66. Stereoselectivity of Dienamine [4 + 2] Cycloadditions

Synthesis of Functionalised Decalins and Drimanes

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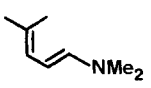
The [4 + 2] cycloaddition stereoselectivity of dienamines **1–4** with dimethyl fumarate and fumaronitrile has been investigated, and functionalised decalins **21–40** have been prepared by elimination of Me_2NH from cycloadducts **7–11** and **15–20**; in the context of the synthesis of drimane sesquiterpenes, the reduction of dienediesters **29** and **30** is also described.

Introduction. – During the past few years, we have investigated synthetic applications related to the use of conjugated dienamines in [4 + 2] cycloaddition reactions. Examples include methodology such as cyclohexannulation [1a] or benzannulation [1b] and syntheses of γ-damascone [2] and specifically substituted decalins [3]. We now report on the cycloaddition stereoselectivity of dienamines **1–4** with dimethyl fumarate and fumaronitrile. In addition, we briefly discuss the synthetic utility of the resulting cycloadducts for the preparation of functionalised decalins[1]) and for the construction of the drimane skeleton **I**[2]).



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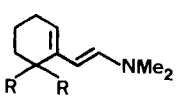
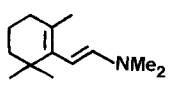


2 R = H
3 R = Me



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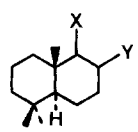

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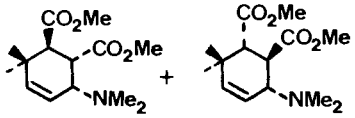
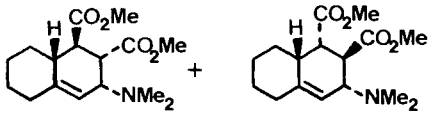
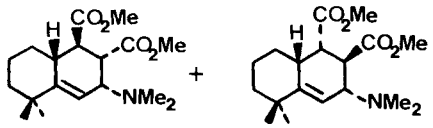
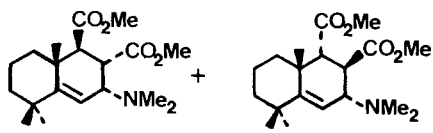
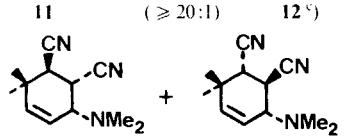
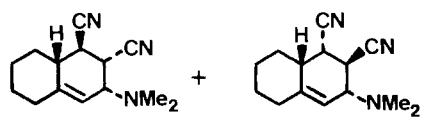
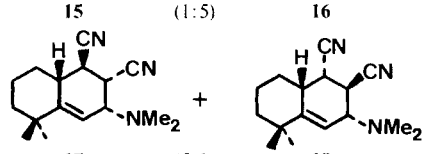
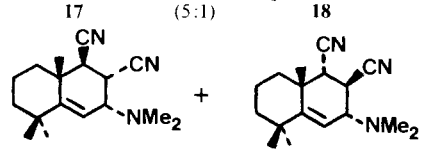
Results and Discussion. – *[4 + 2] Cycloadditions of Dienamines* **1–4** *with Dimethyl Fumarate and Fumaronitrile.* The cycloaddition reactions of dienamines **1–4** with dimethyl fumarate and fumaronitrile are summarised in *Table 1*. In each experiment, the reaction was monitored by GLC[3]), and the resulting product mixture (yield: 82–91%) was analysed by ^{1}H-NMR spectroscopy; the cycloadducts **5–11** and **13–19** were purified by chromatography, characterised, and structural assignments were established by inspection of their ^{1}H- and ^{13}C-NMR data (*cf. Table 2* and the *Fig.*). The reactivity order of **1–4** with both dienophiles is consistent with the relative steric encumbrance of the dienamines (*i.e.* **2** > **3** > **1** > **4**). The situation, however, is more complex with regard to

[1]) For an analogous synthesis of decalins using methyl acrylate as dienophile, see [3b].

[2]) X and Y represent unspecified functionalities; for a recent review of synthetic work concerning drimane-related sesquiterpenes, see [4].

[3]) These *Diels-Alder* reactions are kinetically controlled, the ratio of cycloadducts remaining unchanged throughout the course of the reactions.

Table 1. *[4 + 2] Cylcoadditions of Dienamines* **1–4** *with Dimethyl Fumarate and Fumaronitrile*

Entry	Diene	Reaction conditions[a])	Cycloadducts	Yield [%][b])
1	**1**	*A*, 150°/24 h	 **5** (1:1) **6**	86
2	**2**	*A*, 25°/17 h	 **7** (4:1) **8**	88
3	**3**	*A*, 110°/3 h	 **9** (15:1) **10**	91
4	**4**	*A*, 150°/48 h	 **11** (≥ 20:1) **12**[c])	88
5	**1**	*B*, 110°/3 h	 **13** (1:7) **14**	82
6	**2**	*B*, 25°/1 h	 **15** (1:5) **16**	89
7	**3**	*B*, 25°/1 h	 **17** (5:1) **18**	90
8	**4**	*B*, 110°/17 h	 **19** (≥ 20:1) **20**[d])	85

[a]) *A*: Dimethyl fumarate (1.5 mol-equiv.), toluene; *B*: fumaronitrile (1.5 mol-equiv.), toluene.
[b]) Yields refer to the sum of isolated cycloadducts after chromatography purification.
[c]) Cycloadduct **12** was not detected by ^{1}H-NMR of the crude product mixture.
[d]) Cycloadduct **20** was detected by ^{1}H-NMR of the crude product mixture.

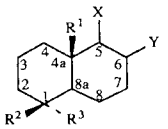


Table 2. *^{13}C-NMR Chemical Shifts* [ppm] *and Assignments for Compounds* **7–11**, **15–19**, **21–23**, **25–27**, **29–33**, and **36–49**

Compound	C(1)	C(2)	C(3)	C(4)	C(4a)	C(5)	C(6)	C(7)	C(8)	C(8a)	CH_3 (R^1)	CH_3 (R^2)	CH_3 (R^3)
7[a])	35.4	27.4	25.8	33.3	40.6	45.2	48.0	58.9	116.1	142.7			
8[a])	36.1	29.3	26.5	30.6	40.2	47.0	41.0	64.2	117.2	143.6			
9[a])	36.5	40.9	21.4	33.6	37.6	45.5	47.9	59.2	114.0	149.4		27.6	29.7
10[a])	37.4	42.6	22.4	31.0	36.0	47.3	40.4	64.5	115.9	149.5		25.4	29.3
11[a])	36.4	40.8	18.2	39.3	37.8	52.0	45.5	58.2	115.3	153.6	22.1	30.8	33.0
15[a])	34.8	26.9	25.4	33.3	40.9	32.9	35.3	58.2	117.2	141.2			
16[a])	35.9	28.8	26.0	31.0	38.3	33.8	28.9	62.4	116.4	143.0			
17[a])	36.5	40.5	21.1	33.8	37.8	33.2	35.0	58.3	115.0	148.0		26.8	29.2
18[a])	37.7	42.3	21.9	31.4	34.6	34.3	28.3	62.9	115.0	149.3		25.1	28.9
19[a])	36.4	40.6	17.8	39.0	37.3	42.5	33.2	57.1	116.0	152.0	22.1	29.7	32.1
21[a])	35.8	30.2	26.6	36.4	42.7	45.5	121.0	134.2	114.8	151.9			
22	29.8	23.0	22.6	28.3	127.4[c])	47.8	124.1[c])	139.0	32.9	127.7[c])			
23[a])	34.2	26.1	25.8	30.1	39.1	44.0	122.5	135.3	117.0	148.9			
25[a])	37.8	43.4	22.4	36.0	38.6	45.3	120.6	134.3	112.6	158.4		25.9	28.4
26	36.8	40.3	21.4	30.5	36.6	44.3	122.2	135.7	114.9	156.5		28.9	28.9
27	33.8	39.2	19.1	27.1	127.2	48.4	124.0	139.9	29.7	134.3		27.2	28.3
29[a])[b])	35.7	39.3	18.0	39.1	38.5	55.5	124.9	133.9	117.0	161.5	18.8	32.1	31.7
30[a])	35.7	38.8	17.9	35.6	38.5	52.5	122.0	135.8	116.7	160.9	26.3	31.1	32.2
31	34.3	27.0	25.3	34.6	40.6	34.0	99.6	140.4	116.5	150.5			
32	33.9	25.4	24.8	29.8	37.8	32.8	99.6	141.5	117.8	150.3			
33[a])	37.3	40.8	20.9	34.5	37.8	34.2	99.3	140.8	114.1	157.7		27.4	28.3
36[a])	136.4	40.9	21.9	34.3	36.6	128.4	123.0	29.6	110.0	142.8		25.0	28.7
37	37.0	39.7	20.5	30.1	35.7	33.2	99.7	141.7	115.6	158.3		28.3	29.1
38[a])	36.4	39.3	17.8	39.1	37.8	43.4	101.4	140.2	117.0	162.8	18.7	31.0	31.4
39[a])	36.2	38.6	17.7	36.3	38.3	41.5	100.2	141.4	117.1	162.2	23.3	31.5	30.6
40[a])	136.4	40.2	18.1	37.8	38.6	136.1	122.8	29.5	114.0	146.9	26.8	30.1	32.2
41[a])	33.0	42.0	18.6	40.3	36.0	57.7	128.7	140.3	24.0	48.9	15.3	22.0	33.3
42[a])	33.2	42.1	18.4	38.6	37.5	56.9	41.3	27.9	18.7	55.5	13.7	21.7	33.6
43[a])	33.0	42.1	18.8	39.4	35.6	54.5	137.1	127.0	23.6	49.5	14.5	21.9	33.2
44	33.0	42.2	18.3	41.3	35.1	52.4	45.4	23.7	18.5	53.9	15.6	21.9	33.4
45[a])[b])	35.5	39.9	18.6	40.0	37.6	52.5	136.0	125.1	117.3	154.9	17.7	31.9	31.8
46[a])	35.9	40.7	18.4	40.3	35.7	51.2	43.7	24.1	118.1	151.5	21.9	31.2	32.3
47[a])	35.1	39.7	18.2	34.1	37.8	49.8	136.9	121.7	116.8	152.6	25.0	31.4	32.4
48[a])	[d])	42.5	19.3	34.2	37.5	50.8	41.2	25.9	119.7	151.0	29.4	27.9	33.7
49[a])	[d])	42.5	19.2	34.4	38.4	54.6	44.2	28.6	119.2	151.6	28.4	27.9	33.7

[a]) C,H-Correlation. [b]) 2D-Inadequate. [c]) Interchangeable. [d]) Unobserved.

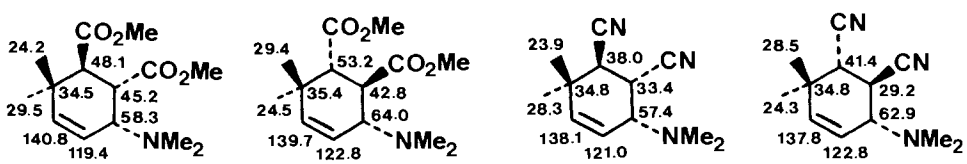
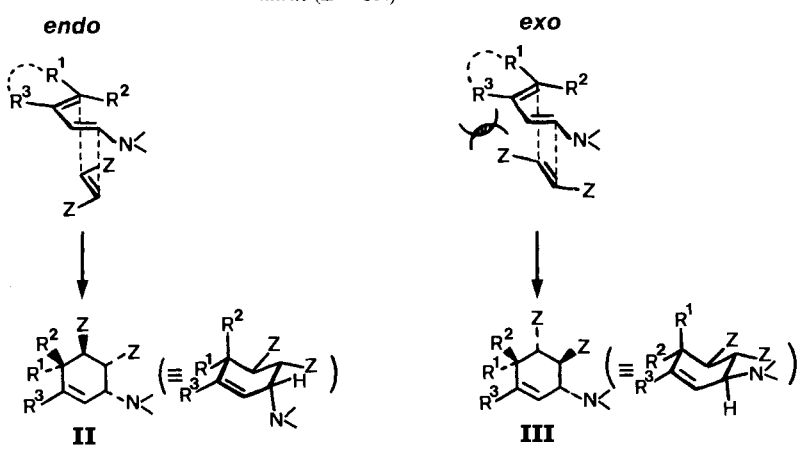


Figure. *^{13}C-NMR Chemical shifts* [ppm] *and assignments* (C,H correlation) *for compounds* **5**, **6**, **13**, *and* **14**

the stereoselectivities of these cycloadditions. Thus, whereas the reaction between **1** and dimethyl fumarate is non-stereoselective, affording a 1:1 mixture **5/6** (86%) *(cf. Entry 1)*, for **2**, **3**, and **4** there is a progressive increase in stereoselectivity with the formation of a 4:1 mixture **7/8** (88%), a 15:1 mixture **9/10** (91%), and a $\geq$ 20:1 mixture **11/12** (88%), respectively *(cf. Entries 2–4)*. With fumaronitrile as dienophile, a different stereochemical behaviour is observed. Similar stereoselectivity to that found for dimethyl fumarate *(vide supra)* is exhibited for **3** and **4**, furnishing a 5:1 mixture **17/18** (90%) and a $\geq$ 20:1 mixture **19/20** (85%), respectively (*cf. Entries 7* and *8*); in contrast, **1** and **2** show reversed stereoselectivity, affording a 1:7 mixture **13/14** (82%) and a 1:5 mixture **15/16** (89%), respectively (*cf. Entries 5* and *6*). These results can be rationalised by consideration of the two possible cycloaddition transition states *(cf. Scheme 1)*. For dimethyl fumarate (Z = COOMe), the preference for the formation of cycloadduct **II** *via* an *endo*-transition state[4]) is positively influenced by the increase in steric bulk of R^3 which causes an unfavourable nonbonding interaction with the COOMe group at C(5) in the *exo*-transition state. In contrast, when fumaronitrile is the dienophile, this influence, although dominant for **3** and **4**, is overridden by a preference for cycloadduct **III** *via* an *exo*-transition state in which both COOMe groups and the Me_2N group occupy pseudoequatorial positions in the newly forming cyclohexene ring.

Scheme 1. Diels-Alder *Transition States for Dienamines* **1–4** *with Dimethyl Fumarate* (Z = CO_2Me) *and Fumaronitrile* (Z = CN)



Synthesis of Decalins **21–40** (*cf. Table 3*). As part of an ongoing program concerning the synthesis of functionalised decalins [3b], we now investigated the elimination of Me_2NH from **7–11** and **15–19** by treatment with silica gel in refluxing cyclohexane. The reactions were followed by GLC analysis and the products isolated by chromatography. Cycloadducts **7**, **9**, and **11** readily underwent elimination to afford a 1.5:1 mixture **21/22** (85%), **25** (84%), and a 20:1 mixture **29/30** (86%)[5]), respectively (*cf. Entries 1, 3,* and *5*).

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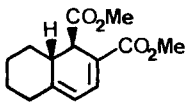
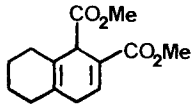
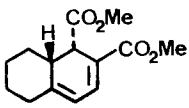
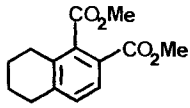
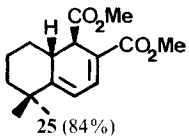
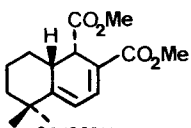
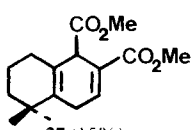
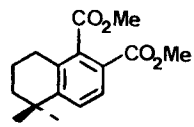
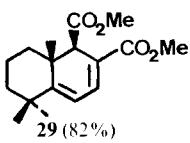
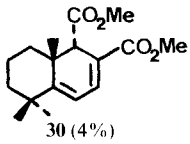
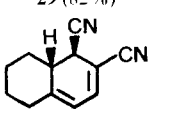
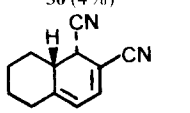
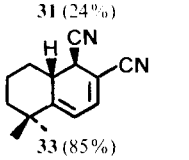
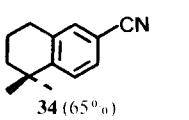
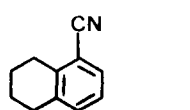
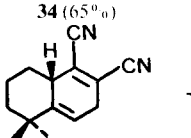
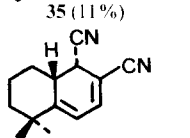
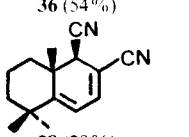
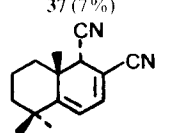
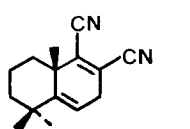
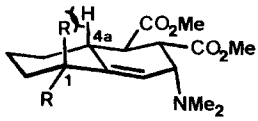
[4]) *endo* and *exo* refer to the orientation of the COOMe group which is adjacent to the Me_2N group.

[5]) The presence of **30** (5%) is explained by partial epimerisation at C(1) under the basic reaction conditions; indeed, treatment of **29/30** (20:1) with MeONa/MeOH at r.t. afforded a 1:5.4 equilibrium mixture **29/30** (*cf. Exper. Part* and [5]).

Table 3. *Synthesis of Functionalised Decalins* **21**–**40**

Entry	Substrate[a])	Reaction time	Products (yield)
1	**7**	6 h	 **21** (51%) +  **22** (34%)
2	**8**	24 h	 **23** (19%) +  **24** (14%) +**22** (26%)
3	**9**	6 h	 **25** (84%)
4	**10**	24 h[b])	 **26** (25%) +  **27** (15%) +  **28** (12%)
5	**11**	6 h	 **29** (82%) +  **30** (4%)
6	**15**/**16** (1:5)	20 h	 **31** (24%) +  **32** (16%)
7	**17**	2 h	 **33** (85%)
8	**18**	20 h	 **34** (65%) +  **35** (11%)
9	**18**	40 h[c])	 **36** (54%) +  **37** (7%) +**33** (11%) + **34**/**35** (7%) (6:1)
10	**19**	2 h	 **38** (39%) +  **39** (40%) +  **40** (10%)

[a]) Reaction conditions: silica gel, cyclohexane, 80° (*cf. Exper. Part*). [b]) *Ca.* 80% conversion. [c]) Reaction temp.: 50°.



7 R = H
9 R = Me

Comparison of substrates **7** and **9** is instructive. Whereas **7** affords **21** *via* 1,2-elimination of Me_2NH and **22**, presumably *via* 1,4-elimination of Me_2NH followed by C=C bond isomerisation[6]), **9** gives exclusively **25** by the former pathway. This difference in behaviour is probably due to the axial *Me*–C(1) group in **9** which sterically disfavours abstraction of H–C(4a). In contrast, cycloadducts **8** and **10** underwent sluggish elimination of Me_2NH, affording complex product mixtures of limited preparative interest (*cf. Entries 2* and *4*). The higher activation energy for *cis*-1,2-elimination accounts for the low yields of **23** and **26** (19 and 26%, respectively) and explains the relatively important amounts of **22** (26%) and **27** (15%), products resulting from 1,4-elimination of Me_2NH[6]). Also formed were the aromatic diesters **24** (14%) and **28** (12%), oxidation products from **22** or **23** and **26** or **27**, respectively.

The cycloadducts **15**–**19** exhibit varying behaviour with respect to the elimination of Me_2NH. For example, **17** and **19** both readily underwent 1,2-elimination, in the former case cleanly affording **33** (85%), but in the latter case giving a 4:4:1 mixture **38**/**39**/**40** (89%), a result which reflects the ready isomerisation of **38** under the reaction conditions[7]) (*cf. Entries 7* and *10*). Slower elimination reactions were observed with **15**/**16** (1:5), which afforded a 1.5:1 mixture **31**/**32** (40%, *cf. Entry 6*), and **18** which, under the same conditions, unexpectedly furnished a 6:1 mixture of the aromatic nitriles **34**/**35** (78%, *cf. Entry 8*), formed by elimination of HCN from the putative intermediate **37**. A second experiment performed at 50° (*cf. Entry 9*) resulted in the isolation of **36** (54%), **33**/**37** (1.6:1, 18%), and **34**/**35** (6:1, 7%), indicating that 1,2-elimination to **37** is followed by isomerisation to **36** and **33**. It is interesting to note that, in contrast to **7**–**11**, 1,4-elimination of Me_2NH is not observed for cycloadducts **15**–**19**. An explanation for this difference may be the relatively higher acidity of H–C(6) in the latter substrates which thus strongly favour the 1,2-elimination.

Synthesis of **41**–**49** (*cf. Scheme 2*). A direct application in the field of natural-product synthesis is the ready access to **29** (*vide supra*)[8]), a known intermediate for the preparation of biologically active drimane sesquiterpenes [5] [8]; in this context, we briefly report on several transformations of **29**[9]) and **30**. Accordingly, chemoselective catalytic hydrogenation of **29** stereoselectively afforded ene-diester **41** (82%) together with diester **42** (3%); subsequent reduction of **41** with $LiAlH_4$ at –30° gave ene-diol **43** (66%) and lactol

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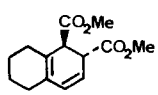
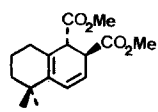
[6]) The putative diene-diester intermediates, **i** and **ii** were not detected in the product mixture.



i



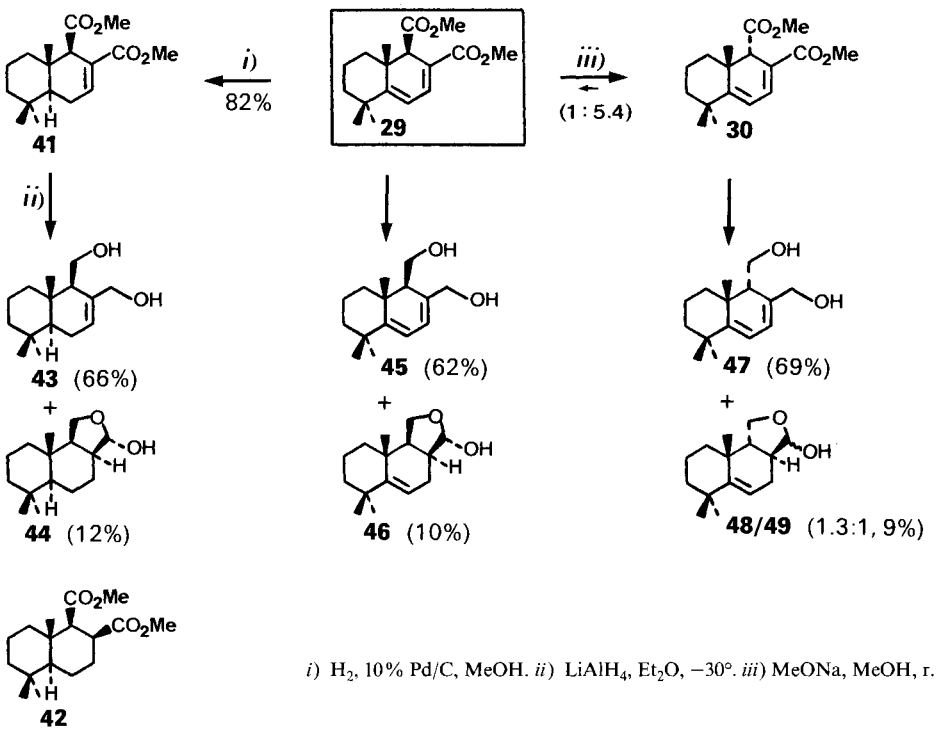
ii

[7]) Prolonged reaction times do not alter the composition of **38**/**39**/**49**, assumed thus to be already at thermodynamic equilibrium.

[8]) For a preliminary communication concerning the preparation of **29** from (*E*)-4-methyl-1-pyrrolidinopenta-1,3-diene and prior *Diels-Alder* approaches for the construction of analogous systems, see [3a] and ref. cit. therein; for more recent examples, see [6]; for related intramolecular *Diels-Alder* cycloadditions directed towards the synthesis of forskolin, see [7].

[9]) These reactions, with slightly different results, have been reported by *Lallemand* and coworkers [5].

Scheme 2



i) H_2, 10% Pd/C, MeOH. *ii*) $LiAlH_4$, Et_2O, −30°. *iii*) MeONa, MeOH, r.t.

44[10]) (12%). Similar reduction of **29** and **30** with $LiAlH_4$ afforded **45** (62%) and **47** (69%), accompanied with minor amounts of the corresponding lactols **46**[10]) (10%) and **48**/**49**[10]) (1.3:1, 9%), respectively.

Experimental Part

General. See [9].

General Procedure for the Preparation of Cycloadducts **5**–**11** *and* **13**–**19**. Dieneamines **1**–**4**[11]) (0.01 mol) were treated with dimethyl fumarate or fumaronitrile (0.015 mol) in either toluene or xylene (50 ml) under the reaction conditions described in *Table 1*. The mixture was then concentrated *i.v.*, and the residue was analysed by ^{1}H-NMR and purified by CC (silica gel, cyclohexane/AcOEt 4:1) to afford **5**–**11** and **13**–**19**.

*Dimethyl (1*RS,*2*SR,*3*RS*)- and (1*RS,*2*SR,*3*SR*)-3-(Dimethylamino)-6,6-dimethylcyclohex-4-ene-1,2-dicarboxylate* (**5** and **6**, resp.; 1:1 diastereoisomeric mixture). Yield from **1**, 86%.

Data of **5**. White crystals. M.p. 78–79°. R_f (cyclohexane/AcOEt 7:3) 0.42. IR ($CHCl_3$): 2950, 1720, 1432, 1320, 1260, 1190, 1160, 1018, 822, 784. ^{1}H-NMR: 0.85 (*s*, 3 H); 1.22 (*s*, 3 H); 2.28 (*s*, 6 H); 2.96 (*d*, *J* = 12.5, H–C(1));

[10]) The configurations of the hitherto unreported lactols **44**, **46**, and **48**/**49** (1.3:1), products of 1,4-hydride reduction, were tentatively assigned by inspection of their ^{1}H- and ^{13}C-NMR spectra.

[11]) Dieneamine **1** was prepared by treating (*E*)-4-methylpent-2-enal with 40% Me_2NH soln. (*Fluka*) [3b]; for **2**–**4**, see [3b]. *Data of* **1**. B.p. 25–28°/0.05 Torr. IR: 1650, 1618, 1432, 1350, 1140, 1082, 1040, 930. ^{1}H-NMR: 1.69 (*s*, 3 H); 1.73 (*s*, 3 H); 2.67 (*s*, 6 H); 5.03 (*dd*, *J* = 13.5, 11, 1 H); 5.72 (br. *d*, *J* = 11, 1 H); 6.13 (*d*, *J* = 13.5, 1 H). MS: 125 (100, $M^{+\cdot}$), 110 (50), 94 (21), 82 (70), 67 (20).

3.15 (*dd*, J = 12.5, 7, H–C(2)); 3.52 (br. *dd*, J = 7, 4.5, H–C(3)); 3.70 (*s*, 6 H); 5.61 (*dd*, J = 11, 4.5, H–C(4)); 5.67 (*d*, J = 11, H–C(5)). ^{13}C-NMR: 174.0 (*s*); 173.8 (*s*); 51.4 (*q*); 51.3 (*q*); 43.2 (2*q*) (for rest of data, *cf.* the *Fig.*). MS: 269 (3, M^+), 155 (29), 125 (100), 110 (39), 91 (18), 82 (64), 72 (21).

Data of **6**. White crystals. M.p. 59–61°. R_f (cyclohexane/AcOEt 7:3) 0.25. IR ($CHCl_3$): 2950, 1720, 1430, 1258, 1198, 1014, 982. ^{1}H-NMR: 0.95 (*s*, 3 H); 1.18 (*s*, 3 H); 2.29 (*s*, 6 H); 2.82 (*d*, J = 11.5, H–C(1)); 2.97 (*dd*, J = 11.5, 11, H–C(2)); 3.47 (br. *d*, J = 11, H–C(3)); 3.68 (*s*, 3 H); 3.70 (*s*, 3 H); 5.51 (*dd*, J = 11, 2, H–C(4)); 5.56 (*d*, J = 11, H–C(5)). ^{13}C-NMR: 175.6 (*s*); 172.8 (*s*); 51.8 (*q*); 51.4 (*q*); 40.2 (2*q*) (for rest of data, *cf.* the *Fig.*). MS: 269 (1, M^+), 155 (28), 125 (100), 110 (29), 91 (11), 82 (54), 72 (13).

*Dimethyl (4a*RS,*5*RS,*6*SR,*7*RS*)- and (4a*RS,*5*SR,*6*RS,*7*RS*)-7-(Dimethylamino)-1,2,3,4,4a,5,6,7-octahydronaphthalene-5,6-dicarboxylate* (**7** and **8**, resp.; 4:1 diastereoisomeric mixture). Yield from **2**, 88%.

Data of **7**. White crystals. M.p. 81–83°. R_f (AcOEt) 0.36. IR ($CHCl_3$): 2910, 2850, 1720, 1430, 1260, 1160, 1020, 980, 850. ^{1}H-NMR: 1.10 (*m*, 1 H); 1.30 (*m*, 2 H); 1.79 (br. *d*, J = 11, 2 H); 1.92–2.12 (3 H); 2.28 (*s*, 6 H); 2.34 (br. *d*, J = 13, 1 H); 2.81 (*dd*, J = 12.5, 9.5, H–C(5)); 2.99 (*dd*, J = 12.5, 6, H–C(6)); 3.52 (*m*, H–C(7)); 3.68 (*s*, 3 H); 3.71 (*s*, 3 H); 5.48 (br. *d*, J = 6, H–C(8)). ^{13}C-NMR: 176.6 (*s*); 173.7 (*s*); 51.8 (*q*); 51.5 (*q*); 43.9 (2*q*) (for rest of data, *cf. Table 2*). MS: 295 (5, M^+), 151 (100), 136 (19), 123 (19), 108 (20), 105 (21), 91 (24).

Data of **8**. White crystals. M.p. 94–95°. R_f (AcOEt) 0.22. IR ($CHCl_3$): 2820, 1720, 1430, 1260, 1180, 990. ^{1}H-NMR: 1.23 (*m*, 2 H); 1.42 (*m*, 2 H); 1.83 (*m*, 2 H); 1.98 (*m*, 1 H); 2.26 (*m*, 1 H); 2.29 (*s*, 6 H); 2.42 (*m*, 1 H); 2.81 (*dd*, J = 11.5, 11, H–C(6)); 3.15 (*dd*, J = 11.5, 6, H–C(5)); 3.44 (br. *d*, J = 11, H–C(7)); 3.67 (*s*, 3 H); 3.71 (*s*, 3 H); 5.36 (br. *s*, H–C(8)). ^{13}C-NMR: 176.2 (*s*); 173.4 (*s*); 51.9 (*q*); 51.7 (*q*); 40.2 (2*q*) (for rest of data, *cf. Table 2*). MS: 295 (2, M^+), 151 (100), 136 (16), 123 (18), 108 (17), 105 (11), 91 (19).

*Dimethyl (4a*RS,*5*RS,*6*SR,*7*RS*)- and (4a*RS,*5*SR,*6*RS,*7*RS*)-7-(Dimethylamino)-1,2,3,4,4a,5,6,7-octahydro-1,1-dimethylnaphthalene-5,6-dicarboxylate* (**9** and **10**, resp.; 15:1 diastereoisomeric mixture). Yield from **3**, 91%.

Data of **9**. White crystals. M.p. 110–111°. R_f (cyclohexane/AcOEt 7:3) 0.19. IR ($CHCl_3$): 2900, 1720, 1432, 1260, 1160, 980, 958, 900, 860. ^{1}H-NMR: 1.01 (*s*, 3 H); 1.07 (*m*, 1 H); 1.13 (*s*, 3 H); 1.31 (*m*, 1 H); 1.49 (br. *d*, J = 14, 1 H); 1.55–1.63 (2 H); 2.04 (*m*, 1 H); 2.24 (*m*, 1 H); 2.29 (*s*, 6 H); 2.76 (*dd*, J = 12.5, 9.5, H–C(5)); 2.92 (*dd*, J = 12.5, 5.5, H–C(6)); 3.53 (br. *dd*, J = 5.5, 5.5, H–C(7)); 3.68 (*s*, 3 H); 3.72 (*s*, 3 H); 5.60 (br. *d*, J = 5.5, H–C(8)). ^{13}C-NMR: 177.0 (*s*); 173.8 (*s*); 51.8 (*q*); 51.5 (*q*); 44.0 (2*q*) (for rest of data, *cf. Table 2*). MS: 323 (5, M^+), 308 (1), 179 (100), 164 (58), 123 (21), 108 (21), 105 (25), 95 (28), 91 (38).

Data of **10**. White crystals. M.p. 91–92°. R_f (cyclohexane/AcOEt 7:3) 0.08. IR ($CHCl_3$): 2900, 2850, 1720, 1430, 1260, 1162, 984. ^{1}H-NMR: 1.09 (2*s*, 6 H); 1.18 (*m*, 2 H); 1.40 (*m*, 1 H); 1.51 (br. *d*, J = 13.5, 1 H); 1.58–1.70 (2 H); 2.30 (*s*, 6 H); 2.70 (*m*, 1 H); 2.80 (*dd*, J = 12, 11, H–C(6)); 3.07 (*dd*, J = 12, 6, H–C(5)); 3.44 (br. *d*, J = 11, H–C(7)); 3.69 (*s*, 3 H); 3.71 (*s*, 3 H); 5.37 (br. *s*, H–C(8)). ^{13}C-NMR: 176.4 (*s*); 173.6 (*s*); 51.9 (*q*); 51.8 (*q*); 40.2 (2*q*) (for rest of data, *cf. Table 2*). MS: 323 (3, M^+), 308 (1), 179 (100), 164 (50), 123 (28), 108 (25), 105 (24), 91 (45).

*Dimethyl (4a*RS,*5*RS,*6*SR,*7*RS*)-7-(Dimethylamino)-1,2,3,4,4a,5,6,7-octahydro-1,1,4a-trimethylnaphthalene-5,6-dicarboxylate* (**11**). Yield from **4**, 88%. Colourless oil. R_f (cyclohexane/AcOEt 4:1) 0.19. IR: 1720, 1430, 1160, 1018, 982, 780, 662. ^{1}H-NMR: 1.10 (*s*, 3 H); 1.15 (*s*, 3 H); 1.16 (*s*, 3 H); 1.10–1.85 (6 H); 2.28 (*s*, 6 H); 2.81 (*d*, J = 13, H–C(5)); 3.33 (*dd*, J = 13, 8, H–C(6)); 3.50 (*dd*, J = 8, 3.5, H–C(7)); 3.67 (*s*, 3 H); 3.68 (*s*, 3 H); 5.61 (*d*, J = 3.5, H–C(8)). ^{13}C-NMR: 174.3 (*s*); 174.0 (*s*); 51.4 (2*q*); 43.1 (2*q*) (for rest of data, *cf. Table 2*). MS: 337 (5, M^+), 322 (10), 193 (100), 178 (36), 122 (17), 105 (17), 91 (16).

*(1*RS,*2*SR,*3*RS*)- and (1*RS,*2*SR,*3*SR*)-3-(Dimethylamino)-6,6-dimethylcyclohex-4-ene-1,2-dicarbonitrile* (**13** and **14**, resp.; 1:7 diastereoisomeric mixture). Yield from **1**, 82%.

Data of **13**. White crystals. M.p. 105–107°. R_f (cyclohexane/AcOEt 7:3) 0.17. IR ($CHCl_3$): 1450, 1360, 1254, 1168, 1020, 940, 816, 740. ^{1}H-NMR: 1.18 (*s*, 3 H); 1.27 (*s*, 3 H); 2.48 (*s*, 6 H); 3.11 (*dd*, J = 11.5, 4.5, H–C(2)); 3.16 (*d*, J = 11.5, H–C(1)); 3.42 (*dd*, J = 4.5, 4.5, H–C(3)); 5.62 (*dd*, J = 11, 4.5, H–C(4)); 5.70 (br. *d*, J = 11, H–C(5)). ^{13}C-NMR: 118.3 (*s*); 117.7 (*s*); 44.0 (2*q*) (for rest of data, *cf.* the *Fig.*). MS: 203 (0, M^+), 125 (100), 110 (56), 82 (51), 42 (17).

Data of **14**. White crystals. M.p. 153–154°. R_f (cyclohexane/AcOEt 7:3) 0.13. IR ($CHCl_3$): 1450, 1364, 1260, 1150, 1026, 972, 838, 620. ^{1}H-NMR: 1.21 (*s*, 3 H); 1.25 (*s*, 3 H); 2.38 (*s*, 6 H); 2.90 (*d*, J = 11.5, H–C(1)); 3.00 (*dd*, J = 11.5, 10, H–C(2)); 3.57 (br. *d*, J = 10, H–C(3)); 5.53 (*dd*, J = 10, 2, H–C(4)); 5.66 (*dd*, J = 10, 2, H–C(5)). ^{13}C-NMR: 119.2 (*s*); 117.2 (*s*); 40.5 (2*q*) (for rest of data, *cf.* the *Fig.*). MS: 203 (0.5, M^+), 125 (100), 110 (53), 82 (45), 42 (17).

*(4a*RS,*5*RS,*6*SR,*7*RS*)- and (4a*RS,*5*SR,*6*RS,*7*RS*)-7-(Dimethylamino)-1,2,3,4,4a,5,6,7-octahydronaphthalene-5,6-dicarbonitrile* (**15** and **16**, resp.; 1:5 diastereoisomeric mixture). Yield from **2**, 89%.

Data of **15**. White crystals. M.p. 76–78°. R_f (cyclohexane/AcOEt 4:1) 0.30. IR ($CHCl_3$): 2920, 2850, 1440, 1260, 1202, 1020, 978, 840, 810. ^{1}H-NMR: 1.10–1.50 (3 H); 1.60–2.05 (3 H); 2.23–2.40 (3 H); 2.48 (*s*, 6 H); 2.95 (*dd*,

J = 11, 4, H–C(6)); 3.02 (*dd*, J = 11, 9, H–C(5)); 3.35 (*m*, H–C(7)); 5.48 (br. *d*, J = 5.5, H–C(8)). ^{13}C-NMR: 119.4 (*s*); 118.5 (*s*); 44.5 (2*q*) (for rest of data, *cf. Table 2*). MS: 229 (0.3, M^{+}), 151 (100), 142 (19), 136 (25), 123 (21), 108 (32), 44 (38).

Data of **16**. White crystals. M.p. 105–107°. R_f (cyclohexane/AcOEt 4:1) 0.21. IR ($CHCl_3$): 2920, 2850, 2780, 1660, 1440, 1260, 1204, 1026, 978, 840, 812. ^{1}H-NMR: 1.27 (*m*, 2H); 1.51 (*m*, 1 H); 1.87–2.04 (3 H); 2.16–2.40 (3 H); 2.37 (*s*, 6 H); 2.87 (*dd*, J = 11.5, 10, H–C(6)); 3.27 (*dd*, J = 11.5, 5.5, H–C(5)); 3.50 (br. *d*, J = 10, H–C(7)); 5.35 (br. *s*, H–C(8)). ^{13}C-NMR: 119.2 (*s*); 117.4 (*s*); 40.5 (2*q*) (for rest of data, *cf. Table 2*). MS: 229 (1, M^{+}), 151 (100), 142 (17), 136 (29), 123 (31), 108 (32), 94 (19), 77 (19), 42 (28).

*(4a*RS,*5*RS,*6*SR,*7*RS*)- and (4a*RS,*5*SR,*6*RS,*7*RS*)-7-(Dimethylamino)-1,2,3,4,4a,5,6,7-octahydro-1,1-dimethylnaphthalene-5,6-dicarbonitrile* (**17** and **18**, resp.; 5:1 diastereoisomeric mixture). Yield from **3**, 90%.

Data of **17**. White crystals. M.p. 103–104°. R_f (cyclohexane/AcOEt 7:3) 0.28. IR ($CHCl_3$): 2920, 1560, 1450, 974, 902, 840, 652. ^{1}H-NMR: 1.03 (*s*, 3 H); 1.12 (*s*, 3 H); 1.30 (*m*, 1 H); 1.55 (br. *d*, J = 12.5, 1 H); 1.63–1.75 (3 H); 2.29 (*m*, 1 H); 2.48 (*s*, 6 H); 2.51 (*m*, 1 H); 2.95 (*dd*, J = 11.5, 3.5, H–C(6)); 3.02 (*dd*, J = 11.5, 11, H–C(5)); 3.39 (*m*, H–C(7)); 5.56 (br. *d*, J = 6.5, H–C(8)). ^{13}C-NMR: 119.8 (*s*); 118.8 (*s*); 44.7 (2*q*) (for rest of data, *cf. Table 2*). MS: 257 (0, M^{+}), 210 (7), 195 (100), 167 (42), 152 (10), 140 (16), 127 (8), 114 (8).

Data of **18**. White crystals. M.p. 120–121°. R_f (cyclohexane/AcOEt 7:3) 0.18. IR ($CHCl_3$): 2910, 2860, 1560, 1446, 1200, 1152, 1040, 840, 820, 798. ^{1}H-NMR: 1.07 (*s*, 3 H); 1.10 (*s*, 3 H); 1.22 (*m*, 1 H); 1.58 (br. *d*, J = 12.5, 1 H); 1.68–1.78 (3 H); 2.21 (*m*, 1 H); 2.39 (*s*, 6 H); 2.64 (*m*, 1 H); 2.85 (*dd*, J = 11.5, 11, H–C(6)); 3.19 (*dd*, J = 11.5, 6, H–C(5)); 3.51 (br. *d*, J = 11, H–C(7)); 5.35 (br. *s*, H–C(8)). ^{13}C-NMR: 119.4 (*s*); 117.7 (*s*); 40.6 (2*q*) (for rest of data, *cf. Table 2*). MS: 257 (1, M^{+}), 195 (100), 179 (12), 167 (41), 152 (10), 140 (21), 76 (15).

*(4a*RS,*5*RS,*6*SR,*7*RS*)- and (4a*RS,*5*SR,*6*RS,*7*RS*)-7-(Dimethylamino)-1,2,3,4,4a,5,6,7-octahydro-1,1,4a-trimethylnaphthalene-5,6-dicarbonitrile* (**19** and **20**, resp.; $\geq$ 20:1 diastereoisomeric mixture). Yield from **4**, 85%.

Data of **19**. White crystals. M.p. 129–130°. R_f (cyclohexane/AcOEt 7:3) 0.27. IR ($CHCl_3$): 2900, 1450, 1270, 1250, 1040. ^{1}H-NMR: 1.13 (*s*, 3 H); 1.14 (*s*, 3 H); 1.14–1.38 (2 H); 1.32 (*s*, 3 H); 1.58 (*m*, 1 H); 1.63 (*m*, 1 H); 1.81 (*m*, 1 H); 2.06 (br. *d*, J = 13.5, 1 H); 2.47 (*s*, 6 H); 2.93 (*d*, J = 13, H–C(5)); 3.26 (*dd*, J = 13, 6.5, H–C6)); 3.41 (*dd*, J = 6.5, 5, H–C(7)); 5.56 (*d*, J = 5, H–C(8)). ^{13}C-NMR: 118.2 (*s*); 118.0 (*s*); 43.4 (2*q*) (for rest of data, *cf. Table 2*). MS: 271 (1, M^{+}), 193 (100), 178 (89), 149 (12), 122 (25), 107 (12), 79 (21), 55 (20), 42 (44).

Data of **20** (not isolated). ^{1}H-NMR: 2.39 (*s*, 6 H); 5.51 (*d*, J = 5, 1 H).

General Procedure for the Elimination of Me_2NH from Cycloadducts **7**–**11** *and* **15**–**19**. *Preparation of* **21**–**40**. A mixture of the cycloadduct (1 mmol) and silica gel (0.06–0.2 mm *(Merck)*; 1 g) in cyclohexane (5 ml) was heated under the reaction conditions described in *Table 3*. After filtration, the filtrate was concentrated *i.v.* and the residue analysed by GLC and ^{1}H-NMR. Purification by CC (silica gel, cyclohexane/AcOEt 7:3) afforded **21**–**40**.

*Dimethyl (4a*RS,*5*RS*)-1,2,3,4,4a,5-Hexahydronaphthalene-5,6-dicarboxylate* (**21**) *and Dimethyl 1,2,3,4,5,8-Hexahydronaphthalene-5,6-dicarboxylate* (**22**). Ratio **21**/**22**, 1.5:1; yield from **7**, 85%.

Data of **21**. Colourless oil. B.p. (bulb-to-bulb distillation) 120–140°/0.05 Torr. R_f (cyclohexane/AcOEt 4:1) 0.12. IR: 2920, 2850, 1730, 1700, 1582, 1428, 1260, 1062, 1002, 840, 758. ^{1}H-NMR: 1.30–1.60 (3 H); 1.75–1.86 (2 H); 1.94 (*m*, 1 H); 2.14 (*m*, 1 H); 2.36 (br. *d*, J = 12, 1 H); 2.73 (*m*, 1 H); 3.38 (*d*, J = 6, H–C(5)); 3.70 (*s*, 3 H); 3.74 (*s*, 3 H); 5.75 (*d*, J = 6, H–C(8)); 7.05 (*d*, J = 6, H–C(7)). ^{13}C-NMR: 174.8 (*s*); 167.6 (*s*); 52.3 (*q*); 51.7 (*q*) (for rest of data, *cf. Table 2*). MS: 250 (1, M^{+}), 191 (55), 159 (46), 131 (33), 105 (100), 91 (21), 59 (23).

Data of **22**. Colourless oil. B.p. (bulb-to-bulb distillation) 120–140°/0.05 Torr. R_f (cyclohexane/AcOEt 4:1) 0.18. IR: 2920, 1730, 1700, 1430, 1256. ^{1}H-NMR: 1.30–2.20 (8 H); 2.71 (*m*, 1 H); 2.91 (*m*, 1 H); 3.70 (*s*, 3 H); 3.74 (*s*, 3 H); 3.88 (br. *dd*, J = 6, 6, H–C(5)); 7.18 (*m*, H–C(7)). ^{13}C-NMR: 172.7 (*s*); 166.5 (*s*); 52.0 (*q*); 51.7 (*q*) (for rest of data, *cf. Table 2*). MS: 250 (0, M^{+}), 191 (38), 159 (19), 131 (32), 105 (100), 91 (19), 59 (20).

*Dimethyl (4a*RS,*5*SR*)-1,2,3,4,4a,5-Hexahydronaphthalene-5,6-dicarboxylate* (**23**), *Dimethyl 1,2,3,4-Tetrahydronaphthalene-5,6-dicarboxylate* (**24**) *and* **22**. Ratio **22**/**23**/**24**, 1.8:1.3:1; yield from **8**, 59%. Colourless oil (b.p. (bulb-to-bulb distillation) 120–140°/0.05 Torr).

Data of **23**. R_f (cyclohexane/AcOEt 4:1) 0.12. IR ($CDCl_3$): 2950, 2860, 1720, 1580, 1440, 1260, 1198, 1168, 840. ^{1}H-NMR: 1.20–1.45 (3 H); 1.75–1.90 (2 H); 1.94 (*m*, 1 H); 2.14 (*m*, 1 H); 2.48 (*d*, J = 14.5, 1 H); 2.75 (*m*, 1 H); 3.66 (*s*, 3 H); 3.73 (*s*, 3 H); 3.80 (*d*, J = 10.5, H–C(5)); 5.78 (*m*, H–C(8)); 7.06 (*d*, J = 6, H–C(7)). ^{13}C-NMR: 172.4 (*s*); 167.3 (*s*); 51.6 (*q*); 51.5 (*q*) (for rest of data, *cf. Table 2*). MS: 250 (2, M^{+}), 216 (6), 190 (20), 159 (11), 131 (100), 105 (95), 91 (27), 59 (28).

Data of **24**. R_f (cyclohexane/AcOEt 4:1) 0.12. ^{1}H-NMR: 7.17 (*d*, J = 8, 1 H); 7.74 (*d*, J = 8, 1 H). MS: 248 (0, M^{+}), 216 (100), 201 (23), 158 (77), 130 (55), 115 (38), 91 (21).

*Dimethyl (4a*RS,*5*RS*)-1,2,3,4,4a,5-Hexahydro-1,1-dimethylnaphthalene-5,6-dicarboxylate* (**25**). Yield from **9**, 84%. Colourless oil. B.p. (bulb-to-bulb distillation) 160–180°/0.08 Torr. R_f (cyclohexane/AcOEt 4:1) 0.13. IR: 2900, 1735, 1702, 1580, 1430, 1264, 1040, 992, 840, 762, 740. ^{1}H-NMR: 1.13 (*s*, 3 H); 1.16 (*s*, 3 H); 1.35 (*m*, 2 H);

1.61 (br. *d*, *J* = 11.5, 2 H); 1.68–1.83 (2 H); 3.06 (*ddd*, *J* = 13, 5.5, 5, 1 H); 3.41 (*d*, *J* = 5.5, H–C(5)); 3.69 (*s*, 3 H); 3.76 (*s*, 3 H); 5.82 (*d*, *J* = 6, H–C(8)); 7.09 (*d*, *J* = 6, H–C(7)). ^{13}C-NMR: 174.5 (*s*); 167.5 (*s*); 52.2 (*q*); 51.7 (*q*) (for rest of data, *cf. Table 2*). MS: 278 (2, M^{+}), 219 (100), 203 (43), 187 (77), 149 (90), 105 (36), 59 (34).

*Dimethyl (4a*RS,*5*SR*)-1,2,3,4,4a,5-Hexahydro-1,1-dimethylnaphthalene-5,6-dicarboxylate* (**26**), *Dimethyl 1,2,3,4,5,8-Hexahydro-1,1-dimethylnaphthalene-5,6-dicarboxylate* (**27**), *and Dimethyl 1,2,3,4-Tetrahydro-1,1-dimethylnaphthalene-5,6-dicarboxylate* (**28**). Ratio **26**/**27**/**28**, 2.1:1.3:1; yield from **10**, 52%. Colourless oil (b.p. (bulb-to-bulb distillation) 160–180°/0.08 Torr).

Data of **26**. R_f (cyclohexane/AcOEt 4:1) 0.13. ^{1}H-NMR: 1.09 (*s* 3 H); 1.18 (*s*, 3 H); 1.24–1.40 (2 H); 1.50 (*m*, 1 H); 1.57–1.70 (2 H); 1.91 (*m*, 1 H); 2.85–3.00 (2 H); 3.66 (*s*, 3 H); 3.74 (*s*, 3 H); 5.94 (*dd*, *J* = 6.5, 2, H–C(8)); 7.08 (*d*, *J* = 6.5, H–C(7)). ^{13}C-NMR: 172.4 (2*s*); 51.6 (*q*); 51.5 (*q*) (for rest of data, *cf. Table 2*). MS: 278 (3, M^{+}), 219 (24), 187 (29), 149 (100), 105 (43), 91 (38), 59 (30).

Data of **27**. R_f (cyclohexane/AcOEt 4:1) 0.23. ^{1}H-NMR: 1.03 (*s*, 6 H); 2.92 (2 H); 3.69 (*s*, 3 H); 3.74 (*s*, 3 H); 3.92 (*dd*, *J* = 6, 6, H–C(5)); 7.23 (*dd*, *J* = 4.5, 4.5, H–C(7)). ^{13}C-NMR: 172.7 (*s*); 166.4 (*s*); 51.6 (*q*); 51.4 (*q*) (for rest of data, *cf. Table 2*). MS: 278 (0, M^{+}), 219 (54), 203 (21), 187 (42), 149 (100), 105 (45), 91 (32).

Data of **28**. R_f (cyclohexane/AcOEt 4:1) 0.22. ^{1}H-NMR: 1.30 (*s*, 6 H); 2.72 (*t*, *J* = 6.5, 2 H); 3.87 (*s*, 3 H); 3.94 (*s*, 3 H); 7.44 (*d*, *J* = 8, 1 H); 7.78 (*d*, *J* = 8, 1 H). MS: 276 (1, M^{+}), 244 (100), 229 (78), 186 (74), 158 (33), 143 (38), 128 (66), 115 (59).

*Dimethyl (4a*RS,*5*RS*)- and (4a*RS,*5*SR*)-1,2,3,4,4a,5-Hexahydro-1,1,4a-trimethylnaphthalene-5,6-dicarboxylate* (**29** and **30**, resp.; 20:1 diastereoisomeric mixture). Yield from **11**, 86%.

Data of **29**. White crystals. M.p. 53–54° ([5]: colourless oil). R_f (cyclohexane/AcOEt 4:1) 0.32. IR: 2900, 1730, 1700, 1560, 1432, 1272, 1190, 1160. ^{1}H-NMR: 1.16 (*s*, 3 H); 1.18 (*s*, 3 H); 1.20 (*s*, 3 H); 1.38 (*m*, 1 H); 1.45–1.75 (5 H); 3.36 (*d*, *J* = 3.5, H–C(5)); 3.73 (2*s*, 6 H); 6.02 (*d*, *J* = 6, H–C(8)); 6.97 (*dd*, *J* = 6, 3.5, H–C(7)): ^{13}C-NMR: 172.9 (*s*); 167.0 (*s*); 51.6 (*q*); 51.4 (*q*) (for rest of data, *cf. Table 2*). MS: 292 (3, M^{+}), 260 (15), 233 (28), 217 (16), 201 (24), 176 (25), 163 (100), 119 (29), 59 (47).

Data of **30** [5]. Viscous colourless oil. B.p. (bulb-to-bulb distillation) 160–180°/0.08 Torr. R_f (cyclohexane/AcOEt 4:1) 0.32. IR: 2920, 1730, 1700, 1564, 1428, 1240, 1140, 1008, 840, 760. ^{1}H-NMR: 1.18 (*s*, 3 H); 1.19 (2*s*, 6 H); 1.20–1.82 (6 H); 3.35 (*s*, H–C(5)); 3.62 (*s*, 3 H); 3.75 (*s*, 3 H); 6.04 (*d*, *J* = 6, H–C(8)); 7.14 (*d*, *J* = 6, H–C(7)). ^{13}C-NMR: 172.0 (*s*); 167.3 (*s*); 51.7 (*q*); 51.4 (*q*) (for rest of data, *cf. Table 2*). MS: 292 (4, M^{+}), 233 (25), 201 (16), 173 (18), 163 (100), 119 (29), 59 (30).

Equilibration of **29**/**30** (20:1). A mixture of **29**/**30** (20:1; 10 g, 0.034 mol) and 15% methanolic NaOMe soln. (120 ml) was stirred at r.t. during 24 h under N_2 and then poured into cold H_2O (200 ml). Acidification (10 N aq. HCl soln.) and extraction (toluene) afforded an org. phase which was washed with sat. aq. $NaHCO_3$ soln., H_2O, sat. aq. NaCl soln., dried (Na_2SO_4), and concentrated. Distillation *i.v.* afforded a 5.4:1 mixture **30**/**29** as a colourless oil (8.2 g, 82%).

*(4a*RS,*5*RS*)- and (4a*RS,*5*SR*)-1,2,3,4,4a,5-Hexahydronaphthalene-5,6-dicarbonitrile* (**31** and **32**, resp., 1.5:1 diastereoisomeric mixture). Yield from **15**/**16** (1:5), 40%. Colourless oil (b.p. (bulb-to-bulb distillation) 160–180°/0.08 Torr). R_f (cyclohexane/AcOEt 4:1) 0.20. IR ($CDCl_3$): 2930, 2850, 1570, 1440, 840.

Data of **31**. ^{1}H-NMR: 1.20–2.80 (9 H); 3.36 (*d*, *J* = 12.5, H–C(5)); 5.85 (*d*, *J* = 6.5, H–C(8)); 6.76 (*dd*, *J* = 6.5, 1.5, H–C(7)). ^{13}C-NMR: 118.1 (*s*) (for rest of data, *cf. Table 2*).

Data of **32**. ^{1}H-NMR: 1.20–2.80 (9 H); 3.60 (*d*, *J* = 8.5, H–C(5)); 5.95 (*m*, H–C(8)); 6.83 (*d*, *J* = 6, H–C(7)). ^{13}C-NMR: 117.2 (*s*) (for rest of data, *cf. Table 2*).

*(4a*RS,*5*RS*)-1,2,3,4,4a,5-Hexahydro-1,1-dimethylnaphthalene-5,6-dicarbonitrile* (**33**). Yield from **17**, 85%. White crystals. M.p. 134–135°. R_f (cyclohexane/AcOEt 4:1) 0.34. IR ($CDCl_3$): 2900, 2850, 1560, 1440, 1360, 972, 840. ^{1}H-NMR: 1.12 (*s*, 3 H); 1.18 (*s*, 3 H); 1.37 (2 H); 1.62 (br. *d*, *J* = 14, 1 H); 1.73 (2 H); 2.23 (*m*, 1 H); 2.91 (*m*, 1 H); 3.34 (*dd*, *J* = 11, 3, H–C(5)); 5.97 (*dd*, *J* = 6, 2, H–C(8)); 6.80 (*dd*, *J* = 6, 3, H–C(7)). ^{13}C-NMR: 118.2 (*s*); 117.2 (*s*) (for rest of data, *cf. Table 2*). MS: 212 (11, M^{+}), 195 (37), 170 (33), 155 (32), 143 (38), 129 (48), 69 (100).

1,2,3,4-Tetrahydro-1,1-dimethylnaphthalene-6-carbonitrile (**34**) *and 1,2,3,4-Tetrahydro-1,1-dimethylnaphthalene-5-carbonitrile* (**35**). Ratio **34**/**35**, 6:1; yield from **18**, 76%. Colourless oil (b.p. (bulb-to-bulb distillation) 140–160°/0.05 Torr). R_f (cyclohexane/AcOEt 4:1) 0.63. IR: 2950, 2240, 1606, 1560, 1498, 1460, 1362, 1080, 1058, 906, 898, 832.

Data of **34**. ^{1}H-NMR: 1.28 (*s*, 6 H); 1.68 (*m*, 2 H); 1.82 (*m*, 2 H); 2.78 (*t*, *J* = 6.5, 2 H); 7.33 (*s*, 1 H); 7.40 (2 H). MS: 185 (13, M^{+}), 170 (100), 142 (28), 115 (15), 77 (11).

Data of **35**. ^{1}H-NMR: 2.96 (*t*, *J* = 6.5, 2 H). MS: 185 (12, M^{+}), 170 (100), 142 (25), 115 (17), 77 (16).

1,2,3,4,4a,7-Hexahydro-1,1-dimethylnaphthalene-5,6-dicarbonitrile (**36**), *(4a*RS,*5*SR*)-1,2,3,4,4a,5-Hexahydro-1,1-dimethylnaphthalene-5,6-dicarbonitrile* (**37**) *and* **33**. Ratio **36**/**37**/**33**, 7.7:1:1.6; yield from **18**, 72%[12]).

[12]) Also detected (GLC, ^{1}H-NMR) was **34**/**35** (6:1; yield from **18**, 7%).

Data of **36**. White crystals. M.p. 76–77°. R_f (cyclohexane/AcOEt 4:1) 0.50. IR ($CHCl_3$): 2940, 1450, 1420, 1386, 1368, 950, 908, 865. ^{1}H-NMR: 1.05 (*s*, 3 H); 1.10 (*s*, 3 H); 1.27 (*m*, 2 H); 1.53 (br. *d*, *J* = 14.5, 1 H); 1.68–1.84 (2 H); 2.29 (br. *d*, *J* = 12, 1 H); 2.98–3.18 (3H); 5.39 (*m*, H–C(8)). ^{13}C-NMR: 115.7 (*s*); 115.4 (*s*) (for rest of data, *cf. Table 2*). MS: 212 (20, $M^{+\cdot}$), 211 (37), 197 (90), 170 (77), 155 (100), 142 (97), 129 (58), 114 (48), 70 (74).

Data of **37**. R_f (cyclohexane/AcOEt 4:1) 0.38. ^{1}H-NMR: 1.10 (*s*, 3 H); 1.23 (*s*, 3 H); 1.20–1.80 (4 H); 2.04 (*m*, 1 H); 2.48 (*m*, 1 H); 2.77 (*m*, 1 H); 3.58 (*d*, *J* = 8, H–C(5)); 6.10 (*m*, H–C(8)); 6.87 (*d*, *J* = 6, H–C(7)). ^{13}C-NMR: 116.4 (*s*) (for rest of data, *cf. Table 2*). MS: 212 (16, $M^{+\cdot}$), 195 (93), 170 (67), 155 (39), 142 (42), 129 (43), 115 (37), 69 (100).

*(4a*RS,*5*RS*)- and (4a*RS,*5*SR*)-1,2,3,4,4a,5-Hexahydro-1,1,4a-trimethylnaphthalene-5,6-dicarbonitrile* (**38** and **39**, resp.) *and 1,2,3,4,4a,7-Hexahydro-1,1,4a-trimethylnaphthalene-5,6-dicarbonitrile* (**40**). Ratio **38**/**39**/**40**, 4:4:1; yield from **19**, 89%.

Data of **38**. White crystals. M.p. 97–98°. R_f (cyclohexane/AcOEt 4:1) 0.32. IR ($CHCl_3$): 2940, 2210, 1550, 1460, 1372, 1272, 840. ^{1}H-NMR: 1.17 (*s*, 3 H); 1.19 (*s*, 3 H); 1.24 (*s*, 3 H); 1.38 (2 H); 1.58 (*m*, 1 H); 1.72 (2 H); 2.18 (br. *d*, *J* = 14, 1 H); 3.49 (*d*, *J* = 3, H–C(5)); 6.08 (*d*, *J* = 6, H–C(8)); 6.85 (*dd*, *J* = 6, 3, H–C(7)). ^{13}C-NMR: 116.9 (*s*); 116.3 (*s*) (for rest of data, *cf. Table 2*). MS: 226 (40, $M^{+\cdot}$), 211 (100), 194 (41), 183 (41), 169 (70), 156 (66), 141 (53), 69 (47), 41 (86).

Data of **39**. White crystals. M.p. 117–118°. R_f (cyclohexane/AcOEt 4:1) 0.39. IR ($CHCl_3$): 2950, 2210, 1560, 1460, 1380, 980, 850. ^{1}H-NMR: 1.17 (*s*, 3 H); 1.19 (*s*, 3 H); 1.24 (*s*, 3 H); 1.20–1.80 (5 H); 2.02 (*m*, 1 H); 3.13 (*s*, H–C(5)); 6.16 (*d*, *J* = 6, H–C(8)); 6.91 (*d*, *J* = 6, H–C(7)). ^{13}C-NMR: 116.4 (*s*) (for rest of data *cf. Table 2*). MS: 226 (21, $M^{+\cdot}$), 211 (24), 184 (30), 169 (22), 156 (28), 141 (27), 131 (21), 115 (21), 69 (100).

Data of **40**. White crystals. M.p. 120–121°. R_f (cyclohexane/AcOEt 4:1) 0.52. IR ($CHCl_3$): 2950, 2230, 1462, 1380, 1010, 980, 720, 662. ^{1}H-NMR: 1.14 (*s*, 3 H); 1.18 (*s*, 3 H); 1.31 (*m*, 1 H); 1.41 (*s*, 3 H); 1.48–1.60 (2 H); 1.67 (*m*, 1 H); 1.84 (*m*, 1 H); 2.05 (br. *d*, *J* = 14, 1 H); 3.05 (*d*, *J* = 4, 2 H–C(7)); 5.61 (*dd*, *J* = 4, 4, H–C(8)). ^{13}C-NMR: 115.8 (*s*); 114.7 (*s*) (for rest of data, *cf. Table 2*). MS: 226 (4, $M^{+\cdot}$), 211 (100), 195 (67), 169 (39), 155 (41), 141 (42), 128 (18), 114 (22), 77 (27), 69 (30), 41 (34).

*Dimethyl (4a*RS,*5*SR,*8a*RS*)-1,2,3,4,4a,5,8,8a-Octahydro-1,1,4a-trimethylnaphthalene-5,6-dicarboxylate* (**41**). A soln. of **29** (2.92 g, 0.01 mol) in MeOH (20 ml) containing 10% Pd/C (40 mg) was hydrogenated at r.t. during 3 h. Filtration *(Hyflo)*, concentration of the filtrate, and recrystallisation of the residue (petroleum ether/ether) afforded **41** as white crystals (2.4 g, 82%). M.p. 80–81° ([8]: 82.5–83°; [5]: 76°). R_f (cyclohexane/AcOEt 4:1) 0.32. IR ($CDCl_3$): 2950, 1720, 1660, 1440, 1260, 1200, 1178, 1142, 1080. ^{1}H-NMR: 0.88 (*s*, 3 H); 0.90 (*s*, 3 H); 0.93 (*s*, 3 H); 1.20–1.60 (6 H); 1.85 (*m*, 1 H); 2.10 (*m*, 1 H); 2.28 (*m*, 1 H); 3.19 (*m*, H–C(5)); 3.66 (*s*, 3 H); 3.69 (*s*, 3 H); 7.04 (*m*, H–C(7)). ^{13}C-NMR: 172.9 (*s*); 167.7 (*s*); 51.6 (*q*); 51.3 (*q*) (for rest of data, *cf. Table 2*). MS: 294 (0.5, $M^{+\cdot}$), 262 (2), 234 (3), 171 (11), 139 (25), 124 (48), 109 (100), 91 (21).

Also isolated by CC (silica gel (200 g), cyclohexane/AcOEt 4:1) of the mother liquour was *dimethyl (1*RS,*2*RS,*4a*RS,*8a*RS*)-1,2,3,4,4a,5,6,7,8,8a-decahydro-5,5,8a-trimethylnaphthalene-1,2-dicarboxylate* (**42**): white crystals (0.1 g, 3%). M.p. 66–68° ([8]: 68–70°). R_f (cyclohexane/AcOEt 4:1) 0.38. IR: 2950, 1740, 1438, 1390, 1370, 1210, 1160, 1098, 1008, 822. ^{1}H-NMR: 0.82 (*s*, 3 H); 0.85 (*s*, 3 H); 1.05 (*s*, 3 H); 0.80–1.70 (9 H); 2.23 (*m*, 1 H); 2.34 (*m*, 1 H); 2.34 (*d*, *J* = 5, H–C(1)); 3.14 (*ddd*, *J* = 5, 2, 2, H–C(2)); 3.64 (*s*, 3 H); 3.66 (*s*, 3 H). ^{13}C-NMR: 174.4 (*s*); 172.4 (*s*); 51.5 (*q*); 51.0 (*q*) (for rest of data, *cf. Table 2*). MS: 296 (3, $M^{+\cdot}$), 281 (9), 264 (10), 159 (15), 145 (53), 123 (92), 113 (100), 107 (57), 93 (63), 81 (64), 69 (74), 55 (69).

*(4a*RS,*5*SR,*8a*RS*)-[1,2,3,4,5,8,8a-Octahydro-6-(hydroxymethyl)-1,1,4a-trimethylnaphthalen-5-yl]methanol* (**43**). A soln. of **41** (1.6 g, 5.4 mmol) in Et_2O (10 ml) was added dropwise within 20 min to a stirred slurry of $LiAlH_4$ (0.38 g, 0.01 mol) in Et_2O (15 ml) at –30° under N_2. The mixture was allowed to attain r.t. during 2 h, cooled to 0°, and H_2O (0.38 ml), 15% aq. NaOH soln. (0.38 ml), and H_2O (1.2 ml) were successively added dropwise. Filtration (*Hyflo*), concentration of the filtrate, and CC of the residue (silica gel (200 g), toluene/AcOEt 1:1) afforded **43** as white crystals (0.85 g, 66%). M.p. 83–84° ([10]: 75.5–77°; [11]: 73–74°; [5]: 63–64°; [8]: 73–74°). R_f (toluene/AcOEt 1:1) 0.30. IR($CDCl_3$): 3380 (br.), 1440, 1390, 1364, 1110, 1040, 980. ^{1}H-NMR (+D_2O): 0.75 (*s*, 3 H); 0.87 (*s*, 3 H); 0.89 (*s*, 3 H); 1.10–1.28 (3 H); 1.40–1.62 (3 H); 1.80–2.15 (4 H); 3.65 (*dd*, *J* = 11, 8.5, 1 H); 3.88 (*dd*, *J* = 11, 2, 1 H); 3.95 (*d*, *J* = 11.5, 1 H); 4.33 (br. *d*, *J* = 11.5, 1 H); 5.79 (*m*, H–C(7)). ^{13}C-NMR: 67.4 (*t*); 61.3 (*t*) (for rest of data, *cf. Table 2*). MS: (0.5, $M^{+\cdot}$), 190 (11), 124 (27), 119 (19), 109 (100), 95 (21), 91 (28), 81 (30), 69 (27).

Also isolated was *(3*RS,*3a*RS,*5a*RS,*9b*RS*)-dodecahydro-6,6-9a-trimethylnaphtho[1,2-c]furan-3-ol* (**44**): white crystals (0.15 g, 12%). M.p. 89–91°. R_f (toluene/AcOEt 1:1) 0.39. IR ($CDCl_3$): 3290 (br.), 1440, 1390, 1365, 1110, 1040, 980, 836. ^{1}H-NMR (+D_2O): 0.84 (*s*, 3 H); 0.88 (*s*, 3 H); 0.90 (*s*, 3 H); 1.00–1.75 (10 H); 1.80 (*dd*, *J* = 6, 6, 1 H); 1.92 (*m*, 1 H); 2.11 (*m*, 1 H); 3.84 (*d*, *J* = 10, 1 H); 4.00 (*dd*, *J* = 10, 5.5, 1 H); 5.21 (*d*, *J* = 7, 1 H). ^{13}C-NMR: 102.3 (*d*); 68.7 (*t*) (for rest of data, *cf. Table 2*). MS: 238 (0, $M^{+\cdot}$), 220 (2), 177 (12), 149 (29), 123 (47), 107 (34), 95 (56), 82 (199), 69 (64).

(4aRS,5RS)-[1,2,3,4,4a,5-Hexahydro-6-(hydroxymethyl)-1,1,4a-trimethylnaphthalen-5-yl]methanol (**45**). As described for **43**, with **29** (5 g, 0.017 mol) in Et_2O (10 ml), $LiAlH_4$ (1 g, 0.026 mol) in Et_2O (35 ml), workup with H_2O (1 ml), 15% aq. NaOH soln. (1 ml) and H_2O (3 ml) and CC (silica gel (350 g), toluene/AcOEt 7:3): **45** as white crystals (2.5 g, 62%). M.p. 106–107° ([5]: 102–103°). R_f (toluene/AcOEt 1:1) 0.30. IR ($CDCl_3$): 3340 (br.), 2925, 1460, 1362, 1032, 980, 840. ^{1}H-NMR (+D_2O): 0.89 (*s*, 3 H); 1.11 (*s*, 3 H); 1.14 (*s*, 3 H); 1.35 (*m*, 2 H); 1.46 (br. *d*, *J* = 13, 1 H); 1.55–1.75 (2 H); 2.00 (br. *d*, *J* = 14, 1 H); 2.41 (*m*, 1 H); 3.91 (*d*, *J* = 11, 1 H); 3.97 (*dd*, *J* = 11, 3.5, 1 H); 4.16 (*d*, *J* = 13, 1 H); 4.38 (*d*, *J* = 13, 1 H); 5.87 (*d*, *J* = 6, 1 H); 6.00 (*dd*, *J* = 6, 3.5, 1 H). ^{13}C-NMR: 65.9 (*t*); 60.0 (*t*) (for rest of data, *cf. Table 2*). MS: 236 (1, $M^{+\cdot}$), 218 (7), 173 (13), 145 (22), 132 (37), 119 (58), 105 (100), 91 (52), 79 (24), 69 (21), 55 (30).

Also isolated was *(3RS,3aRS,9aSR,9bRS)-1,3,3a,4,6,7,8,9,9a,9b-decahydro-6,6,9a-trimethylnaphtho[1,2-c]furan-3-ol* (**46**): viscous, colourless oil (0.4 g, 10%). B.p. (bulb-to-bulb distillation) 180–200°/0.08 Torr. R_f (toluene/AcOEt 1:1) 0.41. IR: 3400 (br.), 2900, 1460, 1372, 1040, 970, 902. ^{1}H-NMR (+D_2O): 1.03 (*s*, 3 H); 1.09 (*s*, 3 H); 1.11 (*s*, 3 H); 1.10–1.85 (6 H); 1.97 (*m*, 1 H); 2.17 (*m*, 1 H); 2.29 (*m*, 1 H); 2.41 (*m*, 1 H); 3.88 (*dd*, *J* = 8.5, 4, 1 H); 4.07 (*dd*, *J* = 8.5, 7, 1 H); 5.21 (*d*, *J* = 3.5, 1 H); 5.62 (*dd*, *J* = 7, 2.5, 1 H). ^{13}C-NMR: 105.7 (*d*); 68.4 (*t*) (for rest of data, *cf. Table 2*). MS: 236 (1, $M^{+\cdot}$), 218 (15), 147 (26), 133 (100), 119 (50), 105 (82), 91 (67), 81 (41), 69 (31), 55 (31).

(4aRS,5SR)-[1,2,3,4,4a,5-Hexahydro-6-(hydroxymethyl)-1,1,4a-trimethylnaphthalen-5-yl]methanol (**47**). As described for **43**, with **30** (1 g, 3.4 mmol) in Et_2O (2 ml), $LiAlH_4$ (0.2 g, 5.2 mmol) in Et_2O (5 ml), workup with H_2O (0.2 ml), 15% aq. NaOH soln. (0.2 ml) and H_2O (0.6 ml) and CC (silica gel (100 g), toluene/AcOEt 4:1): **47** as white crystals (0.55 g, 69%). M.p. 104–105°. R_f (toluene/AcOEt 4:1) 0.23. IR ($CDCl_3$): 3320 (br.), 1450, 1365, 1020, 840. ^{1}H-NMR (+D_2O): 1.10 (*s*, 3 H); 1.12 (*s*, 3 H); 1.13 (*s*, 3 H); 1.20–1.80 (6 H); 1.94 (*dd*, *J* = 9, 5, 1 H); 3.61 (*dd*, *J* = 10, 9, 1 H); 3.82 (*dd*, *J* = 10, 5, 1 H); 4.08 (*d*, *J* = 12.5, 1 H); 4.17 (*d*, *J* = 12.5, 1 H); 5.82 (*d*, *J* = 5.5, 1 H); 5.91 (*d*, *J* = 5.5, 1 H). ^{13}C-NMR: 66.5 (*t*); 61.1 (*t*) (for rest of data, *cf. Table 2*). MS: 236 (1, $M^{+\cdot}$), 48 (3), 173 (11), 145 (18), 132 (39), 118 (49), 105 (100), 91 (40).

Also isolated was *(3RS,3aSR,9aRS,9bRS)- and (3RS,3aRS,9aSR,9bSR)-1,3,3a,4,6,7,8,9,9a,9b-decahydro-6,6,9a-trimethylnaphtho[1,2-c]furan-3-ol* (**48** and **49**, resp.; 1.3:1 diastereoisomeric mixture): viscous, colourless oil (75 mg, 9%). B.p. (bulb-to-bulb distillation) 180–200°/0.08 Torr. R_f (toluene/AcOEt 1:1) 0.44. IR: 3320 (br.), 1460, 1382, 1362, 1282, 1258, 1120, 1082, 980, 906, 820, 670. MS: 236 (1, $M^{+\cdot}$), 218 (10), 175 (12), 147 (16), 133 (53), 119 (51), 105 (100), 91 (89), 79 (43), 55 (50).

Data of **48**. ^{1}H-NMR (+D_2O): 1.08 (*s*, 3 H); 1.18 (*s*, 3 H); 1.28 (*s*, 3 H); 1.00–2.40 (10 H); 3.71 (*dd*, *J* = 11, 8, 1 H); 4.13 (*dd*, *J* = 8, 8, 1 H); 5.36 (*d*, *J* = 5, 1 H); 5.58 (*m*, 1 H). ^{13}C-NMR: 98.6 (*d*); 67.9 (*t*) (for rest of data, *cf. Table 2*).

Data of **49**. ^{1}H-NMR (+D_2O): 1.07 (*s*, 3 H); 1.17 (*s*, 3 H); 1.25 (*s*, 3 H); 1.00–2.40 (10 H); 3.85 (*dd*, *J* = 11, 8, 1 H); 3.91 (*dd*, *J* = 8, 8, 1 H); 5.14 (*d*, *J* = 5, 1 H); 5.59 (*m*, 1 H). ^{13}C-NMR: 103.3 (*d*); 66.6 (*t*) (for rest of data, *cf. Table 2*).

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