Intramolecular Reactions of 1,5-Diaryl-1,5-pentadiyl Radicals

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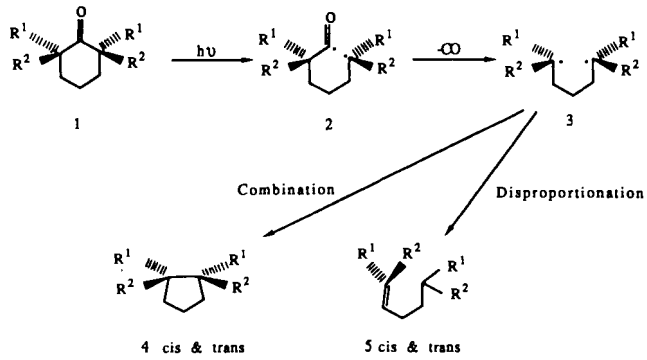
Photochemical decomposition of 2,6-diarylcyclohexanones 1a–d yields 1,2-diarylcyclopentanes 4 and 1,5-diaryl-1-pentenes 5 by intramolecular reaction of the intermediate 1,5-diaryl-1,5-pentadiyls 3. The two stereoisomers *cis*-4 and *trans*-4 are formed in equal amounts. There hence exists a 1:1 equilibrium between the two conformers of 3 which lead to *cis*- and *trans*-4, respectively; the intramolecular combination step itself is not stereoselective. However, the product ratios of 4:5, i. e. combination:disproportionation, depend on the substituents. This regioselectivity is strongly affected by solvent and temperature.

Intramolekulare Reaktionen von 1,5-Diaryl-1,5-pentadiyl-Radikalen

Die 2,6-Diarylcyclohexanone **1a–d** wurden photolysiert und dabei 1,2-Diarylcyclopentane **4** und 1,5-Diaryl-1-pentene **5** als Produkte der intermediären 1,5-Diaryl-1,5-pentadiyle **3** erhalten. Die beiden Stereoisomeren *cis*- und *trans*-**4** entstanden in gleichen Ausbeuten. Demnach besteht ein 1:1-Gleichgewicht zwischen den beiden Konformeren von **3**, aus denen *cis*- bzw. *trans*-**4** entsteht, und auch die Knüpfung der Bindung erfolgt ohne Stereoselektivität. Das Produktverhältnis **4:5** (Kombination/Disproportionierung) ist dagegen abhängig von den Substituenten. Diese Regioselektivität wird zudem stark durch das Lösungsmittel und die Temperatur beeinflußt.

The chemistry of 1,5-diradicals **3** has been the subject of increasing attention during the last few years[1–5]. These radicals can be readily generated from the cyclohexanones **1** by a Norrish-type I photoreaction followed by loss of carbon monoxide from the ketyl-alkyl diradical **2** (Scheme 1).

Scheme 1. Photolysis of 2,6-diarylcyclohexanones **1**



Special interest was given to the lifetimes of the two reactive intermediates, the ketyl-alkyl diradicals **2** and the corresponding 1,5-diradicals **3**. It was shown that the diradicals **3** (R^1 = R^2 = Phenyl, R^1 = Phenyl, R^2 = H) have surprisingly long lifetimes[1,4] of about 900 ns, whereas the ketyl-alkyl diradicals **2** lose carbon monoxide very rapidly within a laser pulse[4]. The latter fact is certainly due to the stabilization of the resulting benzylic radical center[6,7], whereas the lifetimes of the diradicals **3** are mainly controlled by the rate of intersystem crossing[1]. If $R^1 \neq R^2$, four products can be formed by intramolecular reactions: *cis*- and *trans*-cyclopentanes **4** by combination as well as *cis*- and *trans*-1-pentenes **5** by disproportionation.

These diradicals seem to be very suitable for the study of the regioselectivity (combination/disproportionation) and the stereoselectivity (*cis*/*trans*-cyclopentane) of free radical termination reactions. The radicals are easily generated by photolysis and long lifetimes ensure that the conformational equilibrium of the diradical is reached before ring closure. Therefore no memory effect is expected on the configuration (or conformation) of the cyclohexanone. Furthermore, the two reacting radical centers are connected by a "carbon backbone"[1] and consequently only a few restricted conformations have to be considered as transition states. This should facilitate the interpretation relative to structurally related monoradicals[8,9].

The regioselectivity of the termination (com/dis) of monoradicals shows an interesting solvent and temperature dependence[8–10]. For benzylic type radicals, e.g. 1-phenylethyl[9], these effects are especially large.

Although monoradicals normally combine without any stereoselection, 1-arylneopentyl radicals dimerize with considerable stereoselectivity. This seems to be due to steric repulsion between bulky *tert*-butyl groups, which inhibit the rotational motion of the radicals with respect to each other, leading to a conformational restriction in the transition state[11]. Furthermore, combination studies of the 1-arylneopentyl radicals demonstrate that the *d,l*/*meso* diastereomer ratio is greatly influenced by *p*-chloro or *p*-methoxy substituents on the aryl ring[11,12]. We wanted to explore whether similar electronic effects could be observed in the diradical case. We were furthermore interested in observing the steric dependence of the product ratio by replacing the α-hydrogen atoms against bulkier methyl groups. Therefore the cyclohexanones **1a–d** were synthesized. After photolysis the product ratios were determined.

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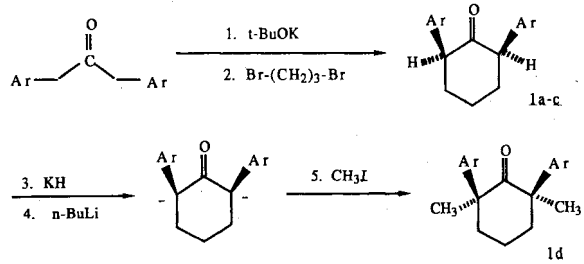
Results

A. Synthesis

The *cis*-cycloalkanones **1a–c** were prepared by the method of Brown involving the condensation of 1,3-diarylacetones with 1,3-dibromopropane[13]. Cyclohexanone **1d** was synthesized by methylation of the dianion of **1a** as described by Baretz and Turro[14].

Scheme 2. Synthesis of **1a–d**



R	1	%
C_6H_5	**a**	22
4-ClC_6H_4	**b**	14
4-$CH_3OC_6H_4$	**c**	29
C_6H_5	**d**	15

B. Photolysis of 1a–d

Thoroughly degassed solutions of **1a–d** in various solvents (0.004–0.14 M) were irradiated (1000 W, Hg high-pressure lamp) at temperatures ranging from −50 to 90 °C. The products were analyzed by GC and GC/MS. The yields were obtained by comparison with an internal standard[15]. Yields and reaction conditions (solvent and temperature) are recorded in Table 1.

The pentenes **5** are not stable to the photolysis conditions: In a control experiment the photolysis of a completely decomposed sample of **1a** showed, that both the *cis*- and *trans*-1-pentenes **5** reacted further. The products could not be detected by GC and the yield of *cis*- and *trans*-cyclopentanes **4** remained unchanged. This decomposition is much slower (ca. 1/20) than that of the cyclohexanone **1a**. As a consequence the values com/dis (see Figure 2) should be regarded as upper limits. The photolyses were carried out only to an extent of about 50% in most cases. The *cis*- and *trans*-cyclopentanes **4** were always obtained in a ratio of 1:1 (see Table 1). The *cis/trans* ratio for the 1-pentenes **5a–c** was not constant. Reasons for this could be due to the decomposition described above or a possible equilibrium between the two isomers under the reaction conditions[16]. At low temperatures the rate of loss of CO from the ketyl-alkyl diradicals **2** decreases markedly, therefore under such conditions intramolecular disproportionation of **2** can compete[17] (Scheme 3).

Scheme 3. Intramolecular reaction of the ketyl-alkyl diradicals **2**

Table 1. Photolysis of the cyclohexanones **1a–d** with the cyclopentanes **4** as dimerization products (com) and the 1-pentenes **5** as disproportionation products (dis)

Cyclo-hexanone	solvent[a] conc[b]	temp. (°C)	progress of reaction(%)	yield % com+dis[c]	com/dis c,d)	cis/trans c,d)	time of irrad. (min)
1a	t-BB	-50.0	42	34	0.83	1.00	30
	(0.14)	g)		35	0.85	1.01	30
		0.0	48	64	1.75	1.00	30
				64	1.79	1.02	30
		90.0	63	88	3.28	0.99	30
				86	3.02	0.99	30
	n-PE	-20.0	90	18	1.28	1.02	30
	(0.04)	g)					
		30.0	87	81	5.20	1.00	30
1b	t-BB	25.0	32	57	2.98	0.95	1
	(0.10)		53	41	2.30	1.08	2
	MEOH	25.0	33	63	5.30	1.02	1
	(0.06)						
1c	THF	25.0	47	82	3.95	0.98	2
	(0.08)		85	83	4.15	0.91	4
	THF[f]	-35.0	98	51	1.70	0.94	60
	(0.004)						
		-50.0	60	43	1.28	0.91	60
	t-BB	25.0	60	86	3.11	0.94	10
	(0.04)	-50.0	95	47	1.10	1.02	60
1d	t-BB	25.0	100	89	7.00	1.00	15
	(0.08)						

[a] t-BB: *tert*-butylbenzene, n-PE: *n*-pentane. – [b] Concentration in mol/l. – [c] Average value from three measurements. – [d] *cis*-**4** and *cis*-**5** products had shorter retention times in the GC analysis than *trans*-**4** and *trans*-**5**, respectively[29]. The ratios *cis/trans* of the disproportionation products **5** were not found to be constant. – [e] Time of irradiation. – [f] To avoid precipitation of the ketone it was diluted by a factor of 20. Later the solvent was removed in vacuo. It was checked repeatedly that no precipitation occured during evaporation. Photolysis was carried out with a 250 W Hg-low-pressure lamp. – [g] Photolysis was carried out in the cavity of an ESR spectrophotometer, 1000 W Hg-high-pressure lamp, no filter.

Products which, on the basis of mass spectroscopy (M^+, fragmentation pattern) are isomers of the cyclohexanones **1**, are found in yields up to 10% at temperatures below 0 °C[18]. They can undergo further reactions to products with higher molecular mass, which again are not detectable by GC.

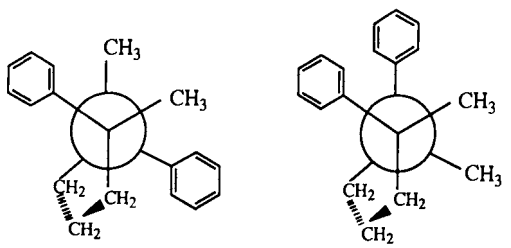
Discussion

In agreement with the earlier results of Overberger[19] and Buchachenko[16] for **4a** we showed that there was equal formation of the *cis* and *trans* diastereomeric cyclopentanes **4a–d** on photolysis of the cyclohexanones **1a–d**. From these results we concluded, that the equilibrium constant K for the *cis/trans* isomerisation of the diradicals **3** is 1.0 and that there is no discrimination in the dimerization step. An alternative explanation of $K \neq 1$ and an exactly compensating discrimination of the diastereomeric transition states seems unlikely. The free-energy difference of 2.7 kcal/mol at 110 °C for *cis/trans*-**4a**[20] does not affect the transition states for the formation of these products. The dimerization step thus seems to be solely controlled by kinetic factors.

These findings are consistent with the results of Turro[4] and Barton et al.[1]. They showed by picosecond spectroscopy, that the rate determining step is the spin inversion from the triplett to the singlet state and not the product formation step. The spin inversion does, however, not depend on the *cis/trans* conformation of the diradical **3**[4], hence the *cis*- to *trans*-product ratio **4** is only determined by the ratio of the two conformers **3**. Our results prove that the lifetimes of the diradicals **3** is indeed long enough to allow complete equilibration between their conformers[21]. Force-field calculations[22], which allow the calculation of standard heats of formation of radicals, showed that both conformations have the same energy, predicting an equilibrium constant of 1. This is again consistent with the experimental findings, assuming the mechanism described above.

Furthermore the results show that aryl-aryl attractions[12], which could be expected in the transition state of the *cis*-cycopentane formation, do not have any stereo-differentiating effect, nor do *p*-substituents on the phenyl rings. The change of stereoselectivity with the *p*-substituent, observed for the dimerization of 1-arylneopentyl radicals[11,12], does not occur here.

Another interesting aspect is that the replacement of the α-hydrogen atoms of **3a** by methyl groups in **3d** does not lead to any change in the selectivity of ring closure. This demonstrates that the methyl groups on the radical centers are not bulky enough to lead to repulsive methyl-methyl interactions in the transition state of the radical dimerization. Considering the Newman projections of the diastereomeric transition states, it seems unlikely that the sum of all repulsive interactions – provided there are any – would be exactly the same in the *cis* and *trans* transition states.



trans transition-state cis transition-state

Figure 1. Newman projections of the diastereomeric transition states for the dimerization of the diradical **3d**

Force-field calculations using a force field for the transition state of radical dimerization[11,23] show that for any chosen distance between the two radical centers on the reaction pathway no energy difference between the two diastereomeric transition states can be detected. The reason for this behaviour is the change in hybridization of about 30% from sp^2 to sp^3 in the transition state. This leads to a considerable back bending of all substituents which decreases any possible interactions between the reacting centers. These calculations have been demonstrated to be very useful in predicting energy differences in transition states, because many interactions cannot be seen by considering projections alone. As expected from studies of comparable systems[1,8,9], the com/dis ratios depend strongly on solvent and temperature (Figure 2). Because of the partial decomposition of the 1-pentenes **5**, the com/dis values should be regarded as upper limits. A simple relationship cannot be given, even if there seems to be a correlation between $\ln(k_{com}/k_{dis})$ and $1/T$: Other hidden parameters, for example solvent viscosity, as shown by Schuh and Fischer[10] for the com/dis ratios of the *tert*-butyl radical, might be the reason for this behaviour. Models dividing the surfaces of the radicals into zones, which on encounter lead to either dimerization or disproportionation[10,24], might be applied here as well.

The results of this work stimulate further investigations. It will be interesting to see, if by appropriate substitution the equilibrium constant $K_{cis/trans}$ of the diradicals **3** can be shifted and if selectivity can be achieved in this way. By introducing bulky groups like *tert*-butyl in the α-position it should be possible to prevent the radicals from bending back (back-strain[25]). Here, in the last step of the reaction sequence, product formation could become rate determining.

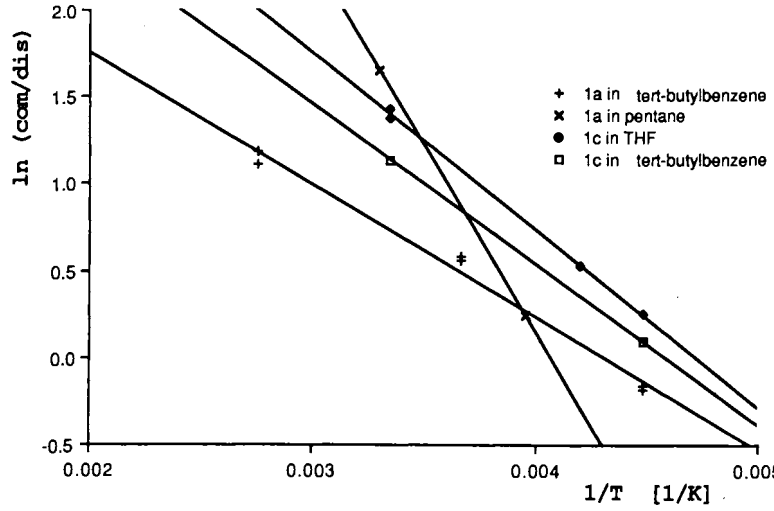


Figure 2. ln(com/dis) vs $1/T$ for the reactions of the diradicals **3a** and **3c** in various solvents

Finally, appropriate substitution on the phenyl rings (for example *p*-methoxy on one and *p*-NO_2 on the other) will show, if transition states and/or equilibrium can be favoured by charge-transfer interactions.

Experimental

1,3-Diphenylacetone was available commercially. 1,3-Bis(4-chlorophenyl)acetone and 1,3-bis(4-methoxyphenyl)acetone were synthesized by condensation of derivatives of the corresponding 4-chloro/4-methoxyphenylacetic acids[11,26-28].

cis-2,6-Diphenylcyclohexanone[13] (**1a**): To 17.0 g (0.44 mol) of potassium 600 ml of *tert*-butyl alcohol was added dropwise under nitrogen in a rate to keep the mixture boiling gently. To the stirred potassium *tert*-butylate solution 48.0 g (0.22 mol) of dibenzyl ketone was added slowly. The reaction mixture turned red during the addition. Stirring was continued for 2 h at room temperature. Then 44.4 g (0.22 mol) of 1,3-dibromopropane was added over 45 min. The red colour disappeared and KBr precipitated. After stirring for additional 2 h at room temperature and 1 h under reflux, 100 ml of H_2O and 3 ml of acetic acid were added. Solvent and water were removed by distillation, and the remainder was dissolved in ether. The ethereal solution was washed with H_2O twice and then dried with $MgSO_4$. The ether was removed in vacuo, and the oily-crystalline product recrystallized three times from ether/petroleum ether (1:1). Yield: 12.5 g (22%) (ref.[13] 25%); m. p. 123–124°C (ref.[13] 123–124°C). – IR (KBr): 1710 cm^{-1} (CO). – ^1H NMR (90 MHz, $CDCl_3$/TMS): δ = 1.73–2.46 (m, 6H, CH_2), 3.46–3.83 (m, 2H, Ar–CH), 6.83–7.26 (m, 10H, Ph). – MS (EI, 70 eV): *m/z* (%) = 250 (M^+, 78), 131 (91), 130 (55), 118 (35), 117 (79), 115 (31), 105 (27), *104 (100)*, 91 (69).

cis-2,6-Bis(4-chlorophenyl)cyclohexanone (**1b**) was synthesized from 9.5 g (0.24 mol) of potassium in 250 ml of *tert*-butyl alcohol, 34.5 g (0.12 mol) of 1,3-bis(4-chlorophenyl)-2-propanone in a mixture of 200 ml of *tert*-butyl alcohol and 150 ml of THF, and 24.1 g (0.12 mol) of 1,3-dibromopropane as described for **1a**. Yield 5.4 g (14%); m. p. 154–155°C. – IR (KBr): 1700 cm^{-1} (CO). – ^1H NMR (250 MHz, $CDCl_3$/TMS): δ = 2.0–2.2 (m, 3,5-H, 4H), 2.30–2.41 (m, 4-H, 2H), 3.70–3.79 (m, 2,6-H, 2H), 7.12–7.29 (m, Ar–H, 8H). – MS (EI, 70 eV): *m/z* (%) = 320 (14, M^+), 318 (41), 165 (48), 164 (14), 152 (10), 151 (48), 140 (21), 139 (14), *138 (100)*, 125 (51).

$C_{18}H_{16}Cl_2O$ (319.2) Calcd. C 67.72 H 5.05 Cl 22.21
Found C 67.37 H 4.53 Cl 21.98

cis-2,6-Bis(4-methoxyphenyl)cyclohexanone (**1c**) was synthesized from 9.8 g (0.25 mol) of potassium in 350 ml of *tert*-butyl alcohol, 34.0 g (0.13 mol) of 1,3-bis(4-methoxyphenyl)-2-propanone in 250 ml of *tert*-butyl alcohol, and 26.2 g (0.13 mol) of 1,3-dibromopropane as described for **1a**. CH_2Cl_2 was used for extraction, the crude product was crystallized twice from toluene. Yield 11.2 g (29%); m. p. 166°C. – IR (KBr): 1710 cm^{-1} (CO). – ^1H-NMR (250 MHz, $CDCl_3$/TMS): δ = 1.95–2.21 (m, 4H, 3,5-H), 2.28–2.45 (m, 2H, 4-H), 3.67–3.85 (m, 2H, Ar–CH), 3.79 (s, 6H, OCH_3), 6.82–7.14 (q, AA'BB', 8H, Ar–H). – MS (EI, 70 eV): *m/z* (%) = 310 (58, M^+), 282 (41), 161 (22), 160 (9), 148 (31), 147 (79), 135 (19), 134 (44), *121 (100)*.

$C_{20}H_{22}O_3$ (310.4) Calcd. C 77.39 H 7.14
Found C 77.18 H 7.05

2,6-Dimethyl-2,6-diphenylcyclohexanone (**1d**): A solution of 7.5 g (30 mmol) of **1a** in 50 ml of THF was added dropwise to a 35% suspension of KH in mineral oil (35 mmol) under nitrogen. The reaction mixture turned yellow, and after 30 min stirring at room temp. the mixture was cooled to 0°C and 50 ml of an *n*-butyllithium solution (1.6 M in *n*-hexane) was added dropwise. The colour of the reaction mixture turned from yellow to red. Stirring was continued for 15 min, then 25.5 g (180 mmol) of CH_3I in 50 ml of THF was added. The colour changed again to yellow. After hydrolysis with 180 ml of ice/water the reaction mixture was neutralized with 2 N HCl. The phases were separated and the aqueous phase was extracted thoroughly with ether. The combined organic phases were dried with $MgSO_4$, the solvent was removed in vacuo. The resulting oil was purified by chromatography (silica, petroleum ether/ethyl acetate 20:1) and was then recrystallized twice from petroleum ether. Yield 1.2 g (15%); m. p. 97°C. – IR (KBr): 1710 cm^{-1} (CO). – ^1H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.38 (s, 6H, CH_3), 1.75–1.3 (m, 3H, 2 3-H_{eq}, 1 4-H_{eq}), 2.16–2.39 (m, 1H, 4-H_{ax}), 2.50–2.65 (m, 2H, 3-H_{ax}), 6.89–7.10 (m, 10H, Ar–H). – MS (EI, 70 eV): *m/z* (%) = 278 (M^+, 19), 250 (11), 145 (54), 144 (26), 132 (22), 131 (31), 129 (9), 119 (15), *118 (100)* 105 (49).

$C_{20}H_{22}O$ (278.4) Calcd. C 86.29 H 7.97
Found C 86.54 H 8.03

Photolysis of **1**: Solutions (0.004–0.14 M, different solvents, see Table 1) of **1a–d** in quartz tubes were thoroughly degassed by repeated freezing in liquid nitrogen, evacuating, venting with nitrogen (99.99% pure), and thawing. The tubes were sealed under nitrogen, and they were irradiated with λ = 254 nm (Gräntzel photoreactor, Hg-low pressure lamp). Reaction conditions as solvent, temperature, time etc. are recorded in Table 1. Products were analyzed and identified by GC and GC/MS[29]. Yields were determined with the help of an internal standard (*n*-alkane)[25], which was added to the reaction mixture. Not listed in Table 1 are isomers of **1** (identical mass spectrum), which were obtained in yields of 0–10%. When the GC columns were cleaned by heating them to 250°C, high boiling products could be observed, however, we were not able to determined their yields. The cyclopentanes **4** and the 1-pentenes **5** showed very similar fragmentation patterns in MS studies. They could be distinguished by shaking the solutions with Br_2 after which the peaks of the 1-pentenes **5** had disappeared from the gas chromatogram. Disproportion products were not stable to the reaction conditions. Photolysis of a completely decomposed sample of **1a** showed that the 1-pentene **5a** disappeared without an increase of any GC-detectable product. However, this reaction is significantly slower than the decomposition of the ketone **1**. The ratios *cis/trans*-**5** were not constant, they varied so strongly with every measurement, that no values can be reported for them.

Results and Conditions of GC/MS Analysis

Products from **1a**: GC conditions: FS-OV-101, 10 m, N_2 flow: 5 ml/min, temp. program: 100 to 150°C with 3°C/min. R_t (min) = 5.5 (**4a**, *cis*); 6.1 (**4a**, *trans*); 7.2 (**5a**, *cis*); 8.1 (**5a**, *trans*); 12.1 (**1a**); 14.3 (*n*-$C_{21}H_{44}$, standard).

cis-**4a**: MS (EI, 70 eV): *m/z* (%) = 222 (M^+, 51), 131 (92), 130 (22), 118 (31), 117 (75), 115 (38), 105 (27), *104 (100)*, 91 (70).

trans-**4a**: Identical mass spectrum.

cis-**5a**: MS (EI, 70 eV): *m/z* (%) = 222 (M^+, 16), 131 (73), 130 (20), 118 (18), 117 (59), 115 (46), 105 (27), 104 (54), *91 (100)*.

trans-**5a**: Identical mass spectrum.

Products from **1b**: GC conditions: FS-OV-101, 10 m, N_2 flow: 5 ml/min, temp. program: 120 to 200°C with 3°C/min. R_t (min) = 2.5 (*n*-$C_{19}H_{40}$, standard); 5.3 (**4b**, *cis*); 5.9 (**4b**, *trans*); 6.4 (**5b**, *cis*); 8.5 (**5b**, *trans*); 15.9 (**1b**).

cis-**4b**: MS (EI, 70 eV): *m/z* (%) = 292 (17), 290 (M – 1, 33), 165 (52), 152 (22), 151 (41), 140 (24), 139 (15), *138 (100)*, 125 (50).

trans-**4b**: Identical mass spectrum.

cis-**5b**: MS (EI, 70 eV): *m/z* (%) = 290 (M − 1, 24), 165 (46), 151 (77), 140 (23), 139 (10), 138 (92), *125 (100)*.

trans-**5b**: Identical mass spectrum.

Products from **1c**: GC conditions: FS-OV-101, 9 m, N_2 flow: 5 ml/min, temp. program: 170 to 220°C with 5°C/min. R_t (min) = 1.50 (**4c**, *cis*); 1.85 (**4c**, *trans*); 2.16 (**5c**, *cis*); 3.08 (**5c**, *trans*); 5.04 (**1c**); 5.89 (n-$C_{28}H_{58}$, standard).

cis-**4c**: MS (EI, 70 eV): *m/z* (%) = 282 (M^+, 43), 161 (23), 148 (28), 147 (73), 135 (17), 134 (49), *121 (100)*.

trans-**4c**: Identical mass spectrum.

cis-**5c**: MS (EI, 70 eV): *m/z* (%) = 282 (M^+, 25), 161 (15), 148 (19), 147 (51), 135 (16), 134 (26), *121 (100)*.

trans-**5c**: Identical mass spectrum.

Products from **1d**: GC conditions: SE 30 2.5%, 2 m, N_2 flow: 24 ml/min, temp. 200°C. R_t (min) = 10.6 (**4d**, *cis*); 11.7 (**4d**, *trans*); 14.0 (**5d**, *cis*); 17.5 (**5d**, *trans*); 20.6 (**1d**); 36.3 (n-$C_{22}H_{46}$, standard).

cis-**4d**: MS (Cl, CH_4): *m/z* (%) = 250 (M^+, 3), 174 (15), *123 (100)*, 131 (5), 119 (5), 117 (11), 105 (12), 95 (6).

trans-**4d**: Identical mass spectrum.

cis-**5d**: MS (Cl, CH_4): *m/z* (%) = 251 (M^+ + 1, 4), 250 (3), 173 (46), 159 (13), 145 (22), 133 (16), 131 (34), 119 (19), 106 (12), *105 (100)*.

trans-**5d**: Identical mass spectrum.

CAS Registry Numbers

1a: 20834-02-0 / **1b**: 113354-65-7 / **1c**: 113354-66-8 / **1d**: 113354-67-9 / (*cis*)-**4a**: 7433-53-6 / (*trans*)-**4a**: 7433-75-2 / (*cis*)-**4b**: 113354-68-0 / (*trans*)-**4b**: 113378-76-0 / (*cis*)-**4c**: 113354-71-5 / (*trans*)-**4c**: 113354-72-6 / (*cis*)-**4d**: 113354-75-9 / (*trans*)-**4d**: 113354-76-0 / (*Z*)-**5a**: 97455-12-4 / (*E*)-**5a**: 97455-11-3 / (*Z*)-**5b**: 113354-69-1 / (*E*)-**5b**: 113354-70-4 / (*Z*)-**5c**: 113354-73-7 / (*E*)-**5c**: 113354-74-8 / (*Z*)-**5d**: 113354-77-1 / (*E*)-**5d**: 113354-78-2 / $(PhCH_2)CO$: 102-04-5 / $Br-(CH_2)_3Br$: 627-15-6 / $(4\text{-}ClC_6H_4CH_2)_2CO$: 65622-34-6 / $(4\text{-}MeOC_6H_4CH_2)_2CO$: 29903-09-1

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