31. Diastereoselective Synthesis of Cyclododeca-1,6-diallenes (= Cyclododeca-1,2,6,7-tetraenes)

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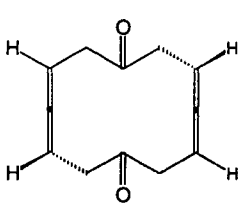
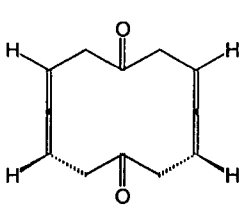
The synthesis of substituted cyclododeca-1,6-diallenes (= cyclododeca-1,2,6,7-tetraenes) from cyclododeca-5,11-diyne-1,4-diols is described (*Schemes 1* and *3*). The *ca.* 1:1 mixtures of the stereoisomers of the cyclododeca-1,6-diallenes were formed in high yields from the *ca.* 1:1 diastereoisomer mixtures of the 1,4-disubstituted cyclododeca-5,11-diynes by reactions with Me_2CuLi or *t*-BuMgCl/$Cu^{I}I$. In mechanistically relevant experiments with the pure diastereoisomers of 1,4-dimethylcyclododeca-5,11-diyne-1,4-diol, it is demonstrated that the configuration is conserved in these reactions. The first synthesis of a 1-substituted cyclododeca-2,8-diyne bearing only one propargylic leaving group gives access to a mixed 12-membered allen-yne (*Scheme 5*).

Introduction. – The intriguing selectivity of allenes in their reactions with electrophiles, radicals, and nucleophiles makes them attractive precursors for C–C bond forming reactions [1]. They are readily available by a variety of methods, many of which make use of S_N2'-type reactions of propargylic precursors or the MeLi-induced opening of geminal dibromocyclopropanes [2–16]. The chiral nature of disubstituted allenes, predicted by *van't Hoff*, led to the investigation of their configuration which clearly shows that 1,3-disubstituted allenes exist as enantiomers. For cyclic compounds, the minimal ring size, which would allow the strainless incorporation of the linear C=C=C structure and isolation of these allenes was of particular interest: cyclonona-1,2-diene is the smallest stable cyclic allene which has been isolated [1] [17].

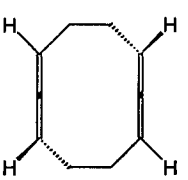
For cyclic diallenes, it has been established by *Sondheimer* that the cyclododeca-1,7-diallene (= cyclododeca-1,2,7,8-tetraene) **1** exist in both, the *meso* and the racemic C_2 form [18]. In the cyclodecane series, only the *meso* form of the cyclodeca-1,6-diallene (= cyclododeca-1,2,6,7-tetraene) **2** had been prepared and its structure determined [19].



rac-**1**



meso-**1**



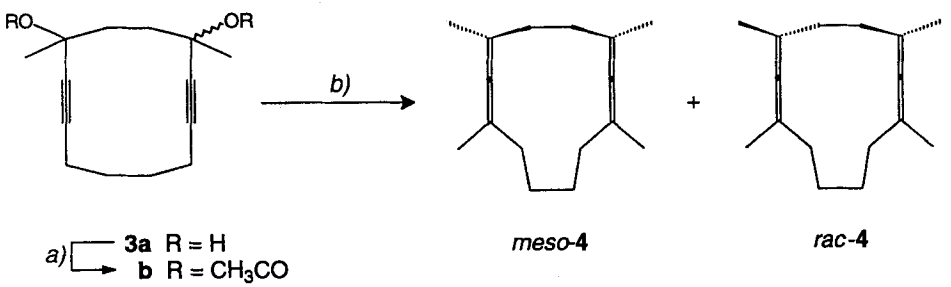
meso-**2**

Recently, we developed efficient synthetic routes to cyclododeca-2,8-diynes with substituents at the propargylic positions of the two alkyne groups [20] and subsequently explored their transformation into cyclic 1,6-diallenes. Due to their ready accessibility

and their stability, the cyclododeca-5,11-diyne-1,4-diols **3a** and **7a** with tertiary- and secondary-alcohol groups, respectively, were chosen as precursors for the synthesis of the cyclododeca-1,6-diallenes **4** and **8**.

Results and Discussion. – When a *ca.* 1:1 mixture of the diastereoisomers of 1,4-dimethylcyclododeca-5,11-diyne-1,4-diyl diacetate (**3b**) was treated with Me_2CuLi, the cyclododeca-1,6-diallene **4** was formed as a *ca.* 1:1 diastereoisomer mixture in 90% yield (*Scheme 1*). The ^{13}C-NMR of **4** showed 16 lines, and the GC analysis revealed two signals in a *ca.* 1:1 ratio which, according to GC/MS, showed both the same fragmentation pattern from *m/z* 216 for M^{+} [1]).

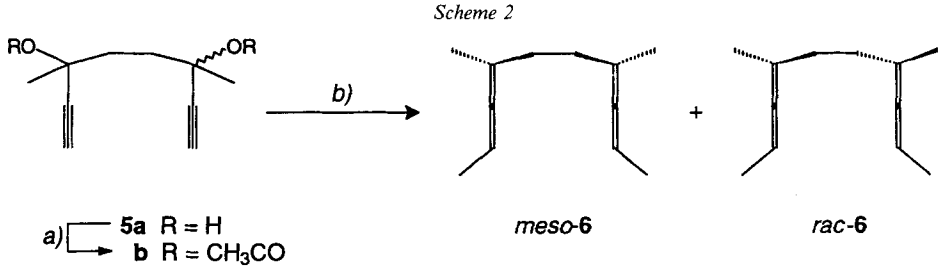
Scheme 1



a) Ac_2O, Et_3N, DMAP, r.t., 10 h. *b*) $LiCuMe_2$, Et_2O, −15°.

When the same reaction conditions were applied to the diastereoisomer mixture (*ca.* 1:1) of the acyclic 3,6-dimethylocta-1,7-diyne-3,6-diyl diacetate (**5b**), the diallene **6** was also obtained as a *ca.* 1:1 diastereoisomer mixture in 91% yield (*Scheme 2*). This was apparent from the double set of signals in the ^{13}C-NMR spectrum of **6**. Due to its thermal lability, **6** could not be analyzed by GC [23] [24].

Scheme 2

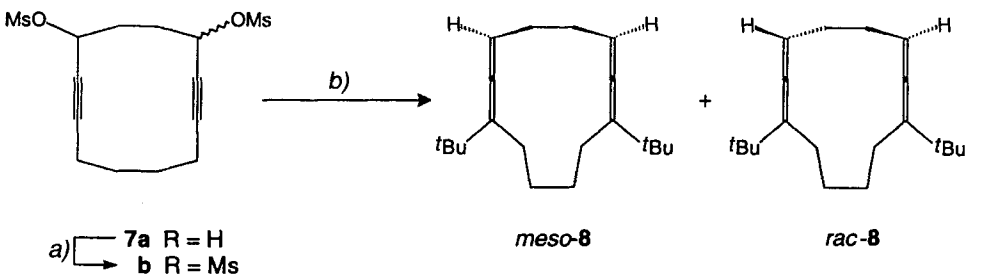


a) Ac_2O, Py, DMAP, 0°, 1.5 h, then r.t., 24 h. *b*) $LiCuMe_2$, Et_2O, −15°.

In a further transformation, a *ca.* 1:1 diastereoisomer mixture **7b** reacted with *t*-BuMgCl and $Cu^{I}I$ to the 1,8-di(*tert*-butyl)cyclododeca-1,6-diallene **8** in 72% yield [8] (*Scheme 3*). The diastereoisomeric *meso*- and *rac*-**8** were formed in a *ca.* 1:1 ratio, which

[1]) The reaction of **3b** with H^- as the nucleophile using SmI_2/Pd^0 remained unsuccessful [21] [22].

Scheme 3



a) Et_3N, MsCl, CH_2Cl_2, THF, 0°. *b*) ^{t}BuMgCl, CuI, THF, −30°.

was confirmed by the double set of signals in the ^{13}C-NMR and the GC analysis with a chiral stationary phase.

In a mechanistically relevant experiment, separate transformations of the pure diastereoisomers of **3b**, obtained by acetylation of the pure diastereoisomers of **3a**, led to products each containing a single diastereoisomer of **4**. The ^{13}C-NMR spectra showed different sets of 8 signals. According to GC analyses on a chiral stationary phase, the precursor *meso*-**3b** was transformed into *meso*-**4**, whereas *rac*-**4** was obtained from the *rac*-precursor[2]).

These results might be interpreted as follows: the S_N2' reactions can overall follow a *trans* or a *cis* pathway, with the *trans* pathway usually being favored [7] [10] [12] (*trans* refers to the incoming nucleophile and the leaving group). For a *trans* pathway, it is reasonable to assume that these substitution reactions occur in a plane perpendicular to the idealized plane of the ring system, because only *cis* substitutions could occur in-plane. For the formation of *meso*-**4** by two sequential *trans*-S_N2' substitutions, the pathway for the second propargylic displacement can be pictured as shown in **9a**. In the case of *rac*-**3b**, the second *trans* substitution reaction with Me_2CuLi may proceed *via* an intermediate with a conformation as depicted in **9b**. Inspection of models indicate that there is severe interaction between the Me group introduced in the first S_N2' reaction and the CH_2 group in the γ-position. The molecule might, therefore, adopt the less strained conformation **9c** where the CH_2 groups now interfere with the *trans*-mode of Me^- attack in the propargylic position. Alternatively, the stereochemical pathway of the transformation **3b** to **4** could proceed similarly to that proposed for **7b** to **8** (see below). The stereospecific results imply that in *rac*-**3b**, the expected steric interaction is not strong enough to change the mode of the S_N2' reaction from *trans* to *cis* as described for other examples [7]. These facts only show that the configuration is preserved in the reactions of *meso*- and *rac*-**3b** but do not answer the question of whether the chirality transfer occurs *via* a *cis* or a *trans* mode in these cyclic systems [25][3]).

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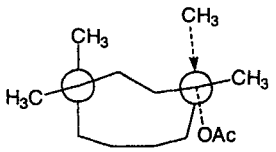
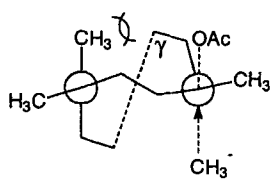
[2]) The GC of *meso*- and *rac*-**4** contained each an additional peak (t_R 20.5 min) of 30–40% intensity, whereas no by-product could be observed in their ^{13}C-NMR spectra. GC/MS Spectra of this peak showed *m/z* 216 for M^+, identical to that of **4**. Therefore, the by-product must correspond to an isomer of **4** of unknown structure [23]. This indicates a limited thermal stability of the diastereoisomers of **4**. No additional peaks could be detected in the GC of **8** and **12**, where the allenic unit is substituted by a *t*-Bu group.

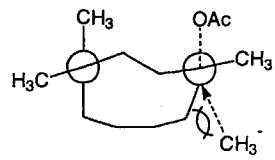
[3]) It is questionable, whether the model calculations which show an angle of 120° for the addition of H^- to HC≡CH [25] are stereoelectronically relevant for the transformation of propargylic compounds like **3b** with R_2CuLi.



9a



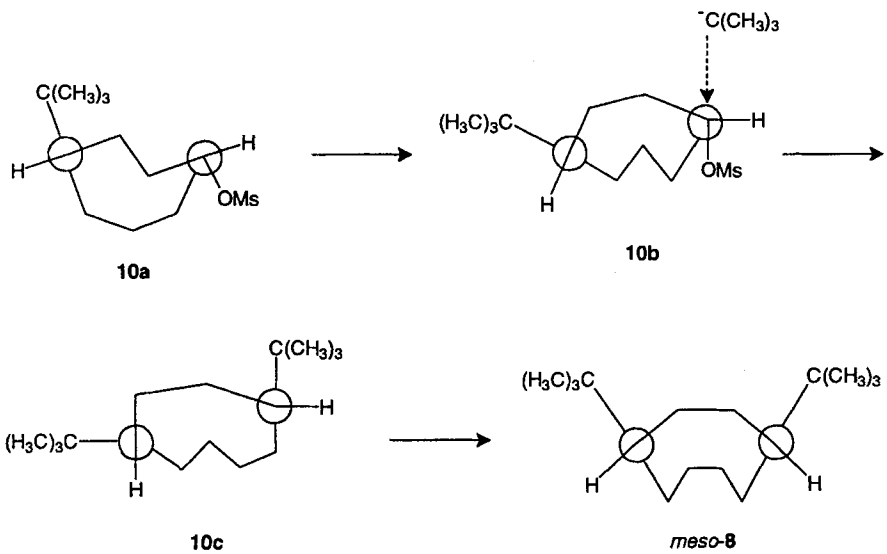
9b



9c

Applying these concepts of steric hindrance to the reaction of **7b** to the diallene **8**, the stereochemical course of the substitution can be rationalized by assuming that a conformational change will occur after the first S_N2' reaction. This would lead to an intermediate with a quasi-equatorial *t*-Bu group and an essentially unhindered alkyne for the second *trans*-substitution proceeding *via* **10b** to **10c** and to the conformation of *meso*-**8** depicted in *Scheme 4*. This interpretation is supported by AM1 calculations of a *tert*-butylcyclododeca-1-allen-7-yne, which gave a conformation with a quasi-equatorial *tert*-butyl group. The transformation of *rac*-**7b** to *rac*-**8** can similarly be analyzed according to this scheme.

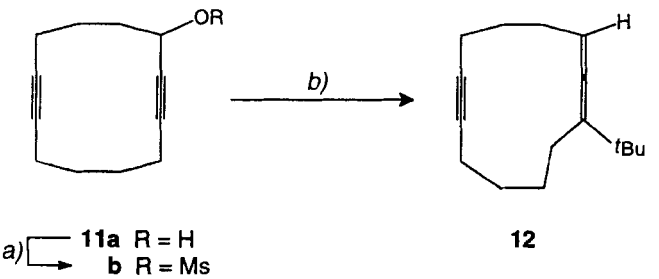
Scheme 4. *Conformational Analysis of the Transformation of* meso-**7b** *to* meso-**8**



As a first example of the 'missing link' between the dialkynes **3a, b** and **7a, b** and the diallenes **4** and **8**, the cyclic allen-yne compound **12** was prepared from the mono-functionalized dialkyne **11b** [20].

Concluding Remarks. – The transfer of chirality from the propargylic positions in the cyclic alkynes by S_N2'-type reactions to the allenes can be explained in terms of the conformational constraints of the ring system and by steric interactions in the course of the second S_N2' reaction. In the case of **3b**, it has been proven that the diastereoisomers

Scheme 5



a) MsCl, Et_3N, CH_2Cl_2, THF, 0°, 2.5 h. *b*) ^{t}BuMgCl, CuI, THF, −30°.

are transformed into the diastereoisomers of the tetramethylcyclododeca-1,6-diallene **4** stereospecifically with conservation of the diastereoisomeric relationship.

The ready access of the cyclic 1,6-diallenes **4** and **8** and the cyclic allen-yne **12** calls for a study of their transannular reactions.

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Experimental Part

General. Chemicals were purchased from commercial suppliers and used without further purification. MeLi (*Fluka pract.*) was used as a 1.6M soln. in Et_2O. THF was dried by distillation from Na, Et_2O from NaH. DMAP = 4-(dimethylamino)pyridine. After workup by pouring the mixture onto sat. NH_4Cl soln. and extraction with Et_2O/pentane 1:1, the solns. were dried ($MgSO_4$). TLC: silica-gel plates *SIL G/UV*$_{254}$ (*Macherey & Nagel*). GC: *Hewlett-Packard-HP-5890* instrument (He, 43 kPa) with a *HP-5-Ultra* capillary column (length 10 m, i.d. 0.2 mm) and a temp. program 40–220° (3°/min); chiral analyses at 20 kPa with a modified cyclodextrin as chiral stationary phase; column *A* (10 m, d.f. 0.25 μm, i.d. 0.3 mm) 100% heptakis{2,3-di-*O*-acetoxy-6-*O*-[(*tert*-butyl)-dimethylsilyl]}-β-cyclodextrin in *OV 1701* and variable temp. programs; t_R in min. Prep. HPLC: *715004 ET.-250/10-Nuc. 50-7* column (*Macherey-Nagel*); flow 12 ml/min. M.p.: *Büchi-510* melting-point apparatus; uncorrected. IR Spectra: in $CHCl_3$; *Perkin-Elmer-782*-IR spectrophotometer. NMR Spectra: in $CDCl_3$ or (D_6) acetone; *Bruker-AC-300* spectrometer (^{1}H, 300 MHz; ^{13}C, 75 MHz); chemical shifts δ in ppm rel. to internal $CHCl_3$ (δ 7.27) or (D_6)acetone (δ 2.04) for ^{1}H-NMR and $CDCl_3$ (δ 77.0) or (D_6)acetone (δ 29.8) for ^{13}C-NMR; stack = heavily overlapping signals. MS: *Varian-MAT-CH7A* (70 eV, EI) and *Fisons-Autospec-Q* spectrometer; in *m/z* (rel. %) GC/MS: *VG-Autospec* spectrometer. Reactions were normally performed under Ar or N_2.

1. *Allene Precursors* **3b**, **5b** *and* **11b**. *1,4-Dimethyl-cyclododeca-5,11-diyne-1,4-diyl Diacetate* (**3b**). Under the same conditions as described for **5b** (see below), 0.2 g (0.91 mmol) of 1,4-dimethylcyclododeca-5,11-diyne-1,4-diol (**3a**) [20] gave 0.083 g (30%) of **3b** as a colorless liquid. Better yields were obtained by dissolving **3a** (0.143 g, 0.65 mmol) in Ac_2O (4 ml) followed by slow addition of Et_3N (0.262 g, 2.29 mmol) and DMAP (0.079 g, 0.65 mmol) and stirring at r.t. for 10 h. Workup and chromatography with AcOEt/hexane 2:1 yielded 0.168 g (85%) of **3b** as a colorless liquid. The pure diastereoisomers of **3b** were obtained by separate transformation of the pure diastereoisomers of **3a**, obtained by crystallization [20]. R_f (*meso/rac*) 0.60 (AcOEt/hexane 2:1). GC (*meso/rac*): t_R 33.98, 34.17 (*ca.* 1:1). IR (*meso/rac*): 2850*s*, 2225*w*, 1710*m*, 1330*s*, 1240v*s*, 1170*s*, 1100*s*, 1080v*s*, 1020*s*, 930*s*. ^{1}H-NMR ((D$_6$)acetone; *meso/rac*): 1.56–1.78 (2*s* + stack; 10H); 1.81–1.89 (*d*, 2H); 2.020 (*s*, 3H), 2.023 (*s*, 3H); 2.12–2.32 (stack, 4H); 2.32–2.43 (stack, 2H). ^{13}C-NMR ((D$_6$)acetone): *rac*-**3b**: 19.10 (*t*); 21.75 (*q*); 26.50 (*q*); 27.67 (*t*); 38.82 (*t*); 76.58 (*s*); 82.15 (*s*); 86.20 (*s*); 167.43 (*s*); *meso*-**3b** 19.00 (*t*); 21.40 (*q*); 25.93 (*q*); 27.56 (*t*); 38.53 (*t*); 76.59 (*s*); 82.04 (*s*); 86.33 (*s*); 167.41 (*s*). MS (*meso/rac*): no M^+, 234(5), 220(3), 219(7), 203(58), 192(29), 187(30), 173(11), 169(11), 159(22), 145(16), 143(18), 131(26), 119(13), 117(13), 105(19), 91(24), 77(13), 43(100).

3,6-Dimethylocta-1,7-diyne-3,6-diyl Diacetate (**5b**). To a soln. of 3,6-dimethylocta-1,7-diyne-3,6-diol (0.5 g, 3.01 mmol; **5a**) [20] in pyridine (25 ml) was slowly added Ac_2O (0.97 g, 9.06 mmol) and DMAP (0.15 g, 1.23 mmol) at 0° and stirred for 1.5 h. The mixture was warmed to r.t. and stirring continued for 24 h. Workup and chromatography with Et_2O gave 0.45 g (60%) of **5b**. White solid. M.p. 52°. R_f 0.68 (Et_2O). GC: t_R 12.45, 12.54 (52:48). IR: 3310*s*, 3000*m*, 2940*m*, 2120*w*, 1740*vs*, 1445*m*, 1370*s*, 1240*vs*, 1175*m*, 1060*m*, 1015*m*, 940*m*. ^{1}H-NMR ($CDCl_3$): 1.59(*s*, 6H); 1.92(*s*, 6H); 1.92–2.11 (stack, 4H); 2.49(*s*, 2H). ^{13}C-NMR ($CDCl_3$): major isomer: 21.80(*q*); 26.42(*q*); 36.05(*t*); 73.66(*s*); 74.10(*d*); 83.32(*s*); 169.20(*s*); minor isomer: 21.80(*q*); 26.32(*q*); 35.99(*t*); 73.64(*s*); 74.06(*s*); 83.29(*s*); 169.20(*s*). GC-MS: 208([*M* – 43]$^+$, 0.5), 166(24), 165([*M* – 43 – 43]$^+$, 27), 149(10), 138(15), 137(10), 133(17), 117(11), 116(11), 105(13), 91(18), 80(19), 79(33), 69(9), 53(13), 43(100). Anal. calc. for $C_{14}H_{18}O_4$ (250.29): C67.18, H7.25; found: C67.46, H7.43.

Cyclododeca-2,8-diyn-1-yl Methanesulfonate (**11b**). As described in [20], cyclododeca-2,8-diyn-1-ol (0.1 g, 0.57 mmol; **11a**) [20] was dissolved in CH_2Cl_2 (7 ml) at –5°. After the addition of Et_3N (0.234 g 2.31 mmol) and MsCl (0.216 g, 1.88 mmol), the mixture was stirred for 4 h at 0°. Workup with 2N HCl and extraction with Et_2O gave 0.132 g (91%) of **11b** as a white powder which could be used without further purification. R_f 0.73 (Et_2O). IR: 2930*vs*, 2860*s*, 2235*m*, 1740*m*, 1680*m*, 1315*m*, 1165*vs*, 1090*m*, 1010*m*, 965*s*, 900*vs*. ^{1}H-NMR ((D$_6$)acetone): 1.59–1.99 (stack, 6H); 2.00–2.40 (stack, 8H); 3.19(*s*, 3H); 5.24(*dm*, 1H). ^{13}C-NMR ((D$_6$)acetone): 19.10(*t*); 19.30(*t*); 19.39(*t*); 24.59(*t*); 27.33(*t*); 28.40(*t*); 35.42(*t*); 39.13(*q*); 73.13(*d*); 78.08(*s*); 81.48(*s*); 82.32(*s*); 90.95(*s*). MS: 255([*M* + 1]$^+$, 0.5), 254(*M*$^+$, 4), 221(5), 220(23), 206(15), 205(77), 189(5), 175(20), 158(24), 157(32), 147(22), 143(33), 131(40), 130(52), 129(77), 128(50), 117(55), 115(66), 105(41), 103(33), 91(87), 81(27), 79(100), 78(36), 77(60), 67(39), 65(42), 55(40), 51(36), 41(61), 39(66).

2. *Acylic and Cyclic Diallenes* **4**, **5**, *and* **8** *and Allen-yne* **12**. *1,3,6,8-Tetramethylcyclododeca-1,2,6,7-tetraene* (**4**). To a slurry of CuI (0.244 g, 1.28 mmol) in Et_2O (2.6 ml) was slowly added MeLi (1.60 ml, 1.6M, 2.56 mmol) at –15°. After 20 min, *meso*-**3b** (0.098 mg, 0.324 mmol) in Et_2O (0.8 ml) was added and stirred at –10° for 30 min. The mixture was warmed to r.t. and stirred for another 24 h. Workup and chromatography with pentane gave *meso*-**4** (63 mg, 90%) as a colorless liquid. Under the same conditions, the transformation of *rac*-**3b** gave *rac*-**4** in 91% yield.

meso-**4**: R_f 0.61 (pentane). GC (*cf. Footnote 2*): t_R 26.49; column *A* (isothermal at 120°): t_R 47.70. IR: 2960*vs*, 2940*vs*, 2900*vs*, 2860*vs*, 1965*w*, 1470*s*, 1455*s*, 1370*s*. ^{1}H-NMR ($CDCl_3$): 1.63(*s*, 6H); 1.67(*s*, 6H); 1.68–1.80 (stack, 4H); 1.93–2.06 (stack, 4H); 2.14–2.36 (stack, 4H). ^{13}C-NMR ($CDCl_3$): 19.48(*q*); 19.70(*q*); 25.61(*t*); 31.82(*t*); 32.25(*t*); 96.35(*s*); 97.64(*s*); 199.40(*s*). MS: 217([*M* + 1]$^+$, 17), 216(*M*$^+$, 100), 201(27), 187(13), 173(20), 161(6), 160(8), 159(49), 146(9), 145(40), 133(17), 131(15), 119(33), 105(18), 91(16), 77(12), 67(5), 41(15). HR-MS: 216.1876 ($C_{16}H_{24}^+$; calc. 216.1878).

rac-**4**: R_f 0.61 (pentane). GC (*cf. Footnote 2*): t_R 25.82; column *A* (60–200° (2°/min)): t_R 47.91, 48.50(1:1). IR: 2960*vs*, 2940*vs*, 2900*vs*, 2860*vs*, 1965*w*, 1470*s*, 1455*s*, 1370*s*. ^{1}H-NMR ($CDCl_3$): 1.628(*s*, 6H); 1.634(*s*, 6H); 1.73–2.03 (stack, 8H); 2.22(*d*, 2H); 2.25(*d*, 2H). ^{13}C-NMR ($CDCl_3$): 18.28(*q*); 20.97(*q*); 26.37(*t*); 32.03(*t*); 33.29(*t*); 96.67(*s*); 97.18(*s*); 199.65(*s*). MS: 217([*M* + 1]$^+$, 18), 216(*M*$^+$, 100), 201(24), 187(10), 173(17), 161(5), 160(7), 159(43), 146(7), 145(35), 133(15), 131(13), 119(30), 105(16), 91(14), 77(10), 67(5), 55(8), 41(15). HR-MS: 216.1877 ($C_{16}H_{24}^+$; calc. 216.1878).

4,7-Dimethyldeca-2,3,7,8-tetraene (**6**). As described for **4**, with **5b** (1.44 g, 5.77 mmol). Workup and chromatography with pentane gave 0.85 g (91%) of **6**. Colorless liquid. R_f 0.72 (pentane). GC: **6** was not stable under GC conditions [23] [24]. IR: 2950*vs*, 2920*vs*, 2900*vs*, 2870*vs*, 1970*m*, 1470*s*, 1445*s*, 1370*s*, 1270*m*, 1145*m*, 995*m*. ^{1}H-NMR ($CDCl_3$): 1.64(*dd*, 6H); 1.69(*d*, 6H); 2.04(*s*, 4H); 5.01 (stack, 2H). ^{13}C-NMR ($CDCl_3$): major isomer: 14.83(*q*); 19.24(*q*); 32.02(*t*); 84.93(*d*); 98.44(*s*); 201.93(*s*); minor isomer: 14.87(*q*); 19.28(*q*); 32.08(*t*); 84.96(*d*); 98.50(*s*); 201.93(*s*). MS: 161([*M* – 1]$^+$, 1), 151(6), 148(8), 147([*M* – 15]$^+$, 93), 137(12), 133(62), 119(17), 105(29), 91(24), 85(17), 71(34), 57(76), 43(100).

*1,8-Di(*tert*-butyl)cyclododeca-1,2,6,7-tetraene* (**8**). To **7b** [20] (84 mg, 0.24 mmol) and CuI (93 mg, 0.45 mmol) in THF (5 ml) was added at –30° a freshly prepared *t*-BuMgCl soln. in Et_2O (1 ml, 1.0 mmol; obtained from Mg (292 mg, 12 mmol) and *t*-BuCl (926 mg, 10 mmol) in Et_2O (10 ml)). The mixture was stirred for 30 min, then warmed to r.t. and stirred for 1 h. Workup and chromatography with pentane gave 47.2 mg (72%) of **8** as a colorless liquid which formed white crystals at –18°. M.p. 48°. R_f 0.55 (pentane). GC: t_R 37.69, 37.58 (1:3); column *A* (isothermal at 110°): t_R 59.93 (74%; *meso* + 1/2 *rac*), 63.24 (26%; 1/2 *rac*): IR: 2975*vs*, 2960*vs*, 2920*vs*, 2880*vs*, 2850*vs*, 1955*m*, 1720*w*, 1465*vs*, 1450*vs*, 1360*s*, 1340*m*, 1290*m*, 1240*s*, 1205*s*, 1090*m*. ^{1}H-NMR ($CDCl_3$): 1.03(*s*, 18H); 1.78–2.34 (stack, 12H); 4.94–5.16 (stack, 2H). ^{13}C-NMR ($CDCl_3$): major isomer: 26.58(*t*); 27.07(*t*); 29.33(*q*); 29.73(*t*); 33.29(*s*); 92.65(*d*); 113.10(*s*); 199.84(*s*); minor isomer: 26.58(*t*); 27.17(*t*); 29.46(*q*); 29.73(*t*); 33.39(*s*); 92.91(*d*); 113.30(*s*); 199.87(*s*). MS: 273([*M* + 1]$^+$, 5), 272(*M*$^+$, 22), 257(5), 216(22), 215(46), 201(20), 193(12), 173(24), 160(20), 159(67), 131(29), 105(17), 95(17), 91(19), 85(36), 57(100), 43(33). HR-MS: 272.2504 ($C_{20}H_{32}^+$; calc. 272.2504).

*1-(*tert*-Butyl)cyclododeca-1,2-dien-7-yne* (**12**). As described for **7b**, with **11b** (0.13 g, 0.512 mmol): 0.06 g (54%) of **12**. Colorless liquid. R_f 0.39 (pentane). GC: t_R 29.86. IR: 2940*m*, 2900*m*, 2820*s*, 2320*m*, 1950*m*, 1450*s*, 1435*vs*, 1390*m*, 1360*vs*, 1330*m*, 1110*vs*, 1020*s*, 980*m*, 900*s*. ^{1}H-NMR ($CDCl_3$): 1.02(*s*, 9H); 1.48–1.98 (stack, 8H); 2.00–2.43 (stack, 6H); 5.10 (stack, 1H). ^{13}C-NMR ($CDCl_3$): 17.89(*t*); 19.19(*t*); 25.15(*t*); 25.18(*t*); 26.44(*t*): 27.92(*t*); 28.54(*t*); 29.29(*q*); 33.53(*s*); 81.22(*s*); 83.08(*s*); 94.56(*d*); 112.74(*s*); 199.41(*s*). MS: 216(M^+, 9), 201(45), 173(26), 159(100), 145(25), 131(63), 117(49), 105(27), 91(49), 79(25), 77(23), 67(20), 57(32), 41(48). HR-MS: 216.1875 ($C_{16}H_{24}^+$; calc. 216.1878).

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