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Formation of 2-Cyclohexenones by Friedel-Crafts Acylation of Alkenes with β,γ -Ethylenic Acyl Halides.[1]

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Abstract : Friedel-Crafts acylation of alkenes with β,γ-alkenoyl halides leads to conjugated Al-trienolates able to cyclize into Al-enolates of 2-cyclohexenones through an allowed thermal disrotatory electrocyclization mechanism. Discussion of the product structure is based on two-dimensional NMR experiments (400 MHz) and molecular mechanics studies (GENMOL and MM2).

Functionalized cyclohexene rings are usually prepared by Diels-Alder reaction[2] or Robinson annulation.[3] In the latter case, they result from the cyclization of δ-diketones yielding Wieland-Miescher ketone or structurally analogous ketones. However no general procedure towards isomeric ketones has yet been developed.

The cyclization of 1,3,5-hexatrienes is a powerful synthetic means towards the stereoselective building of carbon-carbon bonds.[4] Therefore, it seemed to us that the preparation of cyclohexenones by electrocyclization of divinyl ketone enolates (3-oxy-1,3,5-hexatriene anions) was worth exploring. Over the years there have been scattered examples of divinyl- or allylvinylketone cyclization. Thus, isophorone was produced from phorone with basic or acid catalysis[5] (and even neat without catalyst).[6] In a similar manner, various treatments of butanone gave rise to many products, including homoisophorones (3,5-diethyl-2,5-dimethyl-2-cyclohexen-1-one and 3,5-diethyl-5,6-dimethyl-2-cyclohexen-1-one).[7]

In the presence of poor Michael acceptor enones, some Robinson annulation processes can include an aldol condensation followed by the cyclization of the divinylketone enolate intermediates. It was clearly shown that the condensation of 1-acetyl-2-methylcyclohexene with cyclohexanone starts with an aldol reaction leading to a diethylenic ketone which can be cyclized *in situ*.[8,9]

Scanio an Starrett published the first report postulating an electrocyclic reaction.[10] The stereochemistry of a Robinson annulation performed in DMSO and involving 2-methylcyclohexanone and 3-penten-2-one was rationalized by a disrotatory cyclization of a trienolate. In the same way, the bicyclization of the cyclodecadienone enolate into a *cis*-ring junction octalone could result from a disrotatory thermal electrocyclization.[11] Later, Magnus discussed some examples of enolate cyclizations including the griseofulvine synthesis and the methylation of eucarvone enolate into 3-methylcarenone.[12]

The thermal cyclization of N-vinyl-α,β-unsaturated amides could also well be considered as a cyclization of an aza-enolate of divinylketone.[13] More recently, the cyclization under pyrolysis conditions of 3-trimethylsilyloxy-1,3,5-trienes (giving rise to *trans*-octalones) was investigated by Fehr.[14] Finally, Scott has

shown that palladium (II)-catalyzed cyclization of 2- or 3-trimethylsilyloxy-1,3,5-trienes yields cyclohexenones.[15]

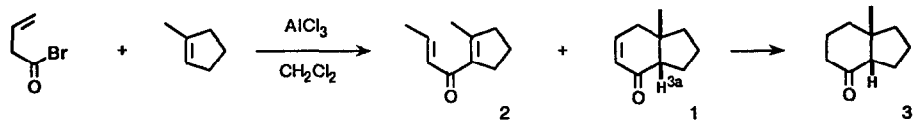
In contrast, thermal cyclization of α,γ-dienone enolates (2-oxy-1,3,5-hexatriene anions) does not occur;[15] photochemical activation being necessary.[16]

In 1979, in a preliminary communication, we suggested that the obtention of octalones or indanones by Friedel-Crafts acylation of cyclohexene or cyclopentene by 3-butenoyl bromide involves the *in situ* enolization of the allylvinylketone intermediates and the allowed thermal cyclization of the Al-trienolates.[17] Soon after, Wolinsky reported similar results but rationalized them by an ionic mechanism (participation reaction).[18] In a second preliminary report,[19] we confirmed the observation of a formal [4 + 2] cycloaddition, which has been, in a particular case, decomposed in the following sequence: acylation reaction, isolation of the intermediate divinylketone and thermal electrocyclization of the corresponding trimethylsilyl enol ether.

In this paper, we explore the potential utility of tandem acylation-cyclization of cycloalkenes to prepare bi- or tricyclic ketones and we discuss the mechanism and the intermediates of the reaction. To do so, the structure of the cyclization products was established with the help of NMR and molecular mechanics studies (both MM2 and GENMOL[20] methods were used).

RESULTS AND DISCUSSION

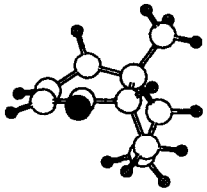
Acylation of 1-methylcyclopentene or 1-methylcyclohexene by 3-butenoyl bromide gives rise to bicyclic products and diethylenic ketones.[17] Yields in bicyclic ketones are increased when using acyl bromide rather than



Scheme 1. Acylation of 1-methylcyclopentene with vinylacetyl bromide.

acyl chloride. Since the indanone moiety is of obvious interest in connection with the synthesis of natural products, such as steroids, we have undertaken the determination of the stereochemistry of the ring junction of enone 1. Enone 1 is obtained from 3-butenoyl bromide and 1-methylcyclopentene (Scheme 1), with 42% yield as a single isomer, along with divinylketone 2 (25%). The major isomer of the corresponding hydrogenated ketone 3 is known[21,22] to have a *cis*-ring junction. As attempts to obtain a crystallized derivative of enone 1 were unsuccessful, we undertook an NMR study of that compound. Proton, carbon, COSY and shift reagent experiments lead us to assign all signals (Figure 5 and exp. part). Moreover, a NOESY experiment has shown a clear interaction between proton H_{3a} and the methyl group implying, therefore, a *cis*-ring junction. It is worth noting that proton H^{3a} appears at 400 MHz as a broad triplet (δ = 2.16 ppm, J = 8.9 Hz) indicating that the ^3J coupling constants between this proton and the two protons on carbon atom C^3 are nearly identical. As a confirmation, we have used molecular mechanics calculations to model energy differences between the two possible geometrical isomers. Both methods (GENMOL and MM2) confirm that the *cis*-isomer (enone 1) is about 1 to 1.5 kcal.mol^{-1} lower in energy than the *trans*-isomer (Figure 1); however, such a difference cannot account, on its own, for the obtention of a single isomer. In addition, it appears from the computed structures of figure 1 that the triplet figure of proton H^{3a} is only possible with the *cis*-isomer (dihedral angles).

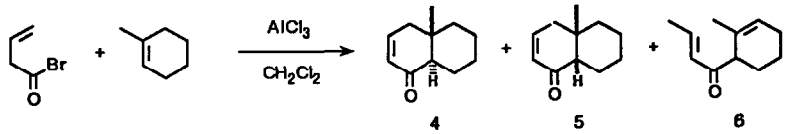
Enone 1:
cis-isomer
GENMOL:
15.4 kcal.mol^{-1}
MM2:
17.6 kcal.mol^{-1}



trans-isomer
GENMOL:
17.0 kcal.mol^{-1}
MM2:
18.5 kcal.mol^{-1}

Fig. 1. Computed structures and energy minima of enone 1 and its *trans*-isomer.

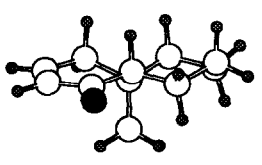
In contrast, acylation of 1-methylcyclohexene leads to a mixture of the two possible diastereoisomers, enones 4 (23%) and 5 (19%) which are obtained along with monocyclic dienone 6 (30%) (Scheme 2).



Scheme 2. Acylation of 1-methylcyclohexene with vinylacetyl bromide.

NMR spectra lead us to propose the *trans*-ring junction for enone 4 and the *cis*-ring junction for enone 5 (signal attribution is based on two-dimensional homo- and heteronuclear proton-carbon correlation spectroscopy experiments : see Figure 5 and exp. part). No NOESY experiments were undertaken, the ^{13}C NMR chemical shifts of the methyl group of enone 4 (17.0 ppm) being characteristic of an axial position.[23] Indeed, the computed structure of the *trans*-isomer (Figure 2) shows that the methyl group is axial with respect to the cyclohexane and the cyclohexenone as well. The value of the methyl chemical shift of enone 5 (28.1 ppm) is comparable to the one obtained with enone 1 (26.0 ppm), in which the *cis*-ring junction was clearly established. Molecular mechanics calculations on enones 4 and 5 gave, depending on the method, a lower energy for *trans*-enone 4 *t*(MM2: 0.6 kcal.mol^{-1}) or for *cis*-enone 5 (GENMOL: 0.7 kcal.mol^{-1}).

Enone 4:
trans-isomer
GENMOL:
19.2 kcal.mol^{-1}
MM2:
13.7 kcal.mol^{-1}



Enone 5 :
cis-isomer
GENMOL:
18.5 kcal.mol^{-1}
MM2:
14.3 kcal.mol^{-1}

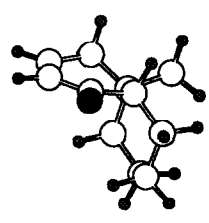
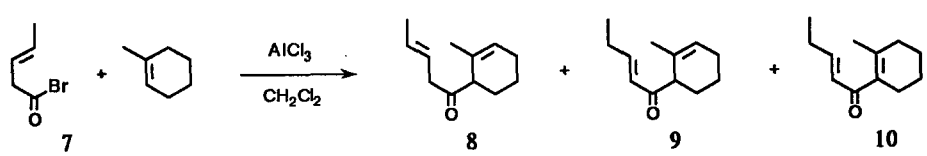


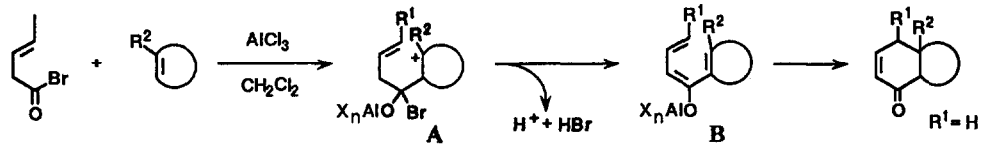
Fig. 2. Computed structures and energy minima of enones 4 and 5 .

Moreover, acylation of 1-methylcyclohexene with 3-pentenoyl bromide 7 leads to a mixture of three dienones 8, 9 and 10 (60%) (Scheme 3). We were not able to isolate any product resulting from a further cyclization.



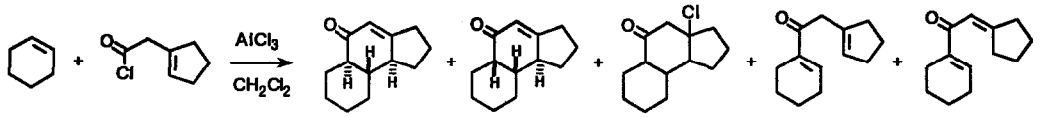
Scheme 3. Acylation of 1-methylcyclohexene with 3-pentenoyl bromide 7.

We propose to rationalize the formation of enones **1**, **4** and **5** with a mechanism involving an allowed thermal disrotatory electrocyclization of Al-enolates **B** (Scheme 4).[24] Enolates **B** are obtained from tetrahedral intermediates **A** by HBr elimination.[25] The introduction of a methyl group (R^1=Me; acyl bromide **7**) generates a strong steric interaction which prevents the cyclization of enolates **B** to occur;[24,26] the reaction leading therefore only to acyclic products, enones **8**, **9** and **10**. The alternative mechanism, namely a participation reaction of carbocations **A**, seems unlikely; indeed, according to Johnson,[27] the presence of a methyl group on the cycle (R^2=Me) should prevent the cyclization to occur when the presence of a methyl group on the side chain (R^1=Me) should, in contrast, favour it. This is not what is observed in our case.



Scheme 4. Mechanism of the formation of indenone **1** or octalones **4** or **5**.

The reaction has then been applied to 1-cyclopentenylacetyl chloride **11** and cyclohexene. It is complex and leads to several tricyclic ketones which are in equilibrium (Scheme 5). Tricyclic enones **12** and **13** (30%)(**12** : **13** *ratio* is generally 2 : 1 but can vary from one experiment to another) are obtained along with chloroketone **14** and dienones **15** and **16**. Acylation in presence of Hünig's base (N-ethyldiisopropylamine)[28] or the use of 1-cyclopentenylacetyl bromide do not modify the results. In contrast, the use of nitromethane as solvent or co-solvent increases the proportion of by-products. Finally, by epimerization, enone **13** leads to enone **12**.



11 **12** **13** **14** **15** **16**

Scheme 5. Acylation of cyclohexene with 1-cyclopentenylacetyl chloride **11**.

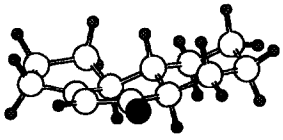
The same mechanism involving an electrocyclization of Al-enolate **B** (Scheme 6) can account for the formation of enones **12** and **13**. It is worthnoting that enolate **B** is not formed from dienone **15** (which proved to be unreactive under the reaction conditions). Two-dimensional NMR experiments (both homo- and heteronuclear correlations) have enabled us to propose the *trans-anti* structure for enone **12** and the *cis-anti* structure for enone **13** (Figures 4 and 5). Indeed, proton H^4 of enone **12** appears at 1.84 ppm as a triplet doublet (J = 11.8; 3.7 Hz) implying a *trans*-ring junction and proton H^9 appears at 1.40 ppm as a quadruplet like figure (J = 11.1 Hz) implying an *anti* relation between H^9 and H^{10} (these observations have been confirmed by selective irradiations of protons H^4, H^9 and H^{10})(Figure 4). On the other hand, proton H^4 of enone **13** appears at 2.25 ppm as a doublet triplet (J = 13.2, 4.5 Hz) implying a *cis*-ring junction. Proton H^9 appears at 1.95 ppm as a broad doublet (J = 11.0 Hz); this coupling constant can be eliminated by selective irradiation of proton H^{10} (2.70 ppm) implying therefore an *anti* relation between protons H^9 and H^{10}.

Molecular mechanics calculations confirmed that the *trans-anti*-isomer (enone **12**) and *cis-anti*-isomer (enone **13**) are the two most stable diastereoisomers out of the four possible ones (Figure 3).

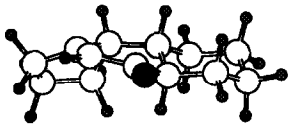
The *cis-syn*-isomer (enone **D**) is most likely the kinetic product of the reaction and is obtained from the hydrolysis of cyclic Al-enolate **C**. The obtention of enone **12** requires therefore two successive epimerizations which occur during workup; molecular mechanics calculations (MM2) on the different enols clearly show that the path to enone **12** through enols **H** (18.7 kcal.mol^{-1}) and **I** (23.2 kcal.mol^{-1}) is lower in energy than the path through enols **E** (22.2 kcal.mol^{-1}) and **G** (18.8 kcal.mol^{-1}).

These observations agree with the formation of **12** and **13** as the only enones of the reaction.

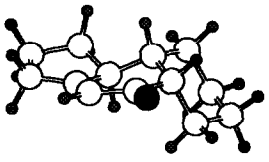
enone **12** :
trans-anti-isomer
GENMOL :
18.7 kcal.mol^{-1};
MM2 :
19.5 kcal.mol^{-1}.



enone **F** :
trans-syn-isomer
GENMOL :
22.9 kcal.mol^{-1};
MM2 :
25.1 kcal.mol^{-1}.



enone **13** :
cis-anti-isomer
GENMOL :
18.7 kcal.mol^{-1}
MM2 :
21.3 kcal.mol^{-1}.



enone **D** :
cis-syn-isomer
GENMOL :
20.6 kcal.mol^{-1}
MM2 :
22.7 kcal.mol^{-1}.

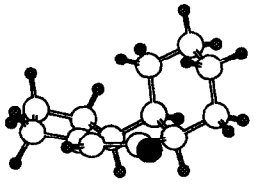
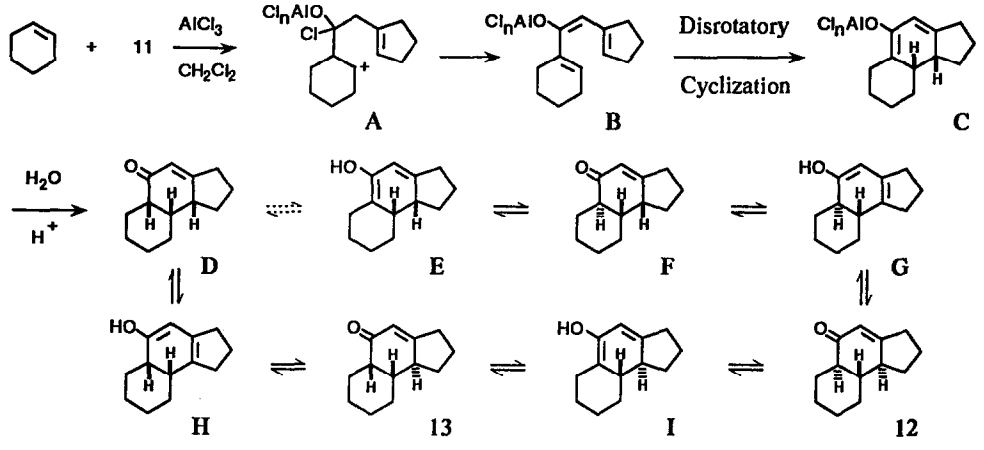


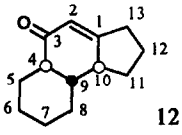
Fig. 3. Computed structures and energy minima of enones **12** , **13**, **D** and **F** .



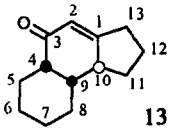
Scheme 6. Mechanism of the formation of tricyclic enones **12** and **13**.

In order to reduce the proportion of side products and to use a regiospecific alkene acceptor, 1-trimethylsilylcyclohexene[29] has been acylated. The orientation of electrophilic vinyl substitution is known to be controllable by the presence of a silicon substituent. Due to the so-called β effect,[30] attack is directed to the carbon atom bonded to silicon.[31] Surprisingly, only diethylenic ketones **15-17** (35% to 65% depending on the reaction conditions) and trimethylsilyldienone **18** (3%) are isolated; the latter probably arises from acyl shift and

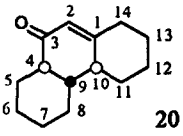
proton elimination. Yield in tricyclic ketone **12** does not exceed 1 % (Scheme 7). This arises probably because the equivalent of carbocation **A** (Scheme 6), although formed, does not lead to trienic enolate **B** and therefore to the products arising from its cyclization into enolate **C**.



12



13



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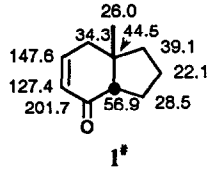
	H^2	H^4	H^9	H^{10}	H^{13}(12, 13), H^{14} (20)	others protons
12	5.84, q, J = 2.2 Hz	1.84, t d, J = 11.8, 3.7 Hz	1.40, q like, J = 11.1 Hz	2.30-2.25, m	2.62, 1/2 AB, d, J = 19.3, 9.4 Hz 2.42, 1/2 AB, t t, J = 19.3, 9.2, 2.2 Hz	2.13 (1, H^{11}, dt, J = 12.0, 6.6 Hz) 1.90 - 1.85 (1, H^{12}, m) 1.90 - 1.80 (2, m.) 1.75 - 1.70 (1, m) 1.67 - 1.57 (1, H^{12}, m) 1.28 - 1.00 (1, H^{11}, m) 1.28 - 1.00 (4, m)
13	5.71, br. s	2.25, d t, J = 13.2, 4.5 Hz	1.95, br. d J = 11.0 Hz	2.70, q like J = 8.0 Hz	2.65, 1/2 AB, d, J = 19.2, 9.7 Hz 2.45, 1/2 AB, t t, J = 19.2, 9.1, 1.9 Hz	2.10 (1, H^{11}, dt, J = 11.9, 6.7 Hz) 1.88 (1, H^{12}, dt, J = 11.6, 7.2 Hz) 1.80 - 1.60 (5, H^5, 2H^{6-7}, H^8, H^{12},m) 1.45 - 1.35 (3, H^5, H^{6-7}, H^8, m) 1.20 - 1.10 (2, H^{6-7}, H^{11}, m)
20	5.76, t J = 2.0 Hz	1.92, d d d, J = 12.7, 11.3, 3.7 Hz	1.35-1.27, m	2.05-1.95, m	2.39, 1/2 AB, quint. like, J = 14.7, 2.0 Hz 2.15-2.05, 1/2 AB, m	2.25-2.18 (2, m) 2.18-1.70 (5, m) 1.46-1.35 (2, m) 1.25-0.88 (5, m)

Fig. 4. ^{1}H NMR (400 MHz) data of enones **12**, **13** and **20**.



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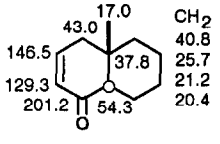
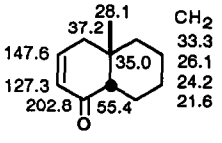
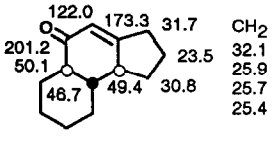


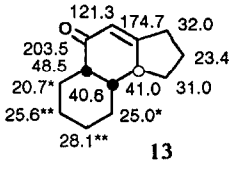
4



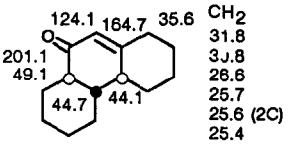
5



12



13



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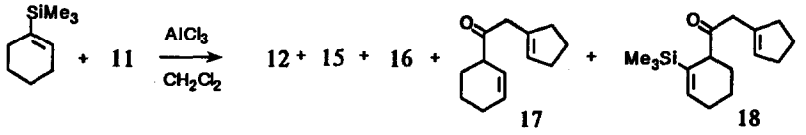
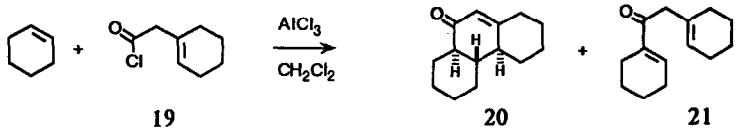
attributions confirmed by the use of shift reagents (Profod and Eufod).

Fig. 5. ^{13}C NMR (100.6 MHz) data of enones **1**, **4**, **5**, **12**, **13** and **20**.



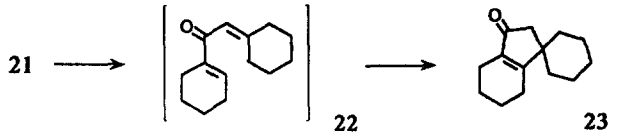
Scheme 7. Acylation of 1-trimethylsilylcyclohexene with 1-cyclopentenylacetyl chloride **11**.

When the acylation was carried out from 1-cyclohexenylacetyl chloride **19** and cyclohexene, only one diastereoisomer of tricyclic enone **20** was isolated (36 %)[8a,32] along with acyclic dienone **21** (22 %) (Scheme 8).



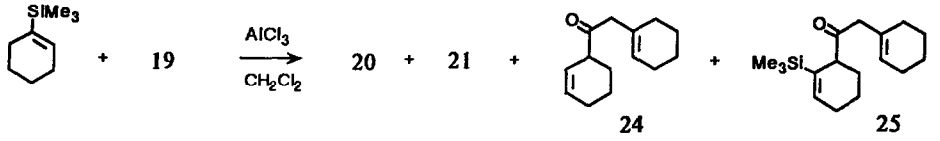
Scheme 8. Acylation of cyclohexene with 1-cyclohexenylacetyl chloride.

Dienone **21** is unreactive under the reaction conditions but, at a higher temperature and in the presence of HCl, it undergoes isomerization into enone **22** which then, yields spiroenone **23** through Nazarov cyclization.[19,33]



Scheme 9. Obtention of spiroenone **23** through Nazarov cyclization.

Again, the use of 1-trimethylsilylcyclohexene favours the formation of acyclic compounds: dienones **21** (40 %) and **24** (30 %) and a small amount of trimethylsilyldienone **25** (3 %) were formed; only 15 % of tricyclic enone **20** were isolated (Scheme 10).



Scheme 10. Acylation of 1-trimethylsilylcyclohexene with 1-cyclohexenylacetyl chloride **19**.

CONCLUSION

The potential use of the aliphatic acylation reaction is compromised by the fact that by-products are commonly obtained. This observation may explain why so few investigations on the mechanism of such reactions have been carried out.[34] Our observation that acylation of alkenes by 3-butenoyl halides leads to Al-enolate formation and, finally, to 2-cyclohexenones represents however a contribution in the synthetic and mechanistic area. On the other hand, acylations of cyclohexene and 1-trimethylsilylcyclohexene occur with different intermediates, the presence of a trimethylsilyl group being of little interest for a greater selectivity of the reaction. Further uses of the electrocyclization of divinyl ketone enolates are currently under investigation.

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EXPERIMENTAL SECTION

General.

CH_2Cl_2 was freshly distilled from P_2O_5 just before being used. 1-Trimethylsilylcyclohexene was prepared according to Paquette's procedure[29]. All reactions were run under an atmosphere of argon in oven-dried glassware. Bulb to bulb distillations were performed with a Büchi GKR-50 microdistillation apparatus. Thin-layer chromatography was performed on silica gel 60 F_{254}. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using Bruker AC 100, Bruker AC 200 or Bruker AM 400-X spectrometers. All two-dimensional experiments were run at 400 MHz. Carbon multiplicities were determined by DEPT sequence experiments and are listed as (s) quaternary, (d) methine, (t) methylene or (q) methyle. Mass spectra were recorded on a Varian MAT 311 mass spectrometer and IR spectra were obtained on a Perkin-Elmer 298 spectrometer.
Calculations were performed on an IBM 3090 200 computer (GENMOL) and a VAX 6320 DEC (MM2). Computed structures were obtained from GENMOL data using EDMOL[35] software.

General Procedure for the Acylation Reactions.

Acyl halide (10 mmol) and cycloalkene (11 mmol) in CH_2Cl_2 (12 mL) were added dropwise to a stirred suspension of $AlCl_3$ (1.47 g, 11 mmol) in CH_2Cl_2 (50 mL) cooled at -80 ° C. The reaction mixture was stirred at -80 ° C for 4 h and then at -20 ° C for 16 h. The cold mixture was then poured into a slurry of ice. Ether (200 mL) was added, the phases were separated, and the aqueous phase was extracted with diethylether (2x40 mL). The combined organic phases were washed with water (2x50 mL), stirred for 0.5 h with saturated solution of $HNaCO_3$ (100 mL) and dried ($MgSO_4$). Concentration in vacuo gave the crude product that was subjected to flash chromatography on silica gel (Merck silica gel 60, 230-400 mesh ASTM).

Acylation of 1-Methylcyclopentene by 3-butenoyl Bromide.

The general procedure was followed with 3-butenoyl bromide (1.5 g, 10 mmol) and 1-methylcyclopentene (0.90 g, 11 mmol). The reaction mixture was stirred at -80 ° C for 4 h and then at -20 ° C for 16 h. Workup as above and flash chromatography on silica gel (pentane/ether, 98/2 and 95/5) afforded **6-methyl-bicyclo[4.3.0]non-3-en-2-one (1)** (630 mg, 42 %) and **1-(2-methylcyclopentenyl)-(*E*)-2-buten-1-one (2)** (375 mg, 25 %). Compound 1 showed: ^1H NMR (400 MHz) δ 6.70 (1, ddd, J = 10.1, 5.0, 3.2 Hz), 5.86 (1, dddd, J = 10.1, 2.6, 1.5, 0.6 Hz), 2.28 (1, 1/2 AB, t , J = 19.3, 3.2 Hz), 2.03 (1, 1/2 AB, dd, J = 19.3, 5.0, 1.5 Hz), 2.16 (1, broad t, J = 8.9 Hz), 1.93 (1, m), 1.79 (1, m), 1.65 (2, m), 1.55 (1, m), 1.36 (1, m), 1.00 (3, s); IR (film) 1670, 1250, 1150 cm^{-1}; mass spectrum, *m/z* 150 (26), 135 (16), 82 (22), 81 (18), 79 (20), 68 (100), 67 (46); HRMS calcd for $C_{12}H_{14}O$ 150.1045, found 150.1051. Compound 2 showed: ^1H

NMR (60 MHz) δ 6.87 (1, dq, J = 14.8, 6.0 Hz), 6.35 (1, dq, J = 14.8, 1.0 Hz), 2.00 (3, br. s), 1.90 (3, dd, J = 6.0, 1.0 Hz); ^{13}C NMR (50.3 MHz) δ 214.0 (s), 60.2 (d), 47.2 (q), 38.8 (t)(2C), 33.7 (t), 27.2 (q), 27.0 (t), 22.5 (t), 22.3 (t). IR (film) 1710, 1670, 1640, 1180, 970 cm^{-1}. Enone **1** in ethanol was hydrogenated (Pd on charcoal) to give ketone **3**.[22a]

Acylation of 1-Methylcyclohexene by 3-Butenoyl Bromide.

The general procedure was followed with vinylacetyl bromide (1.5 g, 10 mmol) and 1-methylcyclohexene (1.06 g, 11 mmol).The reaction mixture was stirred at -80 ° C for 4 h and then at -20 ° C for 16 h. Workup as above and flash chromatography on silica gel (pentane/ether, 98/2 and 95/5) afforded ***trans*-methylbicyclo[4.4.0]dec-3-en-2-one (4)** (377 mg, 23 %), ***cis*-6-methylbicyclo[4.4.0]dec-3-en-2-one (5)** (312 mg, 19 %) and **1-(2-methylcyclohexenyl)-(*E*)-2-buten-1-one (6)** (492 mg, 30 %). Compound **4** showed: ^{1}H NMR (400 MHz) δ 6.73 (1, ddd, J = 10.1, 5.9, 2.3 Hz), 5.93 (1, ddd, J = 10.1, 3.1, 0.6 Hz), 2.27 (1, 1/2 AB, t, J = 18.7, 2.3 Hz), 2.12 (1, 1/2 AB, d, J = 18.7, 5.9 Hz), 2.19 (1, dd, J = 11.6, 3.7 Hz), 2.00-1.10 (8, m), 0.85 (3, s); IR (film) 1678, 1255 cm^{-1}; mass spectrum *m/z* 164 (14), 149 (16), 145 (13), 95 (33), 81 (20), 69 (100); HMRS calcd for $C_{11}H_{18}O$ 164.1201, found 164.1194. Compound **5** showed: ^{1}H NMR (400 MHz) δ 6.78 (1, ddd, J = 10.2, 5.2, 2.8 Hz), 5.88 (1, dm, J = 10.2 Hz), 2.59 (1, 1/2 AB, t, J = 19.6, 2.8Hz), 1.94 (1, dd, J = 11.7, 4.0 Hz), 1.83 (1, 1/2 AB, d, J = 19.6, 5.2 Hz), 1.70-1.10 (8, m), 0.93 (3, s); IR (film) 1678, 1255 cm^{-1}; Compound **6** showed: ^{1}H NMR (60 MHz) δ 6.87 (1, dq, J = 15.8, 6.8 Hz), 6.16 (1, dq, J = 15.8, 1.4 Hz), 5.56 (1, broad s.), 3.27 (1, t. like, J = 6.0 Hz), 1.93 (3, dd, J = 6.8, 1.4 Hz), 1.60 (3, broad s.), 1.65-1.20 (6, m); IR (CCl_4) 1690, 1660, 1630, 1285, 1185, 965 cm^{-1}.

Acylation of 1-Methylcyclohexene with 3-Pentenoyl Bromide 7.

The general procedure was followed with 3-pentenoyl bromide **7** (1.63 g, 10 mmol) and 1-methyl cyclohexene (1.06 g, 11 mmol). The reaction mixture was stirred at -80 ° C for 2 h and at -60 ° C for another 2 h. Workup as above and flash chromatography on silica gel (pentane/ether: 95/5 and 90/10) afforded **1-(2-methyl-2-cyclohexenyl)-(*E*)-3-penten-1-one (8)**, **1-(2-methyl-2-cyclohexenyl)-(*E*)-2-penten-1-one (9)** and **1-(2-methylcyclohexenyl)-(*E*)-2-penten-1-one (10)** (60 %) in a variable *ratio* of about 2:1:1. Compound **8** showed: ^{1}H NMR (100 MHz) δ 5.60 (3,m), 3.15 (3, m), 2.01 (2, m), 1.70 (3, d, J = 4.6 Hz), 1.59 (3, broad s), 1.90-1.50 (4, m); ^{13}C NMR (50.3 MHz) δ 211.2 (s), 130.5 (s), 129.3 (d), 125.4 (d), 123.2 (d), 52.4 (d), 44.9 (t), 26.0 (t), 24.9 (t), 22.4 (q), 19.5 (t), 17.9 (q); IR (film) : 1715, 1670, 975 cm^{-1}. Compound **9** showed: ^{1}H NMR (200 MHz) δ 6.83 (1, dt, J = 15.5, 6.3 Hz), 6.07 (1, broad d, J = 15.5 Hz), 5.53 (1, broad s), 3.11 (1, broad s), 2.11 (2, sextuplet like figure, J = 7 Hz), 1.89 (2, broad s), 1.76-1.37 (4, m), 1.47 (3, broad s), 0.96 (3, t, J = 7 Hz); ^{13}C NMR (50.3 MHz) δ 201.7 (s), 148.7 (d), 130.7 (s), 127.2 (d), 125.2 (d), 51.0 (d), 26.5 (t), 25.3 (t), 24.9 (t), 22.4 (q), 19.5 (t), 12.1 (q); IR (film) : 1695, 1670, 1630, 985 cm^{-1}. Compound **10** showed: ^{1}H NMR (100 MHz) δ 6.82 (1, dt, J = 15.7, 6.2 Hz), 6.13 (1, dt, J = 15.7, 1.5 Hz), 2.35-1.95 (6, m), 1.65 (3, broad s), 1.75-1.50 (4, m), 1.06 (3, t, J = 7.3 Hz); ^{13}C NMR (50.3 MHz) δ 200.5 (s), 151.0 (d), 135.2 (d), 132.7 (s), 129.3 (d), 31.4 (t), 26.9 (t), 25.5 (t), 22.4 (t), 22.2 (t), 21.1 (q), 12.1 (q); IR (film) : 1655, 1620, 1290, 1260, 985 cm^{-1}; Anal. calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.19; Found: C, 80.80; H, 10.20.

Acylation of Cyclohexene by 1-Cyclopentenylacetyl Chloride 11.

The general procedure was followed with 1-cyclopentenylacetyl chloride (1.44 g, 10 mmol) and cyclohexene (0.9 g, 11 mmol). The reaction mixture was stirred at -80 ° C for 4 h and then at -20 ° C for 16 h. Workup as above and flash chromatography on silica gel (pentane/ether, 98/2 and 95/5) afforded **(4*R**,9*S**,10*S**)-tricyclo[8.3.0.0^{4,9}]tridec-1(2)-en-3-one (12)** (380 mg, 20 %) and

(4*S,9*S**,10*S**)-tricyclo-[8.3.0.0^{4,9}]-tridec-1(2)-en-3-one (13)** (190 mg, 10 %) along with **1-(1-cyclohexenyl)-2-(1-cyclopentenyl)ethanone (15)**, **1-(1-cyclohexenyl)-2-cyclopentylidene-ethanone (16)** and **1-chloro-tricyclo[8.3.0.0^{4,9}]tridecan-3-one (14)**(30-40%) in variable proportion. Compound **12** showed: IR (film) 1650 cm^{-1}; mass spectrum, *m/z* 190 (50), 162 (8), 149 (12), 147 (29), 108 (100), 107 (15), 80 (16), 79 (21); HRMS calcd for $C_{13}H_{18}O$ 190.1357, found 190.1368; m.p.: 64-65 ° C. Compound **13** showed: IR (film) 1650 cm^{-1}; mass spectrum, *m/z* 190 (30), 149 (12), 108 (70), 61 (10), 45 (13), 43 (100); HMRS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1368. Compound **14** showed: ^{1}H NMR (200 MHz) δ 2.70 (1, m), 2.50-1.10 (18, m); ^{13}C NMR (50.3 MHz) δ 210.0 (s), 84.0 (s), 51.5 (d), 51.4 (d), 49.7 (d), 44.4 (t), 33.8 (t), 30.8 (t), 28.9 (t), 25.73 (t), 25.67 (t), 25.1 (t), 20.7 (t); IR (film) 1740, 1715, 790, 765 cm^{-1}. Anal. calcd for $C_{13}H_{19}OCl$: C, 68.86; H, 8.44; Cl, 15.63. Found: C, 68.89; H, 8.37; Cl, 15.60. Compound **15** showed: ^{1}H NMR (200 MHz) δ 7.00 (1, br. s), 5.48 (1, br. s), 3.47 (2, s), 2.28 (8, m), 1.91 (2, m), 1.67 (4, m); ^{13}C NMR (50.3 MHz) δ 199.2 (s), 140.6 (d), 139.2 (s), 138.6 (s), 127.5 (d), 40.0 (t), 35.5 (t), 32.6 (t), 26.2 (t), 23.4 (t), 23.2 (t), 22.0 (t), 21.6 (t); IR (film) 1660 cm^{-1}; mass spectrum, *m/z* 190 (11), 110 (6), 109 (100), 81 (67), 79 (24), 77 (6), 53 (18); HRMS calcd for $C_{13}H_{18}O$ 190.1357, found 190.1358. Compound **16** showed: ^{1}H NMR (200 MHz) δ 6.77 (1, m), 6.61 (1,br. s), 2.71 (2, m), 2.40 (2, m), 2.20-1.50 (12, m); IR (film) 1610 cm^{-1}; mass spectrum, *m/z* 190 (10), 110 (8), 109 (100), 81 (47), 79 (27), 53 (17).

Acylation of 1-Trimethylsilylcyclohexene by 1-Cyclopentenylacetyl Chloride 11.

The general procedure was followed with 1-trimethylsilylcyclohexene (1.85 g, 12 mmol) instead of cyclohexene. The reaction mixture was stirred at -80 ° C for 4 h and then from -50 ° C to room temperature in 2 h. Workup as above afforded **12** (20 mg, 1 %), **15** (21 %), **16** (13 %). Reduced reaction time (-80 ° C for 1h and -60 ° C for 3.5 h) led to **15** (760 mg, 40 %), **1-(2-cyclohexenyl)-2-(1-cyclopentenyl)ethanone (17)** (475 mg, 25 %), **1-(2-trimethylsilyl-2-cyclohexenyl)-2-(1-cyclopentenyl)ethanone (18)** (79 mg, 3 %). Compound **17** showed: ^{1}H NMR (200 MHz) δ 5.96 (1, 1/2 AB, *J*= 11 Hz), 5.81 (1, 1/2 AB, *J*= 11 Hz), 5.58 (1, br. s), 3.38 (1, m), 3.35 (2, s), 2.30-1.65 (12, m); ^{13}C NMR (50.3 MHz) δ 209.6 (s), 137.4 (s), 130.2 (d), 128.5 (d), 124.2 (d), 48.5 (d), 43.3 (t), 35.4 (t), 32.6 (t), 24.8 (t)(2C), 23.5 (t), 20.9 (t); IR (film) 1715 cm^{-1}; Compound **18** showed: ^{1}H NMR (200 MHz) δ 6.33 (1, t, *J*= 3.25 Hz), 5.62 (1, br. s), 3.41 (1, m), 3.38 (2, s), 2.41-1.45 (2, m), 0.06 (9, s); ^{13}C NMR (25.1 MHz) δ 209.5 (s), 139.6 (d), 137.3 (s), 135.8 (s), 128.5 (d), 49.1 (d), 43.7 (t), 35.2 (t), 32.4 (t), 26.4 (t), 25.8 (t), 23.4 (t), 16.6 (t), -1.4 (3C) (q) ; IR (film) 1715, 1620, 1250, 840 cm^{-1}; mass spectrum *m/z* 262 (1), 247 (7), 181 (8), 153 (13), 109 (12), 81 (14), 79 (13), 73 (100); HRMS calcd for $C_{16}H_{26}OSi$ 262.1753, found 262.1738.

Acylation of Cyclohexene by 1-Cyclohexenylacetyl Chloride 19.

The general procedure was followed with 1-cyclohexenylacetyl chloride **19** (1.58 g, 10 mmol) and cyclohexene (4.1 g, 50 mmol). The reaction mixture was stirred at -80 ° C for 2 h and -60 ° C for 2 h.Workup as above afforded **(4*R**,9*S**,10*S**)-tricyclo[8.4.0.0^{4,9}]tetradec-1(2)-en-3-one (20)** (734 mg, 36 %) and **1-(1-cyclohexenyl)-2-(1-cyclohexenyl)ethanone (21)** (450 mg, 22 %). Compound **20** showed: IR (film) 1710, 1670 cm^{-1}; mass spectrum, *m/z* 205 (13), 204 (100), 175 (19), 162 (25), 161 (54), 149 (13), 147 (21), 134 (16), 122 (89), 107 (17), 94 (26), 91 (19), 79 (24); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1518; m.p.: 88-89 ° C (reported: 87-88 ° C[32a] ; 85-90 ° C[32b]). Compound **21** showed: ^{1}H NMR (200 MHz) δ 7.00 (1, br. s), 5.52 (1, br. s), 3.32 (2, s), 2.29 (4, m), 2.07-1.96 (4, m), 1.68-1.64 (8, m); ^{13}C NMR δ 199.6 (s), 140.0 (d), 139.1 (s), 132.7 (s), 124.8 (d), 46.1 (t), 28.8 (t), 26.2 (t), 25.5 (t), 23.2 (t), 22.9 (t),

22.2 (t), 22.1 (t), 21.6 (t); IR (film) 1665, 1640 cm^{-1}; mass spectrum, *m/z* 204 (9), 110 (10), 109 (100), 81 (51), 79 (21), 67 (6), 53 (11); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1518.

Acylation of 1-Trimethylsilylcyclohexene by 1-Cyclohexenylacetyl Chloride 19.

The general procedure was followed with 1-trimethylsilylcyclohexene (1.85 g, 12 mmol) and 1-cyclohexenylacetyl chloride **19** (1.58 g, 10 mmol). The reaction mixture was stirred at -80 ° C for 1 h and at -60 ° C for 3.5 h. Workup as above afforded **20** (310 mg, 15 %), **21** (820 mg, 40 %), **1-(2-cyclohexenyl)-2-(1-cyclohexenyl)ethanone (24)** (612 mg, 30 %) and **1-(2-trimethylsilyl-2-cyclohexenyl)-2-(1-cyclohexenyl)ethanone (25)** (83 mg, 3 %). Compound **24** showed: ^1H NMR (200 MHz) δ 5.93 (1, 1/2 AB, *J* = 10.6 Hz), 5.77 (1, 1/2 AB, *J* = 10.6 Hz), 5.52 (1, br. s), 3.21 (1, m), 3.09 (2, s), 2.04-1.53 (14, m); ^{13}C NMR (50.3 MHz) δ 210.4 (s), 131.9 (s), 130.0 (d), 126.1 (d), 124.3 (d), 50.2 (t), 48.14 (d), 28.8 (t), 25.5 (t), 24.9 (t), 24.8 (t), 22.8 (t), 22.1 (t), 20.9 (t); IR (film) 1720 cm^{-1}; mass spectrum *m/z* 204 (8), 123 (11), 109 (14), 95 (100), 81 (64), 79 (14), 67 (11), 53 (11), 44 (54); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1518. Compound **25** showed: ^1H NMR (200 MHz) δ 6.32 (1, t, *J* = 3.1 Hz), 5.64 (1, br. s), 3.50 (1, br. s), 3.18 (2, m), 2.18-1.62 (14, m), 0.08 (9, s); ^{13}C NMR (25.1 MHz) δ 209.9 (s), 139.5 (d), 135.8 (s), 131.6 (s), 126.0 (d), 50.6 (d), 48.6 (t), 28.5 (t), 26.3 (t), 25.6 (t), 25.3 (t), 22.6 (t), 21.9 (t), 18.5 (t), -1.4 (3C) (q); IR (film) 1720, 1270, 1250, 840 cm^{-1}; mass spectrum *m/z* 276 (2), 181 (19), 153 (19), 95 (33), 79 (16), 73 (100), 44 (25); HRMS calcd for $C_{17}H_{28}OSi$ 276.1909, found 276.1905.

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