Diradical-Promoted Two-Carbon Ring-Expansion Reactions by Thermal Isomerization: Synthesis of Functionalized Macrocyclic Ketones

by **Georg Rüedi***[1]) and **Hans-Jürgen Hansen**

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich
(phone: +41 1 635 42 48; fax: +41 1 635 68 53; e-mail: georg@access.unizh.ch)

Dedicated to *Günther Ohloff* on the occasion of his 80th birthday

A new method for the smooth and highly efficient preparation of functionalized macrocyclic ketones has been developed. Pyrolysis of medium- and large-ring 3-vinylcycloalkanones by dynamic gas-phase thermo-isomerization (DGPTI) at 600–630° yielded, under insertion of a previously attached vinyl side chain by means of a 1,3-C shift, the corresponding γ,δ-unsaturated cycloalkanones. The yield of the two-carbon ring-expanded ketones greatly depended on the relative ring strains of substrate and product (5–87%, *cf. Table 5*). The formation of minor amounts of one-carbon ring-expanded cycloalkenes (<10%) can be ascribed to a subsequent decarbonylation step. A reaction mechanism involving initial cleavage of the weakest single bond in the molecule has been established (*cf. Scheme 6*). Recombination within the generated diradical intermediate in terminal vinylogous position led to the observed products, while reclosure gave recovered starting material. Substituents on the vinyl moiety were transferred locospecifically into the ring-expanded products. An isopropenyl group did not significantly affect the isomerization process, whereas substrates bearing a prop-1-enyl group in β-position enabled competing intramolecular H-abstraction reactions, leading to acyclic dienones (*cf. Schemes 9–11*). DGPTI of the 13-membered analogue directly yielded 4-muscenone, which, upon hydrogenation, led to the valuable musk odorant (±)-muscone. Increasing the steric hindrance on the vinyl moiety gave rise to diminishing amounts of the desired γ,δ-unsaturated cycloalkanones. This novel two-carbon ring-expansion protocol was also successfully applied to 3-ethynylcycloalkanones, giving rise to the corresponding ring-expanded cyclic allenes (*cf. Scheme 13*).

1. Introduction. – The construction of medium- and large-ring carbocyclic systems by means of ring expansion has been considered an indispensable tool in synthetic organic chemistry [1–5], and it has become important to develop new synthetic routes to functionalized macrocyclic compounds. Among the many procedures effecting ring expansion, we will focus on isomerization reactions based on chain insertion of previously attached two-carbon units. As we recently reported, a series of medium- and large-ring 1-vinylcycloalkanols were smoothly transformed into the corresponding isomeric, ring-expanded bishomologous macrocyclic ketones by means of dynamic gas-phase thermo-isomerization (DGPTI) at 650° [6–8] (*Scheme 1*). Further, previous work by *Crandall et al.* has shown that cyclooct-4-enone underwent ring contraction to 3-vinylcyclohexanone, when exposed to appropriate heat [9] or light [10]. The thermal behavior of both substrates is interesting in this regard because the formation of their respective isomerization products involves a thermally disallowed concerted 1,3-C shift [11][12]. In both cases, the intermediacy of stabilized diradical intermediates generated

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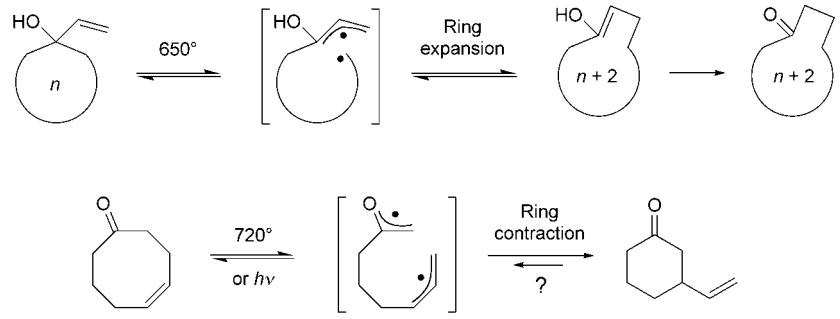
by the homolytic cleavage of the weakest single bond in the substrate molecules was suggested. In the lower case, the α,ω-diradical intermediate should generally be accessible from both directions. The thermal equilibrium may be influenced by both the ring size of the participating structures and substituent effects. The instigating question of the present work was whether medium- and large-ring 3-vinylcycloalkanones might also react in the reverse sense to provide appropriately functionalized γ,δ-unsaturated cycloalkanones.

Scheme 1



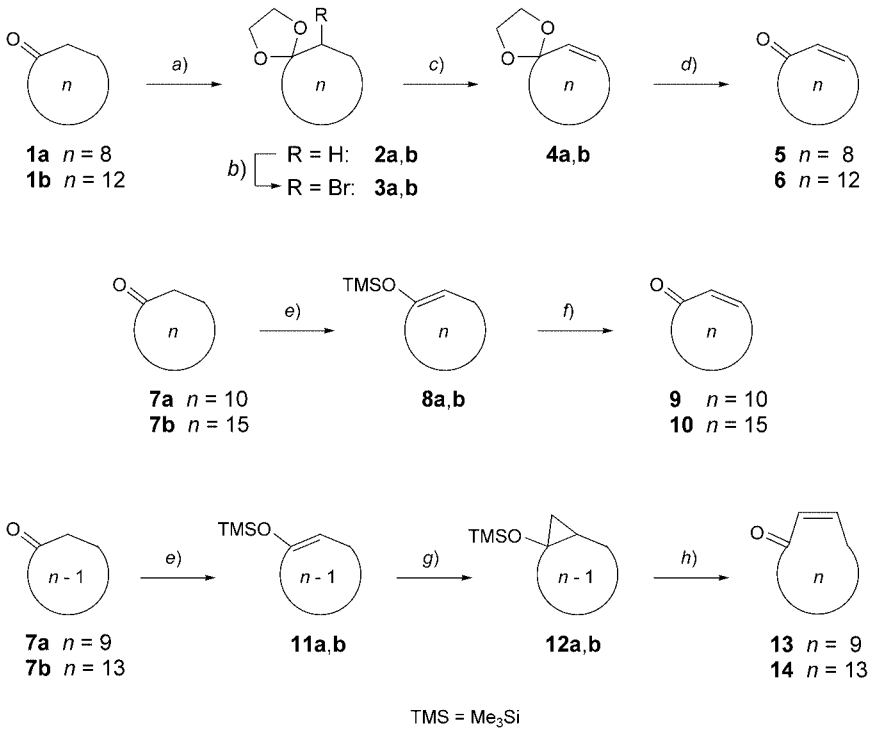
2. Results and Discussion. – 2.1. *Synthesis of Cycloalk-2-enones of Different Ring Size.* Despite their structural simplicity and synthetic utility, the preparation of α,β-unsaturated carbocyclic systems has been considered a challenging task in organic chemistry. Most of the procedures developed over the years are based on halogenation/dehydrohalogenation reactions and S- or Se-mediated methods for oxidations adjacent to the C=O bond [13]. Further, regularly employed methods involve the Pd-assisted oxidation of silyl enol ethers [14] and the oxidative cleavage of 1-(silyloxy)bicyclo-[*n*.1.0]alkanes with $FeCl_3$ *via* C_1 ring enlargement [15][16]. A recently reported procedure developed by *Nicolaou* employs '*o*-iodoxybenzoic acid' (=1-hydroxy-1λ^3,2-benziodoxol-3(1*H*)-one 1-oxide; IBX) to directly transform ketones into the corresponding 2-enones [17][18]. Unfortunately, the IBX-promoted unsaturation method turned out to be inadequate for the preparation of large quantities of material due to the sensitivity of IBX[2]) and the delicate control between single and double unsaturation. As outlined in *Scheme 2*, the requisite α,β-unsaturated cycloalkanones were prepared starting from their saturated analogues. The application of the appropriate dehydrogenation methodology was judged on the basis of the availability of the required cycloalkanones. The low prices of cyclooctanone (**1a**) as well as cyclododecanone (**1b**) allowed a synthetic access to the corresponding α,β-unsaturated target compounds on a multi-gram scale over four steps. The moderate overall yield (45–50%) thus obtained are compensated by both the preparative convenience of this method and the low price of the reagents. Treatment of cycloalkanones **1a**,**b** with ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid (TsOH) in benzene at reflux temperature produced the corresponding ethylene ketals **2a**,**b** in high yields.

[2]) IBX was prepared according to *Frigerio et al.* by oxone oxidation of 2-iodobenzoic acid [19].

Bromination of the ketals **2a**,**b** was accomplished with pyridinium hydrotribromide [20] in THF to afford the crystalline 2-bromoethylene ketals **3a**,**b**, which were subsequently dehydrobrominated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [21][22]. Hydrolysis of the cycloalkenone ketals **4a**,**b** was effected with aqueous acid in a 10 : 1 mixture of THF/acetone, providing the desired α,β-unsaturated cycloalkanones **5** and **6**, respectively. The costs of both the ten- and 15-membered cycloalkanones **7a** and **7b**, respectively, are 20- to 40-times higher than those for **1a** and **1b**. Hence, the corresponding α,β-unsaturated analogues **9** and **10** were prepared *via* a costly two-step procedure entailing high yields. As the second step requires the use of stoichiometric amounts of $Pd(OAc)_2$, the reactions were run on a smaller scale (< 20 mmol). The starting ketones **7a**,**b** were first converted to the corresponding silyl enol ethers **8a**,**b** by LDA (lithium diisopropylamide) deprotonation and subsequent quenching with Me_3SiCl (TMSCl). After oxidation with $Pd(OAc)_2$ in MeCN, the enones **9** and **10** were obtained in almost 90% yield.

Although the nine- and the 13-membered cyclic ketones are commercially available and a similar dehydrogenation sequence would, thus, lead to the desired unsaturated analogues, the exorbitant costs of the starting compounds made such a transformation

Scheme 2



a) Ethylene glycol, TsOH, benzene, reflux; 90–95%. *b*) $PyHBr_3$, THF, r.t.; 75–80%. *c*) DBU, 160°; 80–85%. *d*) 1M HCl, THF/acetone, r.t.; 75–80%. *e*) 1. LDA, THF, −78°; 2. TMSCl, −78°; 90–95%. *f*) $Pd(OAc)_2$, MeCN, r.t.; 85–90%. *g*) Et_2Zn, CH_2I_2, Et_2O, r.t.; 85–90%. *h*) $FeCl_3$, DMF, 60°; 75–80%.

on a larger scale impossible. To circumvent this inconvenience, we chose the approach implying a C_1 ring homologation first reported by *Ito et al.* in 1976 [16][23].

As described above, the readily available starting compounds **1a**,**b** were smoothly transformed into their corresponding silyl enol ethers **11a**,**b**, which were subsequently cyclopropanated in a *Simmons–Smith* reaction using Et_2Zn and CH_2I_2 in Et_2O [24]. Oxidative β-scission of the bridging C–C bond in **12a**,**b** with $FeCl_3$ in DMF at 60° resulted in the direct formation of the ring-expanded α,β-unsaturated cycloalkanones **13** and **14**, respectively. When this reaction was carried out at room temperature, the initially formed 3-chlorocycloalkanones could be isolated and subsequently dehydrochlorinated by treatment with AcONa in boiling MeOH. It is interesting to note that the eight- and nine-membered cycloalkenones **5** and **13**, respectively, were formed only as (*Z*)-isomers for geometric reasons. In contrast, the higher-ring homologues were preferentially obtained in their thermodynamically more-favored (*E*)-forms. However, the presence of minor amounts of the respective (*Z*)-forms was evident from NMR-spectroscopic analyses. In addition, the ^{1}H-NMR spectra of the crude macrocyclic products ($n \geq 13$) **6**, **13**, and **10** indicated a characteristic *doublet* at *ca.* δ(H) 3 (CH_2(2)) with a coupling constant of *ca.* 7.5 Hz, which indicated the presence of the corresponding isomeric β,γ-unsaturated compounds[3]).

2.2. *Preparation of 3-Substituted Cycloalkanone Substrates* **15**–**20**. The synthetic path for the preparation of carbocyclic substrates with a radical-stabilizing substituent at C(3) involved the conjugate 1,4-addition to the α,β-unsaturated cyclic substrates. We started our investigations with the synthesis of 3-vinylcycloalkanones. The vinyl cuprate reagent was prepared by adding a THF solution of vinyl magnesium bromide to a cooled suspension of CuI in THF. The temperature of the resulting solution was maintained below 0° so that the vinylcopper derivative did not undergo thermal decomposition before reaction with the enone substrate. We noticed almost quantitative conversion to **15**–**20**, when the substrates were added in small-scale test runs. However, when the same reactions were run on a larger scale (< 3 g), we observed the competing formation of dimerization products, formed presumably *via* 1,4-addition of the intermediate vinyl enolate to a second substrate molecule, thus leading to dicyclic 1,5-diketones[4]) that exhibited in their ^{13}C-NMR spectrum a characteristic absorption at *ca.* δ(C) 55 (C(2)). We found that the use of a stoichiometric amount of Me_2S under low-concentration conditions (< 0.1M) effected clean transformation to the desired mono-adducts. The results of the 1,4-addition experiments carried out on a multi-gram scale are collected in *Table 1*. The best yield was obtained in the case of the eight-membered **15** (91%). However, the yields decreased slightly with increasing ring size, dropping to 81% in the case of 3-vinylcyclopentadecanone (**20**).

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[3]) As macrocyclic 2-enones are reported to equilibrate to $\alpha,\beta/\beta,\gamma$ mixtures of varying composition, any attempt to isomerize the β,γ-form into the desired α,β-form failed [25].

[4]) Likewise, the formation of such products were formerly observed when α,β-unsaturated carbonyl compounds were treated with organocadmium reagents in the presence of magnesium halides [26].

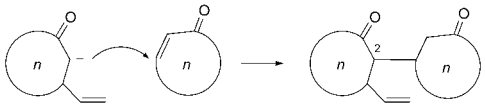
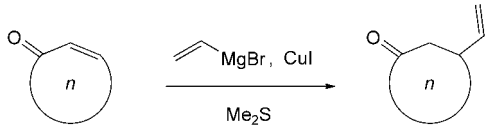


Table 1. *Conjugate 1,4-Addition of Vinyl Cuprate to Different Cycloalk-2-enones*



n	Reactant	Temp. [°]	Product	Yield [%]
8	**5**	– 30	**15**	91
9	**13**	– 20	**16**	88
10	**9**	– 30	**17**	83
12	**6**	– 5	**18**	85
13	**14**	– 10	**19**	82
15	**10**	– 20	**20**	81

Cuprates bearing alkyl substituents on the vinyl moiety were prepared according to *Linstrumelle et al.* [27]. Commercially available 1-alkenyl bromides were added undiluted to a suspension of finely dispersed Li in Et_2O, thus producing the corresponding alk-1-enyl Li reagents, which were added to a suspension of CuI in Et_2O at $-78°$. As summarized in *Table 2*, the enones **6** and **14** were then allowed to react with a series of freshly prepared alkenyl cuprate complexes[5]). As it has long been known, prop-1-enyllithium is formed from 1-bromoprop-1-ene with retention of the double-bond geometry [28–30]. This feature enabled us to diastereoselectively synthesize both (*E*)- and (*Z*)-**21** from **6** using isomerically pure (*E*)- and (*Z*)-bromoalkenes. According to *Scheme 3*, an optically active sample of (*Z*)-**21** was obtained *via* acetalization of (*Z*)-**21** with (−)-butane-2,3-diol [31]. The diastereoisomeric acetals **22** could be separated by repeated chromatography (SiO_2, hexane/AcOEt 80:1), affording enantiomerically pure (−)-(*Z*)-**22**. Removal of the chiral auxiliary provided the optically active ketone (+)-(*Z*)-**21**[6]) in 98% yield. Compounds **23**–**29** were prepared as described above in good to excellent yields. Surprisingly, conjugate addition of (*E*/*Z*)-but-2-en-2-ylcuprate gave rise to (*E*)-**26** and (*E*)-**27** as the single isomers[7]).

Cyclododecanone **31** with an ethynyl moiety in 3-position was prepared accordingly (*Table 2*). However, the use of 1.5 equiv. of Me_3SiI (TMSI) turned out to be essential to achieve 1,4-addition[8]) [34][35]. The TMSI-promoted conjugate addition of copper acetylide, prepared by treatment of a solution of lithium (trimethylsilyl)acetylene in

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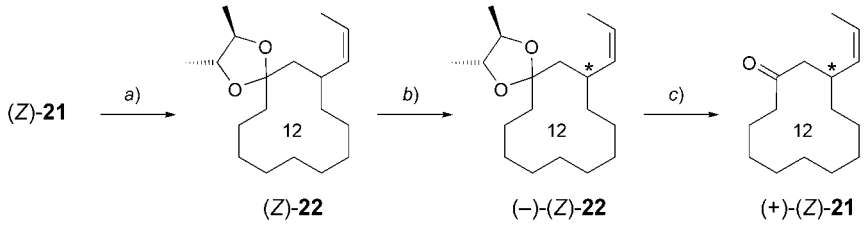
[5]) On adding **6** and **14** to the dark green cuprate preparations, a color change towards red was observed, which disappeared after a few seconds.

[6]) The enantiomeric excess (ee > 95%) was determined by GC analysis. The absolute configuration was not determined.

[7]) This behavior was observed only when excess (*E*/*Z*)-but-2-en-2-yl cuprate was used, and may be explained by the fact that (*Z*)-but-2-en-2-yl lithium is more nucleophilic than its (*E*)-counterpart [32].

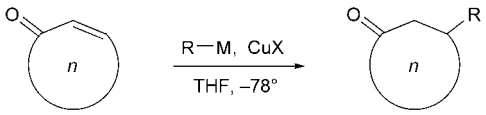
[8]) Coordination of TMSI both to one of the electron pairs to the C=O group and to the alkynyl cuprate (interaction of I-atom with a presumed alkynylcopper π-complex) is considered to be suitable for an addition in a 1,4-manner [33]. An analogous transformation in the absence of TMSI gave only the undesired propargyl alcohol as a result of a 1,2-addition.

Scheme 3

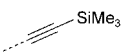


a) (2*R*,3*R*)-Butane-2,3-diol, TsOH, benzene, reflux; 98%. *b*) SiO_2, hexane/AcOEt 80:1. *c*) 1M HCl, THF/acetone, r.t.; 98%.

Table 2. *Conjugate 1,4-Addition of Alk-1-enyl Cuprates to Cycloalk-2-enones* **6** *and* **14**



6 $n = 12$
14 $n = 13$

R	M	X	Product (%)	
			$n = 12$	$n = 13$
	Li	I	(*E*)-**21** (95)	–
	Li	I	(*Z*)-**21** (98)	–
	Li	I	(*E*/*Z*)-**21** (96)	(*E*/*Z*)-**23** (99)
	Li	I	**24** (93)	**25** (94)
	Li	I	(*E*)-**26** (87)	(*E*)-**27** (89)
	Li	I	**28** (81)	**29** (94)
	$SnBu_3$	CN	**30** (78)	–
	Li	I	**31**[a]) (88)	–

[a]) Deprotection of **31** with Bu_4NF afforded the TMS-deprotected analogue **32** (not shown; see *Exper. Part*).

THF with CuI and Me_2S at $-10°$, to enone **6** at $-78°$, and subsequent hydrolysis of the intermediate silyl enol ether with 3M HCl, afforded 3-[(trimethylsilyl)ethynyl]cyclododecanone (**31**) in 88% yield. The TMS group in **31** was then removed by treatment with $Bu_4N^+F^-$ (TBAF) in THF at $-10°$, which led to crystalline 3-ethynylcyclododе-

canone (**32**). In contrast to the acyclic lithium cuprates, we observed no product formation, when 2-cyclododecanone (**6**) was treated in a similar manner with cyclohex-1-enyl cuprate. However, we succeeded in synthesizing 3-(cyclohex-1-en-1-yl-cyclododecanone (**30**) in a yield of 78% by the use of the corresponding Sn reagent [36]. Thereby, 1 equiv. of Bu_3SnCl was added to a solution of freshly prepared cyclohex-1-enyl lithium[9]) to generate a vinylstannane intermediate that was stable at room temperature. Exposure of this reagent to a solution of 1 equiv. of the higher-order (HO) cuprate $Me_2Cu(CN)Li$ in THF effected complete ligand exchange under formation of the HO cyclohex-1-enyl cuprate and tetraalkyltin[10]). Hence, cooling to $-78°$ and subsequent addition of the enone substrate **6** gave rise to 1,4-addition of the cyclohex-1-enyl moiety[11]) to produce **30** as colorless needles (after crystallization from hexane).

The twelve-membered substrate 3-(propa-1,2-dienyl)cyclododecanone (**33**) was synthesized through the following indirect four-step route (*Scheme 4*), because methods for the direct introduction of an allenyl group at the β-position of the α,β-unsaturated ketone moiety had failed. Conjugate 1,4-addition of allenyl cuprate[12]) to **6** was unsuccessful, even with the aid of cuprate-stabilizing additives such as TMSCl or TMSI. On the other hand, direct introduction by means of *Sakurai* reaction [44–47] with propargyl trimethylsilane[13]) and $TiCl_4$ in CH_2Cl_2 provided **33** in only 5% yield, along with the unwanted 1,2-adduct and a dimerization product (*vide supra*). Therefore, the indirect-introduction procedure was adopted. 3-Vinylcyclododecanone (**18**) was converted to the corresponding ethylene ketal **34**, which was cyclopropanated with dibromocarbene (*Scheme 4*). The application of $CHBr_3$/NaOH and benzyl(triethyl)ammonium chloride (TEBA) as a phase-transfer catalyst [50] gave 62% of the corresponding dibromide **35** as a single diastereoisomer[14]). Reaction of **35** with MeLi in Et_2O led to 7-(1,2-propadienyl)-1,4-dioxaspiro[4.11]hexadecane **36**, which was easily deprotected to **33** (50% over 2 steps).

Substrates with a hetero-atom-containing group in β-position were synthesized according to *Scheme 5*. Conjugate addition of KCN to enone **6** quantitatively produced crystalline 3-cyanocyclododecanone (**37**). Treatment of 3-(isopropenyl)cyclododecanone (**24**) with $NaIO_4$ and $KMnO_4$ in a 1:1 mixture of H_2O/acetone at 0° furnished 3-acetylcyclododecanone (**38**) in of 97% yield.

2.3. *Dynamic Gas-Phase Thermo-Isomerization of 3-Substituted Cycloalkanones.* We started our studies on the thermal behavior of cyclic ketones bearing an alk-1-enyl

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9) 1-Chlorocyclohexene was prepared by treating cyclohexanone with PCl_5 [37]. Conversion to the corresponding Li reagent occurred as described for the acyclic derivatives.

10) This high selectivity is due to backbonding effects with Cu [38] as well as the preferential release of a vinyl group from tin [39].

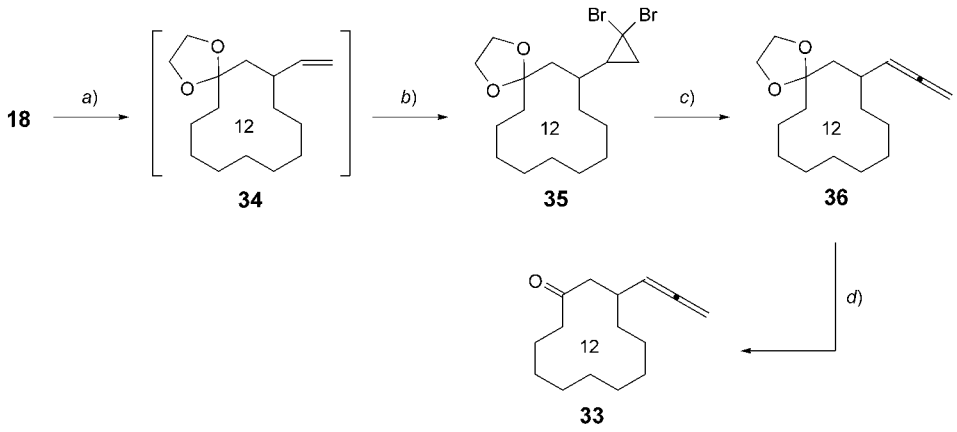
11) Vinyl transfer is favored over alkyl transfer [40].

12) Allenyl bromide was prepared by the CuBr-catalyzed isomerization of propargyl bromide [41]. Conversion to the corresponding Li reagent occurred as described for the alk-1-enyl derivatives. For 1,4-addition procedures of allenyl cuprates, see, *e.g.*, [42][43].

13) Although the use of allyl silanes in *Sakurai* reactions has been extensively described, only very few groups have reported the use of propargyl silanes to prepare 3-allenyl carbonyl compounds [48][49].

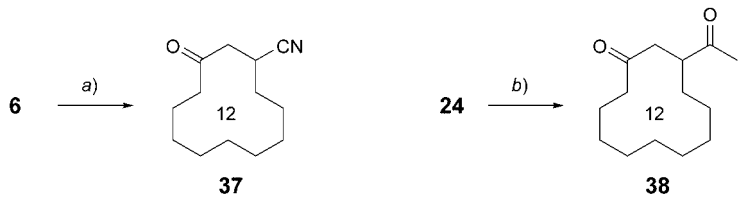
14) The relative configuration was not determined.

Scheme 4



a) Ethylene glycol, TsOH, benzene, reflux; 86%. *b*) $CHBr_3$, 12M NaOH, $BnN^+Et_3Cl^-$, CH_2Cl_2, r.t.; 62%. *c*) MeLi, Et_2O, $-10°$; 56%. *d*) 1M HCl, THF/acetone, r.t.; 89%.

Scheme 5



a) KCN, NH_4Cl, DMF, 70°; 99%. *b*) $NaIO_4$, $KMnO_4$, H_2O/acetone, 0°; 97%.

group in β-position with our model compound 3-vinylcyclododecanone (**18**)[15]). The optimal temperature for the thermal isomerization of **18** was determined by a series of test runs monitored by GC/MS analyses. As compiled in *Table 3*, a reactor temperature of 600° provided the best conversion rates. Besides recovered **18** (6%), the mass spectrum indicated two new isomers (*m*/*z* 206), accounting for 85% of the products observed. Surprisingly, the presence of two additional peaks (7%), exhibiting each a mass of *m*/*z* 180, was evident from the chromatogram. According to *Table 3*, lowering the reactor temperature was adverse to the conversion rate, whereas raising the temperature produced increasing amounts of low-boiling side products, which were not further analyzed. Chromatographic separation of the crude pyrolyzate provided pure samples of both isomerization products (*m*/*z* 206), which were characterized by NMR spectroscopy. The ^{13}C-NMR spectrum of both compounds showed in each case eleven up-field-shifted CH_2 groups, two downfield-shifted CH groups, and a C=O signal.

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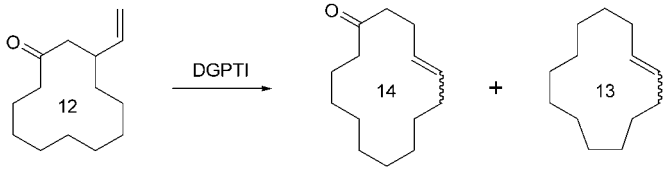
[15]) The substrates were distilled under reduced pressure ($2-4 \times 10^{-2}$ mbar) through a preheated quartz tube (110 cm, 2.5 cm i.d.). The pyrolyzed products were then trapped at low temperature immediately after passing the hot zone. A flow of inert N_2 carrier gas was adjusted to 1.2 l/h. For details, *cf.* [8].

Moreover, the ^{1}H-NMR spectra contained each a signal at *ca.* δ(H) 5.4, indicating olefinic H-atoms. These data are consistent with (*E*)- as well as (*Z*)-cyclotetradec-4-enone ((*E*/*Z*)-**39a**)[16]). Since the olefinic H-atoms appeared as *multiplets*, the C=C bond geometry could not be assigned by means of NOE experiments. However, we succeeded in crystallizing both isomers from hexane, providing in either case colorless needles suitable for X-ray crystal-structure analyses. As depicted in *Fig. 1*, the isomer

Table 3. *Thermal Isomerization of* **18** *at Variable Temperature under Standard Conditions*[15])



18 (*E*/*Z*)-**39a** (*E*/*Z*)-**39b**

	Yield [%]			
Temp. [°]	(*E*)-**39a**	(*Z*)-**39a**	(*E*/*Z*)-**39b**	**18** (recovered)
550	42	19	1	37
580	54	28	5	13
600	57	28	7	6
620	56	24	13	4
650	38	19	18	2
700	17	11	23	0

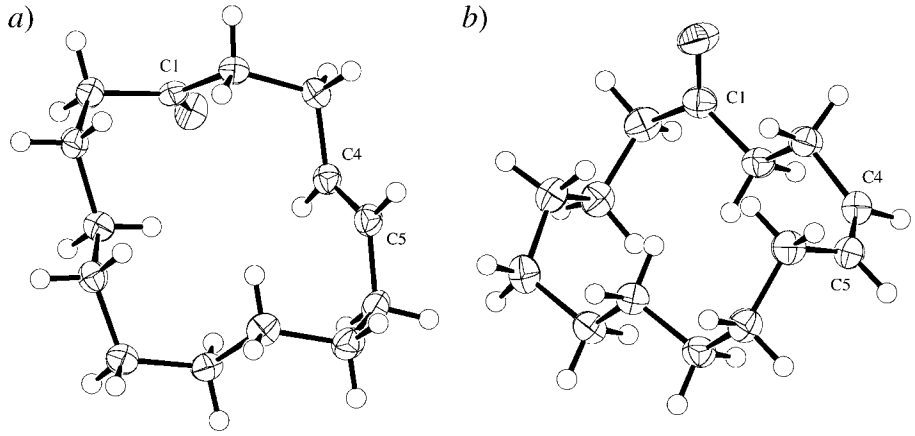


Fig. 1. *ORTEP Plots of the crystal structures of* a) (E)-**39a** *and* b) (Z)-**39a**

[16]) (*E*)-**39a** has been synthesized before by a free-radical macrocyclization procedure utilizing Bu_3SnH/AIBN under high-dilution conditions [51].

that eluted first was (*E*)-**39a**, while its slightly more-polar counterpart exhibited the (*Z*)-configuration.

The missing mass of *m*/*z* 28 in the above side products can be attributed to the loss of CO from (*E*/*Z*)-**39a**, forming thereby the ring-contracted cyclotridecene **39b** as an (*E*/*Z*)-mixture[17]). Indeed, the ^{13}C-NMR spectrum of (*E*/*Z*)-**39b** showed two sets of seven signals only, indicating the inherent symmetry of these cycloalkenes, while the IR spectrum confirmed the absence of a C=O group.

Interestingly, when the above reaction was run at 600°, using a 30-cm quartz tube instead of the standard 110-cm length, we observed significantly larger quantities of starting material **18** (25%), and decreasing amounts of both isomerization products (*E*)- and (*Z*)-**39a** (47 and 22%, respectively), as well as of the decarbonylation products (*E*/*Z*)-**39b** (5%). It was of further interest to subject (*E*)- and (*Z*)-**39a** independently to DGPTI, using quartz tubes of different lengths (110 cm and 30 cm, resp.), as outlined in *Table 4*. To our surprise, when (*E*)-**39a** was pyrolyzed at 600°, we observed a product distribution almost congruent with that obtained by DGPTI of our model compound **18** (*cf. Table 3*). A similar result was observed upon thermolysis of (*Z*)-**39a**, revealing an inverse ratio of (*E*/*Z*)-**39a** 1:1.2. In both cases, upon passing from the 110-cm to the 30-cm tube, increasing amounts of the 14-membered starting components, and decreasing amounts of the ring-contracted compounds **18** and (*E*/*Z*)-**39b** were observed. However, this lower conversion rate could be partly compensated by raising the reactor temperature. Thus, when submitting (*E*)- and (*Z*)-**39a** through the 30-cm tube, preheated at 680°, in both cases, product mixtures comparable to those formed with the 110-cm tube were obtained[18]). The observations that **18** and (*E*/*Z*)-**39** rapidly interconvert indicated the presence of a thermal equilibrium between the twelve-membered **18** and the isomeric fourteen-membered (*E*)- and (*Z*)-**39a**. Since we were limited by the length of the quartz tube, the obtained product mixtures did not exactly represent the total thermal equilibrium. Moreover, as the loss of CO is irreversible under vacuum conditions, the cycloalkene **39b**, once formed, is removed from this equilibrium[19]).

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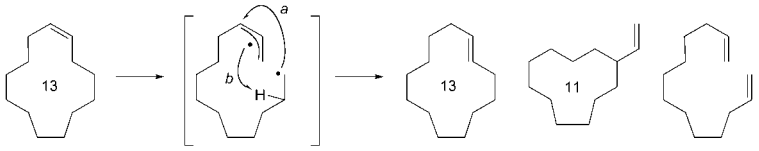
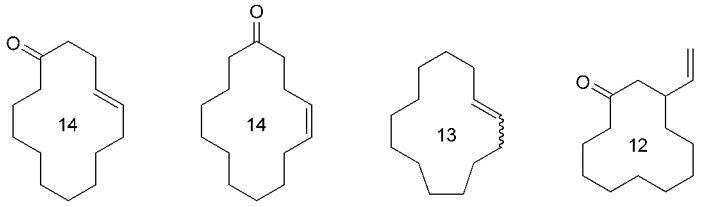
[17]) As exemplified in the case of (*Z*)-cyclotridecene, cyclic olefins may undergo under similar conditions a series of subsequent diradical-mediated isomerization reactions such as (*E*/*Z*)-isomerization, ring contraction to vinylcycloalkanes (path *a*), and stepwise *retro*-ene reaction providing α,ω-dienes (path *b*) [52–54]. We observed the formation of these products only at temperatures > 650°.



[18]) As a result of the higher temperature, the pyrolysate of either experiment contained not identified, low-molecular-mass components (*m*/*z* < 140) accounting for *ca.* 10% of the product mixture.

[19]) Consequently, DGPTI under equal conditions, but using a hypothetical reactor of unlimited length, would result in the sole formation of **39b**, assuming that **39b** undergoes no subsequent reactions.

Table 4. *Product Distribution upon Dynamic Gas-Phase Thermo-Isomerization of (*E*) vs. (*Z*)-***39a*** as a Function of Preheated Quartz-Tube Length*

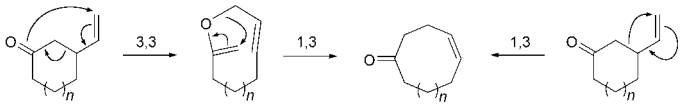


(*E*)-**39a** (*Z*)-**39a** (*E*/*Z*)-**39b** **18**

Substrate	Tube	Products (%)			
		(*E*)-**39a**	(*Z*)-**39a**	(*E*/*Z*)-**39b**	**18**
(*E*)-**39a**	110 cm	63	21	9	4
(*E*)-**39a**	30 cm	68	20	5	2
(*Z*)-**39a**	110 cm	40	47	8	3
(*Z*)-**39a**	30 cm	41	52	4	2

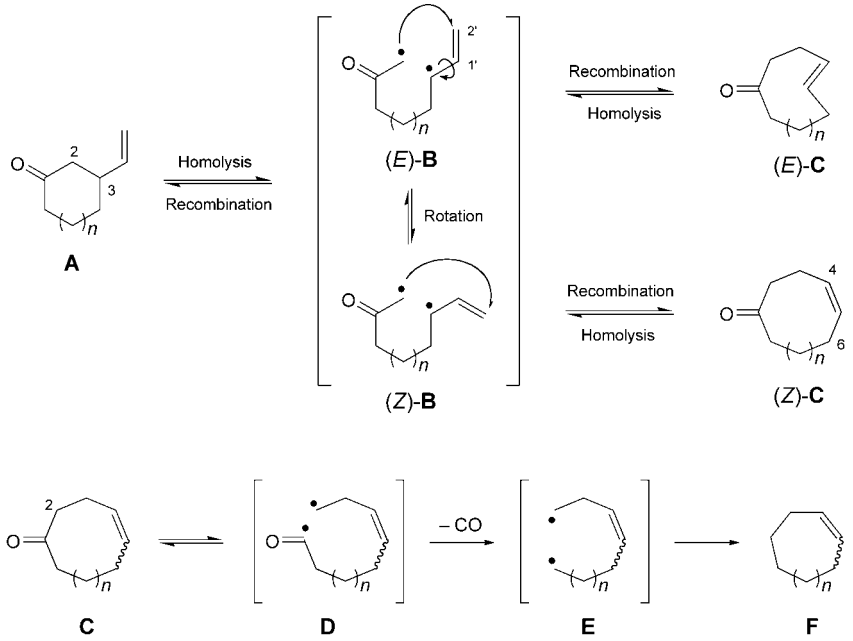
Although a concerted mechanism[20]) has been seriously considered for the DGPTI-mediated thermolysis of cyclic 3-vinyl ketones of type **A**, our data support a stepwise conversion to the ring-expanded product **C** *via* a diradical intermediate **B** (*Scheme 6*). As we have recently observed, when 1-vinylcycloalkanols were pyrolyzed under DGPTI conditions [6–8], homolytic cleavage of the weakest single bond in the substrate **A** is likely to occur. The resulting open-chain intermediate **B**, consisting of two stabilized radicals, an α-acyloyl alkyl radical on one side and an ω-allyl radical on the other side of the chain, undergoes (*E*/*Z*)-isomerization by rotation about the C(3)–C(1′) bond. Intermediate **B** can relax either by going back to starting material **A** by means of reclosing the cleaved single bond, or by going forward to ring-expanded alk-4-enone **C** *via* recombination of C(2) and C(2′) at the terminal vinylic position (*Scheme 6*). Thereby, recombination within (*E*)-**B**, showing (*E*)-arrangement of the allyl radical, leads to the ring-expanded product (*E*)-**C**, while (*Z*)-**B** produces the isomeric (*Z*)-**C**. Although a hypothetical homolytic cleavage of C(6)–C(7) in **C** would result in a partially stabilized diradical intermediate, we did not observe 4-vinyl-cyclododecanone, which would have been formed upon subsequent ring contraction. This further confirms our postulated concept of the cleavage of the weakest single bond in the molecule. On the other hand, homolysis of the C(1)–C(2) bond in **C**, corresponding to a *Norrish* type-I fragmentation, leads to diradical species **D**, which

[20]) There are two concerted mechanisms leading to the ring-expanded enone **C**. However, both pathways involve a thermally disallowed 1,3-shift.



A **A'** **C** **A**

Scheme 6



undergoes a clean decarbonylation reaction. Ring closure of the resulting diradical **E** then produces cycloalkene **F**[21]). As re-opening in the same fashion, giving back intermediate **E**, would involve the cleavage of a nonactivated single bond, the last two steps should be irreversible. It is further noteworthy that no traces of acyclic isomers could be detected, although six-electron processes such as *retro*-ene reactions are generally possible[22]).

The key question, whether the equilibrium between **A** and **C** is shifted to the right or to the left, essentially depends on the relative thermodynamic stability of substrate **A** and its isomerization product **C** at the reactor temperature. The main aspects that have to be taken into account are listed as follows. *1*) A major issue is the degree of double-bond substitution. The monosubstituted olefin **A** is converted into a thermodynamically favored disubstituted olefin **C**. *2*) A further aspect concerns ring-strain effects. The γ,δ-unsaturated ketone **C** exhibits two more cyclic sp^2-hybridized C-atoms than substrate **A**, which adversely affects the flexibility of the skeleton in **C**. In addition,

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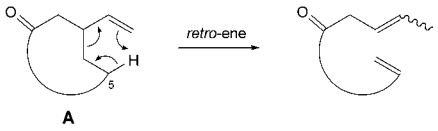
[21]) Alternatively, the formation of **F** is also possible *via Norrish* type-I fragmentation in α'-position of **C**.

[22]) A competing *retro*-ene reaction involving H–C(5) in substrate **A** would lead to open-chain dienones.



passing to the ring-expanded product **C** is accompanied by a change in ring-strain properties. However, whether ring-strain release or increase is observed, largely depends on the ring-strain qualities of the involved carbocyclic systems **A** and **C**, respectively. The activation barrier for the passage through **B** could roughly be evaluated based on the assumption that the activation energy of a specific homolytic process can be approximated by the dissociation energy of the single bond to be cleaved [55–57]. Taking the dissociation energy of an average, unactivated C–C bond (*ca.* 83 kcal · mol^{-1}) and subtracting the radical-stabilization energy[23]) gained by an adjacent acyl group (*ca.* 6 kcal · mol^{-1}) and an allyl group (12 kcal · mol^{-1}), the corresponding activation energy is estimated to be on the order of 65 kcal mol^{-1}[24]). Unfortunately, any attempts to obtain a reliable value for the activation energy by means of computational analyses failed due to the immense number of conformations possible in the investigated macrocyclic systems. The scope and limitations of this clean ring-expansion reaction were explored by extending our studies to substrates of different ring size as well as substrates with vinyl-equivalent C_2-insertion units.

2.3.1. *Thermal Isomerization of 3-Vinylcycloalkanones* **15**–**20**. We subjected a series of 3-vinylcycloalkanones to DGPTI starting with the smallest representative, 3-vinylcyclooctanone (**15**) (*Table 5*)[25]). In remarkable contrast to the smoothly convertible twelve-membered analogue **18**, eight-membered **15** was reluctant to undergo ring expansion upon DGPTI. Only *ca.* 5% (GC/MS) of the expected cyclodec-4-enone (**40a**) could be detected[26]) when **15** was pyrolyzed at 630°. However, this finding is not unexpected, since passing from a cyclooctanone to a cyclodecanone system is accompanied by a ring-strain increase of *ca.* 3 kcal · mol^{-1}.

The next homologous pair was nearly equal in terms of ring-strain properties. Thus, the starting 3-vinylcyclononanone (**16**) (35%) and the isomeric ring-expanded undecanone **41a** (31%) were obtained in similar amounts upon DGPTI at 620°. GC/MS Analysis provided evidence for the presence of a further isomerization product (14%), which was readily purified by column chromatography and characterized as (*E*)-undeca-8,10-dien-2-one ((*E*)-**41c**; *Scheme 7*). The thermodynamically favored (*E*)-form was substantiated in the ^{1}H-NMR spectrum, which exhibited a coupling constant of 15.1 Hz between H–C(8) at δ(H) 6.04 and H–C(9) at δ(H) 5.69. The corresponding ^{13}C-NMR spectrum showed four olefinic signals, among which CH_2(11) appeared at highest field (114.9 ppm), and ^{1}H-NMR showed a characteristic *singlet* at 2.13 ppm, indicating the methyl ketone moiety. As shown in *Scheme 7*, intramolecular[27]) H-abstraction within the generated diradical intermediate **G** leads to the terminal diene (*E*)-**41c**, which represents the thermodynamically most stable constit-

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23) Adjacent functional groups are weakening C–C bonds. Whether the functional group is electron-withdrawing or electron-donating is irrelevant.

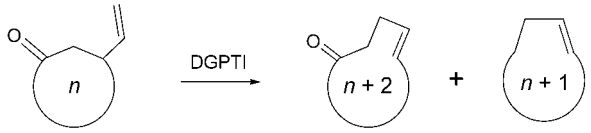
24) Under the reaction conditions (600°, $2-4\times10^{-2}$ mbar, residence time <1 s), an activation barrier of 68 kcal · mol^{-1} can be surmounted with no difficulties.

25) As mentioned in the case of the model compound **18**, the optimal reactor temperature for each substrate was established by a series of test runs.

26) The ^{13}C-NMR spectrum of a chromatographically enriched fraction contained four signals between δ(C) 133–128, accounting for the olefinic C–H groups.

27) Intermolecular processes can be neglected under high-dilution gas-phase conditions.

Table 5. *Effect of Ring Size on the Thermal Isomerization of 3-Vinylcycloalkanones* **15**–**20**

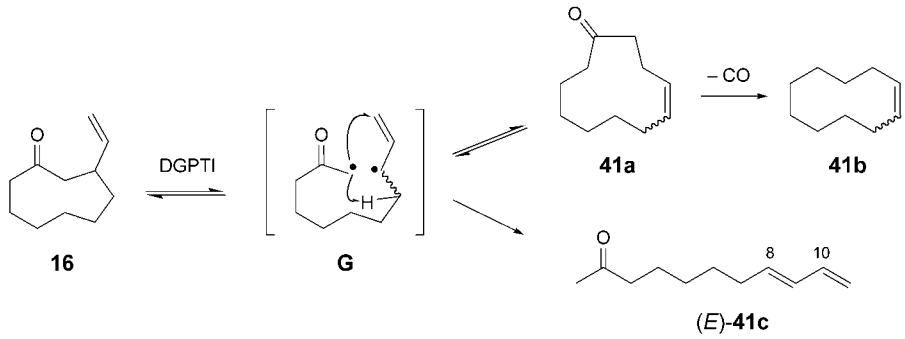


I **II**

n	Substrate	Temp.[a]) [°]	Product **I** (% yield; (*E*)/(*Z*))	Product **II** (% yield)	Substrate[b]) (%yield)
8	**15**	630	**40a** (5; 1.0)[b])	–	90
9	**16**	620	**41a** (35; 1.3)[c])	**41b** (9)[b])	31
10	**17**	610	**42a** (68; 1.7)[d])	**42b** (7)[b])	17
12	**18**	600	**39a** (85; 2.0)[d])	**39b** (7)[c])	6
13	**19**	600	**43a** (87; 1.6)[d])	**43b** (4)[c])	4
15	**20**	600	**44a** (75; 1.7)[c])	**44b** (1)[b])	4

[a]) Optimized temperature. [b]) Not isolated. [c]) Isolated as an (*E*/*Z*)-mixture. [d]) Both isomers could be separated.

Scheme 7



uent since it is acyclic and exhibits a conjugated C=C bond. Hence, the back reaction to **16** or **41a** *via* **G** is unlikely to occur[28]).

As the ring strain decreases by passing from the ten- to the twelve-membered carbocycle, we obtained (*E*/*Z*)-cyclododec-4-enone (**42a**) in a higher yield of 68%. Both isomers could readily be separated by column chromatography, affording 43% of (*E*)- and 25% of (*Z*)-**42a**, respectively. The decarbonylation product **42b** could not be obtained in pure form due to additional nonpolar side products present in the mixture. However, there was still a considerable amount of recovered starting material **17** (17%). Although ring opening by means of intramolecular H-transfer would be

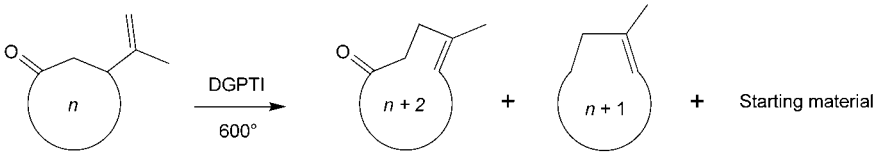
[28]) A control experiment confirmed our assumption. Open-chain (*E*)-**41c** was reluctant to undergo thermal interconversion when submitted to DGPTI at 620°. Furthermore, (*E*)-**41c** showed no (*E*/*Z*)-isomerization at this temperature.

accompanied by a release of ring strain of the tensed cyclodecanone **10**, we could not detect any open-chain products.

Finally, we investigated the thermal behavior of the 13- and 15-membered substrates **19** and **20**, which were cleanly converted to the corresponding ring-expanded bishomologous cycloalkenones **43a** and **44a** in 87 and 75% yield, respectively[29]). In analogy to other 15-membered ketones, cyclopentadec-4-enone (**43a**) smelled fruity and musky. Hydrogenation of its C=C bond yielded the macrocyclic musk odorant cyclopentadecanone, one of the main constituents of naturally occurring musk [58]. In remarkable contrast to the smoothly convertible cyclic 3-vinyl ketones **15**–**20**, DGPTI of comparable acyclic substrates under similar conditions produced only a host of uncharacterized minor components rather than open-chain 4-enones[30]). Also, no reaction or only tar formation was observed when the substrates **15**–**20** were heated under static conditions in a sealed glass tube.

2.3.2. *Thermal Isomerization of 3-(Alk-1-enyl)cycloalkanones* **21** *and* **23**–**30**. With these results in hand, attention could be turned to the question of whether alkyl substituents on the vinyl moiety effect the course of the thermal isomerization reaction. As already summarized in *Table 5*, 3-vinylcycloalkanones **18** and **19** provided best yields in terms of ring-expansion. We, thus, explored a series of twelve- and 13-membered cycloalkanones with an alk-1-enyl group in β-position. With starting compounds comprising an isopropenyl group at C(3), such as in **24** and **25**, we obtained a product distribution resembling that observed for reaction of the vinyl analogues **18** and **19** (*Scheme 8*).

Scheme 8



24 n = 12	(*E*/*Z*)-**45a** (87%)	(*E*/*Z*)-**45b** (6%)	**24** (3%)
25 n = 13	(*E*/*Z*)-**46a** (85%)	(*E*/*Z*)-**46b** (5%)	**25** (4%)

The corresponding ring-expanded products (*E*/*Z*)-**45** and -**46** contain in each case a trisubstituted C=C bond, which complicated the chromatographic separation. However, repeated chromatography of (*E*/*Z*)-**45a** effected enrichment of both isomers, so that further purification of (*Z*)-**45a** was possible by crystallization from hexane. The ^{13}C-NMR spectrum of (*Z*)-**45a** showed two olefinic absorptions at δ(C) 134.6 and 126.6,

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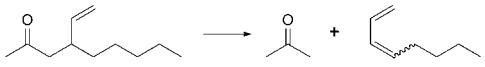
[29]) The lower yield of **44a** may be due to side reactions that already take place in the *Kugelrohr* oven during evaporation of the rather high-boiling substrate **20**.

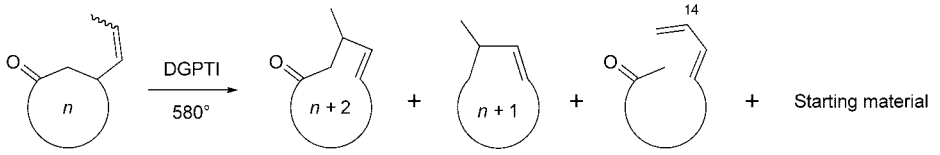
[30]) DGPTI of 3-vinylnonan-2-one at 620° produced several components exhibiting in their GC/MS spectra a molecular peak at m/z 110, which corresponds to the loss of acetone, presumably by the cleavage of the weakest single bond in the substrate.



respectively, the latter appearing as a *doublet* (DEPT experiment). 2D-NOE Measurements exhibited a cross-peak between the Me group at δ(H) 1.69 and the olefinic H-atom at 5.12, in contrast to the isomeric (*E*)-**45a**. The structure of (*Z*)-**45a** was further corroborated by an X-ray crystal-structure analysis (*Fig. 2,a*). Contrarily, the homologous 4-methylcyclopentadec-4-enone (**46a**) could be obtained only as a 1:1 mixture of (*E*)/(*Z*)-isomers. Apparently, an additional Me group at C(1′) on the vinyl moiety did not affect the DGPTI process.

Passing from the isopropenyl to the prop-1-enyl group in β-position of the macrocyclic substrates significantly affected the DGPTI process (*Scheme 9*). Besides the expected ring-expansion products, pyrolysis of **21** and **23** at 580° gave rise to additional isomeric components (*ca.* 30%). Chromatographic separation (silica gel; hexane/AcOEt 50:1) of the crude product mixtures could easily be accomplished due to the large differences in polarity of the individual components. The cyclic olefins **47b** (4%) and **48b** (3%) were eluted first, followed by recovered starting material (16–19%) and the expected cyclic enones **47a** (55%) and **48a** (63%). Finally, the unknown compounds **47c** (10%) and **48c** (9%) were obtained in either case as the last fraction. Surprisingly, apart from the molecular mass and NMR integration, the spectral properties were nearly identical with those of (*E*)-**41c** derived from pyrolysis of **16**. These findings led to the conclusion that (E)-**47c** and (E)-**48c** were pentadeca-12,14-dien-2-one and hexadeca-13,15-dien-2-one, respectively.

Scheme 9



(*E*/*Z*)-**21** *n* = 12 (*E*)-**47a** (55%) (*E*)-**47b** (4%) (*E*)-**47c** (10%) (*E*/*Z*)-**21** (19%)
(*E*/*Z*)-**23** *n* = 13 (*E*)-**48a** (63%) (*E*)-**48b** (3%) (*E*)-**48c** (9%) (*E*/*Z*)-**23** (16%)

The presence of considerable amounts of starting material in the thermodynamic equilibrium is attributable to the lacking driving force of converting a substrate with a disubstituted C=C bond into a ring-expanded product containing a disubstituted C=C bond as well. In remarkable contrast to the isopropenyl case, the ring-expanded products were obtained exclusively in their (*E*)-form, although (*E*/*Z*)-mixtures of the vinyl ketones **21** and **23** were employed. The ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of (*E*)-3-methylcyclotetradec-4-enone ((*E*)-**47a**) exhibited a characteristic *trans*-coupling of 15.4 Hz between the olefinic H-atoms at C(4) and C(5)[31]). In addition, the (*E*)-configuration of the C=C bond was confirmed by an X-ray crystal-structure analysis (*Fig. 2,b*). It is further noteworthy to state that the 3-muscenone (*E*)-**48a** revealed organoleptic properties of musky and fruity quality. Hydrogenation quantitatively afforded the valuable musk odorant (±)-muscone.

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[31]) These signals appear only as a *multiplet*, when recorded at 300 MHz.

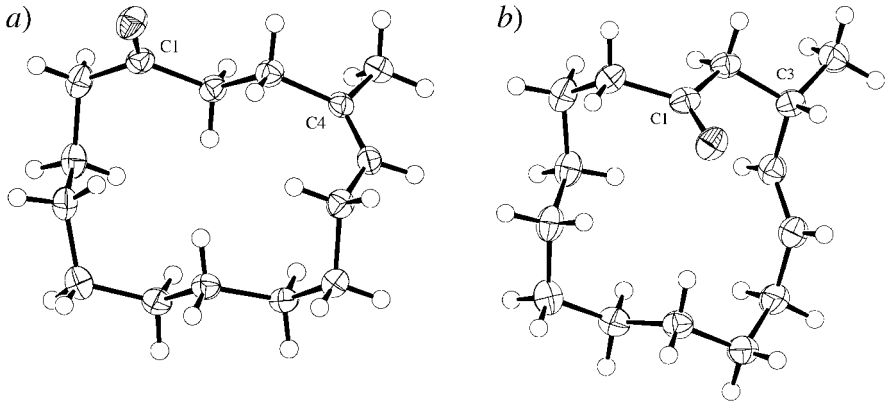
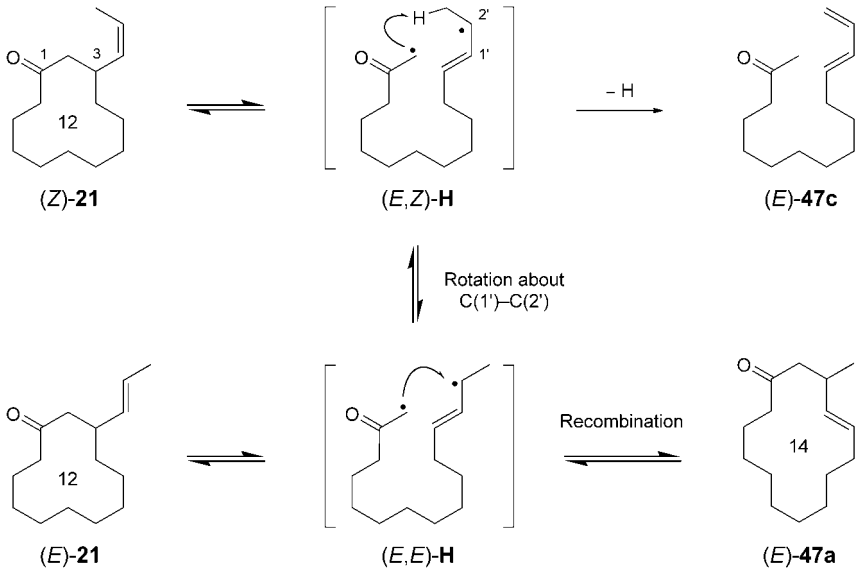


Fig. 2. *ORTEP Plots of the crystal structures of* a) (Z)-**45a** *and* b) (E)-**47a**

To gain insight into mechanistic aspects of this clean transformation, we studied the thermochemical behavior of isomerically pure samples of the twelve-membered prop-1-enyl ketone **21**. To our surprise, when both (*E*)- and (*Z*)-**21** were independently subjected to DGPTI at 580°, we obtained in either case the same product mixture as in the pyrolysis of the 1:1 mixture (*E*)/(*Z*)-**21** (*cf. Scheme 9*). A further striking detail is that the recovered starting material present in both product mixtures consisted each of a 1:1 mixture of (*E*/*Z*)-**21** instead of the initially submitted pure isomers. A plausible mechanism rationalizing these findings is displayed in *Scheme 10*. Initial homolysis of the weakest single bond in both (*Z*)- and (*E*)-**21** results in the formation of their respective diradical intermediates (*E*,*Z*)- and (*E*,*E*)-**H**, which experience rapid interconversion by rotation about C(1′)–C(2′). The (*Z*)-arrangement of the methyl allyl radical in (*E*,*Z*)-**H** is suitable for an intramolecular H-transfer, forming the open-chain dienone (*E*)-**47c**, while intermediate (*E*,*E*)-**H** enables unhindered recombination in the usual manner to give the ring-expanded product (*E*)-**47a**. On the other hand, rotation about C(3)–C(1′) within the diradical intermediate would lead to the (*Z*)-isomers of **47** (*cf. Scheme 6*). However, the formation of the latter could not be observed, presumably due to the thermodynamically disfavored geometry of the required intermediates (*Z*,*E*/*Z*)-**H** compared with (*E*,*E*/*Z*)-**H**. The hypothesis of a fast (*E*/*Z*) isomerization with respect to C(1′)–C(2′) during DGPTI was further supported by pyrolysis of optically active starting material. The entire chiral information was lost when enantiomerically pure (+)-(*Z*)-**21** was thermolyzed at 580°. Even the starting material present in the mixture could be recovered only as a racemic mixture. Hence, H-abstraction and -recombination seem to be the rate-limiting steps, while (*E*/*Z*)-equilibration takes place rapidly. Moreover, the observation that the independent pyrolysis of (*Z*)- and (*E*)-**21** and (+)-(*Z*)-**21** produced exactly the same result strongly speaks for a nonconcerted mechanism involving diradical structures. In contrast, a hypothetical, concerted 1,3-C shift would be accompanied by at least partial conservation of stereochemical information.

Similar results were obtained when an additional Me substituent was placed at C(1′) on the vinyl moiety. According to *Scheme 11*, DGPTI at 590° of the twelve- and 13-membered substrates (*E*)-**26** and (*E*)-**27**, bearing a but-2-en-2-yl group in β-position,

Scheme 10



led to the corresponding C_2 ring-expanded 3,4-dimethylcycloalkenones (*E*)-**49a** and (*E*)-**50a**. In comparison with **47a** and **48a**, the decrease in yield of the former compounds (< 50%) in favor of the acyclic dienones **49c** and **50c** (*ca.* 15%) may be attributed to increased steric hindrance. Even though the substrates were submitted predominantly as (*E*)-isomers ((*E*)/(*Z*) > 9:1), the recovered starting material in the product mixture (*ca.* 20%) was a 1:1 mixture of both isomers. This finding is in excellent agreement with the postulated rapid (*E*) → (*Z*) interconversion by rotation about C(1′)–C(2′) on the stage of the diradical intermediate. But, in contrast to **21** and **23**, the ring-opened products **49c** and **50c** were obtained as (*E*)/(*Z*)-mixtures. Since the difference in thermodynamic stability between the (*E*)- and the (*Z*)-form is relatively small in trisubstituted olefins, the accompanying formation of the (*Z*)-forms might be derived from the initially formed (*E*)-isomers[32]).

Conversely, placing the additional Me group at C(2′) on the vinyl moiety significantly affected the course of the DGPTI process (*Scheme 11*). Pyrolysis of substrates with geminal Me groups at C(2′), such as in **28** and **29**, gave rise to the predominant formation of open-chain dienones (*E*/*Z*)-**51c** and -**52c**. To our surprise, among the expected ring-expanded products, only the 15-membered 3,3-dimethylcycloalkenone (*E*)-**52a** was formed, whereas the analogous 14-membered product was not detected. The ^{1}H-NMR spectrum of (*E*)-**52a** showed a *singlet* at δ(H) 1.09, indicating the six H-atoms of the geminal Me groups, and H–C(4) and H–C(5) exhibited a coupling of 15.7 Hz, providing evidence for an (*E*)-configured endocyclic C=C bond.

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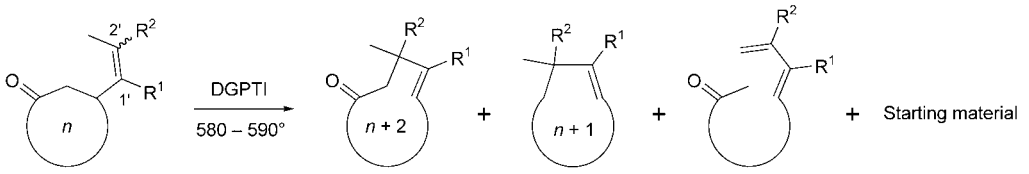
[32]) The activation energy for (*E*/*Z*) isomerization is *ca.* 60 kcal · mol^{-1}, depending on the radical-stabilizing nature of the substituents attached to the olefinic centers [59][60].

Scheme 11



R^1 = Me, R^2 = H:				
(*E*)-**26** *n* = 12	(*E*)-**49a** (46%) +	(*E*)-**49b** (5%) +	(*E*/*Z*)-**49c** (16%) +	(*E*/*Z*)-**26** (22%)
(*E*)-**27** *n* = 13	(*E*)-**50a** (48%)	(*E*)-**50b** (6%)	(*E*/*Z*)-**50c** (14%)	(*E*/*Z*)-**27** (21%)
R^1 = H, R^2 = Me:				
28 *n* = 12	- - - +	- - - +	(*E*/*Z*)-**51c** (38%) +	**28** (28%)
29 *n* = 13	(*E*)-**52a** (15%)	(*E*)-**52b** (2%)	(*E*/*Z*)-**52c** (37%)	**29** (19%)

There are two major reasons responsible for the excessive decrease in yield of the ring-expanded products. First, the sterically demanding $Me_2C(2')$ group renders a recombination in the usual manner difficult, *i.e.*, the forced (*Z*)-arrangement of the methyl-allyl-radical moiety within the diradical intermediate is perfect for intramolecular H-transfer rather than recombination under ring expansion (*cf. Scheme 10*). Second, the ring expansion has no driving force, since it results in the conversion of a trisubstituted into a disubstituted olefin.

The 'perfume qualities' of the macrocyclic compounds have been roughly evaluated. Besides (*E*)-**52a**, (*E*)-**49a** and (E)-**50a** (musky, floral, fruity) were classified as interesting odoriferous compounds[33]).

Finally, we investigated the thermal behavior of 3-(cyclohex-1-enyl)cyclododecanone (**30**) (*Scheme 12*). DGPTI at *ca.* 600° provided only very poor conversion rates. According to GC/MS analysis, the expected bicyclo[12.4.0]octadecane **53a** was obtained as a 1:1 mixture of (*E*/*Z*)-isomers in low yield (22%), accompanied by a double amount of recovered **30**, which could not be removed from **53a**. Furthermore, the product mixture contained an open-chain compound identified as (*E*/*Z*)-**53b** (24%). In contrast to the ring-opened products derived from DGPTI of other alk-1-enyl substrates, intramolecular H-abstraction must have occurred from C(4) of the initially generated diradical intermediate **J**. As C(1′) and C(2′) are both part of the same six-membered ring, rotation about the bond between these two centers cannot be accomplished. H-Abstraction, thus, occurs rather at C(4) than at C(3′). On the other hand, intermediate **J** can undergo rotation about C(3)–C(1′), allowing the formation of the two isomeric intermediates (*E*)- and (*Z*)-**J**. Recombination between the radical at C(2) and the allyl radical at C(2′) gave the corresponding bicyclic (*E*)- as well as (*Z*)-**53a**.

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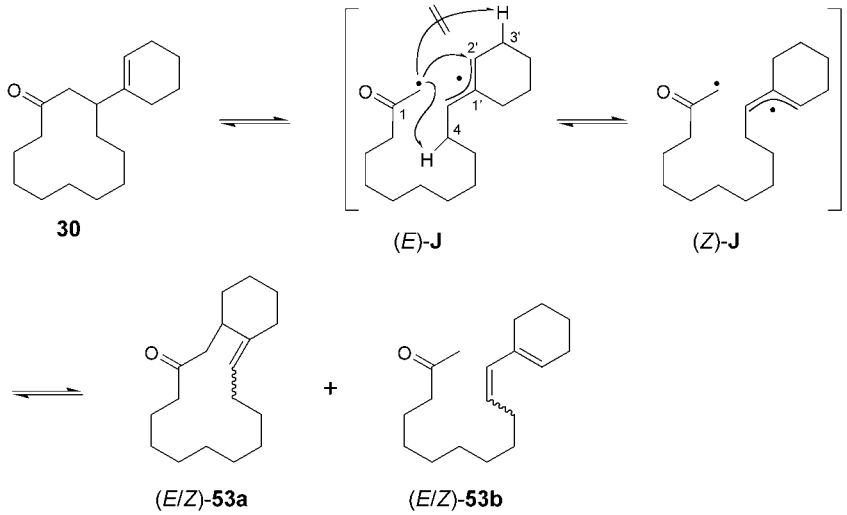
[33]) The 4-muscenone (*E*)-**50a** had already been synthesized *via* macrocyclization [25] and ring expansion [61][62]. Compound (*E*)-**52a** had previously been prepared *via* a multistep ring-expansion procedure with cyclopropene [63]. No items have been recorded, however, for all other substituted macrocyclic ketones.

Scheme 12



2.3.3. *Thermal Isomerization of 3-Ethynylcycloalkanones* **31** *and* **32**. It was of interest to extend our studies to substrates with an ethynyl substituent in β-position. The crucial question was whether 3-ethynylcycloalkanones might react under DGPTI conditions in a similar manner to yield the corresponding cyclic allenes[34]). However, this assumption was based on the mechanistic hypothesis that cleavage of the weakest single bond in **31** or **32** would result in a stabilized α-acyloyl-alkyl ω-propargyl[35]) diradical **K**, undergoing subsequent recombination (*Scheme 13*). Indeed, pyrolysis of **31** at 540° gave rise to the formation of an isomeric compound (13%) besides a large amount of recovered starting material (78%)[36]). Chromatographic separation of the crude product mixture provided a pure sample of the isomerization product, which was found to be cyclotetradeca-3,4-dienone (**54**)[37]). Its IR spectrum exhibited a characteristic band at 1962 cm^{-1}, and the ^{1}H-NMR spectrum showed two signals for olefinic H-atoms at δ(H) 5.31 and 5.11, respectively. The ^{13}C-NMR spectrum of **54** showed a typical low-field-shifted absorption at δ(C) 205.2, indicating the sp-hybridized C(4)-atom.

DGPTI of the trimethylsilyl compound **32** carried out as above led to the isomerization products **55** and **56** in a 4 : 3 ratio, besides recovered **32** (81%). Following chromatographic separation, the structural features of the unknown compounds were established by NMR and IR spectroscopy. Apart from the ^{1}H-NMR spectrum, which

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34) The kinetic stability of cyclic allenes decreases rapidly with diminishing ring size. Unsubstituted cyclic allenes are stable only at room temperature when the number of C-atoms is ≥ 9 [64].

35) A propargyl group is considered to stabilize an adjacent radical center approximately to the same extent as an allyl group (*ca.* 12 kcal · mol^{-1}) [57].

36) Applying a reactor temperature of 600°, as it was the case in DGPTI of most olefin substrates, produced plenty of low-molecular-weight components accounting for 90% of the products observed. Gradually lowering the temperature by steps of 10° eventually led to a value of 540°, at which optimal conversion occurred.

37) The parent compound, cyclotetradeca-1,2-diene, was first synthesized by *Mühlstädt* in 1967 [65].

displayed only one signal for an olefinic H-atom at δ(H) 4.87, the structural properties of **55** were quite similar to those of **54**, in agreement with the expected 3-(trimethylsilyl)cyclotetradeca-3,4-dienone (**55**). On the other hand, the spectral data of the minor component were consistent with the open-chain enyne **56**, which was formed as a 1:1 mixture of (*E*/*Z*)-isomers. The IR spectrum of (*E*/*Z*)-**56** showed two absorptions at 2254 and 2145 cm^{-1}, indicating the presence of two nonequivalent C≡C bonds, one in conjugation with an (*E*)-, the other with a (*Z*)-olefin. Apparently, the bulky TMS group in **32** seems to have an adverse effect on the recombination process, favoring intramolecular H-transfer. In compounds **54** and **55**, 1,3-shift of the cumulene-type β,γ-C=C bond into α,β-position would be accompanied by a large increase in thermodynamic stability. However, the corresponding $\alpha,\beta:\gamma,\delta$-unsaturated isomers of **54** and **55** were not detected[38]).

In the light of the observation that **31** resulted in a host of unidentified side products, when pyrolyzed at 600°, it seemed interesting to subject pure **54** to DGPTI (*Scheme 13*, *a*). However, a similar complex product mixture was obtained. We, therefore, assume that DGPTI of **31** at 600° primarily produced allene **54**, which thermally decomposed, presumably *via* α-cleavage, resulting in a highly reactive butan-2,3-dien-1-yl species. Alternatively, the thermal exposure of a substrate with an allenyl substituent in β-position would represent a further way to generate this reactive radical species. As outlined in *Scheme 13*, *b*, DGPTI of **33** might effect homolysis of the C(2)–C(3) bond under formation of diradical intermediate **L** consisting, on one side, of the mentioned butan-2,3-dien-1-yl radical species. However, recombination to the 14-membered *exo*-methylidene compound **57** could not be observed. Instead, a broad variety of low-molecular-weight products were formed when **33** was pyrolyzed in a temperature range of 450–600°.

In contrast to the highly reactive 3-propargyl- as well as 3-allenylcyclododecanones **31**–**33**, substrates with a heteroatom at the center of recombination, were reluctant to undergo any reaction. DGPTI of both 3-cyano- and 3-acetylcyclododecanone **37** and **38** to yield the corresponding cyclic ketenimine and enol ether, respectively, failed as well.

Conclusions. – We have demonstrated that placing radical-stabilizing groups such as vinyl or ethynyl moieties in β-position of cyclic, medium- and large-ring ketones leads to a clearly defined weakest single bond that undergoes clean homolysis upon exposure to dynamic gas-phase thermo-isomerization conditions. Intramolecular recombination of the generated diradical intermediates affords two-carbon ring-expanded γ,δ-unsaturated cycloalkanones or cyclic allenes. The facility and very high efficiency coupled with the synthetic utility of functionalized, medium- and large-ring carbocyclic systems makes this ring-expansion protocol a valuable method for the construction of synthetically useful macrocyclic target molecules.

We thank *N. Walch*, Dr. *G. Hopp-Rentsch*, and *S. Jurt* for specific NMR measurements, Dr. *A. Linden* for X-ray crystal-structure analyses, and the MS department and the laboratory of microanalysis. Financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

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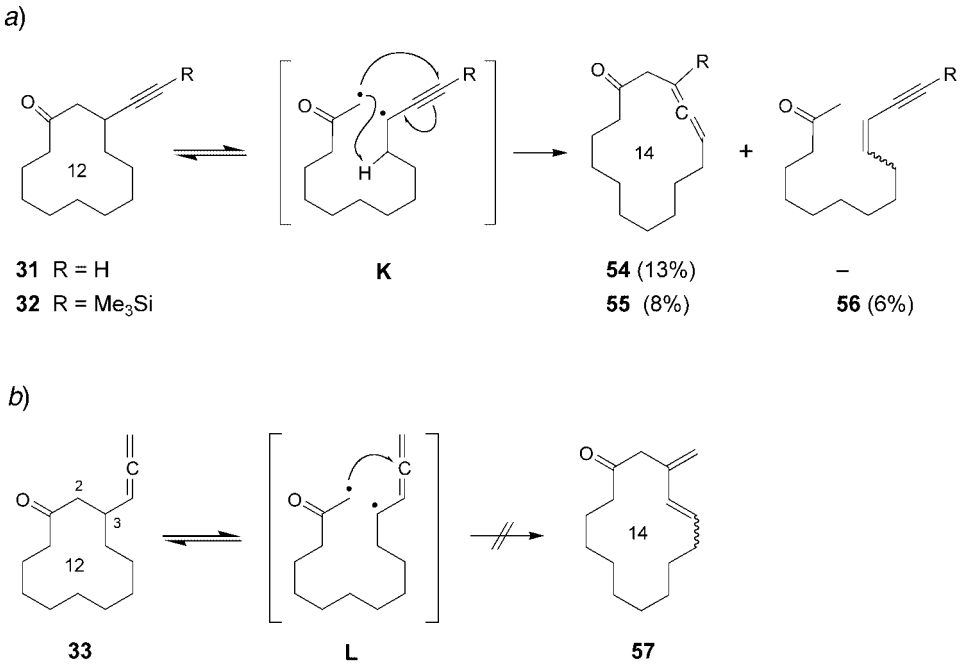
[38]) In contrast, treatment of **55** with catalytic amounts of TBAF in THF at 0° afforded the $\alpha,\beta:\gamma,\delta$-unsaturated isomer of **54**.

Scheme 13



Experimental Part

General. Solvents were purified prior to use by standard procedures. TLC: Glass plates covered with silica gel *60* F_{254} (*Merck*); visualization by UV light or by spraying with 'mostain' solution ($(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ (40 g), $Ce(SO_4)_2$ (0.8 g), 10% H_2SO_4 soln. (800 ml)) and heating (blue spots). Column chromatography (CC): silica gel *60* (*Merck*), 0.040–0.063 mm. M.p. (not corrected): *Mettler FP 5/52*. IR Spectra: *Perkin-Elmer 1600 Series FT-IR* spectrometer; wavenumbers in cm^{-1}; characterization of the band intensities (transmission): 0–20% vs, 20–40% *s*, 40–60% *m*, 60–80% *w*, 80–100% *vw*. NMR Spectra: *Bruker ARX-300* (300/75 MHz), *Avance DRX-500* (500/125 MHz), and *Avance DRX-600* (600/150 MHz); chemical shifts δ (in ppm) relative to $CDCl_3$ (7.27/77.00 ppm), coupling constants *J* in Hz; for complete assignments of ^{1}H-NMR signals, COSY, TOCSY, NOESY, and ROESY 2D- or 1D-NMR methods were applied; for complete assignments of ^{13}C-NMR signals, HMBC and HSQC 2D-NMR methods were employed. If not stated otherwise, the spectra were recorded at 300 and 75 MHz, resp., in $CDCl_3$. MS: *Varian SSQ 700*; ionization by EI (70 eV) or CI (NH_3); in *m*/*z*, rel. intensities (%). GC/MS: *Hewlett Packard HP-5971 Series* (mass-selective detector; EI, 70 eV) and *HP-5890 Series II* (GC); carrier gas, He; *WCOT* capillary column *HP-5*; 25 m × 0.3 mm, 0.2 μm. GC Conditions: injector temp. 280°, starting temp. 60° over 2 min, rate 20°/min, final temp. 250° over 5 min.

1. *Preparation of Cycloalk-2-enones. Representative Procedure (RP 1) for the Preparation of* **5** *and* **6**. – A soln. of cyclooctanone (**1a**; 15.0 g, 118.9 mmol), ethylene glycol (70 ml, 1.2 mol), and TsOH (10 mol-%) in anh. benzene (150 ml) was heated at reflux overnight, using a *Dean–Stark* condenser. The mixture was washed with H_2O, dried ($MgSO_4$), and evaporated under reduced pressure to afford crude **2a**. Pyridinium hydrotribromide (43.9 g, 116.0 mmol) was added to a soln. of crude **2a** in anh. THF (500 ml), giving rise to a white precipitate. After stirring for 1 h at r.t., sat. aq. $NaHCO_3$ soln. (500 ml) was added, and the mixture was extracted with Et_2O. The extract was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by filtration through a short pad of SiO_2, using toluene as eluent, affording crude **3a**. A *Schlenk* flask containing **3a** and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 74 ml, 495.2 mmol) was heated at 160° for 1 h, and allowed to cool. H_2O (300 ml) was added, the mixture was extracted with Et_2O (2 × 150 ml), the combined org. layers were washed with brine, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The resulting crude cyclooctenone

ketal **4a** was dissolved in a 10:1 mixture of THF/acetone (200 ml) and a 1M soln. of HCl (200 ml). The mixture was stirred at r.t. for 5 h. H_2O was then added, and the aq. layer was extracted with Et_2O (2 × 150 ml). The combined org. layers were washed with H_2O and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by CC (hexane/AcOEt 20:1) to afford **5** (6.94 g, 47%) as a colorless oil. An anal. sample was purified by bulb-to-bulb distillation.

(Z)-Cyclooct-2-enone (**5**). IR (film): 3020*s*, 2932v*s*, 2859v*s*, 1689v*s*, 1480*s*, 1455v*s*, 1421*s*, 1398v*s*, 1347*m*, 1324*s*, 1260v*s*, 1226*s*, 1150*s*, 1121*s*, 1029*m*, 929*m*, 845*s*, 832*s*, 775*s*, 749*m*, 722*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.20 (*dt*, $^3J_{cis}$ = 12.5, ^3J = 7.0, H–C(3)); 5.85 (*dt*, $^3J_{cis}$ = 12.5, ^4J = 1.4, H–C(2)); 2.50 (*t*, ^3J = 5.6, CH_2(8)); 2.39–2.32 (*m*, CH_2(4)); 1.77–1.60 (*m*, 2 H); 1.52–1.38 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 204.7 (*s*, C(1)); 140.2 (*d*, C(3)); 131.1 (*d*, C(2)); 41.4 (*t*, C(8)); 27.3 (*t*); 23.9 (*t*); 21.8 (*t*); 21.3 (*t*). EI-MS: 124 (8, $M^{+\cdot}$), 95 (5), 81 (100), 68 (36), 55 (25). Anal. calc. for $C_8H_{12}O$ (124.18): C 77.38, H 9.74; found: C 77.53, H 9.78.

(E)-Cyclododec-2-enone (**6**). According to *RP 1*, starting with *cyclododecanone* (**1b**; 100 g, 548.5 mmol). Yield: 43.5 g (44%) of **6**. Colorless oil. IR (film): 2930v*s*, 2860v*s*, 1691v*s*, 1663v*s*, 1624*s*, 1460*s*, 1447*s*, 1348*s*, 1285*m*, 1235*m*, 1214*m*, 1141*w*, 1037*w*, 987*s*, 739*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.79 (*dt*, $^3J_{trans}$ = 15.6, ^3J = 7.6, H–C(3)); 6.31 (*dt*, $^3J_{trans}$ = 15.6, ^4J = 1.1, H–C(2)); 2.49 (*t*, ^3J = 6.5, CH_2(12)); 2.26 (*qd*, ^3J = 4.8, ^4J = 1.2, CH_2(4)); 1.72 (*quint.*, ^3J = 6.6, CH_2(11)); 1.67–1.56 (*m*, CH_2(5)); 1.44–1.21 (*m*, 10 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 203.4 (*s*, C(1)); 146.8 (*d*, C(3)); 131.3 (*d*, C(2)); 40.0 (*t*, C(12)); 32.6 (*t*, C(4)); 26.6 (*t*); 25.4 (*t*); 25.2 (*t*); 24.85 (*t*); 24.82 (*t*); 24.7 (*t*); 23.9 (*t*). EI-MS: 180 (41, $M^{+\cdot}$), 151 (14), 137 (24), 123 (30), 109 (91), 81 (100), 68 (90), 55 (88). Anal. calc. for $C_{12}H_{20}O$ (180.29): C 79.94, H 11.18; found: C 80.03, H 11.17.

Representative Procedure (*RP 2*) *for the Preparation of* **9** *and* **10**. To a soln. of LDA, freshly prepared by addition of a 2.4M soln. of BuLi in hexane (8.5 ml, 21.4 mmol) to (i-Pr)$_2$NH (3.29 ml, 23.3 mmol) in THF (25 ml) at −78°, was added cyclodecanone (7**a**) (3.0 g, 19.4 mmol) in THF (12 ml) at −78°. After stirring at this temp. for 0.5 h, the soln. was warmed to r.t. and stirred for an additional 0.5 h. After recooling to −78°, Me_3SiCl (4.2 ml, 32.9 mmol) was added, and the mixture was stirred at this temp. for 1 h. The reaction was quenched with a sat. soln. of NH_4Cl and extracted with Et_2O. The org. extract was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give a mixture of *(E)- and (Z)-1-[(trimethylsilyl)oxy]cyclodec-1-ene* (**8a**). The crude silyl enol ether was dissolved in abs. MeCN (30 ml), and $Pd(OAc)_2$ (4.27 g, 19.4 mmol) was added. The mixture was stirred under Ar gas for 24 h, after which Et_2O (100 ml) was added and the Pd removed by filtration. The solvent was evaporated under reduced pressure, and the residual dark-yellow oil was purified by CC (hexane/AcOEt 20:1) to afford **9** (2.60 g, 88%).

(E)-Cyclodec-2-enone (**9**). Colorless oil. IR (film): 2929v*s*, 2862v*s*, 1693v*s*, 1623*s*, 1462*s*, 1440*m*, 1345*s*, 1285*m*, 1234*m*, 1215*s*, 1141*w*, 1037*w*, 988*s*, 732*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.60 (*dt*, $^3J_{trans}$ = 16.0, ^3J = 7.9, H–C(3)); 6.27 (*dt*, $^3J_{trans}$ = 16.0, ^4J = 1.2, H–C(2)); 2.53 (*t*, ^3J = 6.3, CH_2(10)); 2.27 (*qd*, ^3J = 4.9, ^4J = 1.2, CH_2(4)); 1.71–1.60 (*m*, CH_2(5,9)); 1.50–1.17 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 205.0 (*s*, C(1)); 147.0 (*d*, C(3)); 132.0 (*d*, C(2)); 40.0 (*t*, C(10)); 33.8 (*t*, C(4)); 28.2 (*t*); 26.1 (*t*); 25.8 (*t*); 25.7 (*t*); 23.5 (*t*). EI-MS: 152 (5, $M^{+\cdot}$), 134 (6), 123 (4), 109 (16), 98 (76), 81 (100), 68 (48), 55 (26).

(E)-Cyclopentadec-2-enone (**10**). According to *RP 2*, starting with *cyclopentadecanone* (**7b**; 3.0 g, 13.4 mmol). Yield: 2.65 g (89%) of **10**. Colorless oil. IR (film): 2930v*s*, 2858v*s*, 1692v*s*, 1666v*s*, 1624v*s*, 1459*s*, 1444*s*, 1346*m*, 1287*m*, 1208*w*, 1123*w*, 981*s*, 917*m*, 732*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.80 (*dt*, $^3J_{trans}$ = 15.7, ^3J = 7.4, H–C(3)); 6.17 (*dt*, $^3J_{trans}$ = 15.7, ^4J = 1.2, H–C(2)); 2.48 (*t*, ^3J = 5.7, CH_2(15)); 2.21 (br. *q*, ^3J = 5.0, CH_2(4)); 1.66 (*quint.*, ^3J = 6.5, CH_2(14)); 1.55–1.49 (*m*, CH_2(5)); 1.30–1.16 (*m*, 16 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 201.8 (*s*, C(1)); 148.0 (*d*, C(3)); 130.7 (*d*, C(2)); 40.0 (*t*, C(15)); 31.6 (*t*, C(4)); 26.9 (*t*); 26.8 (*t*); 26.67 (*t*); 26.63 (*t*); 26.54 (*t*); 26.50 (*t*); 26.2 (*t*); 26.0 (*t*); 25.4 (*t*); 25.2 (*t*). EI-MS: 222 (68, $M^{+\cdot}$), 164 (8), 137 (7), 123 (14), 109 (82), 96 (93), 81 (100), 68 (64), 55 (89).

Representative Procedure (*RP 3*) *for the Preparation of* **13** *and* **14**. To a soln. of LDA, freshly prepared by addition of a 2.4M soln. of BuLi in hexane (24.1 ml, 60.3 mmol) to (i-Pr)$_2$NH (9.3 ml, 65.8 mmol) in THF (70 ml) at −78°, was added **1b** (10.0 g, 54.9 mmol) in THF (30 ml) at −78°. After stirring at this temp. for 0.5 h, the soln. was warmed to r.t. and stirred for additional 0.5 h. After recooling to −78°, Me_3SiCl (11.8 ml, 93.2 mmol) was added, the mixture was stirred at this temp. for 1 h, and then treated with a sat. soln. of NH_4Cl (100 ml), and extracted with Et_2O. The org. extract was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give crude (*E*/*Z*)-[(trimethylsilyl)oxy]cyclododec-1-ene (**11b**), which was dissolved in anh. Et_2O (70 ml) and cooled to 0°. A 1.1M soln. of Et_2Zn in toluene (58.4 ml, 64.2 mmol) was added, and the soln. was stirred and maintained at 0°, while CH_2I_2 (6.7 ml, 82.4 mmol) was added dropwise *via* syringe. The cloudy mixture was stirred overnight at r.t. The contents of the flask were cooled to 0°, and sat. aq. NH_4Cl soln. (2.9 ml) was slowly added. During hydrolysis, a large amount of gas evolved, and a white precipitate formed. The mixture was filtered, and the solid was washed with Et_2O (2 × 50 ml). The combined filtrates were washed with sat. aq. NH_4Cl soln. (2 × 50 ml) and

brine. The org. layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford crude *1-[(trimethylsilyl)oxy]bicyclo[10.1.0]tridecane* (**12b**) as a yellow oil. A three-necked flask was charged with $FeCl_3$ (22.1 g, 137.2 mmol) and cooled to $-5°$. Under vigorous stirring, DMF (75 ml) was slowly added at this temp. When the solid had dissolved, a soln. of crude **12b** in DMF (22 ml) was added dropwise at r.t., the resulting brown soln. was stirred overnight at 60°, and poured into a separatory funnel containing crushed ice and a 1M soln. of HCl (100 ml). The mixture was extracted with Et_2O (2 × 200 ml) the combined org. layers were washed successively with 1M aq. HCl (100 ml), sat. aq. $NaHCO_3$ (100 ml), and brine (100 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The residual brown oil was purified by CC (hexane/AcOEt 20:1) to afford **14** (6.72 g, 63%).

*(*E*)-Cyclotridec-2-enone* (**14**). Colorless solid. M.p. 28–30°. IR (film): 2930v*s*, 2860v*s*, 1691v*s*, 1663v*s*, 1624*s*, 1460*s*, 1447*s*, 1348*s*, 1285*m*, 1235*m*, 1214*m*, 1141*w*, 1037*w*, 987*s*, 739*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.84 (*dt*, $^3J_{trans}$ = 15.7, ^3J = 7.5, H–C(3)); 6.22 (*dt*, $^3J_{trans}$ = 15.7, ^4J = 1.2, H–C(2)); 2.51 (*t*, ^3J = 6.4, CH_2(13)); 2.27 (*qd*, ^3J = 5.0, ^4J = 1.2, CH_2(4)); 1.75 (*quint.*, ^3J = 6.5, CH_2(12)); 1.62–1.56 (*m*, CH_2(5)); 1.38–1.22 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 203.2 (*s*, C(1)); 148.3 (*d*, C(3)); 132.0 (*d*, C(2)); 38.5 (*t*, C(13)); 32.6 (*t*, C(4)); 26.6 (*t*); 26.5 (*t*); 26.2 (*t*); 25.9 (*t*); 25.8 (*t*); 25.4 (*t*); 25.13 (*t*); 25.07 (*t*), EI-MS: 194 (68, $M^{+\bullet}$), 137 (22), 123 (29), 109 (100), 81 (82), 69 (76), 55 (71). Anal. calc. for $C_{13}H_{22}O$ (194.32): C 80.35, H 11.41; found: C 80.45, H 11.52.

*(*Z*)-Cyclonon-2-enone* (**13**). According to *RP 3*, starting with cycloctanone (**1a**; 6.2 g, 49.2 mmol). Yield: 4.0 g (59%) of **13**. Colorless oil. IR (film): 3017*s*, 2929v*s*, 2858v*s*, 1700v*s*, 1656v*s*, 1472v*s*, 1445v*s*, 1399*s*, 1338*s*, 1325*s*, 1270*s*, 1225v*s*, 1444*s*, 1013*m*, 840*m*, 733*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.28 (*dt*, $^3J_{cis}$ = 12.5, ^3J = 9.3, H–C(3)); 6.05 (*d*, $^3J_{cis}$ = 12.5, H–C(2)); 2.71 (*t*, ^3J = 5.8, CH_2(9)); 2.68–2.52 (*m*, CH_2(4)); 1.97–1.78 (*m*, 2 H); 1.68–1.34 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 205.9 (*s*, C(1)); 142.4 (*d*, C(3)); 133.8 (*d*, C(2)); 41.6 (*t*, C(9)); 28.52 (*t*); 28.46 (*t*); 26.3 (*t*); 26.1 (*t*); 23.9 (*t*). EI-MS: 138 (7, $M^{+\bullet}$), 123 (23), 109 (45), 98 (56), 81 (100), 68 (3), 55 (12).

2. *Preparation of 3-Substituted Cycloalkanone Substrates. General Procedure* (*GP 1*) *for 1,4-Addition of Vinyl Magnesium Bromide Cuprate to Cycloalk-2-enones.* A flame-dried flask was flushed with N_2, charged with CuI (5.72 g, 30 mmol) and anh. THF (400 ml), and cooled to $-5°$. At this temp., a 1M soln. of vinyl magnesium bromide (90 ml) was added with stirring *via* cannula within 10 min. Then, Me_2S (2.2 ml, 30 mmol) was added. The resulting dark-green soln. was stirred for another 15 min at $-5°$, upon which a soln. of the corresponding cycloalkenone (30 mmol) in anh. THF (100 ml) was added at -5 to $-30°$ within 1 h. The mixture was then stirred for 30 min. The reaction was quenched with a sat. aq. soln. of NH_4Cl (200 ml), and then, the mixture was poured into a separatory funnel containing Et_2O (300 ml). The org. layer was separated, and the aq. phase was extracted with Et_2O (3 × 150 ml). The combined org. layers were washed with sat. aq. NH_4Cl soln. and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by CC (hexanes/AcOEt) to afford the products described below.

3-Vinylcyclooctanone (**15**). *GP 1*, with 4.20 g (33.81 mmol) of **5**, at $-30°$. The crude product was purified by CC (hexane/AcOEt 40:1) to give **15** (4.68 g, 91%). Colorless oil. IR (film): 3081*s*, 2924v*s*, 2859v*s*, 1699v*s*, 1640*s*, 1467*s*, 1445v*s*, 1414v*s*, 1359*s*, 1327*s*, 1303*s*, 1281*s*, 1265*s*, 1240v*s*, 1204v*s*, 1170*s*, 1130*m*, 1097*s*, 1081*s*, 1031*m*, 995v*s*, 966*m*, 913v*s*, 832*m*, 746*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.81 (*ddd*, $^3J_{trans}$ = 17.6, $^3J_{cis}$ = 10.4, ^3J(1′,3) = 7.6, H–C(1′)); 5.03 (*dt*, $^3J_{trans}$ = 17.6, ^2J = ^4J = 1.2, 1 H); 5.00 (*dt*, $^3J_{cis}$ = 10.4, ^2J = ^4J = 1.2, 1 H); 2.75–2.61 (*m*, H–3)); 2.57–2.30 (*m*, CH_2(2,8)); 2.06–1.86 (*m*, CH_2(7)); 1.85–1.21 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 217.3 (*s*, C(1)); 142.7 (*d*, C(1′)); 112.6 (*t*, C(2′)); 46.1 (*t*, C(2)); 42.9 (*t*, C(8)); 41.5 (*d*, C(3)); 32.7 (*t*); 27.6 (*t*); 24.4 (*t*); 23.4 (*t*). EI-MS: 152 (26, $M^{+\bullet}$), 137 (21), 123 (85), 109 (41), 95 (69), 81 (100), 67 (67), 55 (53).

3-Vinylcyclononanone (**16**). *GP 1*, with 2.04 g (14.76 mmol) of **13**, at $-20°$. The crude product was purified by CC (hexane/AcOEt 40:1) to give **16** (2.16 g, 88%). Colorless oil. IR (film): 3080*w*, 2928v*s*, 2874v*s*, 1700v*s*, 1639*s*, 1471*s*, 1445*s*, 1417*m*, 1344*m*, 1326*m*, 1273*m*, 1232*s*, 1214*m*, 1185*s*, 1153*m*, 1117*m*, 1067*s*, 995*s*, 913v*s*, 733*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.81 (*ddd*, $^3J_{trans}$ = 17.2, $^3J_{cis}$ = 10.5, ^3J(1′,3) = 7.5, H–C(1′)); 4.98 (*dt*, $^3J_{trans}$ = 17.2, ^2J = ^4J = 1.3, 1 H); 4.94 (*dt*, $^3J_{cis}$ = 10.5, ^2J = ^4J = 1.3, 1 H); 2.88–2.76 (*m*, H–C(3)); 2.59–2.35 (*m*, 4 H, CH_2(2,9)); 1.90–1.81 (*m*, CH_2(8)); 1.70–1.30 (*m*, 8 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 216.1 (*s*, C(1)); 143.3 (*d*, C(1′)); 112.1 (*t*, C(2′)); 48.3 (*t*, C(2)); 43.6 (*t*, C(9)); 39.5 (*d*, C(3)); 32.4 (*t*); 26.2 (*t*); 25.8 (*t*); 24.2 (*t*); 22.7 (*t*). EI-MS: 166 (3, $M^{+\bullet}$), 151 (9), 137 (14), 123 (100), 109 (32), 95 (30), 81 (63), 67 (60), 55 (28).

3-Vinylcyclodecanone (**17**). *GP 1*, with 1.75 g (11.40 mmol) of **9**, at $-30°$. The crude product was purified by CC (hexane/AcOEt 30:1) to give **17** (1.72 g, 83%). Colorless oil. IR (film): 3080*s*, 2923v*s*, 2870*w*, 1699v*s*, 1639v*s*, 1471v*s*, 1444v*s*, 1417v*s*, 1349v*s*, 1266*s*, 1232*s*, 1204*s*, 1185*s*, 1154*s*, 1096*s*, 1031*m*, 995v*s*, 911v*s*, 857*w*, 785*m*, 715*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.85 (*ddd*, $^3J_{trans}$ = 17.1, $^3J_{cis}$ = 10.5, ^3J(1′,3) = 7.5, H–C(1′)); 4.98 (*dd*, $^3J_{trans}$ = 17.1, ^2J = 1.2, 1 H); 4.96 (*dd*, $^3J_{cis}$ = 10.5, ^2J = 1.2, 1 H); 2.91–2.82 (*m*, H–C(3)); 2.69 (*dd*, ^2J = 15.1, ^3J = 9.9, H_a–C(2)); 2.63–2.43 (*m*, CH_2(10)); 2.38 (*dd*, ^2J = 15.1, ^3J = 3.6, H_b–C(2)); 1.94, 1.82 (2m_c, CH_2(9)); 1.78–1.26

(*m*, 10 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 213.1 (*s*, C(1)); 142.9 (*d*, C(1′)); 112.4 (*t*, C(2′)); 46.6 (*t*, C(2)); 42.7 (*t*, C(10)); 38.4 (*d*, C(3)); 30.2 (*t*); 25.6 (*t*); 25.0 (*t*); 24.5 (*t*); 23.9 (*t*); 22.8 (*t*). EI-MS: 180 (5, $M^{+\bullet}$), 165 (8), 151 (21), 137 (26), 123 (71), 109 (33), 98 (50), 95 (51), 81 (86), 67 (91), 55 (100).

3-Vinylcyclododecanone (**18**). *GP 1*, with 10.0 g (55.47 mmol) of **6**, $-5°$. The crude product was purified by CC (hexane/AcOEt 40 :1) to give **18** (9.73 g, 85%). Colorless oil. An anal. sample was further purified by bulb-to-bulb distillation. IR (film): 3078*m*, 2933v*s*, 2865v*s*, 1709v*s*, 1639*s*, 1468v*s*, 1445*s*, 1414*s*, 1364*s*, 1205*s*, 995*s*, 912*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.73 (*ddd*, $^3J_{trans} = 17.2$, $^3J_{cis} = 10.2$, $^3J(1',3) = 7.5$, H–C(1′)); 5.03 (*dd*, $^3J_{trans} = 17.2$, $^2J = 1.4$, 1 H); 5.00 (*dd*, $^3J_{cis} = 10.2$, $^2J = 1.4$, 1 H); 2.76–2.66 (*m*, H–C(3) and H_a–C(12)); 2.52–2.37 (*m*, CH_2(2)); 2.32 (*ddd*, $^2J = 16.8$, $J = 5.9$, 3.3, H_b–C(12)); 1.93, 1.49 (2m_c, CH_2(11)); 1.34–1.29 (*m*, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.2 (*s*, C(1)); 141.7 (*d*, C(1′)); 113.7 (*t*, C(2′)); 46.9 (*t*, C(2)); 39.8 (*t*, C(12)); 37.6 (*d*, C(3)); 29.2 (*t*); 25.1 (*t*); 24.1 (*t*); 23.91 (*t*); 23.89 (*t*); 22.31 (*t*); 22.26 (*t*); 22.0 (*t*). EI-MS: 208 (30, $M^{+\bullet}$), 179 (29), 165 (32), 151 (33), 137 (33), 123 (34), 109 (33), 95 (100), 81 (35), 67 (35), 55 (76). Anal. calc. for $C_{12}H_{22}O$ (182.31): C 79.06, H 12.16; found: C 78.95, H 12.09.

3-Vinylcyclotridecanone (**19**). *GP 1*, with 5.30 g (27.28 mmol) of **14**, at $-10°$. The crude product was purified by CC (hexane/AcOEt 40 :1) to give **19** (4.95 g, 82%). Colorless oil. IR (film): 3078*m*, 2931v*s*, 2862v*s*, 1711v*s*, 1640*s*, 1462v*s*, 1445*s*, 1408*s*, 1362*s*, 1206*s*, 994*s*, 912v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.72 (*ddd*, $^3J_{trans} = 17.1$, $^3J_{cis} = 10.2$, $J(1',3) = 7.4$, H–C(1′)); 5.00 (*dd*, $^3J_{trans} = 17.1$, $^2J = 1.3$, 1 H); 4.97 (*dd*, $^3J_{cis} = 10.2$, $^2J = 1.3$, 1 H); 2.62–2.39 (*m*, H–C(3), H_a–C(2), CH_2(13)); 2.35 (*dd*, $^2J = 13.9$, $J(2_b,3) = 3.4$, H_b–C(2)); 1.78–1.56 (*m*, CH_2(12)); 1.38–1.29 (*m*, 16 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.1 (*s*, C(1)); 142.0 (*d*, C(1′)); 113.4 (*t*, C(2′)); 47.8 (*t*, C(2)); 42.1 (*t*, C(13)); 39.1 (*d*, C(3)); 31.5 (*t*); 26.1 (*t*); 25.8 (*t*); 25.6 (*t*); 25.3 (*t*); 24.4 (*t*); 24.0 (*t*); 23.5 (*t*); 22.4 (*t*). EI-MS: 222 (68, $M^{+\bullet}$), 207 (20), 193 (70), 179 (48), 165 (64), 151 (47), 137 (78), 123 (83), 109 (94), 95 (95), 81 (98), 67 (100), 55 (99).

3-Vinylcyclopentadecanone (**20**). *GP 1*, with 2.33 g (10.48 mmol) of **10**, at $-20°$. The crude product was purified by CC (hexane/AcOEt 40 :1) to give **20** (2.13 g, 81%). Colorless oil. IR (film): 3078*w*, 2929v*s*, 2857v*s*, 1712v*s*, 1640*m*, 1460*s*, 1413*m*, 1358*m*, 1267*w*, 1203*w*, 1131*w*, 1072*m*, 994*m*, 912*s*, 722*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.70 (*ddd*, $^3J_{trans} = 17.2$, $^3J_{cis} = 10.5$, $J(1',3) = 7.5$, H–C(1′)); 4.99 (*dt*, $^3J_{trans} = 17.2$, $^2J = {}^4J = 1.2$, 1 H); 4.96 (*dt*, $^3J_{cis} = 10.5$, $^2J = {}^4J = 1.2$, 1 H); 2.62–2.34 (*m*, H–C(3)); 2.42–2.31 (*m*, 4 H, CH_2(2,15)); 1.71–1.55 (*m*, CH_2(14)); 1.34–1.28 (*m*, 20 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 210.8 (*s*, C(1)); 142.0 (*d*, C(1′)); 113.5 (*t*, C(2′)); 47.7 (*t*, C(2)); 42.1 (*t*, C(15)); 38.4 (*d*, C(3)); 32.9 (*t*); 27.5 (*t*); 26.9 (*t*); 26.6 (*t*); 26.5 (*t*); 26.4 (*t*); 26.3 (*t*); 26.2 (*t*); 26.1 (*t*); 24.7 (*t*); 22.8 (*t*). EI-MS: 250 (68, $M^{+\bullet}$), 235 (11), 221 (49), 207 (6), 193 (4), 179 (4), 165 (5), 151 (5), 137 (9), 123 (16), 109 (56), 95 (92), 81 (81), 67 (74), 55 (100).

General Procedure (*GP 2*) *for 1,4-Addition of Alk-1-enyl Lithium Cuprates to Cycloalk-2-enones.* A flame-dried flask was flushed with Ar gas and charged with Li dispersion (30% in mineral oil, 0.52 g, 75 mmol). The Li was washed three times by transferring 20-ml portions of anh. Et_2O into the flask and withdrawing the major part of the solvent after the resulting suspension had separated. Then, Et_2O (15 ml) was transferred into the flask, and the corresponding alkenyl bromide (30 mmol) was added dropwise under vigorous stirring at r.t. The resulting grey suspension was stirred for 2 h at r.t. The precipitated LiBr was allowed to settle, and the resulting alk-1-enyl lithium soln. was directly transferred by cannula through a glass-wool pad into a flame-dried flask cooled to $-78°$, containing a suspension of CuI (2.86 g, 15 mmol) in Et_2O (18 ml). The mixture was then warmed to $-30°$ for 45 min and subsequently recooled to $-78°$. A soln. of the corresponding cycloalkenone (15 mmol) in Et_2O (20 ml) was added at this temp. within 30 min, and the mixture was stirred for an additional 30 min. The reaction was quenched with a sat. soln. of NH_4Cl (30 ml). The mixture was poured into a separatory funnel containing Et_2O (50 ml), the org. layer was separated, and the aq. phase was extracted with Et_2O (3 × 40 ml). The combined org. layers were washed with sat. NH_4Cl soln. and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by CC to afford the products described below.

*(*E*)-3-(Prop-1-enyl)cyclododecanone* ((*E*)-**21**). *GP 2*, with 3.78 g (20.97 mmol) of **6** and (*E*)-1-bromopropene. The crude product was purified by CC (hexane/AcOEt 40 :1) to give (*E*)-**21** (4.43 g, 95%). Colorless oil. IR (film): 3010*s*, 2931v*s*, 2864v*s*, 1709v*s*, 1469v*s*, 1445v*s*, 1414*s*, 1361*s*, 1259*s*, 1204*s*, 1133*m*, 1099*m*, 1016*m*, 967*m*, 927*m*, 917*m*, 733v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.52–5.41 (*m*, H–C(2′)); 5.30 (*ddd*, $J(1',2') = 15.2$, $J =$ 7.6, 1.4, H–C(1′)); 2.79–2.63 (*m*, H–C(3), H_a–C(12)); 2.40 (*d*, $J(2_a,3) = 2.0$, H_a–C(2)); 2.38 (*s*, H_b–C(2)); 2.31–2.22 (*m*, H_b–C(12)); 2.02–1.91 (*m*, H_a–C(11)); 1.66 (*dd*, $J = 3.2$, 2.0, Me); 1.48–1.20 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.4 (*s*, C(1)); 134.5 (*d*, C(1′)); 124.4 (*d*, C(2′)); 48.1 (*t*, C(2)); 39.4 (*t*, C(12)); 36.8 (*d*, C(3)); 29.7 (*t*); 25.3 (*t*); 23.9 (*t*); 22.91 (*t*); 22.90 (*t*); 22.5 (*t*); 22.3 (*t*); 21.9 (*t*, C(11)); 17.7 (*q*, Me). EI-MS: 222 (8, $M^{+\bullet}$), 193 (7), 179 (8), 151 (5), 123 (12), 109 (16), 95 (50), 81 (49), 67 (88), 55 (100).

*(*Z*)-3-(Prop-1-enyl)cyclododecanone* ((*Z*)-**21**). *GP 2*, with 4.21 g (23.35 mmol) of **6** and (*Z*)-1-bromopropene. The crude product was purified by CC (hexane/AcOEt 40 :1) to give (*Z*)-**21** (5.09 g, 98%). Colorless

oil. IR (film): 3009*s*, 2932v*s*, 2864v*s*, 1709v*s*, 1468v*s*, 1445v*s*, 1414*s*, 1361*s*, 1258*s*, 1204*s*, 1133*m*, 1016*m*, 967*m*, 927*m*, 919*m*, 733v*s*, 720v*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.50–5.44 (*m*, H–C(2′)); 5.19 (*tq*, J = 11.2, ^4J(1,Me) = 1.5, H–C(1′)); 3.06 (m_c, H–C(3)); 2.83 (*ddd*, ^2J = 15.8, J = 11.8, 3.0, H_a–C(12)); 2.35 (*d*, $J(2_a,3)$ = 4.4, H_a–C(2)); 2.34 (*s*, H_b–C(2)); 2.25 (*ddd*, ^2J = 15.8, J = 5.3, 3.5, H_b–C(12)); 2.00, 1.42 ($2m_c$, CH_2(11)); 1.69 (*dd*, ^3J(Me,2′) = 6.7, ^4J(Me,1′) = 1.5, Me); 1.41–1.21 (*m*, 14 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 211.6 (*s*, C(1)); 134.4 (*d*, C(1′)); 124.0 (*d*, C(2′)); 48.8 (*t*, C(2)); 39.3 (*t*, C(12)); 31.7 (*d*, C(3)); 30.3 (*t*); 25.8 (*t*); 24.2 (*t*); 24.0 (*t*); 23.9 (*t*); 23.2 (*t*); 22.6 (*t*); 22.2 (*t*, C(11)); 13.4 (*q*, Me). EI-MS: 222 (8, $M^{+\bullet}$), 193 (10), 179 (10), 151 (7), 137 (8), 123 (12), 109 (18), 95 (50), 81 (52), 67 (69), 55 (100). Alternatively, a 1:1 mixture (*E*)/(*Z*)-**21** (96% yield) was prepared accordingly from a 1:1 mixture of (*E*)/(*Z*)-1-bromopropene.

*(*E/Z*)-3-(Prop-1-enyl)cyclotridecanone* (**23**). *GP 2*, with 1.56 g (8.03 mmol) of **14** and a 1:1 mixture of (*E*/*Z*)-1-bromopropene. The crude product was purified by CC (hexane/AcOEt 40:1) to give a 1:1 mixture of (*E*)/(*Z*)-**23** (1.88 g, 99%). Colorless solid. M.p. 27°. IR (film): 3008*s*, 2932v*s*, 2861v*s*, 1710v*s*, 1461v*s*, 1445v*s*, 1407*s*, 1360*s*, 1206*s*, 1166*m*, 1125*m*, 1079*m*, 1067*m*, 1033*m*, 966*m*, 731*s*, 712*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.49–5.39 (*m*, H–C(2′)); 5.19 (*td*, J = 10.7, 1.4, H–C(1′)); 2.91 (m_c, H–C(3) of (*Z*)-isomer); 2.52–2.20 (*m*, H–C(3) of (*E*)-isomer, CH_2(2,13)); 1.78–1.68 (*m*, H_a–C(12)); 1.67 (*dd*, J = 6.8, 1.7, Me); 1.45–1.12 (*m*, 17 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.3, 211.2 (2*s*, C(1)); 134.8, 134.4 (2*d*, C(1′)); 124.1, 123.5 (2*d*, C(2′)); 48.8, 48.7 (2*t*, C(2)); 42.04, 41.96 (2*t*, C(13)); 38.3, 31.9 (2*d*, C(3)); 33.0 (*t*); 32.4 (*t*); 26.4 (*t*); 26.2 (*t*); 25.9 (*t*); 25.5 (*t*); 25.4 (*t*); 25.3 (*t*); 24.4 (*t*); 24.0 (*t*); 23.9 (*t*); 23.6 (*t*); 22.3 (*t*); 17.7, 13.0 (2*q*, Me). EI-MS of (*Z*)-**23**: 236 (38, $M^{+\bullet}$), 207 (40, $[M - CHO]^+$), 193 (52, $[M - CHO - CH_2]^+$), 137 (48), 123 (51), 109 (52), 95 (52), 81 (100), 67 (55), 55 (53). EI-MS of (*E*)-**23**: 236 (26, $M^{+\bullet}$), 207 (32, $[M - CHO]^+$), 193 (52, $[M - CHO - CH_2]^+$), 179 (11, $[M - CHO - 2CH_2]^+$), 165 (6), 137 (35), 123 (45), 109 (44), 95 (48), 81 (100), 67 (48), 55 (51).

3-(Isopropenyl)cyclododecanone (**24**). *GP 2*, with 2.25 g (12.48 mmol) of **6**. The crude product was purified by CC (hexane/AcOEt 40:1) to give **24** (2.58 g, 93%). Colorless oil. IR (film): 3074*w*, 2933v*s*, 2866v*s*, 1709v*s*, 1645*s*, 1469v*s*, 1445*s*, 1374*s*, 1256*m*, 1205*m*, 1131*m*, 889v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.78, 4.74 (2*quint.*, J = 1.4, CH_2(2′)); 2.81–2.71 (*m*, H–C(3) and H_a–C(12)); 2.56 (*dd*, ^2J = 13.6, ^3J = 11.9, H_a–C(2)); 2.36 (*dd*, ^2J = 13.6, ^3J = 3.0, H_b–C(2)); 2.31 (*ddd*, ^2J = 16.2, J = 5.8, 2.2, H_b–C(12)); 1.97 (m_c, H_a–C(11)); 1.63 (*t*, J = 0.7, Me); 1.51–1.20 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.4 (*s*, C(1)); 147.1 (*s*, C(1′)); 110.6 (*t*, C(2′)); 47.0 (*t*, C(2)); 40.5 (*d*, C(3)); 39.3 (*t*, C(12)); 27.1 (*t*); 25.2 (*t*); 24.0 (*t*); 23.9 (*t*); 23.7 (*t*); 22.5 (*t*); 22.4 (*t*); 22.0 (*t*); 19.7 (*q*, Me). EI-MS: 222 (15, $M^{+\bullet}$), 207 (29), 179 (30), 151 (28), 137 (35), 123 (42), 109 (39), 95 (50), 81 (100), 67 (45), 55 (41).

3-(Isopropenyl)cyclotridecanone (**25**). *GP 2*, with 1.20 g (6.18 mmol) of **14**. The crude product was purified by CC (hexane/AcOEt 40:1) to give **25** (1.37 g, 94%). Colorless solid. M.p. 34–36°. IR (film): 3074*w*, 2932v*s*, 2860v*s*, 1710v*s*, 1645*s*, 1461*s*, 1445*s*, 1408*m*, 1375*m*, 1245*m*, 889*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.75 (*s*, CH_2(2′)); 2.62–2.39 (*m*, H–C(3), H_a–C(2), CH_2(13)); 2.35 (*dd*, ^2J = 12.9, $J(2_b,3)$ = 1.9, H_b–C(2)); 1.75–1.56 (*m*, CH_2(12)); 1.68 (*s*, Me); 1.41–1.29 (*m*, 16 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.2 (*s*, C(1)); 147.7 (*s*, C(1′)); 110.4 (*t*, C(2′)); 47.8 (*t*, C(2)); 42.2 (*d*, C(3)); 42.0 (*t*, C(13)); 30.1 (*t*); 26.2 (*t*); 25.7 (*t*); 25.4 (*t*); 25.3 (*t*); 24.4 (*t*); 24.0 (*t*); 23.8 (*t*); 22.4 (*t*); 19.6 (*q*, Me). EI-MS: 236 (56, $M^{+\bullet}$), 221 (49), 207 (10), 193 (88), 179 (51), 165 (65), 151 (76), 137 (71), 123 (78), 109 (85), 95 (100), 81 (96), 67 (99), 55 (92).

*(*E*)-3-(1-Methylprop-1-enyl)cyclododecanone* ((*E*)-**26**). *GP 2*, with 2.96 g (16.42 mmol) of **6** and a 1:1 mixture of (*E*/*Z*)-2-bromobutene. The crude product was purified by CC (hexane/AcOEt 40:1) to give (*E*)-**26** (3.37 g, 87%). (The presence of < 10% of the (*Z*)-isomer was detected by GC- as well as ^{13}C-NMR analyses). Colorless oil. IR (film): 2932v*s*, 2860v*s*, 1709v*s*, 1667*m*, 1469v*s*, 1445v*s*, 1377v*s*, 1261*s*, 1205*s*, 1132*s*, 1024*m*, 952*s*, 814*s*, 711*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.34–5.27 (*m*, H–C(2′)); 3.26–3.17 (*m*, H–C(3)); 3.07–2.96 (*m*, H_a–C(12)); 2.45–2.04 (*m*, 4 H); 1.68 (*dd*, J = 6.8, 1.4, Me–C(2′)); 1.57 (*t*, J = 1.5, Me–C(1′)); 1.40–1.16 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.7, 211.5 (2*s*, C(1)); 137.2, 137.0 (2*s*, C(1′)); 120.4, 119.3 (2*d*, C(2′)); 48.5, 48.1 (2*t*, C(2)); 42.4, 33.6 (2*d*, C(3)); 38.5, 37.6 (2*t*, C(12)); 27.0 (*t*); 26.2 (*t*); 25.6 (*t*); 24.0 (*t*); 23.8 (*t*); 23.5 (*t*); 23.2 (*t*); 23.1 (*t*); 22.9 (*t*); 22.4 (*t*); 22.3 (*t*); 21.8 (*t*); 21.6 (*t*); 18.6, 13.9, 13.1, 12.6 (4*q*, Me). EI-MS of (*E*)-**26**: 236 (8, $M^{+\bullet}$), 123 (18), 109 (33), 95 (44), 81 (57), 67 (68), 55 (100). EI-MS of (*Z*)-**26**: 236 (22, $M^{+\bullet}$), 207 (40), 179 (19), 151 (13), 137 (16), 123 (45), 109 (68), 95 (84), 81 (89), 67 (90), 55 (100).

*(*E*)-3-(1-Methylprop-1-enyl)cyclotridecanone* ((*E*)-**27**). *GP 2*, with 1.09 g (5.61 mmol) of **14** and a 1:1 mixture of (*E*/*Z*)-2-bromobutene. The crude product was purified by CC (hexane/AcOEt 40:1) to give (*E*)-**27** (1.25 g, 89%). (The presence of < 10% of the (*Z*)-isomer was detected by GC as well as ^{13}C-NMR analyses). Colorless oil. IR (film): 2930v*s*, 2860v*s*, 1709v*s*, 1460*s*, 1445*s*, 1407*m*, 1375*m*, 1250*s*, 1185*s*, 1124*m*, 1066*m*, 844*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.28 (*qd*, ^3J(2′,Me) = 6.8, J(2′,3) = 1.4, H–C(2′)); 3.12–3.06 (*m*, H–C(3)); 2.59–2.44 (*m*, H_a–C(2), CH_2(13)); 2.17 (*dd*, ^2J = 12.8, $J(2_b,3)$ = 2.9, H_b–C(2)); 1.79–1.67 (*m*, H_a–C(12)); 1.65 (*dd*, J = 6.8, 1.5, Me–C(2′)); 1.57 (*t*, J = 1.4, Me–C(1′)); 1.40–1.28 (*m*, 17 H). ^{13}C-NMR (75 MHz, $CDCl_3$):

211.4 (*s*, C(1)); 137.5 (*s*, C(1′)); 120.0 (*d*, C(2′)); 47.7 (*t*, C(2)); 42.0 (*t*, C(13)); 35.4 (*d*, C(3)); 29.6 (*t*); 26.6 (*t*); 25.8 (*t*); 25.2 (*t*); 25.3 (*t*); 24.4 (*t*); 24.3 (*t*); 23.0 (*t*); 22.0 (*t*); 18.6 (*q*, Me–C(1′)); 13.0 (*q*, Me–C(2′)). EI-MS: 250 (11, $M^{+\bullet}$), 235 (7), 221 (19), 193 (12), 137 (14), 123 (21), 109 (32), 95 (45), 81 (54), 67 (66), 55 (100).

3-(2-Methylprop-1-enyl)cyclododecanone (**28**). *GP 2*, with 1.69 g (9.37 mmol) of **6**. The crude product was purified by CC (hexane/AcOEt 40 :1) to give **28** (1.79 g, 81%). Colorless oil. IR (film): 2930v*s*, 2863v*s*, 1709v*s*, 1468*m*, 1445*m*, 1415*w*, 1376*w*, 1258*w*, 1204*w*, 1126*w*, 837*m*, 727*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.92 (*dsept.*, $J(1',3) = 9.4$, $^4J(1',Me) = 1.4$, H–C(1′)); 2.89 (*quint.*, $J = 7.9$, H–C(3)); 2.82 (*ddd*, $^2J = 16.5$, $J = 12.0$, 3.1, H_a–C(12)); 2.33 (*s*, H_a–C(2)); 2.30 (*d*, $J(2_b,3) = 1.9$, H_b–C(2)); 2.23 (*ddd*, $^2J = 16.5$, $J = 5.1$, 3.3, H_b–C(12)); 2.05–1.99 (*m*, H_a–C(11)); 1.70 (*t*, $J = 1.5$, 2 Me); 1.46–1.20 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.4 (*s*, C(1)); 131.3 (*s*, C(2′)); 128.4 (*d*, C(1′)); 48.9 (*t*, C(2)); 38.9 (*t*, C(12)); 32.6 (*d*, C(3)); 31.4 (*t*); 30.3 (*t*); 25.58 (*q*, Me); 25.53 (*t*); 23.9 (*t*); 23.7 (*t*); 23.0 (*t*); 22.3 (*t*); 21.8 (*t*); 18.0 (*q*, Me). EI-MS: 236 (22, $M^{+\bullet}$), 221 (18), 193 (27), 179 (10), 151 (6), 137 (19), 123 (15), 109 (44), 95 (65), 81 (72), 67 (82), 55 (100).

3-(2-Methylprop-1-enyl)cyclotridecanone (**29**). *GP 2*, with 1.36 g (7.00 mmol) of **14**. The crude product was purified by CC (hexane/AcOEt 40 :1) to give **29** (1.47 g, 84%). Colorless solid. IR (film): 2931v*s*, 2861v*s*, 1710v*s*, 1461*s*, 1445*s*, 1408*m*, 1376*m*, 1263*m*, 1045*w*, 812*w*, 716*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.92 (*d* × *sept.*, $J(1',3) = 9.5$, $^4J(1',Me) = 1.4$, H–C(1′)); 2.81–2.72 (*m*, H–C(3)); 2.58–2.40 (*m*, CH_2(13)); 2.38 (*dd*, $^2J = 13.6$, $J(2_a,3) = 10.4$, H_a–C(2)); 2.22 (*dd*, $^2J = 13.6$, $J(2_b,3) = 3.4$, H_b–C(2)); 1.79–1.55 (*m*, CH_2(12)); 1.68 (*dd*, $J = 5.0$, 1.2, 2 Me); 1.45–1.18 (*m*, 16 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.4 (*s*, C(1)); 131.1 (*s*, C(2′)); 128.8 (*d*, C(1′)); 49.2 (*t*, C(2)); 42.0 (*t*, C(13)); 34.3 (*d*, C(3)); 32.6 (*t*); 26.4 (*t*); 25.9 (*t*); 25.6 (*q*, Me); 25.4 (*t*); 25.3 (*t*); 24.4 (*t*); 24.0 (*t*); 23.9 (*t*); 22.3 (*t*); 18.0 (*q*, Me). EI-MS: 250 (20, $M^{+\bullet}$), 235 (18), 207 (33), 193 (15), 137 (22), 123 (19), 109 (47), 95 (67), 81 (70), 67 (76), 55 (100).

3-(Cyclohex-1-enyl)cyclododecanone (**30**). A flame-dried flask was flushed with Ar, charged with CuCN (0.84 g, 9.32 mmol) and THF (10 ml), and cooled to −30°. A 1.20M soln. of MeLi in Et_2O (17.1 ml, 20.51 mmol) was added. The resulting soln. was warmed to −5° and stirred for 1 h at this temp. A soln. of cyclohex-1-en-1-yl(tributyl)stannane (10.47 mmol), freshly prepared by adding 1 equiv. of cyclohex-1-en-1-yl lithium to a soln. of Bu_3SnCl (2.82 ml, 10.47 mmol) in THF (20 ml), was slowly added *via* syringe to the above mixture at −5°. After 1.5 h at ambient temp. the mixture was cooled to −78°, and **6** (1.20 g, 6.66 mmol) in THF (5 ml) was added. The green-yellow suspension was stirred for 30 min at −78°. The reaction was quenched with a sat. soln. of NH_4Cl (40 ml), and the mixture was poured into a separatory funnel containing crushed ice and Et_2O (50 ml). The org. layer was separated, and the aq. phase was extracted with Et_2O (3 × 20 ml). The combined org. layers were washed with a sat. soln. of NH_4Cl and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by CC (hexane/AcOEt 50 :1) to afford **30** (1.54 g, 88%) as a colorless liquid. An anal. sample was crystallized from hexane to give colorless needles. M.p. 58–61° (hexane). IR (KBr): 2926v*s*, 2862v*s*, 1699v*s*, 1469*s*, 1445*m*, 1410*m*, 1372*m*, 1257*m*, 1211*m*, 1137*m*, 930*w*, 729*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.47 (m_c, H–C(2′)); 2.81 (*ddd*, $^2J = 15.1$, $J = 11.6$, 2.7, H_a–C(12)); 2.66–2.55 (*m*, H–C(3)); 2.48 (*t*, $^2J = J(2_a,3) = 13.0$, H_a–C(2)); 2.35 (*dd*, $^2J = 13.0$, $J(2_b,3) = 3.0$, H_b–C(2)); 2.24 (*ddd*, $^2J = 15.1$, $J = 4.6$, 3.1, H_b–C(12)); 2.03–1.83 (*m*, CH_2(3′,6′)); 1.65–1.26 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.9 (*s*, C(1)); 139.0 (*s*, C(1′)); 121.8 (*d*, C(2′)); 47.7 (*t*, C(2)); 40.9 (*d*, C(3)); 38.8 (*t*, C(12)); 27.1 (*t*); 25.5 (*t*); 25.2 (*t*); 24.9 (*t*); 24.6 (*t*); 23.9 (*t*); 23.7 (*t*); 23.4 (*t*); 22.9 (*t*); 22.6 (*t*); 22.4 (*t*); 21.9 (*t*). EI-MS: 262 (100, $M^{+\bullet}$), 234 (35), 219 (41), 205 (9), 179 (26), 163 (50), 149 (82), 123 (81), 107 (96), 95 (82), 81 (85), 70 (81), 55 (83).

3-[(Trimethylsilyl)ethynyl]cyclododecanone (**31**). To a stirred soln. of trimethylsilyl acetylene (2.45 g, 25 mmol) in anh. THF (100 ml), a 2.4M soln. of BuLi in hexane (10.15 ml, 25 mmol) was added slowly *via* syringe at −10°. The resulting pale yellow lithium acetylide soln. was stirred for 30 min at −10°. Then, CuI (5.23 g, 27.5 mmol) and Me_2S (1.51 ml, 20.6 mmol) were added at this temp. The resulting copper acetylide suspension was stirred for 1 h at −20°, then the temp. was lowered to −78°. Me_3SiI (3.4 ml, 25.0 mmol) was added. After stirring for another 10 min at −78°, a soln. of **6** (3.0 g, 16.6 mmol) in anh. THF (15 ml) was added dropwise. The dark suspension was stirred for 1 h at −78° for completion of the reaction. The mixture was quenched with a sat. NH_4Cl soln. (30 ml), and stirring was continued for 30 min at r.t. To the resulting bright orange suspension containing the silyl enol ether of **31**, 3M aq. HCl (10 ml) was added, whereupon the color turned immediately to pale yellow, and the mixture was stirred for another 30 min at r.t. The biphasic mixture was then poured into a separatory funnel containing Et_2O (40 ml). The org. layer was separated, and the aq. phase was extracted with Et_2O (3 × 20 ml). The combined org. layers were washed once with 5% $Na_2S_2O_3$ and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by CC (hexane/AcOEt 50 :1) to afford **31** (3.61 g, 78%). Colorless solid. M.p. 60–63°. IR (KBr): 2933v*s*, 2856v*s*, 2167*s*, 1701v*s*, 1471*s*, 1443*s*, 1421*s*, 1370*m*, 1250v*s*, 1206*m*, 1133*m*, 901*m*, 848v*s*, 760v*s*, 698*s*, 649*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.10–3.30 (*m*, H–C(3)); 2.74 (*dd*, $^2J = 15.9$, $J(2_a,3) = 11.7$, H_a–C(2)); 2.37–2.76 (*m*, H_b–C(2), CH_2(12)); 1.75–1.30 (*m*, CH_2(11)); 1.30–1.18

(*m*, 14 H); 0.14 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.6 (*s*, C(1)); 109.1 (*s*, C(2′)); 85.0 (*s*, C(1′)); 45.1 (*t*, C(2)); 41.1 (*t*, C(12)); 28.8 (*t*); 26.4 (*d*, C(3)); 25.0 (*t*); 24.8 (*t*); 24.0 (*t*); 23.9 (*t*); 22.4 (*t*); 22.1 (*t*); 21.1 (*t*); 0.0 (*q*, Me_3Si). EI-MS: 278 (5, $M^{+\bullet}$), 205 (9), 179 (10), 167 (18), 151 (6), 123 (15), 115 (51), 109 (29), 95 (14), 81 (17), 73 (100), 55 (28).

3-Ethynylcyclododecanone (**32**). To a stirred soln. of **31** (1.93 g, 6.9 mmol) in THF (150 ml), $Bu_4NF \cdot 3\ H_2O$ (2.18 g, 6.9 mmol) was added at $-10°$. The colorless soln. was allowed to warm to r.t. and was then stirred at this temp. for 30 min. The mixture was poured into a separatory funnel containing crushed ice and Et_2O (100 ml). The org. layer was separated, and the aq. phase was extracted with Et_2O (3×40 ml). The combined org. layers were washed with H_2O and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was crystallized from hexane to give **32** (1.30 g, 91%). Colorless needles. M.p. 46–48° (hexane). IR (KBr): 3310v*s*, 2927v*s*, 2866v*s*, 2113*w*, 1701v*s*, 1471v*s*, 1445*m*, 1418*s*, 1368*s*, 1230*m*, 951*w*, 733*w*, 638v*s*, 620v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.23–3.14 (*m*, H–C(3)); 2.91 (*dd*, $^2J = 16.0$, $J(2_a,3) = 11.6$, H_a–C(2)); 2.53–2.43 (*m*, H_b–C(2), CH_2(12)); 2.05 (*d*, $J(2',3) = 2.5$, H–C(2′)); 1.92–1.78 (*m*, H_a–C(11)); 1.63–1.21 (*m*, 15 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.5 (*s*, C(1)); 86.5 (*s*, C(1′)); 68.9 (*d*, C(2′)); 44.8 (*t*, C(2)); 41.3 (*t*, C(12)); 28.8 (*t*); 25.3 (*d*, C(3)); 25.1 (*t*); 24.9 (*t*); 24.1 (*t*); 23.9 (*t*); 22.5 (*t*); 22.2 (*t*); 21.1 (*t*). EI-MS: 206 (2, $M^{+\bullet}$), 163 (16), 149 (20), 135 (34), 121 (68), 109 (70), 95 (100), 79 (92), 67 (86), 55 (88). Anal. calc. for $C_{14}H_{22}O$ (206.33): C 81.50, H 10.75; found: C 81.49, H 10.66.

*(−)-(2*R*,3*R*)-2,3-Dimethyl-7-(prop-1-enyl)-1,4-dioxaspiro[4.11]hexadecane* ((−)-(*Z*)-**22**). A soln. of (*Z*)-**21** (2.23 g, 10.03 mmol), (2*R*,3*R*)-butane-2,3-diol (1.08 ml, 11.03 mmol), and a catalytic amount of *p*-toluenesulfonic acid in anh. benzene (25 ml) was heated at reflux for 6 h, using a *Dean–Stark* condenser. The mixture was washed with H_2O, dried ($MgSO_4$), and evaporated under reduced pressure to afford a 1:1 diastereoisomer mixture of racemic (*Z*)-**22** (2.89 g, 98%). This mixture was subjected to CC (hexane/AcOEt 80:1) to afford a 3:1 mixture (−)-(*Z*)-**22**/(+)-(*Z*)-**22**. The enriched material was resubjected to CC (hexane/AcOEt 80:1) to afford optically pure (−)-(*Z*)-**22** (> 95% ee according to GC. $[\alpha]_D^{23} = -43.0$ ($c = 1.0$, hexane). IR (film): 3005*m*, 2931v*s*, 2864v*s*, 1469v*s*, 1445*s*, 1374*s*, 1350*m*, 1310*m*, 1286*m*, 1266*m*, 1234*m*, 1216*m*, 1168*m*, 1100v*s*, 982*s*, 931*s*, 731*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.36–5.18 (*m*, H–C(1′,2′)); 3.65–3.52 (*m*, H–C(2,3)); 2.62–2.57 (*m*, H–C(7)); 2.00 (*dd*, $^2J = 14.1$, $^3J = 2.7$, H_a–C(6)); 1.95–1.88 (*m*, H_b–C(6)); 1.62 (*d*, $^3J = 5.0$, Me(3′)); 1.60–1.17 (*m*, 18 H); 1.21, 1.17 (2*d*, $^3J = 5.6$, 6 H, Me–C(2,3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.3 (*d*, C(1′)); 120.6 (*d*, C(2′)); 111.3 (*s*, C(5)); 78.4, 77.4 (2*d*, C(2,3)); 39.9 (*t*, C(6)); 35.3 (*t*, C(12)); 34.5 (*t*, C(8)); 30.1 (*d*, C(7)); 26.3 (*t*); 25.7 (*t*); 23.5 (*t*); 22.5 (*t*); 22.3 (*t*); 22.2 (*t*); 20.3 (*t*); 16.6 (*q*, Me–C(2,3)); 13.1 (*q*, C(3′)). EI-MS: 294 (70, $M^{+\bullet}$), 265 (35), 251 (66), 239 (68), 225 (53), 221 (30), 205 (18), 183 (77), 167 (86), 153 (28), 141 (60), 55 (100).

*(+)-(*Z*)-3-(Prop-1-enyl)cyclododecanone* ((+)-(*Z*)-**21**). To a stirred soln. of (−)-(*Z*)-**22** (0.76 g, 2.58 mmol) in a 10:1 mixture of THF/acetone (5 ml), a 1M soln. of HCl (5 ml) was added at 5°. The mixture was stirred for 3 h at r.t. H_2O was added, and the aq. layer was extracted with Et_2O (2×20 ml). The combined org. layers were washed with H_2O and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was filtered through a short pad of silica gel, with hexane/AcOEt 40:1 as eluent, to give (+)-(*Z*)-**21** (0.56 g, 98%), which was identical in all respects with an authentic sample of racemic (*Z*)-**21**. Colorless oil. $[\alpha]_D^{23} = +28.3$ ($c = 1.0$, hexane).

7-(2,2-Dibromocyclopropyl)-1,4-dioxaspiro[4.11]hexadecane (**35**). A soln. of **18** (4.10 g, 19.68 mmol), ethylene glycol (1.44 ml, 25.58 mmol), TsOH (cat. amount) in anh. benzene (50 ml) was heated at reflux for 12 h, using a *Dean–Stark* condenser. The mixture was washed with H_2O, dried ($MgSO_4$), and evaporated under reduced pressure to afford crude *7-vinyl-1,4-dioxaspiro[4.11]hexadecane* (**34**) (4.27 g, 86%) as a colorless oil, which was directly used in the next step without further purification. A 12M NaOH soln. (7 ml) was added dropwise to a cooled (0°) soln. of **34** (3.85 g, 15.25 mmol), a catalytic amount of benzyl(triethyl)ammonium chloride (TEBA), and $CHBr_3$ (5.80 g, 22.88 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 2 d at r.t., washed with H_2O, dried ($MgSO_4$), and evaporated under reduced pressure. The residual brown oil was purified by CC (hexane/AcOEt 20:1) to afford **35** (4.01 g, 62%). Colorless solid. M.p. (96–98°). IR (KBr): 2981*s*, 2942v*s*, 2866v*s*, 2849v*s*, 1471*s*, 1443*m*, 1356*m*, 1253*m*, 1227*m*, 1179*s*, 1172*s*, 1113v*s*, 1100v*s*, 1070v*s*, 943*s*, 689*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.06–3.74 (*m*, 4 H, CH_2(2,3)); 2.18–2.10 (*m*, 1 H); 1.93–1.87 (*m*, 1 H); 1.76–1.70 (*m*, 1 H); 1.62–1.20 (*m*, 21 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 111.7 (*s*, C(5)); 64.5, 64.1 (2*t*, C(2,3)); 37.6, 36.5 (2*d*, C(7,1′)); 36.8 (*t*); 35.2 (*t*); 31.0 (*s*, C(2′)); 30.8 (*t*); 28.0 (*t*); 25.8 (*t*); 24.5 (*t*); 23.8 (*t*); 22.1 (*t*); 21.7 (*t*); 20.8 (*t*); 20.2 (*t*). EI-MS: 343 (12, $[M - Br]^+$), 297 (8), 237 (14), 197 (15), 183 (5), 155 (18), 99 (100), 86 (53), 65 (15), 55 (42).

3-(Propa-1,2-dien-1-yl)cyclododecanone (**33**). To a stirred soln. of **35** (3.85 g, 9.08 mmol) in anh. Et_2O (25 ml), a 1.20M soln. of MeLi in Et_2O (11.4 ml, 13.62 mmol) was added slowly *via* syringe at $-10°$. The cooling

bath was removed, and the mixture was allowed to warm to r.t. within 40 min. Under ice cooling, H_2O was carefully added, and the aq. layer was extracted with Et_2O (2 × 20 ml). The combined org. layers were washed with H_2O and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by CC (hexane/AcOEt 40:1) to afford **36** (1.34 g, 56%) as a colorless oil, which was immediately used in the next step. To a stirred soln. of **36** (1.32 g, 4.98 mmol) in a 10:1 mixture of THF/acetone (10 ml) a 1M soln. of HCl (10 ml) was added at 5°. The mixture was stirred for 4 h at r.t. H_2O was added, and the aq. layer was extracted with Et_2O (2 × 30 ml). The combined org. layers were washed with H_2O and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by CC (hexane/AcOEt 20:1) to afford **33** (0.98 g, 89%). Colorless oil. IR (film): 2933v*s*, 2865v*s*, 1956*s*, 1708v*s*, 1469v*s*, 1445*s*, 1414*m*, 1367*s*, 1263*m*, 1204*m*, 1170*m*, 1131*m*, 916*m*, 845*s*, 732*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.12 (*q*, J = 5.6, H–C(1′)); 4.74, 4.73 (2*d*, ^4J = 5.6, CH_2(3′)); 2.86–2.77 (*m*, H–C(3)); 2.67–2.40 (*m*, CH_2(2), H_a–C(12)); 2.37 (*ddd*, ^2J = 16.8, J = 5.7, 3.3, H_b–C(12)); 1.96–1.81 (*m*, CH_2(11)); 1.58–1.21 (*m*, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.2 (*s*, C(1)); 207.5 (*s*, C(2′)); 93.8 (*d*, C(1′)); 76.1 (*t*, C(3′)); 46.3 (*t*, C(2)); 40.3 (*t*, C(12)); 32.5 (*d*, C(3)); 29.6 (*t*); 24.8 (*t*); 24.4 (*t*); 24.0 (*t*); 22.4 (*t*); 22.2 (*t*); 22.0 (*t*). EI-MS: 219 (30, $[M-H]^+$), 205 (18), 177 (6), 163 (16), 149 (13), 135 (26), 121 (100), 107 (51), 95 (64), 79 (90), 67 (72), 55 (83).

3-Cyanocyclododecanone (**37**). A soln. of **6** (1.00 g, 5.55 mmol) in DMF (10 ml) and H_2O (1.7 ml) was warmed to 70°. Then, KCN (7.22 g, 11.10 mmol) and NH_4Cl (0.46 g, 8.65 mmol) were added. The resulting cloudy soln. was then heated at 80° for 12 h. The mixture was poured into a separatory funnel containing ice-water (100 ml) and Et_2O (60 ml). The aq. layer was extracted with Et_2O (2 × 40 ml), the combined org. layers were washed with H_2O and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give **37** (1.14 g, 99%) as a slightly yellow oil that solidified after a few days. M.p. 57–60° IR (film): 2946v*s*, 2864*s*, 2852*s*, 2239*m*, 1709v*s*, 1472v*s*, 1440*s*, 1411*s*, 1364*m*, 1266*m*, 1234*m*, 1199*m*, 1171*m*, 1125*m*, 1018*m*, 944*m*, 732*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.42–3.34 (*m*, H–C(3)); 3.16 (*dd*, ^2J = 17.1, ^3J = 1.2, H_a–C(2)); 2.62–2.52 (*m*, H_a–C(12), H_b–C(2)); 2.40–2.29 (*m*, H_b–C(12)); 1.83–1.20 (*m*, 16 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 207.3 (*s*, C(1)); 121.4 (*s*, CN); 42.4 (*t*, C(2)); 40.0 (*t*, C(12)); 26.2 (*t*); 25.7 (*t*); 25.3 (*t*); 24.7 (*d*, C(3)); 23.9 (*t*); 23.2 (*t*); 22.7 (*t*); 22.0 (*t*); 20.5 (*t*). EI-MS: 207 (7, $M^{+\bullet}$), 164 (64), 150 (48), 136 (33), 108 (26), 97 (75), 81 (86), 69 (43), 55 (100).

3-Acetylcyclododecanone (**38**). To a soln. of $NaIO_4$ (3.88 g, 18.14 mmol) in a 1:1 mixture H_2O/acetone (20 ml) was added a soln. of **24** (1.09 g, 4.90 mmol) in acetone (10 ml). The soln. was cooled to 0°, and a soln. of $KMnO_4$ (0.77 g, 4.90 mmol) in H_2O (20 ml) was added dropwise over 30 min. The mixture was stirred at r.t. for 10 min and then poured into a separatory funnel containing H_2O (30 ml) and Et_2O (40 ml). The aq. layer was extracted with Et_2O (2 × 20 ml), the combined org. layers were washed with H_2O and brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give **38** (3.94 g, 97%). Slightly yellow oil. IR (film): 2946v*s*, 2862*s*, 1710v*s*, 1472v*s*, 1448*s*, 1417*s*, 1276*w*, 1233*s*, 1202*m*, 1125*m*, 1019*m*, 945*m*, 732*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.17–3.10 (*m*, H–C(3)); 2.98 (*dd*, ^2J = 17.5, ^3J = 1.5, H_a–C(2)); 2.59–2.31 (*m*, H_a–C(12), H_b–C(2)); 2.39–2.30 (*m*, H_b–C(12)); 2.19 (*s*, Me); 1.82–1.64 (*m*, CH_2(11)); 1.59–1.15 (*m*, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 210.9, 210.3 (2*s*, C(1,2′)); 46.4 (*d*, C(3)); 42.8, 39.0 (2*t*, C(2,12)); 27.9 (*q*, Me); 26.5 (*t*); 25.6 (*t*); 25.4 (*t*); 24.5 (*t*); 23.4 (*t*); 22.9 (*t*); 22.6 (*t*); 21.0 (*t*). EI-MS: 224 (91, $M^{+\bullet}$), 180 (100), 135 (45), 111 (96), 81 (87), 55 (65).

3. *Thermal Isomerization Reactions. General Procedure* (*GP 3*) *for Isomerization of 3-Substituted Cycloalkanones.* The thermo-isomerization device consisted of an electrically heatable tube furnace (1-m length), a condenser unit with a cooling trap at the outlet side, and a *Kugelrohr* oven as the evaporation unit at the inlet side. A quartz tube (110 cm, 2.5 cm i.d.) fitting into the furnace was connected to a trap (cooled with liquid N_2) on one side and to a bulb placed in the *Kugelrohr* oven on the other. The starting material (typically 1–2 g) was placed in the bulb equipped with a capillary inlet device for the inert flow gas (N_2) and a magnetic stirrer. After evacuation of the apparatus with a high-vacuum oil pump, the starting material was distilled directly through the preheated reactor tube (1–3 g/h). After all of the starting material had been distilled, the apparatus was vented, and the frozen products were transferred to a bulb with Et_2O as solvent. The resulting soln. was dried ($MgSO_4$) and evaporated under reduced pressure. The following parameters are typical for the DGPTI process: *1*) the *Kugelrohr* oven was heated up to 140–160°; *2*) a flow of N_2 was adjusted from 0.8–1.4 l/h; *3*) the reactor tube was heated up to 580–630°; *4*) the vacuum was adjusted from $2-4 \times 10^{-2}$ mbar.

*(*E/Z*)-Cycloundec-4-enone* (**41a**) *and (*E*)-Undeca-8,10-dien-2-one* ((*E*)-**41c**). *GP 3*, from **16** (0.86 g, 5.17 mmol), at 620°. The dark yellow crude product was purified by CC (hexane/AcOEt 50:1) to afford a 1.3:1 mixture of (*E*/*Z*)-**41a** (0.30 g, 35%) followed by (*E*)-**41c** (0.12 g, 14%). A minor amount (9%) of a 1:1 mixture (*E*)/(*Z*)-**41b** (*cyclodecene*) was detected by GC/MS analysis.

*Data of (*E/Z*)-***41a***.* Colorless oil. IR (film): 2933v*s*, 2858*s*, 1702v*s*, 1461*m*, 1446*m*, 1410*w*, 1366*m*, 1215*w*, 1201*w*, 1144*w*, 1122*w*, 1053*w*, 981*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.49–5.26 (*m*, H–C(4,5)); 2.50–2.46 (*m*, CH_2(2)); 2.41–2.36 (*m*, CH_2(3,11)); 2.09–1.95 (*m*, CH_2(6)); 1.61–1.55 (*m*, CH_2(10)); 1.47–1.22

(*m*, CH_2(7,8,9)). ^{13}C-NMR (75 MHz, $CDCl_3$): 214.0 (*s*); 213.3 (*s*); 132.7 (*d*); 131.4 (*d*); 128.7 (*d*); 128.1 (*d*); 42.5 (*t*); 41.5 (*t*); 40.4 (*t*); 34.0 (*t*); 30.6 (*t*); 26.7 (*t*); 25.9 (*t*); 25.2 (*t*); 24.5 (*t*); 24.2 (*t*); 23.8 (*t*); 22.3 (*t*). EI-MS of (*E*)-isomer: 166 (48, $M^{+\bullet}$), 137 (12, $[M - CHO]^+$), 123 (33, $[M - CHO - CH_2]^+$), 109 (43, $[M - CHO - 2CH_2]^+$), 98 (70), 81 (66), 67 (100), 55 (89). EI-MS of (*Z*)-isomer: 166 (32, $M^{+\bullet}$), 137 (12, $[M - CHO]^+$), 123 (31, $[M - CHO - CH_2]^+$), 111 (40), 98 (62), 81 (57), 67 (100), 55 (82).

*Data of (*E*)*-**41c**. Colorless oil. IR (film): 2934v*s*, 2861v*s*, 1709v*s*, 1445*s*, 1363*s*, 1262*s*, 1163*m*, 1010*w*, 973*m*, 809*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.30 (*ddd*, $^3J_{trans} = 16.8$, $^3J_{cis} = 9.2$, $J(10,9) = 10.0$, H–C(10)); 6.04 (*dd*, $J(9,8) = 15.1$, $J(9,10) = 10.0$, H–C(9)); 5.69 (*td*, $J(8,9) = 15.1$, $J(8,7) = 6.9$, H–C(8)); 5.08 (*d*, $^3J_{trans} = 16.8$, 1 H); 4.95 (*d*, $^3J_{cis} = 9.2$, 1 H); 2.42 (*t*, $J(3,4) = 7.4$, CH_2(3)); 2.13 (*s*, Me(1)); 2.09–2.05 (*m*, CH_2(7)); 1.60–1.56 (*m*, CH_2(4)); 1.42–1.37 (*m*, CH_2(6)); 1.31–1.25 (*m*, CH_2(5)). ^{13}C-NMR (150 MHz, $CDCl_3$): 209.3 (*s*, C(2)); 137.4 (*d*, C(10)); 135.3 (*d*, C(8)); 131.3 (*d*, C(9)); 114.9 (*t*, C(11)); 43.9 (*t*, C(3)); 32.5 (*t*, C(7)); 29.8 (*q*, C(1)); 29.1 (*t*); 28.9 (*t*); 23.8 (*t*). EI-MS: 166 (6, $M^{+\bullet}$), 137 (15), 123 (100), 109 (39), 95 (40), 81 (62), 67 (62), 55 (61).

*(*E*)- and (*Z*)-Cyclododec-4-enone* ((*E*)- and (*Z*)-**42a**). *GP 3*, from **17** (1.30 g, 7.21 mmol), at 610°. The dark-yellow crude product was purified by CC (hexane/AcOEt 30:1) to give (*E*)-**42a** (0.56 g, 43%) and (*Z*)-**42a** (0.33 g, 25%). A minor amount (7%) of a 1:1 mixture of (*E*/*Z*)-**42b** (*cycloundecene*) was detected by GC/MS analysis.

*Data of (*E*)*-**42a**. Colorless oil. IR (film): 3025*w*, 2925v*s*, 2853v*s*, 1712v*s*, 1457*s*, 1438*s*, 1363*m*, 1290*w*, 1219*m*, 1110*m*, 1050*w*, 975v*s*, 948*m*, 918*m*, 733*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.41–5.33 (*m*, H–C(4,5)); 2.43–2.39 (*m*, CH_2(2,12)); 2.37–2.33 (*m*, CH_2(3)); 2.03–2.00 (*m*, CH_2(6)); 1.66 (*quint.*, $J = 6.0$, CH_2(11)); 1.44–1.38 (*m*, CH_2(7)); 1.35–1.29 (*m*, CH_2(8)); 1.28–1.23 (*m*, CH_2(9,10)). ^{13}C-NMR (150 MHz, $CDCl_3$): 212.9 (*s*, C(1)); 134.4 (*d*, C(5)); 128.0 (*d*, C(4)); 42.5 (*t*, C(12)); 41.5 (*t*, C(2)); 31.9 (*t*, C(6)); 29.4 (*t*, C(3)); 26.9 (*t*, C(8)); 25.3 (*t*, C(10)); 25.0 (*t*, C(7)); 24.6 (*t*, (C(9)); 21.1 (*t*, C(11)). EI-MS: 180 (100, $M^{+\bullet}$), 151 (27, $[M - CHO]^+$), 137 (46, $[M - CHO - CH_2]^+$), 123 (65, $[M - CHO - 2CH_2]^+$), 111 (50), 95 (81, $[M - CHO - 4CH_2]^+$), 81 (89, $[M - CHO - 5CH_2]^+$), 67 (96, $[M - CHO - 6CH_2]^+$), 55 (70).

*Data of (*Z*)*-**42a**. Colorless oil. IR (film): 3002*m*, 2927v*s*, 2856v*s*, 1710v*s*, 1460*s*, 1440*s*, 1361*m*, 1216*m*, 1181*w*, 1096*m*, 976*m*, 917*m*, 732*s*, 712*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.41–5.25 (*m*, H–C(4,5)); 2.54–2.39 (*m*, CH_2(2,12)); 2.11 (*q*, $J = 6.3$, CH_2(3)); 1.69 (*q*, $J = 6.3$, CH_2(6)); 1.49–1.17 (*m*, 10 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.7 (*s*, C(1)); 131.4 (*d*, C(5)); 128.1 (*d*, C(4)); 43.2 (*t*, C(12)); 38.9 (*t*, C(2)); 26.63 (*t*); 26.57 (*t*); 24.9 (*t*); 24.5 (*t*); 23.54 (*t*); 23.51 (*t*); 19.7 (*t*). EI-MS: 180 (78, $M^{+\bullet}$), 151 (21, $[M - CHO]^+$), 137 (35, $[M - CHO - CH_2]^+$), 123 (49, $[M - CHO - 2CH_2]^+$), 111 (50), 95 (80, $[M - CHO - 4CH_2]^+$), 81 (92, $[M - CHO - 5CH_2]^+$), 67 (100, $[M - CHO - 6CH_2]^+$), 55 (82).

*(*E*)- and (*Z*)-Cyclotetradec-4-enone* ((*E*)- and (*Z*)-**39a**) *and (*E*/*Z*)-Cyclotridecene* (**39b**). *GP 3*, from **18** (4.82 g, 23.14 mmol), at 600°. The pale-yellow crude product was purified by CC (hexane/AcOEt 40:1) to give a 1.3:1 mixture of (*E*/*Z*)-**39b** (0.92 g, 7%), (*E*)-**39a** (1.96 g, 37%), followed by a mixed fraction of (*E*/*Z*)-**39a** (1.13 g, 28%). Finally, pure (*Z*)-**39a** (0.83 g, 20%) was obtained. Both (*E*)- and (*Z*)-**39a** could be crystallized from hexane.

*Data of (*E*)*-**39a**. Colorless needles. M.p. 40° (hexane). IR (KBr): 3030*w*, 2928v*s*, 2848*s*, 1703v*s*, 1456*m*, 1431*s*, 1407*m*, 1361*m*, 1213*m*, 1185*w*, 1092*w*, 1003*w*, 977*m*, 967*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.41–5.30 (*m*, H–C(4,5)); 2.51 (*t*, $^3J(2,3) = 5.7$, CH_2(2)); 2.41 (*t*, $J(14,13) = 6.2$, CH_2(14)); 2.32 (*q*, $J = 6.5$, CH_2(3)); 2.00 (*q*, $J = 5.9$, CH_2(6)); 1.68–1.64 (*m*, CH_2(13)); 1.38–1.32 (*m*, 4 H); 1.24–1.12 (*m*, 8 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 211.4 (*s*, C(1)); 131.9 (*d*, C(5)); 130.1 (*d*, C(4)); 42.2 (*t*, C(14)); 42.0 (*t*, C(2)); 30.8 (*t*, C(6)); 27.2 (*t*, C(7)); 26.9 (*t*); 26.8 (*t*, C(3)); 26.0 (*t*); 25.9 (*t*); 24.9 (*t*); 24.4 (*t*, C(8)); 24.2 (*t*, C(13)). EI-MS: 208 (11, $M^{+\bullet}$), 165 (10, $[M - CHO - CH_2]^+$), 151 (7, $[M - CHO - 2CH_2]^+$), 121 (12, $[M - CHO - 4CH_2]^+$), 109 (23, $[M - CHO - 5CH_2]^+$), 95 (42, $[M - CHO - 6CH_2]^+$), 81 (55, $[M - CHO - 7CH_2]^+$), 67 (82), 55 (100). Anal. calc. for $C_{14}H_{24}O$ (208.34): C 80.71, H 11.61; found: C 80.45, H 11.47. X-Ray crystal-structure analysis: see *Fig. 1*, *a*.

*Data of (*Z*)*-**39a**. Colorless needles. M.p. 58–59° (hexane). IR (KBr): 3006*w*, 2923v*s*, 2846v*s*, 1701v*s*, 1465*s*, 1452*m*, 1429*m*, 1405*s*, 1356*s*, 1263*m*, 1203*m*, 1158*w*, 1128*w*, 1112*w*, 1067*w*, 850*w*, 732*s*, 704*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.45 (m_c, H–C(4)); 5.35 (m_c, H–C(5)); 2.45 (*t*, $J(2,3) = 7.4$, CH_2(2)); 2.40 (*t*, $J(14,13) = 6.7$, CH_2(14)); 2.33 (*q*, $J = 7.7$, CH_2(3)); 2.07 (*q*, $J = 7.4$, CH_2(6)); 1.67 (*quint.*, $J = 6.7$, CH_2(13)); 1.41 (*quint.*, $J = 7.0$, CH_2(7)); 1.35–1.32 (*m*, 4 H); 1.29–1.22 (*m*, 6 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 212.5 (*s*, C(1)); 131.4 (*d*, C(5)); 128.5 (*d*, C(4)); 42.7 (*t*, C(14)); 41.7 (*t*, C(2)); 27.8 (*t*, C(7)); 26.6 (*t*); 26.13 (*t*); 26.07 (*t*); 25.8 (*t*); 25.6 (*t*); 25.4 (*t*, C(6)); 23.5 (*t*, C(13)); 22.3 (*t*, C(3)). EI-MS: 208 (15, $M^{+\bullet}$), 165 (12, $[M - CHO - CH_2]^+$), 151 (10, $[M - CHO - 2CH_2]^+$), 121 (18, $[M - CHO - 4CH_2]^+$), 109 (30, $[M - CHO - 5CH_2]^+$), 95 (62, $[M - CHO - 6CH_2]^+$), 81 (75, $[M - CHO - 7CH_2]^+$), 67 (98), 55 (100). Anal. calc. for $C_{14}H_{24}O$ (208.34): C 80.71, H 11.61; found: C 80.72, H 11.52. X-Ray crystal-structure analysis: see *Fig. 1*, *b*.

*Data of (*E/Z*)-***39b***.* Colorless oil. IR (film): 3077*w*, 2999*s*, 2924v*s*, 2855v*s*, 1641*w*, 1461v*s*, 1447v*s*, 1349*w*, 1305*w*, 971*s,* 909*s*, 721*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.35–5.29 (*m*, H–C(1,2)); 2.14–1.99 (*m*, CH_2(3,13)); 1.52–1.26 (*m*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 131.5 (*d*); 130.8 (*d*); 31.4 (*t*); 28.6 (*t*); 28.1 (*t*); 27.5 (*t*); 26.9 (*t*); 26.0 (*t*); 25.8 (*t*); 25.5 (*t*); 25.2 (*t*); 25.1 (*t*); 24.9 (*t*). EI-MS of (*E*)-isomer: 180 (81, $M^{+\bullet}$), 137 (10, $[M-3CH_2]^+$), 123 (25), 109 (62), 96 (96), 81 (100), 67 (98), 55 (93). EI-MS of (*Z*)-isomer: 180 (78, $M^{+\bullet}$), 137 (5, $[M-3CH_2]^+$), 123 (12), 109 (22), 96 (54), 81 (88), 67 (99), 55 (100).

*(*E*)- and (*Z*)-Cyclopentadec-4-enone* ((*E*)-**43a** and (*Z*)-**43a**) *and (*E/Z*)-Cyclotetradecene* (**43b**). *GP 3*, from **19** (1.80 g, 8.09 mmol), at 600°. The pale-yellow crude product was purified by CC (hexane/AcOEt 60:1) to give a 1.7:1 mixture of (*E*/*Z*)-**43b** (63 mg, 4%), followed by pure (*E*)-**43a** (0.79 g, 44%). Finally, a 1:1 fraction of (*E*)- and (*Z*)-**43a** (0.78 g, 43%) was obtained. An enriched sample of (*Z*)-**43a** ((*Z*)/(*E*) 3:1) was obtained by CC (hexane/AcOEt 60:1).

*Data of (*E*)-***43a***.* Colorless oil. IR (film): 3027*w*, 2927v*s*, 2855v*s*, 1714v*s*, 1459*s*, 1441*s*, 1406*s*, 1367*s*, 1292*w*, 1207*w*, 1124*m*, 1073*m*, 970v*s*, 917*w*, 733*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.44–5.36 (*m*, H–C(4,5)); 2.48 (*m*, *t*-like, *J*(2,3) = 5.9, CH_2(2)); 2.40 (*t*, *J*(15,14) = 7.0, CH_2(15)); 2.32 (*q*, *J* = 5.3, CH_2(3)); 2.02 (*q*, *J* = 5.4, CH_2(6)); 1.63 (*quint.*, *J* = 6.8, CH_2(14)); 1.39–1.32 (*m*, 6 H); 1.30–1.17 (*m*, 8 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 211.6 (*s*, C(1)); 132.1 (*d*, C(5)); 129.5 (*d*, C(4)); 42.8 (*t*, C(2)); 42.6 (*t*, C(15)); 31.3 (*t*, C(6)); 28.2 (*t*); 27.6 (*t*); 27.4 (*t*, C(3)); 27.3 (*t*); 26.7 (*t*); 26.4 (*t*); 26.1 (*t*); 26.0 (*t*); 21.9 (*t*, C(14)). EI-MS: 222 (60, $M^{+\bullet}$), 193 (48, $[M-CHO]^+$), 179 (20, $[M-CHO-CH_2]^+$), 165 (18, $[M-CHO-2CH_2]^+$), 151 (14), 135 (23), 121 (30), 109 (45), 95 (87), 81 (94), 67 (97), 55 (100).

*Data of (*Z*)-***43a***.* Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.54–5.35 (*m*, H–C(4,5)); 2.50–2.45 (*m*, CH_2(11)); 2.40 (*t*, *J*(15,14) = 6.9, CH_2(15)); 2.32 (*t*, *J* = 6.0, CH_2(3)); 2.09 (*m*, CH_2(6)); 1.67–1.22 (*m*, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.2 (*s*, C(1)); 131.2 (*d*, C(5)); 128.1 (*d*, C(4)); 43.1 (*t*, C(15)); 41.8 (*t*, C(2)); 27.3 (*t*); 27.1 (*t*); 27.0 (*t*); 26.8 (*t*); 26.43 (*t*); 26.37 (*t*); 25.8 (*t*); 25.7 (*t*); 23.7 (*t*); 22.4 (*t*). EI-MS: 222 (99, $M^{+\bullet}$), 193 (47, $[M-CHO]^+$), 179 (63, $[M-CHO-CH_2]^+$), 165 (50, $[M-CHO-2CH_2]^+$), 151 (39), 135 (70), 123 (78), 109 (85), 95 (94), 81 (95), 67 (100), 55 (95).

*Data of (*E/Z*)-***43b***.* Colorless oil. IR (film): 3078v*w*, 2999*m*, 2930v*s*, 2858v*s*, 1640v*w*, 1461*m*, 1445*m*, 1349v*w*, 971*m*, 910*m*, 721*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.42–5.27 (*m*, H–C(1,2)); 2.03–2.00 (*m*, CH_2(3,14)); 1.36–1.24 (*m*, 20 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 131.5 (*d*); 129.9 (*d*); 33.7 (*t*); 27.5 (*t*); 27.4 (*t*); 26.8 (*t*); 26.3 (*t*); 25.8 (*t*); 25.3 (*t*); 25.2 (*t*); 25.0 (*t*); 24.3 (*t*); 24.1 (*t*); 23.6 (*t*). EI-MS of (*E*)-isomer: 194 (81, $M^{+\bullet}$), 151 (8, $[M-3CH_2]^+$), 137 (23), 123 (41), 109 (54), 95 (93), 81 (100), 67 (96), 55 (88). EI-MS of (*Z*)-isomer: 194 (55, $M^{+\bullet}$), 151 (5, $[M-3CH_2]^+$), 137 (18), 123 (30), 109 (49), 95 (90), 81 (100), 67 (98), 55 (84).

*(*E/Z*)-Cycloheptadec-4-enone* (**44a**). *GP 3*, from **20** (1.72 g, 6.87 mmol), at 600°. The yellow crude product was purified by CC (hexane/AcOEt 40:1) to afford a 1.7:1 mixture of (*E*/*Z*)-**44a** (1.29 g, 75%). A trace amount (1%) of a 1:1 mixture of (*E*/*Z*)-**44b** (*cyclohexadecene*) was detected by GC/MS analysis. Colorless oil. IR (film): 2962v*s*, 2855v*s*, 1714v*s*, 1459*m*, 1407*m*, 1365*m*, 1204*w*, 1079*w*, 969*m*, 915*m*, 733*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.43–5.35 (*m*, H–C(4,5)); 2.50–2.45 (*m*, CH_2(2)); 2.44–2.35 (*m*, CH_2(17)); 2.34–2.26 (*m*, CH_2(3)); 2.07–1.95 (*m*, CH_2(6)); 1.65–1.57 (*m*, CH_2(16)); 1.39–1.28 (*m*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.3 (*s*); 211.0 (*s*); 131.7 (*d*); 131.1 (*d*); 128.7 (*d*); 127.9 (*d*); 43.2 (*t*); 42.9 (*t*); 42.4 (*t*); 41.9 (*t*); 31.6 (*t*); 28.5 (*t*); 28.3 (*t*); 27.8 (*t*); 27.6 (*t*); 27.5 (*t*); 27.4 (*t*); 27.23 (*t*); 27.15 (*t*); 27.1 (*t*); 27.01 (*t*); 26.96 (*t*); 26.90 (*t*); 26.8 (*t*); 26.7 (*t*); 26.3 (*t*); 23.5 (*t*); 23.2 (*t*). EI-MS of (*E*)-**44a**: 250 (63, $M^{+\bullet}$), 221 (10, $[M-CHO]^+$), 207 (9, $[M-CHO-CH_2]^+$), 193 (5), 179 (4), 151 (7), 135 (14), 123 (15), 109 (28), 95 (50), 81 (61), 67 (79), 55 (100). EI-MS of (*Z*)-**44a**: 250 (70, $M^{+\bullet}$), 221 (8, $[M-CHO]^+$), 207 (9, $[M-CHO-CH_2]^+$), 193 (2), 179 (3), 165 (4), 151 (7), 135 (10), 123 (13), 109 (24), 95 (54), 81 (59), 67 (75), 55 (100).

*(*E*)- and (*Z*)-4-Methylcyclotetradec-4-enone* ((*E*)-**45a** and (*Z*)-**45a**) *and (*E/Z*)-1-Methylcyclotridecene* (**45b**). *GP 3*, from **12** (1.43 g, 6.43 mmol), at 600°. The colorless crude product was purified by CC (hexane/AcOEt 50:1) to give a 1.2:1 mixture of (*E*/*Z*)-**45b** (73 mg, 6%), enriched (*E*)-**45a** (0.29 g, 20%), followed by a mixed fraction of (*E*)-**45a** and (*Z*)-**45a** (0.54 g, 38%), and then enriched (*Z*)-**45a** (0.41 g, 29%). The enriched sample of (*Z*)-**45a** could be crystallized from hexane, and the enriched sample of (*E*)-**45a** was resubjected to CC to give the pure isomer.

*Data of (*E*)-***45a***.* Colorless oil. IR (film): 2931v*s*, 2856v*s*, 1702v*s*, 1442*m*, 1425*m*, 1360*m*, 1221*w*, 875*w*, 732*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.13 (*td*, *J*(5,6) = 7.4, *J* = 1.1, H–C(5)); 2.54 (*t*, *J*(2,3) = 6.0, CH_2(2)); 2.43 (*t*, *J*(14,13) = 6.1, CH_2(14)); 2.36 (*t*, *J*(3,2) = 6.1, CH_2(3)); 1.99 (*q*, *J* = 6.9, CH_2(6)); 1.62 (*s*, Me); 1.62 (*quint.*, *J* = 5.9, CH_2(13)); 1.38–1.10 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 210.6 (*s*, C(1)); 133.4 (*s*, C(4)); 126.5 (*d*, C(5)); 41.1 (*t*, C(14)); 39.8 (*t*, C(2)); 33.4 (*t*); 27.6 (*t*); 26.4 (*t*); 25.6 (*t*); 25.4 (*t*); 25.2 (*t*); 24.8 (*t*); 24.3 (*t*); 22.3 (*t*); 19.7 (*q*, Me). EI-MS: 222 (8, $M^{+\bullet}$), 164 (15, $[M-CHO-2CH_2]^+$), 152 (12), 134 (16, $[M-CHO-4CH_2]^+$), 109 (31), 95 (58), 81 (51), 67 (70), 55 (100).

Data of (Z)-**45a**. Colorless needles. M.p. 69–70° (hexane). IR (KBr): 2960*s*, 2929v*s*, 2853v*s*, 1701v*s*, 1465*m*, 1451*m*, 1408*m*, 1349*m*, 1268*m*, 1208*w*, 1071*w*, 877*m*, 752*w*, 706*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.12 (*t*, *J*(5,6) = 7.7, H–C(5)); 2.50 (*t*, *J*(2,3) = 7.8, CH_2(2)); 2.39 (*t*, *J*(14,13) = 6.8, CH_2(14)); 2.29 (*t*, *J*(3,2) = 7.8, CH_2(3)); 1.99 (*q*, *J* = 7.2, CH_2(6)); 1.69 (*d*, ^{4}*J*(Me,5) = 1.0, CH_3); 1.68 (*quint.*, *J* = 7.1, CH_2(13)); 1.39–1.22 (*m*, 12 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 212.8 (*s*, C(1)); 134.6 (*s*, C(4)); 126.6 (*d*, C(5)); 42.9 (*t*, C(14)); 40.2 (*t*, C(2)); 28.1 (*t*); 26.9 (*t*); 26.4 (*t*); 26.3 (*t*, C(6)); 26.1 (*t*, (C3)); 25.80 (*t*); 25.78 (*t*); 25.5 (*t*); 23.8 (*t*, C(13)); 23.5 (*q*, CH_3). EI-MS: 222 (5, $M^{+\bullet}$), 164 (24, $[M - CHO - 2CH_2]^+$), 152 (23), 137 (25, $[M - CHO - 4CH_2]^+$), 108 (91), 93 (90), 82 (98), 67 (100), 55 (99). Anal. calc. for $C_{15}H_{26}O$ (222.37): C 81.02, H 11.78; found: C 80.86, H 11.73. X-Ray crystal-structure analysis: see *Fig. 2*, *a*.

*Data of (*E/Z*)*-45b. Colorless oil. IR (film): 3077*m*, 2925v*s*, 2853v*s*, 1641*m*, 1447v*s*, 1376*s*, 1349*s*, 1310*m*, 990*m*, 964*m*, 909v*s*, 887v*s*, 736*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.19–5.98 (*m*, H–C(1,2)); 2.10–1.97 (*m*, CH_2(3,13)); 1.67 (*d*, ^{4}*J*(Me,1) = 1.3, Me of isomer 1); 1.58 (*d*, ^{4}*J*(Me,1) = 0.6, Me of isomer 2); 1.35–1.23 (*m*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.4 (*s*); 134.2 (*s*); 127.1 (*d*); 126.4 (*d*); 38.2 (*t*); 29.6 (*t*); 28.1 (*t*); 28.0 (*t*); 27.7 (*t*); 27.4 (*t*); 27.0 (*t*); 26.8 (*t*); 26.4 (*t*); 26.1 (*t*); 25.7 (*t*); 25.6 (*t*); 25.5 (*t*); 25.2 (*t*); 24.6 (*t*); 23.4 (*q*); 15.3 (*q*). EI-MS of (*E*)-isomer: 194 (89, $M^{+\bullet}$), 138 (10, $[M - 4CH_2]^+$), 123 (36), 109 (88), 95 (100), 81 (97), 67 (96), 55 (96). EI-MS of (*Z*)-isomer: 194 (55, $M^{+\bullet}$), 138 (8, $[M - 4CH_2]^+$), 123 (27), 109 (54), 95 (100), 81 (96), 67 (96), 55 (92).

*(*E/Z*)-4-Methylcyclopentadec-4-enone* (**46a**) *and (*E/Z*)-1-Methylcyclotetradecene* (**46b**). *GP 3*, from **25** (0.77 g, 3.26 mmol), at 600°. The colorless crude product was purified by CC (hexane/AcOEt 50:1) to give a 1.2:1 mixture of (*E*/*Z*)-**46b** (34 mg, 5%), recovered starting material (31 mg, 4%), and a 1:1 mixture of (*E*/*Z*)-**46a** (0.65g, 85%).

Data of (E/Z)-**46a**. Colorless oil. IR (film): 2928v*s*, 2857v*s*, 1713v*s*, 1458*s*, 1446*s*, 1408*m*, 1367*m*, 1275*w*, 1110*w*, 1082*m*, 860*w*, 723*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.18 (*t*, *J*(5,6) = 7.5, H–C(5) of isomer 1); 5.11 (*td*, *J*(5,6) = 6.9, *J* = 1.3, H–C(5) of isomer 2); 2.53–2.49 (*m*, CH_2(2)); 2.42–2.26 (*m*, CH_2(3,15)); 2.01–1.92 (*m*, CH_2(6)); 1.69 (*d*, ^{4}*J*(Me,5) = 1.2, Me of isomer 1); 1.63 (*d*, ^{4}*J*(Me,5) = 0.4, Me of isomer 2); 1.40–1.18 (*m*, 16 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 212.2 (2*s*, C(1)); 134.1, 125.9 (2*s*, C(4)); 126.2, 125.9 (2*d*, C(5)); 42.4 (*t*); 41.8 (*t*); 41.7 (*t*); 40.3 (*t*); 34.0 (*t*); 28.6 (*t*); 28.0 (*t*); 27.0 (*t*); 26.9 (*t*); 26.5 (*t*); 26.4 (*t*); 26.3 (*t*); 26.0 (*t*); 25.2 (*t*); 25.0 (*t*); 24.0 (*t*); 23.0 (*q*, Me); 20.6 (*t*); 16.1 (*q*, Me). EI-MS: 236 (42, $M^{+\bullet}$), 193 (15, $[M - CHO - CH_2]^+$), 179 (19, $[M - CHO - 2CH_2]^+$), 165 (6, $[M - 3CH_2]^+$), 149 (20), 135 (23), 122 (33), 109 (63), 95 (97), 81 (100), 67 (99), 55 (99).

*Data of (*E/Z*)*-**46b**. Colorless oil. IR (film): 3077*w*, 2924v*s*, 2858v*s*, 1640*s*, 1447*s*, 1378*w*, 1349*w*, 996*w*, 907*m*, 731*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.16–4.90 (*m*, H–C(1,2)); 2.01–1.89 (*m*, CH_2(3,13)); 1.68 (*d*, ^{4}*J*(Me,2) = 2.0, Me of isomer 1); 1.56 (*d*, ^{4}*J*(Me,2) = 0.9, Me of isomer 2); 1.45–1.15 (*m*, 20 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.7 (*s*); 134.4 (*s*); 126.5 (*d*); 125.0 (*d*); 38.5 (*t*); 30.6 (*t*); 28.0 (*t*); 27.6 (*t*); 27.0 (*t*); 26.9 (*t*); 26.7 (*t*); 25.9 (*t*); 25.5 (*t*); 25.4 (*t*); 25.0 (*t*); 24.8 (*t*); 24.4 (*t*); 24.3 (*t*); 24.0 (*t*); 23.8 (*t*); 22.5 (*q*); 15.1 (*q*). EI-MS of (*E*)-isomer: 208 (61, $M^{+\bullet}$), 165 (13, $[M - 3CH_2]^+$), 124 (56), 109 (89), 95 (97), 81 (98), 67 (100), 55 (98). EI-MS of (*Z*)-isomer: 208 (44, $M^{+\bullet}$), 151 (10, $[M - 4CH_2]^+$), 123 (20), 109 (48), 95 (86), 81 (98), 67 (100), 55 (99).

*(*E*)-3-Methylcyclotetradec-4-enone* ((*E*)-**47a**), *(*E*)-3-Methylcyclotridecene* ((*E*)-**47b**), *and (*E*)-Pentadeca-12,14-dien-2-one* ((*E*)-**47c**). *GP 3*, from (*E*/*Z*)-**21** (5.70 g, 25.63 mmol), at 580°. The orange crude product mixture was purified by CC (hexane/AcOEt 70:1) to give, in the following order, (*E*)-**47b** (0.18 g, 4%), recovered starting material (1.08 g, 19%), (*E*)-**47a** (3.14 g, 55%), and (*E*)-**47c** (0.57 g, 10%), which solidified below 17°. An anal. sample of (*E*)-**47a** was crystallized from hexane.

*Data of (*E*)*-**47a**. Colorless needles. M.p. 48° (hexane). IR (KBr): 2925v*s*, 2858v*s*, 1703v*s*, 1456*s*, 1432*m*, 1408*s*, 1365*s*, 1276*m*, 1163*m*, 971v*s*, 742*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.33 (*ddd*, *J*(5,4) = 15.4, ^{3}*J* = 8.2, 2.6, H–C(5)); 5.26 (*dd*, *J*(4,5) = 15.4, *J*(4,3) = 7.8, H–C(4)); 2.80 (m_c, H–C(3)); 2.48 (*dd*, ^{2}*J* = 16.3, *J*(2_a,3) = 11.2, H_a–C(2)); 2.45, 2.35 (2*ddd*, ^{2}*J* = 16.8, ^{3}*J* = 8.4, 4.2, CH_2(14)); 2.28 (*dd*, ^{2}*J* = 16.3, *J*(2_b,3) = 3.0, H_b–C(2)); 2.07, 1.90 ($2m_c$, CH_2(6)); 1.70, 1.53 ($2m_c$, CH_2(13)); 1.42–1.38 (*m*, 1 H); 1.39–1.32 (*m*, 10 H); 1.15–1.07 (*m*, 1 H); 1.02 (*d*, ^{3}*J*(Me,3) = 7.0, Me). ^{13}C-NMR (150 MHz, $CDCl_3$): 210.8 (*s*, C(1)); 135.4 (*d*, C(4)); 129.9 (*d*, C(5)); 50.2 (*t*, C(2)); 42.0 (*t*, C(14)); 32.9 (*d*, C(3)); 31.1 (*t*, C(6)); 27.4 (*t*, C(7)); 26.5 (*t*); 25.8 (*t*); 25.3 (*t*); 25.2 (*t*); 24.4 (*t*); 23.3 (*t*, C(13)); 21.3 (*q*, Me). EI-MS: 222 (10, $M^{+\bullet}$), 137 (8, $[M - CHO - 4CH_2]^+$), 123 (11), 109 (20), 95 (40), 81 (45), 67 (81), 55 (100). Anal. calc. for $C_{15}H_{26}O$ (222.37): C 81.02, H 11.78; found: C 81.11, H 11.61. X-Ray crystal-structure analysis: see *Fig. 2*, *b*.

*Data of (*E*)*-**47b**. IR (film): 3077*w*, 2925v*s*, 2856v*s*, 1641*w*, 1460v*s*, 1367*m*, 1349*w*, 971*s*, 909*m*, 728*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.30 (*td*, *J*(1,2) = 15.3, *J*(1,13) = 4.0, H–C(1)); 5.16 (*dd*, *J*(2,1) = 15.3, *J*(2,3) = 8.4, H–C(2)); 2.12–1.89 (*m*, H–C(3), CH_2(13)); 1.51–1.18 (*m*, 18 H); 0.95 (*d*, ^{3}*J*(Me,3) = 6.7, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.4 (*d*, C(2)); 129.3 (*d*, C(1)); 37.2 (*d*, C(3)); 36.9 (*t*); 31.2 (*t*); 27.6 (*t*); 27.0 (*t*); 26.3 (*t*); 25.79 (*t*); 25.76 (*t*); 25.0 (*t*); 24.7 (*t*); 24.2 (*t*); 23.6 (*q*, Me). EI-MS: 194 (32, $M^{+\bullet}$), 137 (7, $[M - 4CH_2]^+$), 123 (11), 109 (48), 95 (92), 81 (99), 67 (100), 55 (91).

*Data of (*E*)-***47c***.* M.p. 17°. IR (film): 3085*w*, 3015*s*, 2927v*s*, 2855v*s*, 1718v*s*, 1463*s*, 1410*m*, 1359*s*, 1163*s*, 1004*s*, 987*s*, 949*m*, 897*w*, 719*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 6.30 (*ddd*, $^3J_{trans}$ = 16.5, $^3J_{cis}$ = 10.2, *J*(14,13) = 9.7, H–C(14)); 6.04 (*ddd*, *J*(13,12) = 15.2, *J*(13,14) = 9.7, ^4J = 0.6, H–C(13)); 5.70 (*td*, *J*(12,13) = 15.2, *J*(12,11) = 6.9, H–C(12)); 5.08 (*dd*, ^2J = 0.6, $^3J_{trans}$ = 16.5, 1 H); 4.94 (*dd*, ^2J = 0.6, $^3J_{cis}$ = 10.2, 1 H); 2.41 (*t*, *J*(3,4) = 7.5, CH_2(3)); 2.13 (*s*, Me(1)); 2.07 (*q*, *J* = 7.2, CH_2(11)); 1.56 (*quint.*, *J* = 7.3, CH_2(4)); 1.38 (*quint.*, *J* = 7.0, CH_2(10)); 1.29–1.24 (*m*, 10 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 209.3 (*s*, C(2)); 137.3 (*d*, C(14)); 135.5 (*d*, C(12)); 130.8 (*d*, C(13)); 114.5 (*t*, C(15)); 43.8 (*t*, C(3)); 32.5 (*t*, C(11)); 29.8 (*q*, C(1)); 29.38 (*t*); 29.35 (*t*); 29.34 (*t*); 29.30 (*t*); 29.13 (*t*); 29.08 (*t*); 23.8 (*t*). EI-MS: 222 (46, $M^{+\bullet}$), 164 (21), 135 (24), 125 (30), 109 (28), 95 (39), 81 (64), 67 (75), 55 (48), 43 (100).

*(*E*)-3-Methylcyclopentadec-4-enone* ((*E*)-**48a**), *(*E*)-3-Methylcyclotetradecene* ((*E*)-**48b**), *and (*E*)-Hexadeca-13,15-dien-2-one* ((*E*)-**48c**). *GP 3*, from **23** (1.21 g, 5.12 mmol), at 580°. The yellow-orange crude product mixture was purified by CC (hexane/AcOEt 50:1) to give, in the following order, (*E*)-**48b** (32 mg, 3%), recovered starting material (0.19 g, 16%), (*E*)-**48a** (0.76 g, 63%), and (*E*)-**48c** (0.11 g, 9%), which solidified below 23°.

*Data of (*E*)-***48a***.* Colorless oil. IR (film): 2928v*s*, 2856v*s*, 1714v*s*, 1458*s*, 1407*s*, 1367*s*, 1276*m*, 1090*m*, 1056*m*, 969v*s*, 728*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.37 (*ddd*, *J*(5,4) = 15.4, ^3J = 8.1, 5.2, H–C(5)); 5.30 (*dd*, *J*(4,5) = 15.4, *J*(4,3) = 8.0, H–C(4)); 2.67 (m_c, H–C(3)); 2.43 (*dd*, ^2J = 14.7, *J*(2_a,3) = 10.8, H_a–C(2)); 2.39–2.31 (*m*, CH_2(15)); 2.28 (*dd*, ^2J = 14.7, *J*(2_b,3) = 3.1, H_b–C(2)); 2.06, 1.96 ($2m_c$, CH_2(6)); 1.68, 1.53 ($2m_c$, CH_2(14)); 1.40–1.16 (*m*, 1 H); 1.15–1.07 (*m*, 14 H); 1.02 (*d*, ^3J(Me,3) = 6.9, Me). ^{13}C-NMR (150 MHz, $CDCl_3$): 211.2 (*s*, C(1)); 135.1 (*d*, C(4)); 130.4 (*d*, C(5)); 50.8 (*t*, C(2)); 42.8 (*t*, C(15)); 34.1 (*d*, C(3)); 31.5 (*t*, C(6)); 28.5 (*t*); 27.3 (*t*); 27.1 (*t*); 26.8 (*t*); 26.4 (*t*); 25.8 (*t*); 25.7 (*t*); 22.3 (*q*, Me); 21.2 (*t*, C(14)). EI-MS: 236 (78, $M^{+\bullet}$), 207 (24, $[M - CHO]^+$), 193 (62, $[M - CHO - CH_2]^+$), 178 (55), 165 (43), 151 (47), 137 (74), 123 (76), 109 (89), 95 (97), 81 (93), 67 (98), 55 (100).

*Data of (*E*)-***48b***.* Colorless oil. IR (film): 3077v*w*, 2929v*s*, 2857v*s*, 1640v*w*, 1458*s*, 1378*w*, 1350v*w*, 973*m*, 908*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.25 (*td*, *J*(1,2) = 15.1, *J*(1,14) = 5.1, H–C(1)); 5.11 (*dd*, *J*(2,1) = 15.1, *J*(2,3) = 7.9, H–C(2)); 2.16–1.88 (*m*, H–C(3), CH_2(14)); 1.44–1.14 (*m*, 20 H); 0.96 (*d*, ^3J(Me,3) = 6.7, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.5 (*d*, C(2)); 129.3 (*d*, C(1)); 37.1 (*d*, C(3)); 36.2 (*t*); 33.7(*t*); 31.8 (*t*); 29.2 (*t*); 26.4 (*t*); 26.3 (*t*); 25.3 (*t*); 24.8 (*t*); 24.1 (*t*); 23.9 (*t*); 23.4 (*t*); 23.3 (*t*); 21.6 (*q*, Me). EI-MS: 208 (60, $M^{+\bullet}$), 165 (11, $[M - 3CH_2]^+$), 151 (23), 124 (50), 109 (75), 95 (88), 81 (100), 67 (99), 55 (98).

*Data of (*E*)-***48c***.* Colorless solid. M.p. 23°. IR (film): 3085v*w*, 3016*m*, 2927v*s*, 2854v*s*, 1719v*s*, 1463*s*, 1410*s*, 1359*s*, 1164*s*, 1004*s*, 987*s*, 949*s*, 897*m*, 718*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.30 (*ddd*, $^3J_{trans}$ = 15.8, $^3J_{cis}$ = 10.0, *J*(15,14) = 9.2, H–C(15)); 6.02 (*ddd*, *J*(14,13) = 15.6, *J*(14,15) = 9.2, ^4J = 0.6, H–C(14)); 5.69 (*td*, *J*(13,14) = 15.6, *J*(13,12) = 6.9, H–C(13)); 5.07 (*dd*, ^2J = 0.4, $^3J_{trans}$ = 15.8, 1 H); 4.94 (*dd*, ^2J = 0.4, $^3J_{cis}$ = 10.0, 1 H); 2.41 (*t*, *J*(3,4) = 7.4, CH_2(3)); 2.13 (*s*, Me(1)); 2.10–2.03 (*m*, CH_2(12)); 1.56 (*quint.*, *J* = 7.2, CH_2(4)); 1.40–1.27 (*m*, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.1 (*s*, C(2)); 137.3 (*d*, C(15)); 135.5 (*d*, C(13)); 130.7 (*d*, C(14)); 114.4 (*t*, C(16)); 43.7 (*t*, C(3)); 32.4 (*t*, C(12)); 31.7 (*t*); 30.0 (*t*); 29.6 (*q*, C(1)); 29.3 (*t*); 29.2 (*t*); 29.0 (*t*); 28.9 (*t*); 23.7 (*t*). EI-MS: 236 (59, $M^{+\bullet}$), 178 (15), 149 (11), 135 (13), 121 (15), 109 (26), 95 (66), 81 (100), 67 (93), 55 (52).

*(*E*)-3,4-Dimethylcyclotetradec-4-enone* ((*E*)-**49a**), *(*E*)-1,13-Dimethylcyclotridecene* ((*E*)-**49b**), *and (*E/Z*)-13-Methylpentadeca-12,14-dien-2-one* (**49c**). *GP 3*, from (*E*)-**26** (2.50 g, 10.58 mmol), at 580°. The colorless crude product was purified by CC (hexane/AcOEt 70:1) to give (*E*)-**49b** (0.11 g, 5%), recovered starting material (0.55 g, 22%), (*E*)-**49a** (1.15 g, 46%), and a 1:1 mixture of (*E*/*Z*)-**49c** (0.40 g, 16%), which solidified below 21°.

*Data of (*E*)-***49a***.* Colorless oil. IR (film): 2931v*s*, 2859v*s*, 1713v*s*, 1458*s*, 1407*m*, 1364*s*, 1275*w*, 1211*w*, 1154*w*, 1111*m*, 1049*w*, 878*w*, 738*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.19 (*td*, *J*(5,6) = 6.8, *J* = 0.7, H–C(5)); 2.83 (m_c, H–C(3)); 2.68 (*dd*, ^2J = 15.4, *J*(2_a,3) = 11.8, H_a–C(2)); 2.43–2.38 (*m*, CH_2(14)); 2.16 (*dd*, ^2J = 15.4, *J*(2_b,3) = 3.1, H_b–C(2)); 2.03, 1.93 ($2m_c$, CH_2(6)); 1.63, 1.51 ($2m_c$, CH_2(13)); 1.57 (*s*, Me–C(4)); 1.40–1.10 (*m*, 12 H); 1.02 (*d*, ^3J(3-Me,3) = 7.0, Me–C(3)). ^{13}C-NMR (150 MHz, $CDCl_3$): 210.6 (*s*, C(1)); 137.9 (*s*, C(4)); 125.9 (*d*, C(5)); 48.3 (*t*, C(2)); 41.2 (*t*, C(14)); 39.6 (*d*, C(3)); 28.1 (*t*); 26.6 (*t*, C(6)); 25.78 (*t*); 25.76 (*t*); 25.73 (*t*); 24.8 (*t*); 24.6 (*t*); 22.1 (*t*, C(13)); 21.0 (*q*, Me–C(3)); 12.4 (*q*, Me–C(4)). EI-MS: 236 (70, $M^{+\bullet}$), 193 (30, $[M - CHO - CH_2]^+$), 165 (62, $[M - CHO - 3CH_2]^+$), 149 (69), 137 (75), 123 (89), 109 (100), 95 (96), 81 (99), 67 (98), 55 (96).

*Data of (*E*)-***49b***.* Colorless oil. IR (film): 3077*w*, 2928v*s*, 2857v*s*, 1641*w*, 1456*s*, 1376*m*, 1312*w*, 1137*w*, 1095*w*, 992*w*, 909*m*, 727*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.16–4.88 (*m*, H–C(2)); 2.22–1.90 (*m*, H–C(13), CH_2(3)); 1.58 (*t*, *J* = 1.5, Me–C(1)); 1.45–1.10 (*m*, 18 H); 0.96 (*d*, ^3J = 6.9, Me–C(13)). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.2 (*s*, C(1)); 126.1 (*d*, C(2)); 42.1 (*d*, C(13)); 33.8 (*t*); 28.3 (*t*); 28.1 (*t*); 27.2 (*t*); 25.5 (*t*); 25.3 (*t*); 25.1 (*t*); 25.0 (*t*); 24.5 (*t*); 23.8 (*t*); 20.5 (*q*, Me–C(13)); 14.0 (*q*, Me–C(1)). EI-MS: 208 (32, $M^{+\bullet}$), 137 (9, $[M - 5CH_2]^+$), 123 (10), 109 (29), 95 (46), 81 (75), 67 (86), 55 (100).

*Data of (*E/Z*)-***49c**. M.p. 21°. IR (film): 2927v*s*, 2854v*s*, 1718v*s*, 1456v*s*, 1359v*s*, 1227*m*, 1167*s*, 1065*w*, 989*s*, 963v*s*, 911*m*, 733*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.35–6.08 (*m*, 1 H); 5.80–5.14 (*m*, 1 H); 5.15–4.91 (*m*, CH_2(15)); 2.41 (*t*, *J*(3,4) = 7.4, CH_2(3)); 2.12 (*s*, Me(1)); 2.12–2.08 (*m*, CH_2(11)); 1.79–1.77 (*m*, 6 H, Me–C(13)); 1.56 (*quint.*, *J* = 7.1, CH_2(4)); 1.37–1.28 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.1 (*s*, C(2)); 138.7 (*s*); 138.6 (*s*); 134.5 (*d*); 133.4 (*d*); 132.1 (*d*); 132.0 (*d*); 110.1 (*t*); 43.7 (*t*, C(3)); 33.1 (*t*); 32.7 (*t*); 29.6 (*q*, C(1)); 29.4 (*t*); 29.2 (*t*); 29.1 (*t*); 29.0 (*t*); 28.9 (*t*); 25.7 (*t*); 12.7, 12.4 (2*q*, *Me*–C(13)).

*(*E*)-3,4-Dimethylcyclopentadec-4-enone* ((*E*)-**50a**), *(*E*)-1,14-Dimethylcyclotetradecene* ((*E*)-**50b**), *and (*E/Z*)-14-Methylhexadeca-13,15-dien-2-one* (**50c**). *GP 3*, from (*E*)-**27** (0.91 g, 3.59 mmol), at 580°. The colorless crude product mixture was purified by CC (hexane/AcOEt 40:1) to give (*E*)-**50b** (48 mg, 6%), recovered starting material (0.19 g, 21%), (*E*)-**50a** (0.43 g, 48%), and a 1:1 mixture of (*E*/*Z*)-**50c** (0.14 g, 14%).

*Data of (*E*)-***50a**. Colorless oil. IR (film): 2930v*s*, 2858v*s*, 1712v*s*, 1458*s*, 1408*m*, 1367*m*, 1280*w*, 1078*w*, 917*m*, 734*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.19 (*td*, *J*(5,6) = 6.8, *J* = 0.7, H–C(5)); 2.72 (*m*, H–C(3)); 2.62 (*dd*, ^2J = 13.6, *J*(2_a,3) = 11.2, H_a–C(2)); 2.40–2.34 (*m*, CH_2(15)); 2.20 (*dd*, ^2J = 13.6, *J*(2_b,3) = 2.6, H_b–C(2)); 2.08–1.93 (*m*, CH_2(6)); 1.72–1.51 (*m*, CH_2(14)); 1.58 (*d*, ^4J(4-Me,5) = 0.6, Me–C(4)); 1.43–1.15 (*m*, 14 H); 1.04 (*d*, ^3J(3-Me,3) = 7.0, Me–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 210.7 (*s*, C(1)); 137.9 (*s*, C(4)); 125.4 (*d*, C(5)); 48.4 (*t*, C(2)); 41.5 (*t*, C(15)); 39.8 (*d*, C(3)); 28.7 (*t*); 26.8 (*t*); 26.6 (*t*); 26.4 (*t*); 25.9 (*t*); 25.2 (*t*); 24.8 (*t*); 24.3 (*t*); 21.0 (*q*, Me–C(3)); 20.8 (*t*); 12.6 (*q*, Me–C(4)). EI-MS: 250 (56, $M^{+\cdot}$), 221 (49, $[M - CHO]^+$), 207 (45, $[M - CHO - CH_2]^+$), 179 (40), 165 (34), 149 (32), 137 (45), 123 (50), 109 (49), 95 (97), 81 (100), 67 (73), 55 (52).

*Data of (*E*)-***50b**. Colorless oil. IR (film): 3077v*w*, 2928v*s*, 2857*s*, 1639v*w*, 1457*m*, 1378*m*, 1157*w*, 997*m*, 907*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.17–4.86 (*m*, H–C(2)); 2.15–1.87 (*m*, H–C(14), CH_2(3)); 1.57 (*s*, Me–C(1)); 1.48–1.12 (*m*, 20 H); 0.97 (*d*, ^3J = 6.9, Me–C(14)). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.3 (*s*, C(1)); 126.4 (*d*, C(2)); 42.4 (*d*, C(14)); 30.2 (*t*); 29.6 (*t*); 28.1 (*t*); 27.1 (*t*); 25.8 (*t*); 25.3 (*t*); 24.7 (*t*); 24.3 (*t*); 23.8 (*t*); 23.3 (*t*); 22.6 (*t*); 20.4 (*q*, Me–C(14)); 14.0 (*q*, Me–C(1)). EI-MS: 222 (5, $M^{+\cdot}$), 109 (10), 95 (24), 81 (39), 67 (73), 55 (100).

*Data of (*E/Z*)-***50c**. Colorless oil. IR (film): 2928v*s*, 2855v*s*, 1720v*s*, 1459*s*, 1358*s*, 1225*w*, 1166*m*, 988*m*, 963*s*, 891*w*, 733*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.27–5.99 (*m*, 1 H); 5.82–5.40 (*m*, 1 H); 5.10–4.88 (*m*, CH_2(16)); 2.41 (*t*, *J*(3,4) = 7.4, CH_2(3)); 2.12 (*s*, Me(1)); 2.12–2.07 (*m*, CH_2(12)); 1.74–1.71 (*m*, 6 H, Me–C(14)); 1.58–1.53 (*m*, CH_2(4)); 1.39–1.27 (*m*, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.1 (*s*, C(2)); 138.7 (*s*); 138.5 (*s*); 134.5 (*d*); 133.7 (*d*); 133.4 (*d*); 132.6 (*d*); 110.1 (*t*); 43.7 (*t*, C(3)); 33.2 (*t*); 32.7 (*t*); 29.6 (*q*, C(1)); 29.5 (*t*); 29.4 (*t*); 29.2 (*t*); 29.0 (*t*); 28.9 (*t*); 25.7 (*t*); 23.7 (*t*); 12.7, 12.4 (2*q*, *Me*–C(14)).

*(*E/Z*)-14-Methylpentadeca-12,14-dien-2-one* (**51c**). *GP 3*, with **28** (0.95 g, 4.02 mmol), at 590°. The colorless crude product mixture was purified by CC (hexane/AcOEt 70:1) to give recovered starting material (0.27 g, 28%) and a 1:1 mixture of (*E*/*Z*)-**51c** (0.36 g, 38%). Colorless oil. IR (film): 3017*s*, 2928v*s*, 2854v*s*, 1720v*s*, 1459*s*, 1410*s*, 1358*s*, 1224*m*, 1165*s*, 987*m*, 963*m*, 881*m*, 720*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.22–5.97 (*m*, 1 H); 5.85–5.56 (*m*, 1 H); 4.85 (*s*, CH_2(15)); 2.41 (*t*, *J*(3,4) = 7.4, CH_2(3)); 2.12 (*s*, Me(1)); 2.11–2.04 (*m*, CH_2(11)); 1.75, 1.73 (2*s*, Me–C(14)); 1.56 (*quint.*, *J* = 7.2, CH_2(4)); 1.39–1.28 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.1 (*s*, C(2)); 142.1 (*s*); 134.6 (*d*); 131.9 (*d*); 130.9 (*d*); 129.5 (*d*); 113.9 (*t*); 43.7 (*t*, C(3)); 32.7 (*t*); 32.6 (*t*); 29.7 (*q*, C(1)); 29.6 (*t*); 29.5 (*t*); 29.3 (*t*); 29.24 (*t*); 29.20 (*t*); 29.1 (*t*); 29.0 (*t*); 28.9 (*t*); 27.4 (*t*); 22.3 (*t*); 18.6, 18.0 (2*q*, *Me*–C(14)).

*(*E*)-3,3-Dimethylcyclopentadec-4-enone* ((*E*)-**52a**) *and (*E/Z*)-15-Methylhexadeca-13,15-dien-2-one* (**52c**). *GP 3*, from **29** (0.86 g, 3.43 mmol), at 590°. The colorless crude product mixture was purified by CC (hexane/AcOEt 50:1) to give recovered starting material (0.16 g, 19%), (*E*)-**52a** (0.13 g, 15%), and a 1:1 mixture of (*E*/*Z*)-**52c** (0.32 g, 37%). A trace amount (2%) of (*E*)-3,3-dimethylcyclotetradecene ((*E*)-**52b**) was detected by GC/MS analysis.

*Data of (*E*)-***52a**. Colorless oil. IR (film): 2933v*s*, 2859v*s*, 1703v*s*, 1469v*s*, 1460v*s*, 1446v*s*, 1366*s*, 978*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.56 (*dt*, *J*(4,5) = 15.7, *J*(4,6) = 1.4, H–C(4)); 5.32 (*dt*, *J*(5,4) = 15.7, *J*(5,6) = 6.7, H–C(5)); 2.46–2.31 (*m*, CH_2(2,15)); 2.12–2.02 (*m*, CH_2(6)); 1.67–1.49 (*m*, CH_2(14)); 1.44–1.14 (*m*, 14 H); 1.09 (*s*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 210.4 (*s*, C(1)); 138.7 (*d*, C(4)); 127.4 (*d*, C(5)); 55.9 (*t*, C(2)); 43.3 (*t*, C(15)); 36.9 (*t*); 35.8 (*s*, C(3)); 31.4 (*t*); 28.4 (*q*, Me_2C(3)); 27.0 (*t*); 26.9 (*t*); 26.4 (*t*); 25.7 (*t*); 25.5 (*t*); 25.3 (*t*); 24.4 (*t*). EI-MS: 250 (16, $M^{+\cdot}$), 123 (8), 109 (20), 95 (48), 81 (49), 67 (73), 55 (100).

*Data of (*E/Z*)-***52c**. Colorless oil. IR (film): 3018*s*, 2927v*s*, 2855v*s*, 1720v*s*, 1456v*s*, 1411*s*, 1359v*s*, 1224*m*, 1166*s*, 987*s*, 964v*s*, 882*s*, 733*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.18–6.03 (*m*, 1 H); 5.85–5.50 (*m*, 1 H); 4.84 (*s*, CH_2(15)); 2.41 (*t*, *J*(3,4) = 7.3, CH_2(3)); 2.12 (*s*, Me(1)); 2.11–2.03 (*m*, CH_2(12)); 1.75, 1.73 (2*s*, Me–C(15)); 1.59–1.54 (*m*, CH_2(4)); 1.39–1.27 (*m*, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.0 (*s*, C(2)); 142.1 (*s*); 134.6 (*d*); 132.6 (*d*); 130.9 (*d*); 129.6 (*d*); 113.9 (*t*); 43.7 (*t*, C(3)); 32.7 (*t*); 32.6 (*t*); 29.7 (*q*, C(1)); 29.6 (*t*); 29.5 (*t*); 29.31 (*t*); 29.26 (*t*); 29.0 (*t*); 27.4 (*t*); 26.1 (*t*); 22.3 (*t*); 18.5, 18.0 (2*q*, *Me*–C(15)).

(E/Z)-Bicyclo[12.4.0]octadec-13-en-3-one (**53a**) *and (E/Z)-12-(Cyclohexen-1-yl)dodec-11-en-2-one* (**53b**). *GP 3*, from **30** (1.26 g, 4.80 mmol), at 570°. The yellow crude product mixture was purified by CC (hexane/AcOEt 70:1) to give an inseparable 1:3 mixture of (*E*/*Z*)-**53a** and starting material (0.82 g, 65%), followed by pure (*E*/*Z*)-**53b** (0.30 g, 24%, (*E*)/(*Z*) 1:1). A trace amount (2%) of a 1:1 mixture of (*E*/*Z*)-bicyclo[11.4.0]-heptadec-12-ene was detected by GC/MS analysis.

MS Data of **53a**. EI-MS ((*E*)-isomer): 262 (52, $M^{+\cdot}$), 149 (15, $[M - CHO - 6CH_2]^+$), 135 (51), 121 (29), 107 (50), 94 (100), 79 (94), 67 (72), 55 (77). EI-MS ((*Z*)-isomer): 262 (55, $M^{+\cdot}$), 234 (9, $[M - CO]^+$), 219 (11, $[M - CHO - CH_2]^+$), 163 (14, $[M - CHO - 5CH_2]^+$), 149 (38, $[M - CHO - 6CH_2]^+$), 135 (44), 121 (100), 107 (60), 94 (66), 79 (98), 67 (78), 55 (83).

*Data of (E/Z)-***53b**. IR (film): 2928*vs*, 2855*vs*, 1716*vs*, 1674*s*, 1456*s*, 1411*s*, 1359*vs*, 1167*vs*, 1070*s*, 967*s*, 918*m*, 722*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.81–5.60 (*m*, H–C(12)); 5.22, 5.10 (2*t*, $^3J = 6.5$, H–C(2′) of both isomers); 2.41 (*t*, *J*(3,4) = 7.4, CH_2(3)); 2.33–2.14 (*m*, 2 H); 2.12 (*s*, Me(1)); 2.11–2.02 (*m*, CH_2(11)); 1.73–1.62 (*m*, 2 H); 1.60–1.54 (*m*, CH_2(4)); 1.38–1.27 (*m*, 16 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.1 (*s*, C(2)); 135.6 (*s*); 134.6 (*s*); 131.1 (*d*); 127.3 (*d*); 126.8 (*d*); 125.5 (*d*); 43.7 (*t*, C(3)); 32.2 (*t*); 29.8 (*t*); 29.6 (*q*, C(1)); 29.5 (*t*); 29.3 (*t*); 29.2 (*t*); 29.1 (*t*); 29.0 (*t*); 27.2 (*t*); 26.7 (*t*); 26.1 (*t*); 25.5 (*t*); 25.1 (*t*); 24.5 (*t*); 23.7 (*t*); 23.2 (*t*); 22.4 (*t*).

Cyclotetradeca-3,4-dienone (**54**). *GP 3*, from **31** (1.12 g, 5.43 mmol), at 540°. The crude product mixture was purified by CC (hexane/AcOEt 70:1) to give recovered starting material (0.87 g, 78%) followed by **54** (146 mg, 13%). Colorless oil. IR (film): 2935*vs*, 2858*vs*, 1962*w*, 1707*vs*, 1469*s*, 1446*s*, 1414*m*, 1360*m*, 1266*m*, 1071*w*, 1019*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.31 (m_c, H–C(3)); 5.11 (m_c, H–C(5)); 3.24 (*ddd*, $^2J = 16.4$, $J(2_a,3) = 10.4$, $J(2_a,5) = 0.8$, H_a–C(2)); 2.97 (*ddd*, $^2J = 16.4$, $J(2_b,3) = 8.9$, $J(2_b,5) = 2.5$, H_b–C(2)); 2.58, 2.38, (2m_c, CH_2(14)); 2.03–1.91 (m_c, CH_2(6)); 1.73–1.65 (m_c, CH_2(13)); 1.40–1.15 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.5 (*s*, C(1)); 205.2 (*s*, C(4)); 91.2 (*d*, C(3)); 84.6 (*d*, C(5)); 42.7 (*t*, C(2)); 41.3 (*t*, C(14)); 28.8 (*t*); 27.0 (*t*); 26.9 (*t*); 26.3 (*t*); 25.9 (*t*); 25.8 (*t*); 25.6 (*t*); 23.3 (*t*). EI-MS: 206 (43, $M^{+\cdot}$), 177 (10, $[M - CHO]^+$), 163 (21, $[M - CHO - CH_2]^+$), 149 (30), 135 (26), 121 (29), 107 (100), 93 (68), 81 (80), 67 (59), 55 (70).

3-Trimethylsilylcyclotetradeca-3,4-dienone (**55**) *and (E/Z)-14-Trimethylsilyltetradec-11-en-13-yn-2-one* (**56**). *GP 3*, from **32** (1.73 g, 6.21 mmol), at 540°. The crude product mixture was purified by CC (hexane/AcOEt 60:1) to give **55** (138 mg, 8%), recovered starting material (1.40 g, 81%), and a 1:1 mixture of (*E*/*Z*)-**56** (104 mg, 6%).

Data of **55**. Colorless oil. IR (film): 2930*vs*, 2857*vs*, 1936*s*, 1715*vs*, 1460*m*, 1443*m*, 1406*m*, 1247*vs*, 1001*w*, 841*vs*, 756*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 4.87 (m_c, H–C(5)); 3.19 (*dd*, $^2J = 15.1$, $J(2_a,5) = 1.7$, H_a–C(2)); 2.94 (*dd*, $^2J = 15.1$, $J(2_b,5) = 2.7$, H_b–C(2)); 2.56, 2.40 (2*dt*, $^2J = 15.8$, $J(14,13) = 7.2$, CH_2(14)); 2.03, 1.97 (2m_c, CH_2(6)); 1.65 (m_c, CH_2(13)); 1.47 (m_c, H_a–C(7)); 1.39–1.23 (*m*, 11 H); 0.10 (*s*, Me_3Si). ^{13}C-NMR (150 MHz, $CDCl_3$): 210.1 (*s*, C(1)); 207.8 (*s*, C(4)); 91.2 (*s*, C(3)); 86.1 (*d*, C(5)); 44.6 (*t*, C(2)); 41.2 (*t*, C(14)); 27.7 (*t*, C(7)); 27.0 (*t*, C(6)); 26.15 (*t*); 26.14 (*t*); 25.8 (*t*); 25.6 (*t*); 25.5 (*t*); 22.7 (*t*, C(13)); −1.1 (*q*, Me_3Si). EI-MS: 278 (75, $M^{+\cdot}$), 263 (60, $[M - Me]^+$), 235 (37, $[M - CHO - CH_2]^+$), 221 (48), 205 (53), 179 (70), 169 (68), 151 (52), 131 (50), 119 (36), 107 (44), 91 (56), 73 (100), 55 (53).

*Data of (E/Z)-***56**. Colorless oil. IR (film): 2932*vs*, 2858*s*, 2254*w*, 2145*w*, 1710*s*, 1464*w*, 1360*m*, 1251*s*, 1084*w*, 958*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.06 (*dt*, *J*(11,12) = 15.9, *J*(11,10) = 6.9, H–C(11) of (*E*)-isomer); 5.79 (*dt*, *J*(11,12) = 10.9, *J*(11,10) = 6.9, H–C(11) of (*Z*)-isomer); 5.35 (*dt*, *J*(12,11) = 15.9, *J*(12,10) = 1.5, H–C(12) of (*E*)-isomer); 5.32 (*dt*, *J*(12,11) = 10.9, *J*(12,10) = 1.1, H–C(12) of (*Z*)-isomer); 2.27 (*t*, *J*(3,4) = 7.4, CH_2(3)); 2.16 (*qd*, *J* = 7.4, *J*(10,12) = 1.1, CH_2(10) of (*Z*)-isomer); 1.98 (*s*, Me(1)); 1.95 (*qd*, *J* = 7.4, *J*(10,12) = 1.5, CH_2(10) of (*E*)-isomer); 1.49–1.33 (*m*, CH_2(4)); 1.32–1.10 (*m*, 10 H); 0.05, 0.03 (2*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.2 (*s*, C(2)); 146.2, 145.6 (2*d*, C(11)); 109.6, 109.2 (2*d*, C(12)); 104.2, 102.2, 97.9, 92.5 (4*s*, C(13,14)); 43.8 (*t*, C(3)); 33.0 (*t*, C(10)); 30.2 (*t*); 29.8 (*q*, C(1)); 29.2 (*t*); 29.0 (*t*); 28.64 (*t*); 28.56 (*t*); 23.8 (*t*); 0.0 (*q*, Me_3Si). EI-MS: 278 (9, $M^{+\cdot}$), 263 (8, $[M - Me]^+$), 221 (4), 205 (7), 179 (18), 167 (18), 151 (5), 131 (3), 119 (3), 107 (4), 91 (6), 73 (100), 55 (8).

4. *X-Ray Crystal-Structure Determination*. Compounds (*E*)-**39a**, (*Z*)-**39a**, (*Z*)-**45a**, and (*E*)-**47a** (see *Table 6* and *Figs. 1* and *2*) were analyzed crystallographically[39]). All measurements were conducted on a *Nonius*

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[39]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication Nos. CCDC-229915, -229916, -229917, and -229918 for (*E*)-**39a**, (*Z*)-**39a**, (*Z*)-**45a**, and (*E*)-**47a**, respectively. These data can be obtained, free of charge, *via* www.ccdc.cam.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

KappaCCD diffractometer [66] using graphite-monochromated Mo$K\alpha$ radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream-700* cooler. Data reduction was performed with HKL DENZO and Scalepack [67], and equivalent reflections were merged. The intensities for each structure were corrected for *Lorentz* and polarization effects, but not for absorption. Each structure was solved by direct methods using SIR92 [68], which revealed the positions of all non-H-atoms. The C=O O-atom in (*Z*)-**39a** is disordered over two positions in the macrocyclic ring, appearing at C(1) and C(8). These positions are unequally occupied, and refinement of the site-occupation factors yielded a value of 0.902(3) for the major orientation. A bond-length restraint was applied to the C=O bond of the minor component. The non-H-atoms of each structure were refined anisotropically. All H-atoms were placed in geometrically calculated positions. The structures of (*E*)-**39a**, (*Z*)-

Table 6. *Crystallographic Data of Compounds* (E)-**39a**, (Z)-**39a**, (Z)-**45a**, *and* (*E*)-**47a**

	(*E*)-**39a**	(*Z*)-**39a**	(*Z*)-**45a**	(*E*)-**47a**
Crystallized from	hexane	hexane	hexane	hexane
Empirical formula	$C_{14}H_{24}O$	$C_{14}H_{24}O$	$C_{15}H_{26}O$	$C_{15}H_{26}O$
M_r [g mol^{-1}]	208.34	208.34	222.37	222.37
Crystal color, habit	colorless prism	colorless prism	colorless prism	colorless prism
Crystal size [mm]	0.07 × 0.12 × 0.30	0.05 × 0.17 × 0.25	0.10 × 0.15 × 0.25	0.05 × 0.12 × 0.20
Temp. [K]	160 (1)	160 (1)	160 (1)	160 (1)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\,2_1$	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$
Z	2	4	4	4
Reflections for cell determination	1588	2281	2949	3429
2θ range for cell determination [°]	4–55	4–50	4–52	4–55
Unit-cell parameters:				
a [Å]	7.6071 (1)	5.3093 (1)	17.0393 (4)	9.2119 (2)
b [Å]	5.4093 (1)	27.4049 (4)	5.2743 (1)	5.5706 (1)
c [Å]	15.3602 (3)	8.6425 (2)	15.7306 (3)	26.6534 (6)
β [°]	90.9070 (7)	91.5122 (6)	108.818 (1)	95.4013 (9)
V [Å^3]	631.98 (2)	1257.05 (4)	1338.15 (5)	1361.67 (5)
$F(000)$	232	464	496	496
D_x [g cm^{-3}]	1.095	1.101	1.104	1.085
μ(Mo$K\alpha$) [mm^{-1}]	0.0659	0.0663	0.0660	0.0649
Scan type	ϕ and ω	ϕ and ω	ω	ω
$2\theta_{(max)}$ [°]	55	50	52	55
Total refl. measured	13874	19811	25538	29044
Symmetry-independent reflections	2853	2218	2653	3112
R_{int}	0.044	0.050	0.072	0.074
Reflections [$I > 2\sigma(I)$]	2515	1630	1788	1654
Parameters refined	136	147	146	145
Final R	0.0397	0.0397	0.0461	0.0561
wR	0.0373	–	0.0472	0.0532
$wR(F^2)$	–	0.1063	–	–
Weights: p in $w = [\sigma^2(F_0) + (\,p\,F_0)^2]^{-1}$	0.005	$w = [\sigma^2(F_0^2) + (0.0512P)^2 + 0.1823P]^{-1}$, where $P = (F_0^2 + 2F_C^2)/3$	0.013	0.020
Goodness of fit	1.931	1.055	1.805	1.533
Secondary ext. coeff.	2.4 (4) × 10^{-6}	0.017(5)	2.4 (4) × 10^{-6}	–
Final Δ_{max}/σ	0.0004	0.001	0.0003	0.0002
$\Delta\rho$ (max; min) [e Å^3]	0.16; −0.14	0.16; −0.16	0.18; −0.15	0.28; −0.19
σ ($d_{(C-C)}$) [Å]	0.002	0.002	0.002	0.003

45a, and (*E*)-**47a** were refined on *F* means of full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o|-|F_C|)^2$. For (*Z*)-**39a**, the refinement was carried out on F^2 by minimizing the corresponding function based on F^2. Corrections for secondary extinction were applied in the case of (*E*)-**39a**, (*Z*)-**39a**, and (*Z*)-**45a**. For (*E*)-**39a** and (*Z*)-**39a**, three low-angle reflections were omitted from the final refinement of each structure, because the observed intensities of these reflections were much lower than the calculated values as a result of being partially obscured by the beam stop. The absolute structure has not been determined and the absolute direction of the polar axis has been assigned arbitrarily. Neutral-atom scattering factors for non-H-atoms were taken from *Maslen et al.* [69], and the scattering factors for H-atoms were taken from *Stewart et al.* [70]. The values of the mass-attenuation coefficients are those of *Creagh* and *Hubbel* [71]. The calculation of the structure of (*Z*)-**39a** was performed with SHELXL97 [72], and the teXsan [73] crystallographic-software package was used for the remaining structures. The crystallographic diagrams were drawn with ORTEPII [74].

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