (345.83) Calc. C 55.57 H 7.00 N 4.05% Found C 55.39 H 7.18 N 4.05%

2.5. *2-Bromo-6,6-dimethyl-5-morpholino-cyclohex-2-enone* (**8b**). From 1.83 g (10 mmol) of 2-bromo-2-butenoyl chloride (**4b**) and 1.46 g (10.3 mmol) of 2-methyl-1-morpholinopropene (**3**) was obtained, after 6 h, 2.00 g (69%) of **8b** as pale yellow crystals, m.p. 115–118° ($CHCl_3$/hexane). – UV. (C_2H_5OH): 249 (4600). – IR. ($CHCl_3$): 1680*s*, 1110*s*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.29 (*t*, J=4.5, 1 H, H–C(3)); 3.8–3.5 (*m*, 4 H, 2 H–C(β,β')); 2.82 (*t*, J=5, 1 H, H–C(5)); 2.7–2.2 (*m*, 6 H, 2 H–C(α,α') and 2 H–C(4)); 1.25 (*s*, 3 H, H_3C–C(6)); 1.18 (*s*, 3 H, H_3C–C(6)). – MS. (70 eV): 289 (60), 287 (60, *M*), 246 (50), 244 (50), 208 (100), 141 (50).

$C_{12}H_{18}BrNO_2$ (288.19) Calc. C 50.01 H 6.30 N 4.86% Found C 49.84 H 6.40 N 5.07%

2.6. *2-Bromo-3,6,6-trimethyl-5-morpholino-cyclohex-2-enone* (**8c**). From 1.97 g (10 mmol) of 2-bromo-3-methyl-2-butenoyl chloride (**4c**) [11] and 1.41 g (10 mmol) of 2-methyl-1-morpholinopropene (**3**) was obtained, after 36 h, 1.91 g (63%) of **8c** as a light yellow oil. – IR. (film): 1680*s*, 1620*m*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 3.8–3.5 (*m*, 4 H, 2 H–C(β,β')); 2.8–2.2 (*m*, 7 H, 2 H–C(α,α'), 2 H–C(4) and H–C(5)); 2.18 (*s*, 3 H, H_3C–C(3)); 1.22 (*s*, 3 H, H_3C–C(6)); 1.17 (*s*, 3 H, H_3C–C(6)). – MS. (70 eV): 216 (29), 214 (29), 135 (89), 91 (90), 83 (100).

Perchlorate, m.p. 195–197°. – UV. (C_2H_5OH): 257 (6000).

$C_{13}H_{21}BrClNO_6$ (402.68) Calc. C 38.78 H 5.26 N 3.48% Found C 39.23 H 5.33 N 3.40%

3. Cycloadditions leading to 4,4-dialkyl-3-dialkylamino-2-vinylcyclobutanones (10d and 10e). – 3.1. *4,4-Dimethyl-3-morpholino-2-vinylcyclobutanone* (**10d**)[2]. To 1.41 g (10 mmol) 2-methyl-1-morpholinopropene (**3**) in 20 ml hexane containing 2.8 ml (20 mmol) triethylamine was added, over 4 h with stirring, 2.06 g (20 mmol) 2-butenoyl chloride (**4d**) in 10 ml of hexane. After 24 h at RT. the mixture was cooled to 0°, washed with 20 ml of water, 20 ml sat. $NaHCO_3$-solution and the product

extracted into 15 ml 5% HCl-solution, all solutions being kept at 0°. The ice-cold aqueous extract was basified with solid K_2CO_3 and extracted twice with 15 ml ether each. The combined ether layers were dried and evaporated to give 0.97 g of a pale yellow oil, which contained ≈50% (by ^{1}H-NMR.) **10d** (23%). – IR. (film): 1780*s*, 1640*m*. – ^{1}H-NMR. (360 MHz, $CDCl_3$, signals assigned to **10d**): 5.78 ($d\times d\times d$, J = 17.5, 10 and 7.5, 1 H, H–C(5)); 5.22 ($d\times t$, J = 17.5 and ≈1, 1 H, H–C(6)); 5.18 ($d\times t$, J = 10 and ≈1, 1 H, H–C(6)); 3.85 (br. $d\times d$, J = 8 and 7.5, 1 H, H–C(2)); 3.7–3.5 (*m*, 4 H, 2 H–C(α,α')); 2.52 (*d*, J = 8, 1 H, H–C(3)); 2.5–2.3 (*m*, 4 H, 2 H–C(β,β')); 1.26 (*s*, 3 H, H_3C–C(4)); 1.19 (*s*, 3 H, H_3C–C(4)). Due to instability it was not possible to obtain an analytically pure sample (compare [2] for this reaction).

3.2. *2-Isopropenyl-4,4-dimethyl-3-morpholino-cyclobutanone* (**10e**) *and 2-isopropylidene-4,4-dimethyl-3-morpholino-cyclobutanone* (**11**)[2]. From 1.18 g (10 mmol) 3-methyl-2-butenoyl chloride (**4e**), 1.41 g (10 mmol) 2-methyl-1-morpholinopropene (**3**) and 1.4 ml (10 mmol) triethylamine in 30 ml of CH_2Cl_2 was obtained, as described in *Exper. 3.1*, 1.50 g (67%) of **10e** as a yellow oil. – IR. (film): 1780*s*, 1640*m*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 4.82 (split *s*, 1 H, H–C(6)); 4.75 (split *s*, 1 H, H–C(6)); 3.76 (*d*, J = 8.3, 1 H, H–C(2)); 3.7–3.5 (*m*, 4 H, 2 H–C(α,α')); 2.69 (*d*, J = 8.3, 1 H, H–C(3)); 2.6–2.2 (*m*, 4 H, 2 H–C(β,β')); 1.78 (*s*, 3 H, H_3C–C(5)); 1.22 (*s*, 3 H, H_3C–C(4)); 1.15 (*s*, 3 H, H_3C–C(4)).

On standing at 0° during 5 days in the absence of solvent, **10e** was spontaneously converted to **11**. – UV. (C_2H_5OH): 242 (10000). – IR. (film): 1745*s*, 1660*s*, 1115*s*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 3.9–3.5 (*m*, 4 H, 2 H–C(β,β')); 3.28 (split *s*, 1 H, H–C(3)); 2.8–2.3 (*m*, 4 H, 2H–C(α,α')); 2.12 (*s*, 3 H, H_3C–C(5)); 1.88 (*s*, 3 H, H_3C–C(5)); 1.20 (*s*, 3 H, H_3C–C(4)); 1.15 (*s*, 3 H, H_3C–C(4)). – MS. (70 eV): 223 (25, *M*); 180 (100), 138 (45), 82 (13).

$C_{13}H_{21}NO_2$ (223.32) Calc. C 69.92 H 9.48 N 6.27% Found C 69.86 H 9.49 N 5.99%

4. Cycloadditions leading to mixtures of 5-dialkylamino-6,6-dialkylcyclohex-2-enones and 3-dialkylamino-4,4-dialkyl-2-vinylcyclobutanones *6a/9a* and *8a/10a*. – 4.1. *Mixture of 2,6,6-trimethyl-5-pyrrolidino-cyclohex-2-enone* (**6a**) *and 2,4,4-trimethyl-5-pyrrolidino-2-vinylcyclobutanone* (**9a**). To a refluxing solution of 1.25 g (10 mmol) of **1** and 1.4 ml (10 mmol) of triethylamine in 20 ml of hexane was added dropwise 1.18 g (10 mmol) of (*E*)-2-methyl-2-butenoyl chloride (**4a**) in 10 ml of hexane. After 24 h reflux the solution was cooled, washed with water and with sat. $NaHCO_3$-solution, dried and evaporated to yield 1.17 g (56%) of a red oil. The IR.- and ^{1}H-NMR.-spectra (60 MHz, $CDCl_3$) of this crude material showed it to consist of an approximately 5:4:1 mixture of **6a** and the two diastereoisomers **A** and **B** of **9a**. – IR. (film): 1770*s*, 1660*s*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 6.60 (split *t*, J = 4); 6.35 ($d\times d$, J = 17.5 and 10); 5.83 ($d\times d$, J = 17.5 and 10); 5.3–4.9 (*m*); 3.2–2.1 (*m*); 2.2–1.4 (*m*); 1.5–0.8 (*m*). These 7 signals appeared in intensity ratios of 1:0.8:0.2:2:12:11:15. The ratios of **6a**:**9aA**:**9aB** were derived from the intensity ratios of the signals at 6.60, 6.35 and 5.83. After subtracting the signals of **6a** (which are known from *Exper. 2.2*), using the intensity ratio of the signal at 6.60 to the sum of those at 6.35 and 5.83, the following signals are assigned (for multiplets only approximately) to **9a**(**A**/**B**): 6.35 ($d\times d$, J = 17.5 and 10, 0.8 H, H–C(5) of **A**); 5.83 ($d\times d$, J = 17.5 and 10, 0.2 H, H–C(5) of **B**); 5.3–4.7 (*m*, 2 H, 2 H–C(6)); under 3.2–2.3 (*m*, 5 H, H–C(3), 2H–C(α,α')); under 2.2–1.4 (*m*, 4 H, 2 H–C(β,β')); under 1.5–0.8 (*m*, 9 H, H_3C–C(2), 2 H_3C–C(4)).

4.2. *Mixture of 2,6,6-trimethyl-5-morpholino-cyclohex-2-enone* (**8a**) *and 2,4,4-trimethyl-3-morpholino-2-vinylcyclobutanone* (**10a**). – 4.2.1. *In hexane*. To a refluxing solution of 1.41 g (10 mmol) **3** and 1.4 ml (10 mmol) of triethylamine in 20 ml hexane was added with stirring, over a 5 min period 1.18 g (10 mmol) (*E*)-2-methyl-2-butenoyl chloride (**4a**) in 10 ml of hexane. After 48 h at reflux, the mixture was cooled and washed twice with water. The organic layer was extracted with 2×20 ml of 5% HCl-solution and the aqueous phase washed with ether. After addition of excess solid K_2CO_3 to the aqueous phase, the liberated amine was extracted with 2×20 ml of CH_2Cl_2, the resulting organic phase dried and evaporated to yield 0.59 g (26%) of a yellow oil which consisted by its ^{1}H-NMR. spectrum of a 1:3:7 mixture of **8a** and the diastereoisomers **A** and **B** of **10a** (compare also [2]). – IR. (film): 1775*s*, 1635*s*, 1115*s*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): After subtracting the signals for **8a** (known from a comparison with *Exper. 4.2.2*), the following signals are attributed to **10aA** and **10aB**: 6.38 ($d\times d$, J = 17.5 and 10.5, 0.3 H, H–C(5) of **A**); 5.82 ($d\times d$, J = 17.5 and 10.5, 0.7 H, H–C(5) of **B**); 5.3–4.9 (*m*, 2 H, 2 H–C(6)); 3.8–3.5 (*m*, 4 H, 2 H–C(β,β')); 2.62 (*s*, 0.7 H, H–C(3) of **B**); 2.6–2.2 (*m*, 4.3 H, H–C(3) of **A**, 2 H–C(α,α')); 1.40 (*s*), 1.33 (*s*), 1.28 (*s*), 1.18 (*s*) and 1.15 (*s*) (together 9 H, H_3C–C(2), 2 H_3C–C(4)). – MS. (70 eV): 223 (18, *M*), 141 (100), 138 (28), 83 (41).

4.2.2. *In CH_2Cl_2.* To a solution of 1.41 g (10 mmol) of **3** and 1.4 ml triethylamine in 20 ml CH_2Cl_2 was added at RT. with stirring over a 5 min period 1.18 g (10 mmol) of **4a** in 10 ml CH_2Cl_2. After 24 h at RT. the mixture was washed twice with water and the organic layer extracted with 2×20 ml of 5% HCl-solution. The aqueous phase was washed with ether, basified with solid K_2CO_3 and extracted with 2×20 ml CH_2Cl_2. The extract was dried, concentrated and the residue distilled in a Kugelrohr at 80–100°/0.05 Torr to yield 0.58 g (26%) of a pale yellow oil which consisted, according to its ^{1}H-NMR. spectrum, of a 65:22:13 mixture of **8a**, **10aA** and **10aB**. – IR. (film): 1775*m*, 1668*s*, 1630*m*, 1115*s*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): After substracting the signals of **10a(A/B)** (known form a comparison with *Exper. 4.2.1*) the following signals are assigned to **8a**: 6.60 (split *t*, *J* = 4, H–C(3)); 3.8–3.5 (*m*, 4 H, 2 H–C(β,β')); 2.75 (*t*, *J* = 5, 1 H, H–C(5)); 2.7–2.2 (*m*, 6 H, 2 H–C(4) and 2 H–C(α,α')); 1.72 (split *s*, 3 H, H_3C–C(2)); 1.20 (*s*, 3 H, H_3C–C(6)); 1.10 (*s*, 3 H, H_3C–C(6)).

This reaction had been reported to yield 12% **8a** and 10% **10a** when performed in benzene at reflux [2].

5. Preparation of 6,6-dialkylcyclohexa-2,4-dienones (*12a, 12b, 12c* and 13a). – 5.1. *General procedure.* To a cooled solution of the 5-dialkylamino-cyclohex-2-enone in CH_2Cl_2 (20 ml) was added sufficient *m*-chloroperbenzoic acid to ensure complete oxidation of the amine (usually 2–5 mol-equiv. of peracid), while the reaction was followed by TLC. (acetone/hexane 1:9). After 0.25–0.50 h the solution was poured into 25 ml of 10% $NaHSO_3$-solution and extracted with CH_2Cl_2. The organic phase was washed with 10% $NaHCO_3$-solution, dried and evaporated to yield the 6,6-dialkylcyclohexa-2,4-dienone.

5.2. *2,6,6-Trimethylcyclohexa-2,4-dienone* (**12a**) *and 1,4,6,6,9,9-hexamethyl-tricyclo[6.2.2.0^{2,7}]-dodeca-3,11-diene-5,10-dione* (**15a**). Oxidation of 0.52 g (2.5 mmol) of 2,6,6-trimethyl-5-pyrrolidino-cyclohex-2-enone (**6a**) yielded 0.28 g (82%) of **12a** as a pale yellow oil. – UV. (C_2H_5OH): 308 (5100) ([4]: 308 (4700)). – IR. ($CHCl_3$): 1655*s*, 1640*s*, 1600*m* ([4]: 1655, 1640). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 6.9–6.7 (*m*, 1 H, H–C(3)); 6.3–5.9 (*m*, 2 H, H–C(4) and H–C(5)); 1.87 (*d*, *J* = 1, 3 H, H_3C–C(2)); 1.15 (*s*, 6 H, 2 H_3C–C(6)).

This compound dimerized on standing at RT. for several days: 0.25 g (1.8 mmol) of **12a** yielded, after chromatography over silica (ethyl acetate/hexane 1:4), 0.12 g (48%) of the dimer **15a** as colourless cubes, m.p. 110–115° (CH_3OH/H_2O) ([4]: 110–110.5°). – IR. ($CHCl_3$): 1715*s*, 1675*s* ([4]: 1723, 1682). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 6.30 (*d*×*d*, *J* = 8 and 7, 1 H, H–C(11)); 6.20 (br. *s*, 1 H, H–C(3)); 5.45 (*d*, *J* = 8, 1 H, H–C(12)); 2.8–2.4 (*m*, 3 H, H–C(2), H–C(7) and H–C(8)); 1.80 (*s*, 3 H, H_3C–C(4)); 1.30 (*s*, 3 H); 1.26 (*s*, 3 H); 1.15 (*s*, 6 H) and 1.03 (*s*, 3 H) (together 2 H_3C–C(6), 2 H_3C–C(9) and H_3C–C(1)). – MS. (70 eV): 136 (100, *M* of monomer).

5.3. *2-Bromo-6,6-dimethylcyclohexa-2,4-dienone* (**12b**) *and 1,4-dibromo-6,6,9,9-tetramethyl-tricyclo-[6.2.2.0^{2,7}]dodeca-3,11-diene-5,10-dione* (**15b**). From 300 mg (1.0 mmol) of 2-bromo-6,6-dimethyl-5-morpholinocyclohex-2-enone (**8b**) was obtained 130 mg (62%) **12b** as a yellow oil. – IR. ($CHCl_3$): *3160w*, 1666*s*, 1620*m*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 7.42 (*d*×*d*, *J* = 6 and 2, 1 H, H–C(3)); 6.37 (*d*×*d*, *J* = 10.5 and 2, 1 H, H–C(5)); 6.05 (*d*×*d*, *J* = 10.5 and 6, 1 H, H–C(4)); 1.28 (*s*, 6 H, 2 H_3C–C(6)).

On standing at RT. for 0.5 h, dimerization took place to yield 130 mg (100%) of **15b**, m.p. 168–170° (CH_3OH). – UV. (C_2H_5OH): 255 (3400). – IR. (Nujol): 1735*s*, 1695*s*, 1620*m*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.29 (*d*, *J* = 4.2, 1 H, H–C(3)); 6.28 (*d*×*d*, *J* = 8.4 and 7.2, 1 H, H–C(11)); 5.98 (*d*, *J* = 8.4, 1 H, H–C(12)); 3.34 (*d*×*d*, *J* = 8.4 and 4.2, 1 H, H–C(2)); 2.9–2.5 (*m*, 2 H, H–C(7) and H–C(8)); 1.23 (*s*, 9 H) and 1.12 (*s*, 3 H) (together 2 H_3C–C(6) and 2 H_3C–C(9)). – MS. (70 eV): 202 (41), 200 (40, *M* of monomer), 121 (100), 93 (48).

$C_{16}H_{18}Br_2O_2$ (402.14) Calc. C 47.80 H 4.51 Br 39.74% Found C 48.03 H 4.62 Br 41.10%

The dienone **12b** and its dimer **15b** was also obtained from 2-bromo-6,6-dimethyl-5-pyrrolidino-cyclohex-2-enone (**6b**) by using the same procedure.

5.4. *2-Bromo-3,6,6-trimethylcyclohexa-2,4-dienone* (**12c**). From 157 mg (0.52 mmol) of 2-bromo-3,6,6-trimethyl-5-morpholinocyclohex-2-enone (**8c**) was obtained, after 0.5 h, 71 mg (63%) of **12c** as a yellow oil. – UV. (C_2H_5OH): 314 (2380). – IR. ($CHCl_3$): 1660. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 6.25 (*d*, *J* = 9.3, 1 H, H–C(5)); 6.05 (*d*, *J* = 9.3, 1 H, H–C(4)); 2.27 (*s*, 3 H, H_3C–C(3)); 1.24 (*s*, 6 H, 2 H_3C–C(6)). – MS. (70 eV): 216 (53), 214 (51, *M*), 135 (100), 107 (38), 91 (53).

$C_9H_{11}BrO$ (215.10) Calc. C 50.26 H 5.16 Br 37.15% Found C 50.37 H 5.57 Br 37.33%

This compound did not dimerize rapidly at room temperature.

5.5. *2-Methyl-spiro[5.5]undeca-2,4,8-trienone* (**13a**). From 310 mg (1.26 mmol) of 2-methyl-5-pyrrolidino-spiro[5.5]undeca-2,8-dienone (**7a**) (2:1 mixture of the diastereoisomers **A** and **B**), allowing 0.75 h, was obtained, after chromatography over silica (acetone/hexane 1:9), 150 mg (68%) of **13a** as a pale yellow oil. – UV. (CH_3OH): 308 (5700). – IR. ($CHCl_3$): 3150*w*, 1660*s*, 1635*m*, 1585*m*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 6.80 ($d \times qi$, $J = 6.0$ and 1.5, 1 H, H–C(3)); 6.51 (split *d*, $J = 9.3$, 1 H, H–C(5)); 6.15 ($d \times d$, $J = 9.3$ and 6.0, 1 H, H–C(4)); 5.9–5.5 (*m*, 2 H, H–C(8) and H–C(9)); 2.9–1.2 (*m*, 6 H, 2 H–C(7), 2 H–C(10) and 2 H–C(11)); 1.89 (*s*, 3 H, H_3C–C(2)). – MS. (70 eV): 174 (100, *M*), 159 (34), 121 (10), 91 (13).

$C_{12}H_{14}O$ (174.24) Calc. C 82.72 H 8.10% Found C 82.44 H 8.17%

This compound did not dimerize rapidly at room temperature.

6. Preparation of 4,4-dialkyl-2-vinylcyclobutenones (*14d* and *14e*). – 6.1. *General procedure.* To a solution of the 3-morpholino-2-vinylcyclobutanone in 25 ml of CCl_4 at RT. were added, in portions, 3 mol-equiv. of *m*-chloroperbenzoic acid, keeping the temp. below 40° during the addition. The mixture was allowed to stir for 0.75 h at RT. and then washed with 50 ml of 10% $NaHSO_3$-solution and 50 ml of sat. $NaHCO_3$-solution. Drying over K_2CO_3 and careful evaporation of the solvent at 25–30°/100 Torr afforded the crude 4,4-dialkyl-2-vinylcyclobutenone.

6.2. *4,4-Dimethyl-2-vinylcyclobutenone* (**14d**). From 0.94 g (4.5 mmol) of crude 4,4-dimethyl-3-morpholino-2-vinylcyclobutanone (**10d**) was obtained, after column chromatography (*Woelm* neutral alumina, activity grade I, 35 g, elution with ether) and Kugelrohr distillation at 40–50°/50 Torr, 166 mg (30%) of **14d** as a colourless oil. – IR. (CCl_4): 3100*w*, 3050*w*, 1760*s*. – ^{1}H-NMR. (90 MHz, CCl_4): 7.70 (*s*, 1 H, H–C(3)); 6.15 ($d \times d$, $J = 17.4$ and 9, 1 H, H–C(5)); 5.88 ($d \times d$, $J = 17.4$ and 4.2, 1 H, H–C(6)); 5.38 ($d \times d$, $J = 9$ and 4.2, 1 H, H–C(6)); 1.23 (*s*, 6 H, 2 H_3C–C(4)).

Good analytical and mass spectral data could not be obtained on this compound because of its instability.

6.3. *2-Isopropenyl-4,4-dimethylcyclobutenone* (**14e**). From 1.00 g (4.5 mmol) of 2-isopropenyl-4,4-dimethyl-3-morpholino-cyclobutanone (**10e**) was obtained, after Kugelrohr distillation at 45–55°/15 Torr, 0.45 g (74%) of **14e** as a pale yellow, lachrymatory oil. – IR. (film): 3090*w*, 1760*s*, 1670*w*, 1635*w*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 7.71 (*s*, 1 H, H–C(3)); 5.65 (split *s*, 1 H, H–C(6)); 5.09 (split *s*, 1 H, H–C(6)); 1.80 (*t*, $J = 1.5$, 3 H, H_3C–C(5)); 1.22 (*s*, 6 H, 2 H_3C–C(4)). – MS. (70 eV): 136 (98, *M*); 108 (36), 91 (100), 77 (98).

$C_9H_{12}O$ (136.20) Calc. C 79.37 H 8.88% Found C 79.45 H 9.02%

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