235. Nucleophilic Addition to C,C-Double Bonds

Part IX[1])

Kinetics and Mechanism of the Base-Catalyzed Intramolecular Cyclization of Olefinic Alcohols

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The base-catalyzed intramolecular cyclization of polycyclic olefinic alcohols of type **a** (10-*endo*-hydroxy-*anti*^{9,10}-tricyclo[4.2.1.1^{2,5}]dec-7-en-9-ones (type **h**), *anti*^{9,10}-tricyclo[4.2.1.1^{2,5}]dec-3-en-9-*endo*-ols (type **j**), and *anti*^{10,11}-tricyclo[4.3.1.1^{2,5}]undec-3-en-10-*endo*-ols (type **l**)) to the ethers **d** and **f**, resp., has been studied. A mechanism for the nucleophilic addition of the corresponding alkoxide anion **b** to the isolated C,C-double bond is discussed. It is proposed that **b** is formed (fast acid/base equilibrium) in the first step. For the subsequent reaction sequence, there are two well distinguishable pathways: a) Compounds with an additional carbonyl group (**h**) cyclize *via* a homoenolate-like intermediate **c**, which is protonated stereoselectively on the *exo*-side by the hydroxylic solvent. b) Compounds without a carbonyl group (**j** and **l**) cyclize 10^2–10^4 times slower, and the reaction proceeds *via* a carbanion-like transition state **e**. The proton transfer from the hydroxylic solvent is clearly coupled with the C,O-bond formation. Steric compression in the olefinic alcohols **a** influences the cyclization rate: a) Alcohols with a smaller ring (**h**, X = CH_2CH_2) cyclize 70–200 times faster than the ones with a larger ring (**1**, X = $CH_2CH_2CH_2$). b) Replacement of the H-atom at the carbinol C-atom by a CH_3 group enhances the rate of ether formation by a factor of 50–100. Due to through-bond interactions between the C,C-double bonds, olefinic alcohols with an additional endocyclic C,C-double bond (**h** and **j**, X = CH=CH) cyclize 20–300 times faster than the corresponding monoolefinic ones (**h** and **j**, X = CH_2CH_2).

In previous communications[1]), we have shown that in polycyclic olefinic alcohols of the general type **a**, the structurally close proximity of the reacting centers allows base-catalyzed intramolecular nucleophilic addition of an alkoxide anion to a C,C-double bond bearing no electron-attracting substituents (→**d** and **f**, resp.). Continuing our studies, we present a mechanistic model *(Sect. 1)* for this uncommon reaction, based on kinetic data *(Sect. 2)*.

1. Mechanistic Model *(Scheme 1)*. – The ether formation **a**→**d** and **f**, resp., is initiated by the deprotonation of the alcohol **a** by the base B^- (→**b**) and the establishment of a fast acid/base equilibrium. For the subsequent reaction sequence, two distinct pathways have to be considered: a) In compounds with Y = O, the negative charge at the β-C-atom, generated by nucleophilic attack of the alkoxide anion **b** on the C,C-double bond in the rate determining step, is stabilized by homoconjugation with the carbonyl group with

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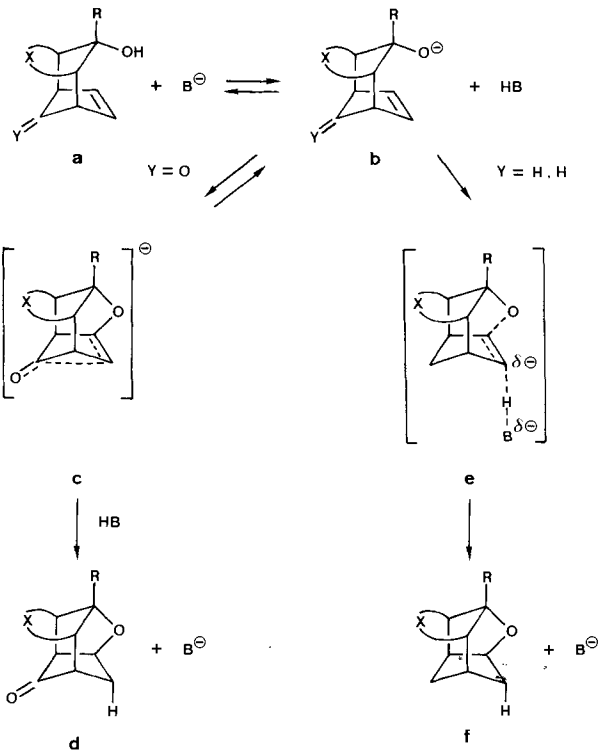
Scheme 1



R = H or alkyl
X = CH=CH, CH_2CH_2, CH_2CH_2CH
Y = O; H,H

formation of a homoenolate-like intermediate[3]) **c**. This is finally protonated stereoselectively from the *exo*-side (= from the outside of the cage-like skeleton; →**d**) by the hydroxylic solvent. Thus, the formation of the ether **d** can be regarded as the reverse of an E_lcB-elimination [3]. b) In compounds with Y = H,H, *i.e.* in the absence of any homoconjugative effect, a carbanionic intermediate is very unlikely and indeed, all experimental evidence supports an ether formation **b**→**f** *via* a carbanion-like transition state *e*[4]). According to the variable transition state theory [5], this process implies the reverse of an E_lcB-like elimination with a transition state **e** having a strong carbanionic character[5]).

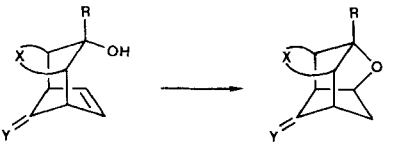
2. Results and Discussion. – 2.1. *General.* All the investigated conversions (see *Scheme 2*) exhibit a linear relationship between the pseudo-first-order rate constant (k_{obs}) and the base concentration, and the cyclization rates are not influenced by the nature of

[3]) For a review on homoenolization/homoketonization, see [2].

[4]) As we described earlier [4], the protonation of **e** must be either concerted or occur after the nucleophilic attack of the alcoholate anion on the C,C-double bond.

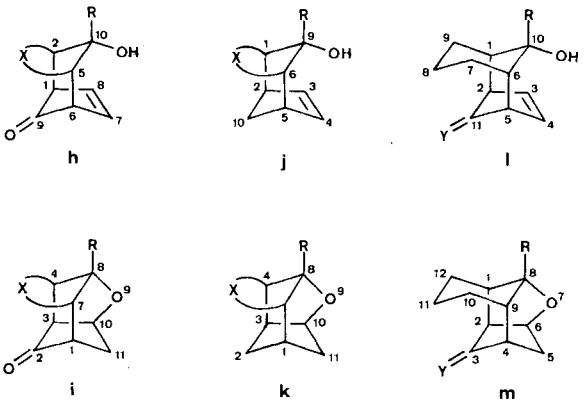
[5]) On carbanionic intermediates and transition states, see [6].

Scheme 2



a **g**

Reactant	Atom numbering	Y	X	R	Product	Atom numbering
1	**h**	O	CH=CH	H	**2**	**i**
3	**h**	O	CH=CH	CH_3	**4**	**i**
5	**h**	O	CH_2CH_2	H	**6**	**i**
7	**h**	O	CH_2CH_2	CH_3	**8**	**i**
9	**j**	H,H	CH=CH	H	**10**	**k**
11	**j**	H,H	CH=CH	CH_3	**12**	**k**
13	**j**	H,H	CH_2CH_2	H	**14**	**k**
15	**j**	H,H	CH_2CH_2	CH_3	**16**	**k**
17	**l**	H,H	$CH_2CH_2CH_2$	H	**18**	**m**
19	**l**	H,H	$CH_2CH_2CH_2$	CH_3	**20**	**m**
21	**l**	$C(CH_3)_2$	$CH_2CH_2CH_2$	H	**22**	**m**



h **j** **l**

i **k** **m**

the cation of the base. This is illustrated for the transformation **3**→**4** in *Fig. 1* (see also *Table 4, Runs 13–17,* in the *Exper. Part*) and *Table 1.*

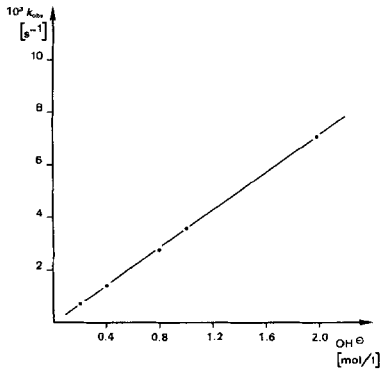


Fig. 1. *Rate of the cyclization* **3**→**4** *as a function of the* OH^- *concentration in aq. NaOH/*CH_3OH *1:1 at r.t.*

Table 1. *Cyclization* **3**→**4** *in aq. MOH/CH_3OH 1:1*

Run	Reaction conditions			$10^3 \cdot k_B$[a])	Correlation
	Temp. [°C]	Base MOH	Concentration [mol/kg]	[kg/s·mol]	
1	20.1	NaOH	1.120	3.2	0.999
2	20.8	NaOH	0.448	3.3	0.992
3	20.1	LiOH	0.528	3.2	0.999
4	20.7	CsOH	0.416	3.5	0.998

[a]) Average values out of 3 measurements.

2.2. *Temperature Dependence.* The second-order rate constants $k_B = k_{obs}/[B^-]$ for the cyclizations **1**→**2**, **3**→**4**, **5**→**6**, **7**→**8**, **13**→**14**, and **19**→**20** at different temperatures fitted the *Arrhenius* relationship [7]. The results are listed in *Table 2* (see also *Table 4* in the *Exper. Part*).

Table 2. *Activation Parameters for the Cyclization of* **1**, **3**, **5**, **7**, **13**, *and* **19**

Run	Conversion	Base[a])	E_a [kcal/mol]	A [s^{-1}]	$\Delta H^{\neq}$ [kcal/mol]	$\Delta S^{\neq}$ [cal/K·mol]	$\Delta G^{\neq}$ [kcal/mol]	Correlation
1	**1**→ **2**	A	25.9	$5.5 \cdot 10^{16}$	25.3	+16.1	20.6	−0.959
2	**3**→ **4**	B	19.7	$1.5 \cdot 10^{12}$	19.1	−4.8	20.5	−0.999
3	**5**→ **6**	A	27.5	$5.0 \cdot 10^{16}$	26.9	+15.9	22.2	−0.995
4	**7**→ **8**	B	21.7	$1.6 \cdot 10^{12}$	21.1	−4.6	22.5	−0.999
5	**13**→**14**	A	21.2	$3.5 \cdot 10^{8}$	20.6	−21.4	26.9	−0.968
6	**19**→**20**	A	22.7	$1.3 \cdot 10^{9}$	22.1	−18.9	27.6	−0.991

[a]) A: *t*-BuOK/*t*-BuOH; B: CH_3ONa/CH_3OH.

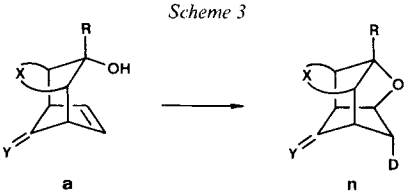
The keto alcohols **1** and **3** contain a second C,C-double bond at C(3),C(4) in addition to the one at C(7),C(8). This lowers $\Delta G^{\neq}$ by *ca.* 2 kcal/mol in *t*-BuOK/*t*-BuOH (*Runs 1* and *3*) as well as in CH_3ONa/CH_3OH (*Runs 2* and *4*). A carbonyl group in homoconjugation to the C(7),C(8)-double bond lowers $\Delta G^{\neq}$ by 4.7 kcal/mol (*Runs 3* and *5*).

The $\Delta\Delta G^{\neq}$ of 0.7 kcal/mol for the reactions **13**→**14** and **19**→**20** (*Runs 5* and *6*) is correlated to the difference in steric compression between the two olefinic alcohols **13** and **19**. The cyclizations of compounds **a** bearing a carbonyl group (Y = O) show either positive (*Runs 1* and *3*) or slightly negative (*Runs 2* and *4*) $\Delta S^{\neq}$ values which, in analogy to E_1cB base-catalyzed eliminations [8], can be attributed to the reversible formation of an intermediate of type **c**. On the other hand, the ether formations starting from compounds **a** lacking the additional carbonyl group (Y = H,H) exhibit strongly negative $\Delta S^{\neq}$ values (*Runs 5* and *6*).

2.3. Solvent Isotope Effect (*Scheme 3, Table 3;* see also *Table 4* in the *Exper. Part*). The experimental rate-constant ratios k_{OH}/k_{OD} of 1.7 and 1.5 for the cyclizations of **1** and **5**, respectively, are characteristic for solvent isotope effects in E_1cB-eliminations, which proceed *via* a carbanionic intermediate [9]. This is very remarkable because the conversions **1**→(11-*exo*-$^2H_1$)-**2** (*Run 1*) and **5**→(11-*exo*-$^2H_1$)-**6** (*Run 2*) yet represent multistep processes.

The cyclization **19**→(5-*exo*-$^2H_1$)-**20** in the range of 80–130° (*Table 3, Runs 3–6*) shows a temperature-dependent rate-constant ratio, which in part is attributable to the solvent

Scheme 3



	Y	X	R		
1	O	CH=CH	H	(11-*exo*-$^2H_1$)-**2**	(i)
5	O	CH_2CH_2	H	(11-*exo*-$^2H_1$)-**6**	(i)
19	H,H	$CH_2CH_2CH_2$	CH_3	(5-*exo*-$^2H_1$)-**20**	(m)

Table 3. *Solvent Isotope Effects (k_{OH}/k_{OD}) for the Cyclization* **a**→**n** *of* **1**, **5** *and* **19** *in* t-*BuOK*/t-*BuOD*

Run	Reactant **a**	Product **n**	Temp. [°C]	k_{OH}/k_{OD}
1	**1**	(11-*exo*-$^2H_1$)-**2**	30	1.7
2	**5**	(11-*exo*-$^2H_1$)-**6**	34	1.5
3	**19**	(5-*exo*-$^2H_1$)-**20**	80	0.6
4	**19**	(5-*exo*-$^2H_1$)-**20**	100	0.9
5	**19**	(5-*exo*-$^2H_1$)-**20**	120	1.6
6	**19**	(5-*exo*-$^2H_1$)-**20**	130	4.5

isotope effect in the acid/base equilibrium **a**⇄**b** (Y = H,H; X = $CH_2CH_2CH_2$)[6]). At temperatures up to *ca.* 100° (*Runs 3* and *4*), the k_{OH}/k_{OD} ratios are indicative of a transition state with strong carbanionic character[5]). Above *ca.* 100° (*Runs 5* and *6*), the protonation of the C,C-double bond is obviously coupled with the C,O-bond formation.

2.4. *Steric Compression.* With regards to steric compression between the OH group and the C,C-double bond in olefinic alcohols **a**, two factors which influence the cyclization rate were studied: the substitution pattern at the carbinol C-atom and the size of the X bridge.

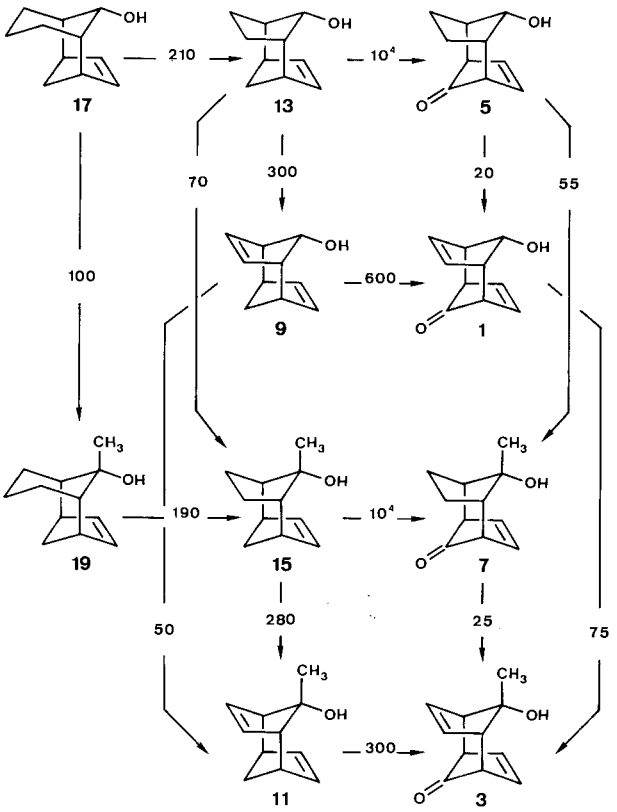
The correlation between structure and reactivity for several olefinic alcohols listed in *Scheme 4* was studied by X-ray analysis [11] [12]. Substitution of the H-atom by a CH_3 group causes a strong pyramidalization of the carbinol C-atom, which increases the steric compression between the OH group and C,C-double bond.

For different pairs of secundary and tertiary alcohols **a**, a CH_3 group instead of a H-atom at the carbinol C-atom increases the cyclization rate by a factor of 50–100 *(Scheme 4)*. The ratio k_{CH_3}/k_H is quite insensitive to small structural and/or electronic changes in the model compounds.

The change from an *anti*[10,11]-tricyclo[4.3.1.$1^{2,5}$]undecane (X = $CH_2CH_2CH_2$: **17** and **19**) to an *anti*[9,10]-tricyclo[4.2.1.$1^{2,5}$]decane system (X = CH_2CH_2: **13** and **15**) enhances the steric compression *(Scheme 4)*. By consequence the latter alcohols undergo base-catalyzed ether formation *ca.* 200 times faster.

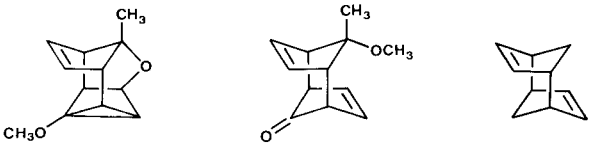
[6]) For solvent isotope effects in acid/base equilibria, see [10].

Scheme 4



2.5. *Homoconjugative Effects (Scheme 4;* see also *Table 4* in the *Exper. Part).* In addition to structural parameters (see *2.4*), electronic through-space and through-bond interactions can influence the rate of base-catalyzed ether formation.

Olefinic alcohols **a** with Y = O (additional carbonyl group: **1**, **3**, **5**, and **7**) cyclize *ca.* 10^2–10^4 times faster than the corresponding reactants with Y = H,H (**9**, **11**, **13**, and **15**). This is due to through-space homoconjugative stabilization of the negative charge, generated at the β-C-atom in the rate-determining addition step. The homoenolization[3]) **b**→**c** as well as the stereochemical course of the homoketonization **c**→**d** have already been studied extensively for compounds of type **a** with Y = O [13]. In the case of **3**, the intermediate homoenolate anion **c** could even be trapped with dimethylsulfate as the homoenol ether **23** (56%) besides of the methyl ether **24** (32%) [13]. A similar through-



space interaction was also observed in the diolefinic alcohol **21** (Y = $(CH_3)_2C$) between the two C,C-double bonds. Formation of the ether **22** in *t*-BuOK/*t*-BuOH at 90° is *ca.* 20 times faster than the corresponding cyclization **17**→**18** (Y = H,H).

Through-bond interactions are operative in compounds with a second endocyclic C,C-double bond[7]). The diolefinic alcohols **1**, **3**, **9**, and **11** cyclize 20–300 times faster than the corresponding monoolefinic ones **5**, **7**, **13**, and **15**.

A qualitative theoretical inspection of the through-bond interaction in *anti*[9,10]-tricyclo[4.2.1.$1^{2,5}$]deca-3,7-diene (**25**) leads to the prediction of a high reactivity for the diolefinic alcohols **1**, **3**, **9**, and **11**[8]). As shown in *Fig. 2*[9]), the $a_g(\pi)$ orbital is destabilized by the interaction with the $a_g(\sigma)$ orbital, while $b_g(\pi^*)$ is stabilized by the interaction with $b_g(\sigma^*)$.

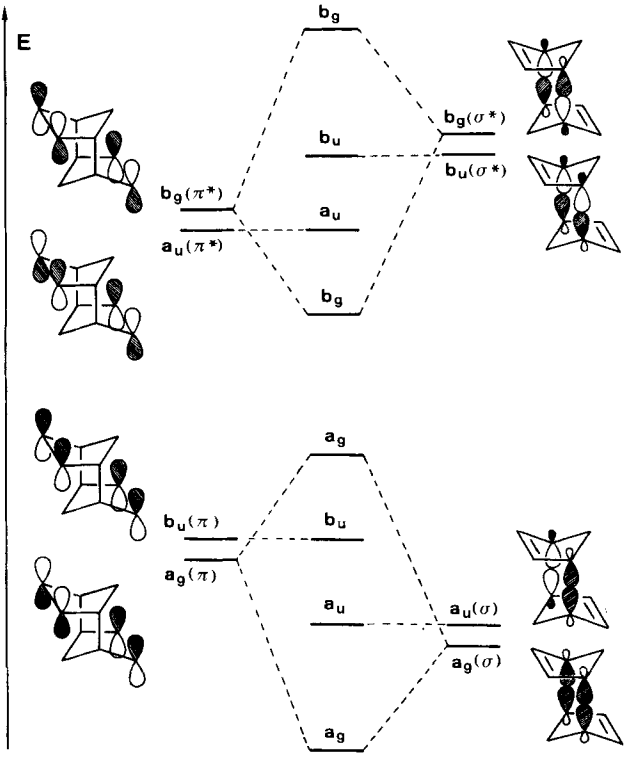


Fig. 2. Qualitative correlation diagrams for the orbitals of the π-systems at C(3),C(4) and C(7),C(8) as well as the σ-bonds between C(1),C(2) and C(5),C(6) in **25**

The interactions between the other orbitals are, due to symmetry and energy reasons, negligible. This qualitative analysis implies that a diolefine with through-bond interactions like **25**, should be more reactive towards a nucleophilic attack than a corresponding compound without such interactions[10]).

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[7]) For structural reasons, through-space interactions are negligible in such compounds.

[8]) A steric effect was not detected by X-ray analysis.

[9]) The interaction diagram was constructed according to the usual theoretical considerations [14] [15].

[10]) These results were also confirmed quantitatively by MINDO/3 calculations [16] [17].

It is noteworthy that the combined through-bond and through-space interactions are not exactly multiplicative. This might be a consequence of geometrical deformations as well as different energies of the basis orbitals.

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Experimental Part

1. General. – See [4].

2. Kinetic Measurements. – 2.1. *General.* The time dependence of the product/internal standard[11]) ratio was followed by cap. GLC. The samples were taken in intervals of *ca.* ½–⅓ half-life time ($t_{½}$), diluted with ice-water and extracted with pentane at −10°. The org. layer was analyzed by cap. GLC (*UCON HB 5100*, 25 m × 0.33 mm) and a *Hewlett-Packard 3390A* integrator. The extraction and the analysis procedure was calibrated for each product/internal standard[11]) mixture by using mixtures of known compositions (error limit $< \pm 1\%$).

2.2. *Cyclizations at* $T \leq 70°$ *in aq. NaOH/CH₃OH 1:1 or* t-*BuOK*/t-*BuOH.* Under Ar, a 1:1 mixture of reactant and internal standard[11]) was dissolved (*ca.* 0.1 mmol/ml) in CH_3OH or *t*-BuOH, resp., and thermostated in a water bath. The reaction was started by injection of a thermostated aq. NaOH or *t*-BuOK/*t*-BuOH soln. The mixture was stirred under Ar, and the samples were withdrawn through a septum at intervals of *ca.* ⅓ $t_{½}$.

2.3. *Cyclizations at* $T > 70°$ *in* t-*BuOK*/t-*BuOH.* An O_2-free soln. (*ca.* 0.1 mmol/ml) of reactant (or a mixture of reactants for the determination of relative reaction rates) and internal standard[11]) in *t*-BuOK/*t*-BuOH was distributed in several tubes. The latters were sealed under Ar and heated in an oil ($T < 150°$) or salt ($T \geq 150°$) bath. At intervals of *ca.* ½ $t_{½}$, one tube was taken out, rapidly cooled to 0° to quench the reaction, and opened for analysis.

2.4. *Determination of* k_{obs}, k_B, *and* k_{rel}. All investigated reactions showed pseudo-first-order kinetics with linear time dependence of $\ln c$[12]) for 10–90% of conversion.

The *pseudo*-first-order rate constants (k_{obs}) were determined by linear regression. Division of k_{obs} by the concentration of the base gave the second-order rate constants (k_B).

The relative reaction rates (k_{rel}) were directly determined by treatment of a mixture of the corresponding two alcohols with an O_2-free *t*-BuOK/*t*-BuOH soln. in sealed tubes followed by cap. GLC analysis of the product distribution. The measurements of k_{obs} (and k_B, resp.) for different preference compounds allowed the transformations of relative into absolute rate constants.

The results of all the kinetic measurements are summarized in *Table 4*.

Table 4. *Kinetic Data for the Cyclizations of* **1**, **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17**, **19**, *and* **21**

Run	Conversion	Reaction conditions			$10^3 \cdot k_B$[b])[c])	Correlation
		Temp. [°C]	Base[a])	Concentration [mol/kg]	[kg/s·mol]	
1	**1**→**2**	20.5	A	0.94	2.2	0.997
2	**1**→**2**	25.5	A	0.45	9.1	0.998
3	**1**→**2**	31.7	A	0.45	16.4	0.993
4	**1**→**2**	35.5	A	0.21	22.7	0.994
5	**1**→**2**	27.9	B	0.28	25.5	0.996
6	**1**→**2**	51.4	C	0.33	1.8	0.999
7	**1**→**2**	21.2	C	0.93	0.2	0.998
8	**1**→**2**	31.7	C	0.66	0.7	0.998
9	**1**→**2**	36.1	C	0.34	1.7	0.999
10	**1**→**2**	42.2	C	0.17	5.0	0.999

[11]) Internal standard: 9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-en-2-one (**2**) [18] or naphthalene.

[12]) $c = a_\infty/a_\infty - a_t$, whereby a_t and a_∞ mean the ratio [product]/[internal standard] at the time t and ∞, resp.

Table 4 (cont.)

Run	Conversion	Reaction conditions			$10^3 \cdot k_B$[b])[c])	Correlation
		Temp. [°C]	Base[a])	Concentration [mol/kg]	[kg/s · mol]	
11	**1**→**2**	49.5	C	0.09	9.3	0.999
12	**1**→(11-*exo*-$^2H_1$)-**2**	30	D	0.13	930	0.983
13	**3**→**4**	20.1	E	0.224	3.3	0.999
14	**3**→**4**	20.8	E	0.448	3.3	0.992
15	**3**→**4**	20.8	E	0.896	3.1	0.999
16	**3**→**4**	20.1	E	1.120	3.2	0.999
17	**3**→**4**	20.8	E	2.24	7.0	0.999
18	**3**→**4**	24.1	E	0.448	3.4	0.999
19	**3**→**4**	28.2	E	0.224	7.4	0.996
20	**3**→**4**	23.5	F	0.436	4.4	0.989
21	**3**→**4**	32.3	F	0.198	12.1	0.998
22	**3**→**4**	41.5	F	0.059	29.2	0.996
23	**3**→**4**	20.1	G	0.528	3.2	0.999
24	**3**→**4**	20.7	H	0.416	3.5	0.998
25	**5**→(11-*exo*-$^2H_1$)-**6**	34	D	0.13	73	0.999
26	**7**→**8**	27.8	F	0.436	0.3	0.998
27	**7**→**8**	37.5	F	0.997	0.9	0.998
28	**7**→**8**	42.4	F	0.218	1.5	0.996
29	**7**→**8**	49.6	F	0.108	3.3	0.998
30	**7**→**8**	25.3	A	0.05	1.7	0.997
31	**7**→**8**	20.8	E	2.240	0.2	0.999
32	**9**→**10**	60.1	A	0.79	1.3	0.999
33	**11**→**12**	22.8	A	0.79	1.6	
34	**13**→**14**	90	A	0.07	0.1	0.999
35	**13**→**14**	120	A	0.07	0.3	0.991
36	**13**→**14**	150	A	0.02	5.7	0.998
37	**15**→**16**	70	A	0.02	0.8	0.998
38	**17**→**18**	130	A	1.00	50	
39	**19**→**20**	80	A	1.00	140	0.998
40	**19**→**20**	100	A	0.25	390	0.984
41	**19**→**20**	120	A	0.25	2500	0.945
42	**19**→**20**	130	A	0.25	22600	0.999
43	**19**→**20**	150	A	0.01	26600	0.976
44	**19**→(5-*exo*-$^2H_1$)-**20**	80	D	1.11	2	0.996
45	**19**→(5-*exo*-$^2H_1$)-**20**	100	D	0.28	5	0.984
46	**19**→(5-*exo*-$^2H_1$)-**20**	120	D	0.28	16	0.988
47	**19**→(5-*exo*-$^2H_1$)-**20**	130	D	0.28	51	0.996
48	**21**→**22**	90	A	0.99	40	

[a]) A: *t*-BuOK/*t*-BuOH; B: *t*-BuOK in *t*-BuOH/DMSO 1:1; C: CH_3ONa in CH_3OH/DMSO 1:1; D: *t*-BuOK/*t*-BuOD; E: aq. NaOH/CH_3OH 1:1; F: CH_3ONa/CH_3OH; G: aq. LiOH/CH_3OH 1:1; H: aq. CsOH/CH_3OH 1:1.

[b]) $k_B = k_{obs}$/[base].

[c]) Average values from at least 3 measurements. For the *Runs 38* and *48*, k_B was evaluated by calculation from the corresponding k_{rel}.

3. Analytical and Spectral Data[13]). – *(11-exo-$^2H_1$)-9-Oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-en-2-one ((11-exo-$^2H_1$)-2)* [12] [13]. IR: 3148*w*, 3070*m*, 2172*w*, 1807*w*, 1759*s*, 1573*w*, 1348*s*, 1340*w*, 1259*w*, 1241*w*, 1229*w*, 1187*w*, 1168*m*, 1147*m*, 1107*w*, 1096*s*, 1084*m*, 1053*w*, 1042*m*, 1013*w*, 978*s*, 970*w*, 959*w*, 923*w*, 893*s*, 871*m*, 642*w*. ^{1}H-NMR (100 MHz, CCl_4): 1.88 (*m*, $w_{1/2} \approx 5$, H_{endo}–C(11)); 2.45 (*m*, $w_{1/2} \approx 8$, H–C(1)); 2.5–2.75 (*m*, H–C(3), H–C(7)); 3.05 (*m*, $w_{1/2} \approx 18$, H–C(4)); 4,38 (*t*, *J*(4,8) = *J*(7,8) = 4, H–C(8)); 4.84 (*dd*, *J*(3,10) = 4.5, *J*(1,10) = 1.5, H–C(10)); 5.92 (*dd*, *J*(5,6) = 6, *J*(4,5) = 3, H–C(5)); 6.02 (*dd*, *J*(5,6) = 6, *J*(6,7) = 3, H–C(6)). MS: 164 (10), 163 (83, M^+, $C_{10}H_9DO_2$), 162 (3.5), 134 (23), 116 (6), 106 (100), 92 (24), 85 (53), 81 (44), 80 (35), 78 (46), 67 (11), 66 (11), 56 (41), 51 (17).

*10-*endo*-Hydroxy-*anti*^{9,10}-tricyclo[4.2.1.1^{2,5}]dec-7-en-9-one* (**5**) [12] [13] [21]. Decomposition > 216°. IR: 3622*s*, 3058*w*, 1856*w*, 1785*m*, 1768*s*, 1470*m*, 1453*w*, 1436*w*, 1332*w*, 1262*m*, 1219*w*, 1175*s*, 1155*w*, 1126*w*, 1090*s*, 1025*w*, 986*m*, 923*m*, 678*s*. ^{1}H-NMR (100 MHz): 1.5–1.8 (*m*, 2 H–C(3), 2 H–C(4)); 2.56 (*m*, $w_{1/2} \approx 12$, H–C(2), H–C(5)); 2.88 (*dm*, *J*(1,2) = *J*(5,6) = 6, $w_{1/2} \approx 5$, H–C(1), H–C(6)); 2.88 (*d*, *J*(10, HO–C(10)) = 11, HO–C(10)); 3.72 (*dm*, *J*(10, HO–C(10)) = 11, $w_{1/2} \approx 8$, H–C(10)); 6.66 (*t*, *J*(1,7) = *J*(6,7) = *J*(1,8) = *J*(6,8) = 2, H–C(7), H–C(8)). ^{13}C-NMR: 25.43 (*t*, C(3), C(4)); 44.11 (*d*, C(2), C(5)); 53.87 (*d*, C(1), C(6)); 77.65 (*d*, C(10)); 134.89 (*d*, C(7), C(8)); 206.40 (*s*, C(9)). MS: 164 (2, M^+), 136 (65), 118 (78), 117 (52), 108 (36), 107 (37), 95 (53), 91 (50), 80 (45), 79 (100), 77 (47), 67 (24), 53 (20), 51 (22). Anal. calc. for $C_{10}H_{12}O_2$ (164.21): C 73.14, H 7.37; found: C 73.30, H 7.35.

9-Oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undecan-2-one (**6**) [12] [13]. M.p. 197° (sealed tube). IR: 1755*s*, 1464*w*, 1444*w*, 1353*m*, 1290*w*, 1244*w*, 1177*m*, 1148*w*, 1127*m*, 1078*s*, 1058*m*, 1025*w*, 998*w*, 985*m*, 955*m*, 931*m*, 895*s*, 878*w*, 849*w*, 648*w*. ^{1}H-NMR (100 MHz): 1.4–2.0 (*m*, H_{exo}–C(11), 2 H–C(5), 2 H–C(6)); 2.10 (*d*, J_{gem} = 13, H_{endo}–C(11)); 2.1–2.4 (*m*, H–C(1), H–C(7)); 2.5–2.9 (*m*, H–C(3), H–C(4)); 4.59 (*m*, $w_{1/2} \approx 9$, H–C(8)), 4.74 (*m*, $w_{1/2} \approx 8$, H–C(10)). MS: 165 (12), 164 (100, M^+, $C_{10}H_{12}O_2$), 136 (24), 121 (11), 108 (35), 107 (49), 96 (36), 94 (30), 92 (34), 91 (31), 82 (85), 81 (57), 80 (47), 79 (76), 77 (35), 69 (32), 67 (35), 53 (32), 43 (34).

*10-*endo*-Hydroxy-10-*exo*-methyl-*anti*^{9,10}-tricyclo[4.2.1.1^{2,5}]dec-7-en-9-one* (7) [12] [13]. M.p. 85°. IR: 3616*s*, 3022*w*, 1817*w*, 1770*s*, 1481*m*, 1441*w*, 1379*m*, 1346*s*, 1301*m*, 1287*w*, 1203*s*, 1148*w*, 1125*s*, 1103*w*, 1053*s*, 1034*w*, 1008*m*, 973*w*, 955*w*, 642*m*, 602*w*. ^{1}H-NMR (100 MHz): 1.20 (*d*, *J*(CH_3–C(10), HO–C(10)) = 1.5, CH_3–C(10)); 1.5–2.1 (*m*, 2 H–C(3), 2 H–C(4)); 2.27 (*m*, $w_{1/2} \approx 12$, H–C(2), H–C(5)); 2.91 (*dt*, *J*(1,2) = *J*(5,6) = 6, *J*(1,7) = *J*(1,8) = *J*(6,7) = *J*(6,8) = 2, H–C(1), H–C(6)); 3.83 (*q*, *J*(CH_3–C(10), HO–C(10)) = 1.5, HO–C(10)); 6.79 (*t*, *J*(1,7) = *J*(6,7) = *J*(1,8) = *J*(6,8) = 2, H–C(7), H–C(8)). MS: 178 (12, M^+, $C_{11}H_{14}O_2$), 150 (69), 135 (38), 132 (35), 117 (54), 108 (38), 107 (86), 92 (36), 91 (49), 80 (41), 79 (100), 77 (36), 71 (46), 43 (98).

8-Methyl-9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undecan-2-one (**8**) [12] [13]. M.p. 117°. UV: 290 (25). IR: 1753*s*, 1470*m*, 1442*m*, 1379*s*, 1340*m*, 1323*m*, 1289*w*, 1244*w*, 1211*w*, 1158*m*, 1132*s*, 1117*w*, 1048*w*, 1037*w*, 1026*s*, 1014*w*, 985*m*, 964*w*, 946*m*, 922*w*, 899*s*, 876*w*, 852*w*, 610*w*. ^{1}H-NMR (100 MHz): 1.35 (*s*, CH_3–C(8)); 1.4–2.0 (*m*, H–C(7), 2 H–C(5), 2 H–C(6)); 1.65 (*dt*, J_{gem} = 12.5, *J*(1,11-*exo*) = *J*(10,11-*exo*) = 4, H_{exo}–C(11)); 2.11 (*d*, J_{gem} = 12.5, H_{endo}–C(11)); 2.15–2.4 (*m*, H–C(1), H–C(4)); 2.66 (*ddd*, *J*(3,4) = 8.5, *J*(3,10) = 5, *J*(1,3) = 2.5, H–C(3)); 4.68 (*ddd*, *J*(3,10) = 5, *J*(10,11-*exo*) = 4, *J*(1,10) = 2, H–C(10)). MS (directly, < 100°): 178 (100, M^+, $C_{11}H_{14}O_2$), 150 (60), 135 (25), 121 (20), 120 (23), 117 (15), 108 (53), 107 (50), 96 (56), 95 (34), 94 (81), 91 (37), 82 (48), 79 (92), 71 (33), 67 (22), 53 (19), 43 (70).

9-Oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-ene (**10**). IR: 3058*w*, 1468*w*, 1440*w*, 1350*s*, 1341*w*, 1314*w*, 1279*w*, 1241*w*, 1171*w*, 1128*m*, 1096*w*, 1080*w*, 1073*s*, 1039*w*, 1019*w*, 998*w*, 989*w*, 980*w*, 961*w*, 940*m*, 924*w*, 900*w*, 885*w*, 867*w*, 853*w*, 673*w*, 614*w*. ^{1}H-NMR (300 MHz): 1.15 (*dm*, J_{gem} = 11, $w_{1/2} \approx 11$, each, H_{exo}–C(11)); 1.57 (*dt*, J_{gem} = 11, *J*(1,2-*exo*) = *J*(2-*exo*, 3) = 4, H_{exo}–C(2)); 1.75 (*ddd*, J_{gem} = 11, *J*(2-*endo*, 11-*endo*) = 3.5, further *J* = 1, H_{endo}–C(11)); 1.79 (*dd*, J_{gem} = 11, *J*(2-*endo*, 11-*endo*) = 3.5, H_{endo}–C(2)); 1.89 (*m*, $w_{1/2} \approx 10$, H–C(1)); 2.25–2.4 (*m*, H–C(6), H–C(7)); 2.54 (*ddd*, *J*(3,4) = 7.5, *J*(4,8) = 4.5, *J*(4,5) = 3, H–C(4)); 4.32 (*t*, *J*(4,8) = *J*(7,8) = 4.5, H–C(8)); 4.81 (*td*, *J*(3,10) = *J*(10,11) = 4.5, *J*(1,10) = 1.5, H–C(10)); 5.82 (*dd*, *J*(5,6) = 6, *J*(6,7) = 3, H–C(6)); 5.87 (*dd*, *J*(5,6) = 6, *J*(4,5) = 3, H–C(5)). MS: 148 (90, M^+, $C_{10}H_{12}O$), 130 (5), 129 (5), 120 (8), 119 (53), 117 (15), 115 (9), 107 (5), 105 (17), 104 (22), 103 (8), 94 (6), 92 (22), 91 (85), 83 (8), 82 (9), 81 (42), 80 (16), 79 (100), 78 (72), 77 (32), 70 (37), 67 (10), 66 (46), 65 (21), 63 (8), 55 (6), 53 (14), 52 (8), 51 (17), 50 (7), 41 (58), 40 (7), 39 (41).

8-Methyl-9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undec-5-ene (**12**). IR: 3058*m*, 1465*w*, 1446*w*, 1439*w*, 1374*m*, 1333*s*, 1311*w*, 1302*w*, 1294*w*, 1275*w*, 1265*w*, 1243*w*, 1220*w*, 1204*w*, 1775*w*, 1151*s*, 1131*m*, 1100*w*, 1095*w*, 1065*m*, 1038*w*, 1002*s*, 980*w*, 968*w*, 958*w*, 939*w*, 921*w*, 909*w*, 880*m*, 694*s*, 628*w*. ^{1}H-NMR (300 MHz): 1.06 (*ddd*, J_{gem} = 11, *J*(10,11-*exo*) = 5.5, *J*(1,11-*exo*) = 2.5, H_{exo}–C(11)); 1.52 (*dt*, J_{gem} = 11, *J*(1,2-*exo*) = *J*(2-*exo*,3) ≈ 5, H_{exo}–C(2)); 1.62 (*ddd*, J_{gem} = 11, *J*(2-*endo*, 11-*endo*) = 3.5, further *J* = 1.5, H_{endo}–C(11)); 1.69 (*dd*, J_{gem} = 11, *J*(2-*endo*, 11-

[13]) Literature references: **1** and **2** [18], **3** and **4** [4] [13], **17** and **18** [19], and **19** [20]. Forthcoming paper: **9**, **11**, and **21**.

endo) = 3.5, H_{endo}–C(2)); 1.88 (*m*, $w_{1/2} \approx 10$, H–C(1)); 2.01 (*m*, $w_{1/2} \approx 10$, H–C(7)); 2.24 (*ddd*, *J*(3,4) = 7.5, *J*(4,5) = 3, *J*(4,7) = 1, H–C(4)); 2.43 (*ddd*, *J*(3,4) = 7.5, *J*(2,3) = 5, *J*(3,10) = 2, H–C(3)); 4.76 (*ddd*, *J*(10,11-*exo*) = 5.5, *J*(1,10) = 3.5, *J*(3,10) = 2, H–C(10)); 5.81 (*dd*, *J*(5,6) = 6, *J*(6,7) = 3, H–C(6)); 5.88 (*dd*, *J*(5,6) = 6, *J*(4,5) = 3, H–C(5)). MS: 162 (76, M^+, $C_{11}H_{14}O$), 147 (5), 119 (66), 118 (9), 117 (17), 115 (9), 105 (12), 104 (16), 103 (7), 97 (7), 95 (41), 93 (9), 92 (55), 91 (100), 84 (28), 80 (11), 79 (54), 78 (13), 77 (26), 71 (10), 69 (17), 67 (7), 66 (16), 65 (18), 63 (8), 57 (11), 55 (12), 53 (12), 51 (14), 43 (60), 41 (66), 39 (33).

anti-*Tricyclo[4.2.1.1^{2,5}]dec-3-en-9*-endo-*ol* (**13**) [13] [21]. M.p. 191–194°. IR: 3615*s*, 3053*w*, 3012*m*, 2958*s*, 2946*s*, 2900*m*, 2885*m*, 2848*w*, 1490*w*, 1462*m*, 1445*w*, 1344*m*, 1388*m*, 1300*w*, 1270*m*, 1264*m*, 1182*s*, 1157*s*, 1103*m*, 1092*m*, 1082*s*, 1055*m*, 996*m*, 982*w*, 972*w*, 960*w*, 898*w*, 872*m*, 720*m*, 666*w*, 642*m*. ^{1}H-NMR (100 MHz): 1.1–2.0 (*m*, 2 H–C(7), 2 H–C(8), H_{exo}–C(10)); 2.0–2.3 (*m*, H–C(1), H–C(6), H_{endo}–C(10)); 2.54 (*m*, $w_{1/2} \approx 12$, H–C(2), H–C(5)); 3.19 (*m*, $w_{1/2} \approx 17$, among others *J*(*endo*-HO–C(9),9-*exo*) = 11, *endo*-HO–C(9)); 3.58 (*m*, $w_{1/2} \approx 17$, among others *J*(*endo*-HO–C(9),9-*exo*) = 11, H_{exo}–C(9)); 6.3–6.7 (*m*, $w_{1/2} \approx 4$, H–C(3), H–C(4)). ^{13}C-NMR: 27.49 (*t*, C(7), C(8)); 40.74, 43.70 (2*d*, C(1), C(6), C(2), C(5)); 42.37 (*t*, C(10)); 79.48 (*d*, C(9)); 138.96 (*d*, C(3), C(4)). MS: 150 (12, M^+), 132 (55), 131 (13), 117 (36), 106 (10), 104 (23), 93 (24), 91 (48), 84 (12), 83 (27), 80 (18), 79 (39), 78 (17), 77 (33), 67 (98), 66 (100), 65 (16), 57 (14), 55 (15), 53 (12), 51 (10), 41 (24), 39 (31). Anal. calc. for $C_{10}H_{14}O$ (150.22): C 79.95, H 9.39; found: C 79.80, H 9.38.

9-Oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undecane (**14**) [12] [13] [21]. M.p. 160–162°. IR: 1487*w*, 1461*m*, 1450*w*, 1358*m*, 1335*w*, 1269*w*, 1182*w*, 1133*m*, 1072*s*, 1065*w*, 1045*m*, 1003*m*, 991*m*, 980*w*, 965*w*, 951*m*, 933*m*, 897*w*, 881*w*, 867*w*, 853*m*, 683*w*, 608*w*. ^{1}H-NMR (100 MHz): 1.1–2.3 (*m*, 11 H); 2.48 (*q*-like *m*, $w_{1/2} \approx 20$, H–C(3)); 4.33 (*tm*, *J*(4,8) = *J*(7,8) = 4, $w_{1/2} \approx 4$, H–C(8)); 4.64 (*ddd*, *J*(3,10) = 5, *J*(10,11-*exo*) = 4, *J*(1,10) = 1.5, H–C(10)). MS: 150 (79, M^+, $C_{10}H_{14}O$), 121 (14), 106 (100), 93 (37), 91 (58), 79 (89), 78 (84), 67 (71), 55 (21), 54 (20), 53 (23).

9-exo-*Methyl*-anti-*tricyclo[4.2.1.1^{2,5}]dec-3-en-9*-endo-*ol* (**15**) [12] [13]. IR: 3605*s*, 3025*m*, 1496*w*, 1464*w*, 1376*m*, 1345*s*, 1339*m*, 1305*m*, 1290*w*, 1228*w*, 1200*s*, 1160*w*, 1115*m*, 1051*s*, 977*m*, 960*w*, 941*w*, 900*w*, 612*w*, 601*w*. ^{1}H-NMR (100 MHz): 1.0–2.3 (*m*, 7 H): 1.15 (*d*, *J*(CH_3–C(9), HO–C(9)) = 2, CH_3–C(9)); 2.17 (*dm*, J_{gem} = 10, $w_{1/2} \approx 4$, H_{endo}–C(10)); 2.59 (*m*, $w_{1/2} \approx 11$, H–C(2), H–C(5)); 4.40 (*q*, *J*(CH_3–C(9), HO–C(9)) = 2, HO–C(9)); 6.50 (*m*, $w_{1/2} \approx 4$, H–C(3), H–C(4)). MS: 164 (23, M^+, $C_{11}H_{16}O$), 149 (20), 146 (13), 131 (46), 121 (22), 117 (17), 109 (46), 104 (31), 91 (54), 81 (83), 80 (100), 79 (78), 71 (75), 67 (26), 66 (26), 55 (17), 53 (17), 43 (89).

8-Methyl-9-oxatetracyclo[5.4.0.0^{3,10}.0^{4,8}]undecane (**16**) [12] [13]. IR: 1489*w*, 1463*m*, 1442*w*, 1378*s*, 1344*w*, 1322*w*, 1308*w*, 1276*w*, 1210*w*, 1164*m*, 1148*s*, 1120*m*, 1076*m*, 1027*s*, 1019*s*, 984*s*, 947*w*, 908*w*, 903*w*, 886*m*, 846*w*, 619*m*. ^{1}H-NMR (100 MHz): 1.0–2.1 (*m*, 11 H); 1.20 (*s*, CH_3–C(8)); 2.53 (*q*-like *m*, $w_{1/2} \approx 20$, H–C(3)); 4.53 (*ddd*, *J*(3,10) = 5, *J*(10,11-*exo*) = 4, *J*(1,10) = 1.5, H–C(10)). MS: 165 (12), 164 (83, M^+, $C_{11}H_{16}O$), 163 (2), 149 (10), 146 (4), 135 (6), 131 (7), 121 (29), 106 (38), 97 (30), 94 (100), 92 (58), 79 (60), 71 (52), 67 (23), 55 (12), 53 (13), 43 (55).

8-Methyl-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane (**20**) [12] [13]. IR: 3022*m*, 1493*w*, 1466*m*, 1437*w*, 1375*s*, 1349*w*, 1316*w*, 1295*w*, 1205*w*, 1151*w*, 1127*w*, 1119*m*, 1077*w*, 1058*m*, 1001*s*, 961*w*, 951*w*, 932*w*, 911*w*, 887*m*, 863*w*. ^{1}H-NMR (100 MHz, CCl_4): 1.0–2.0 (*m*, H–C(1), H_{exo}–C(3), H_{endo}–C(5), H–C(9), 2 H–C(10), 2 H–C(11), 2 H–C(12)); 1.08 (*s*, CH_3–C(8)); 1.30 (*dt*, J_{gem} = 11, *J*(4,5-*exo*) = *J*(5-*exo*,6) = 3.5, H_{exo}–C(5)); 2.11 (*m*, $w_{1/2} \approx 8$, H–C(4)); 2.30 (*ddd*, J_{gem} = 12, *J*(3-*endo*,5-*endo*) = 3.5, *J* = 1, H_{endo}–C(3)); 2.57 (*q*-like *m*, *J*(1,2) ≈ *J*(2,3-*exo*) ≈ *J*(2,6) ≈ 6, $w_{1/2} \approx 4$, H–C(2)); 4.32 (*ddd*, *J*(2,6) = 5, *J*(5-*exo*,6) = 4, *J*(4,6) = 1.5, H–C(6)). ^{13}C-NMR: 18.28 (*t*, C(11)); 21.55 (*q*, CH_3–C(8)); 22.75, 27.07 (2*t*), C(10), C(12)); 33.88 (*t*, C(3)); 40.67, 41.48, 45.55, 46.55 (4*d*, C(1), C(2), C(4), C(9)); 43.21 (*t*, C(5)); 78.44 (*d*, C(6)); 81.03 (*s*, C(8)). MS: 179 (2), 178 (13, M^+, $C_{12}H_{18}O$), 163 (1), 149 (2), 134 (100), 119 (31), 105 (18), 95 (22), 79 (16), 67 (11), 55 (7), 53 (7), 43 (18).

3-Isopropylidene-7-oxatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane (**22**). IR: 1459*w*, 1438*w*, 1371*m*, 1368*w*, 1347*w*, 1330*w*, 1316*w*, 1310*w*, 1298*w*, 1289*w*, 1281*w*, 1240*w*, 1231*w*, 1194*w*, 1186*w*, 1159*w*, 1090*m*, 1062*w*, 1039*s*, 1015*w*, 1006*m*, 975*w*, 967*m*, 921*w*, 902*m*, 881*w*, 871*w*, 859*w*, 851*w*, 655*w*. ^{1}H-NMR (300 MHz): 1.1–1.35 (*m*, H_{endo}–C(11)); 1.29 (*dt*, J_{gem} = 11.5, (4,5-*exo*) = *J*(5-*exo*, 6) = 3.5, further *J* ≈ 1, H_{exo}–C(5)); 1.4–1.9 (*m*, 5 H); 1.64 1.66 (2*s*, $(CH_3)_2$ = C(3)); 1.91 (*d*, J_{gem} = 11.5, H_{endo}–C(5)); 1.95 (*m*, $w_{1/2} \approx 12$, H–C(9)); 2.30 (*m*, $w_{1/2} \approx 14$, H–C(1)); 2.82 (*m*, $w_{1/2} \approx 9$, H–C(4)); 3.19 (*ddd*, *J*(1,2) = 7, *J*(2,6) = 5, *J*(2,4) = 2, H–C(2)); 3.85 (*t*, *J*(1,8) = *J*(8,9) = 4, H–C(8)); 4.57 (*ddd*, *J*(2,6) = 5, *J*(5-*exo*,6) = 3.5, *J*(4,6) = 2, H–C(6)). MS: 204 (47, M^+, $C_{14}H_{20}O$), 171 (15), 162 (34), 161 (37), 160 (80), 159 (36), 147 (34), 146 (13), 145 (100), 134 (11), 133 (24), 132 (20), 131 (28), 130 (10), 120 (14), 119 (85), 118 (17), 117 (34), 115 (10), 107 (10), 105 (40), 93 (14), 92 (15), 91 (73), 81 (10), 79 (29), 78 (9), 77 (29), 67 (16), 65 (16), 55 (15), 53 (16), 43 (15), 41 (44), 39 (23).

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