172. The Synthesis of 4,7-Bis(dialkylamino)tricyclo[5.2.1.$0^{4,10}$]deca-1(10),2,5,8-tetraenes and their Reduction with Alkali Metal

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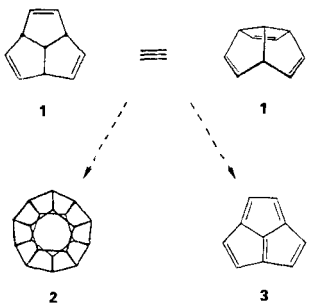
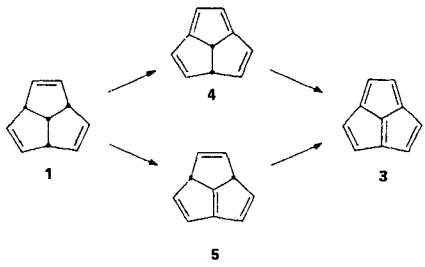
The synthesis and characterization of the novel 4,7-bis(dialkylamino)tricyclo[5.2.1.$0^{4,10}$]deca-1(10), 2,5,8-tetraenes **12** from 1,4,7-trihalotriquinacenes **8** and secondary amines is reported. The structural and electronic characteristics of these as well as the acepentalene dianion (3^{2-}) and some related systems as determined by semiempirical (MNDO) calculations are discussed. Thereby, 3^{2-} should be a triply etheno-bridged trimethylenemethane dianion exhibiting Y-delocalization favored over the formation of a peripheral 10π-electronic system. Attempts directed towards the generation of 3^{2-} by reacting tetraenes **12** with Na led to the formation of tris(dialkylamino)triquinacenes **9**, presumably by a kind of reduction/disproportionation mechanism.

1. Introduction. – Triquinacene (**1**), when it was first prepared by *Woodward* and coworkers [1] in 1964, was not only conceived as an ideal precursor of the elusive dodecahedrane (**2**) [2] [3], but also as a potential precursor to the highly unsaturated acepentalene (**3**) *(Scheme 1)*.

Scheme 1



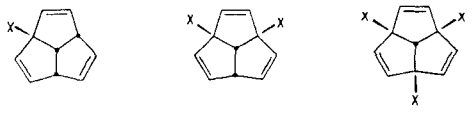
Scheme 2



It is easily recognized that **1** and **3** have identical C-skeletons, and **1** already contains three of the five double bonds present in **3**. One is, therefore, surprised to find almost no reports [4] [5] on this possible approach to **3**, which is of great theoretical interest. In such a concept, the tetraenes **4** and **5** would have to be intermediates on the route from **1** to **3** *(Scheme 2)*.

Here, we present a facile synthesis of the first stable derivatives of tetraene **5**, along with semiempirical calculations on **4** and **5**, the acepentalene dianion (3^{2-}), and related systems, and finally some results of the attempted generation of 3^{2-}.

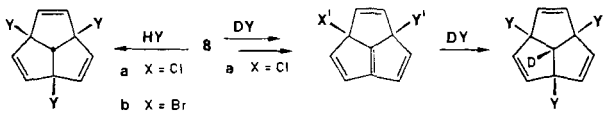
2. Synthesis of 4,7-Bis(dialkylamino)tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraenes (12). – The 1-halotriquinacenes (**6**) and 1,4-dihalotriquinacenes (**7**) on the one hand and 1,4,7-trihalotriquinacenes (**8**) on the other show fundamentally different chemical behaviors.



6 **7** **8a** X = Cl **b** X = Br

Upon nucleophilic substitution, mono- and dihalotriquinacenes **6** and **7** differentiate between hard and soft nucleophiles. With hard nucleophiles only bridgehead substitution (S_N1 type) products are formed [6], soft nucleophiles yield *exo*-3-isotriquinacene [7] derivatives instead [4] [5] [8]. In contrast, compounds **8** [4] [6] [8] with almost all sorts of nucleophiles[1]) yield bridgehead substitution products, *e.g.* 1,4,7-trimethoxy- (**9c**) [6] and 1,4,7-tris(dimethylamino)triquinacene (**9d**) with NaOMe/MeOH and Me_2NH, respectively *(Scheme 3)*.

Scheme 3

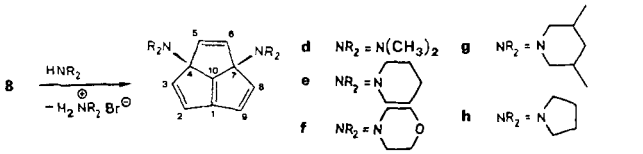


9c Y = OMe **d** Y = NMe_2 **10** X', Y' = X, Y **11c** Y = OCD_3 **d** Y = NMe_2

As had been demonstrated by D labelling, the methoxide substitution does not follow a S_N1-type mechanism but rather an elimination-addition sequence to yield **11c** [7]. The same results has now been obtained in the reaction of **8a** with Me_2ND, yielding tris(dimethylamino)[10-D]triquinacene (**11d**).

The D incorporation at C(10) strongly suggests the existence of tetraene intermediates of type **10**. The olefinic protons of symmetrically 1,4,7-trisubstituted derivatives **8**, **9**, and **11** show a singlet in their ^{1}H-NMR spectra. Surprisingly, the trichloride **8a** and the tribromide **8b** upon reaction with piperidine, formed a new product in good yields (86%), which showed a singlet and an *AB*-line system (integrated ratio 1:1:1) in the olefinic region of its ^{1}H-NMR spectrum. On the basis of this and other spectral data (IR, MS, ^{13}C-NMR), the product was identified as 4,7-dipiperidinotricyclo[5.2.1.0^{4,10}]-deca-1(10)2,5,8-tetraene (**12e**, *Scheme 4*).

Scheme 4



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[1]) Compounds **6** and **7** react with OH^-, leading to hydroxytriquinacenes. Compounds **8** do not react with OH^- (*cf.* [6]).

Piperidine is sterically more demanding than Me_2NH. It could, therefore, be rationalized that the steric bulk of the two piperidino groups in **12e** inhibits a third molecule of piperidine from adding to the strained central double bond. The scope and limitations of this new reaction were tested with other secondary amines [9]. Morpholine, which is similar to piperidine by its molecular shape, gave the corresponding 4,7-dimorpholinotetraene **12f** in 86% yield. The sterically more crowded 3,5-dimethylpiperidine (mixture of *cis*- and *trans*-isomers) yielded tetraene **12g** only in 36% yield, which is less stable and more sensitive to heat and air than **12e** and **12f**. One can only speculate that the bulkier substituents in **12g** are more easily eliminated, followed by decomposition through polymerization.

The even more crowded 2,6-dimethylpiperidine and 2,2,6,6-tetramethylpiperidine do not react with **8b** to give a corresponding tetraene derivative **12**. Instead, differing amounts of starting material **8b** were isolated together with polymeric material. It is assumed that these amines are basic enough to eliminate HBr from **8b** and form unstable tetraene **10** (X′ = Y′ = Br), which polymerizes faster than it reacts with these bulky amines by addition.

The reaction of **8b** with pyrrolidine leads to tetraene **12h** only in trace amounts; an addition product could be isolated, which was most likely the tripyrrolidino derivative **9h** (Y = pyrrolidino), along with a large amount of polymeric material. Surprisingly, a very satisfactory yield (77%) of 4,7-bis(diethylamino)tricyclo[5.2.1.$0^{4,10}$]deca-1(10),2,5,8-tetraene (**12i**) was obtained from **8b** and Et_2NH (see *Table 1*). When carefully monitored, the reaction of **8b** with Me_2NH yielded the corresponding tetraene **12d** (47%) and the tris(dimethylamino) compound **9d** (31%).

Table 1. *4,7-Bis(dialkylamino)tricyclo[5.2.1.$0^{4,10}$]deca-1(10),2,5,8-tetraenes* **12**, *from 1,4,7-trihalotriquinacenes* **8**

Educt	*sec*-Amine	Product	Yield [%]	React. cond.	Workup[a])
8b	Me_2NH	**12d**	47[b])	25°, 14d	I
8a	Piperidine	**12e**	86	25°, 14d	I, II
8b	Piperidine	**12e**	86	25°, 1d	I, II
8b	Morpholine	**12f**	86	25°, 1d	I, II
8b	3,5-Dimethylpiperidine	**12g**	36	25°, 1d	I, II
8b	Et_2NH	**12i**	77	25°, 4d	I, II, III

[a]) I: Extraction pentane/H_2O; II: low-temperature liquid chromatography, −30°, silica gel, *t*-BuOMe/Me_3N 10:1; III: *Kugelrohr* distillation, 100°/0.01 Torr.

[b]) By-product **9d** (31%).

Tetraenes **12** can conveniently be isolated as colorless oils by low-temperature column chromatography. The bis(diethylamino) compound **12i**, however, is best purified by *Kugelrohr* distillation. All tetraenes **12**, which slowly decompose in solution or in the presence of air are easily identified by their characteristic ^{1}H-NMR signals in the olefinic region (*Table 2*). Compound **12i** contains two sets of diastereotopic methylene protons which appear, in the 400-MHz ^{1}H-NMR spectrum, as a nicely resolved ABX_3-line system.

Compared to **1** with its pyramidal shape, tetraenes **12** are forced by their additional double bond to have a more planar C-skeleton. This is evidenced by their ^{13}C-NMR data (see *Table 3*).

Table 2. *^{1}H-NMR* (270 MHz) *Data of the Tetraenes* **12**. Chemical shift δ_{TMS} in ppm, coupling constants see *Exper. Part.*

Compound	Solvent	H–C(5(6))[a]	H–C(3(8))[b]	H–C(2(9))[b]	NR_2
12d	$CDCl_3$	5.68	6.21	6.75	2.34 (*s*, 6H) 2.41 (*s*, 6H)
e	C_6D_6	5.50	6.20	6.69	1.25–1.70 (*m*, 12H) 2.70–2.95 (*m*, 8H)
f	C_6D_6	5.41	6.27	6.56	2.57–2.79 (*m*, 8H) 3.67 (*t*, 8H)
g	C_6D_6	5.60	6.21	6.72	0.80–0.87 (*2d*, 12H) 1.50–2.14 (*m*, 8H) 3.04–3.45 (*dm*, 8H)
i	C_6D_6	5.47	6.14	6.61	1.09 (*t*, 12H) 2.66–2.93 (*m*, 8H)

[a]) *Singlet.*
[b]) *AB*-line system, $^3J(2(9), 3(8)) = 5.0$ Hz in all cases.

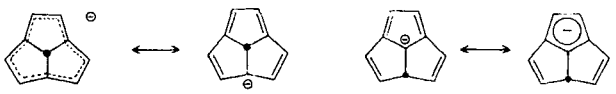
Table 3. *^{13}C-NMR Data of the Tetraenes* **12**. Solvent: (D_6) benzene, chemical shift δ_{TMS} in ppm, Obs. = observable, Mult. = multiplicity, *J* in Hz.

Compound	*v* [MHz]	Obs.	C(1)	C(2(9))	C(3(8))	C(4(7))	C(5(6))	C(10)	C(2')	C(3')	C(4')
12e	67.91	δ	163.2	135.9	147.8	82.1	129.6	163.4	50.6	27.1	25.5
f	67.91	δ	161.5	135.6	147.3	81.6	130.8	164.9	50.0	67.6	–
i	100.63	δ	162.2	136.2	148.5	82.0	128.8	165.2	45.6	15.8	–
e	67.91	Mult.	*s*	*d*	*d*	*s*	*d*	*s*	*t*	*t*	*t*
		^1J(C,H)	–	165.4	165.4	–	165.4	–	131.9	128.0	128.0
i	100.63	Mult.	*tt*	*dd*	*dd*	*t*	*dd*	*t*	*tq*	*qt*	–
		^1J(C,H)	–	166.2	165.5	–	164.2	–	131.6	125.2	–
		^2J(C,H)	11	2.5	3	~6	5	–	4.3	2	–
		^3J(C,H)	5	–	–	–	–	4	–	–	–

The chemical shifts of C(2,3,5,6,8,9) and those of C(4,7) are within the usual range. The two signals above 160 ppm are assigned to C(1) and C(10), as they do not show a ^1J(C,H) coupling. For the bis(diethylamino) compound **12i**, the 100.63-MHz gated ^{13}C-NMR spectrum showed coupling constants ^2J(C,H) = 11 Hz and ^3J(C,H) = 5 Hz for C(1), and ^3J(C,H) = 4 Hz for C(10). This indicates a partial planarization of the C-skeleton, as the arguments leading to the *Karplus* relationship between interplanar angles and H,H-coupling constants apply to C,H couplings as well [10].

The tetraenes **12** are the first spectroscopically completely characterized derivatives of the parent hydrocarbon **5**. Only *Jacobson* reported in 1974 a [4 + 2] cycloaddition dimer of the octachloro derivative, which was characterized only by IR, MS, and chemical transformation [11]. The stable tetraenes **12** should be potential precursors for the preparation of acepentalene (**3**) and its dianion ($\mathbf{3}^{2-}$).

3. Calculations. – With regard to the stability of polyenes **3–5**, two aspects have to be taken into account, the destabilizing strain and the stabilizing conjugative effect. Force-field calculations of **3–5** and related olefins have been reported [8]; according to these results the olefinic strain (OS) [12] of **3–5** should be so high as to preclude the possibility



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for these to be isolated as such. Among all, **4** ought to be substantially more strained than **5**, due to the impossibility of releasing strain by independent bridgehead double bond deformation.

To obtain some insight into their electronic nature, MNDO calculations [13] were performed for the tetraenes **4**, **5**, and the anions **13**, **14**, the conjugate bases of **4** *(Table 4)*.

The MNDO-calculated enthalpies of formation ΔH_f° of both **4** and **5** are about the same. Because of its larger HOMO-LUMO energy gap (8.53 *vs.* 7.64 eV), however, **5** should be less reactive than **4**. This must be due to the fact that **4** is linearly conjugated tetraene whereas **5** contains only a cross-conjugated triene unit[2]). Yet the HOMO-LUMO energy gap for **5** is smaller than the usual 9.2 eV for 2-vinyl substituted dienes [15]. The

Table 4. *MNDO-Calculated Enthalpies of Formation* ΔH_f° *and Orbital Energies OE of* **4**, **5**, **13**, *and* **14**

Compound:	**4**	**5**	**13**	**14**
ΔH_f° (kcal/mol):	109.92	110.50	100.21	110.92
OE (eV)				
LUMO + 4			+8.78	+8.49
LUMO + 3	+ 1.65	+ 1.79	+6.88[a])	+7.10
LUMO + 2	+ 1.32	+ 0.97	+6.87[a])	+7.02
LUMO + 1	+ 0.67	+ 0.74	+4.91[a])	+5.36
LUMO	− 0.49	− 0.16	+4.90[a])	+4.97
HOMO	− 8.13	− 8.69	−2.37[a])	−2.47
HOMO-1	− 9.43	− 9.74	−2.40[a])	−2.85
HOMO-2	−10.28	− 9.86	−5.17[a])	−4.66
HOMO-3	−11.11	−11.12	−5.17[a])	−5.79
HOMO-4			−6.76	−6.81

[a]) Degenerate.

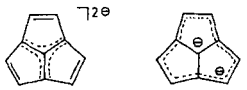
Table 5. *MNDO-Calculated Bond Lengths* [pm] *of* $\mathbf{3}^{2-}$, **13** *and* **14**

Bond	$\mathbf{3}^{2-}$	**13**	**14**
1–10	141.6	152.3	142.3
4–10	141.6	152.3	142.3
7–10	141.6	152.5	150.9
1–2	144.5	141.8	143.8
2–3	143.4	143.4	143.1
3–4	144.5	141.2	143.5
4–5	144.5	141.6	145.2
5–6	143.5	143.4	139.4
6–7	144.5	141.6	152.3
7–8	144.5	141.6	152.0
8–9	144.5	143.4	139.5
9–1	144.6	141.6	145.2

[2]) Compound **5** may be regarded as a 'dendralene' (*cf.* [14]).

LUMO's of both **4** and **5** have negative energy values, indicating thermodynamic stabilization of the respective hydrocarbons by reduction to the corresponding anions.

Among the two isomeric conjugated bases of **4** (**13** and **14**), **13** should be thermodynamically more stable. Both the orbital energies *(Table 4)* as well as the molecular geometry *(Table 5)* indicate an aromatic, delocalized peripheral 10π-electron system. The peripheral bond lengths converge, the system realizes C_{3v} symmetry, and the molecular orbitals degenerate. In contrast, **14** is only a 1,3-divinylcyclopentadienide with alternating bond lengths and nondegenerate MO's. In **13**, a higher degree of charge delocalization is possible, while **14** has the steric problem to form a more or less planar cyclopentadienide system within the rigid nonplanar C-skeleton.



(a) (b)

3^{2-}

Table 6. *MNDO-Calculated Charge Distribution in* 3^{2-}

Atom	Abs.[a])	Rel.[b])
C(10)	−0.150	7.51
C(1,4,7)	−0.246	12.31
C(2,3,5,6,8,9)	−0.145	7.26
H–C(2,3,5,6,8,9)	−0.040	2.00

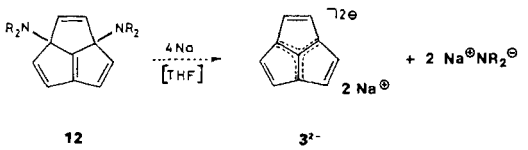
[a]) Charge excess in elemental charges. [b]) Charge excess in % of gross charge.

MO calculations predict acepentalene (**3**) to have a triplet ground state [16]. Therefore, 3^{2-} should be a closed-shell system. According to our MNDO calculation, 3^{2-} has an enthalpy of formation $\Delta H_f^\circ = 199.49$ kcal/mol, and a trigonally planar geometry (for bonds lengths see *Table 5*). The calculated charge densities *(Table 6)* with the largest excess on the peripheral bridgehead C-atoms C(1,4,7) exclude a delocalization like in (**b**), which would be analogous to that found in the aceheptalene dianion [17]. Instead, 3^{2-} delocalizes the two excess charges like in (**a**), which corresponds to a Y delocalization [18–23]. Accordingly, 3^{2-} should be regarded as a triply etheno-bridged trimethylenemethane dianion. This may be due to *Coulomb* interactions [24] which should be more dominant in 3^{2-} with its three ethylene units than in the aceheptalene dianion, which has two butadiene and one ethylene unit on the perimeter allowing a wider spread of charge density.

4. Attempted Generation of the Acepentalene Dianion (3^{2-}). – The ideal precursor to 3^{2-} would be a bisquaternary ammonium salt of one of the tetraenes **12**, which upon reduction would expell two molecules of the tertiary amine. However, several attempts to quaternize the aminotetraenes **12** lead to polymeric materials only. In a few experiments, some weak evidence (^{1}H-NMR, solubility) was obtained for the formation of an ammonium salt. Apparently, quaternary ammonium derivatives of **12** are rather sensitive and readily cleave to form unstable intermediates.

Therefore, the tetraenes **12** themselves were reduced with Na wire hoping that the amino substituents would be activated enough in their triply allylic positions to leave the molecule as amide anions *(Scheme 5)*.

Scheme 5



12 **3^{2-}**

These reductions were performed in (D_8) THF with NMR control [25], as the trigonally symmetric $\mathbf{3}^{2-}$ (see *Chap. 3*) should give rise to characteristically simple ^{1}H- and ^{13}C-NMR spectra. With the three tetraenes **12e, f, i** the Na wire showed dark points after 6–8 h, later signs of dissolution. The color of the reaction mixture changed from colorless/pale yellow to a dark red-brown.

In all three cases, a decrease in starting material signals, and an interesting singlet in the olefinic region was observed *(Table 7)*. The chemical shifts of these new singlets were close to the expected value 5.73 ppm, calculated for $\mathbf{3}^{2-}$ by the *Schaefer-Schneider* correlation [26][3]).

Table 7. *^{1}H-NMR* (270 MHz) *Data of the Na-Reduction Products of* **12**. Spectra of the reaction mixture after complete reaction; chemical shift δ_{TMS} in ppm; solvent: (D_8)THF.

Educt	Observable signals
12e	1.48 (*m*); 2.34–2.63 (*m*); 3.30 (*s*); 5.31 (*s*)
12f	2.37–2.76 (*m*); 3.63 (*m*); 5.45 (*s*)
12i	1.03 (*t*, ^3J = 7.2); 2.71 (*q*); 5.55 (*s*)

The simplicity of the ^{1}H-NMR spectra proves that the products were C_3-symmetrical and bore either three identical substituents at C(1,4,7) or none. Interestingly, the diastereotopicity of the CH_2 protons in the Et_2N groups of **12i** disappeared in the course of the reaction, leading to a quadruplet for these protons in the product spectrum.

The ^{13}C-NMR data *(Table 8)* of all three products are in accord with a C_3 symmetry. The peripheral olefinic C-atoms give rise to a doublet around 133 ppm, some spectra show an additional signal 0.2 ppm upfield from this. All three products show one signal for quaternary C-atoms around 88 ppm proved by DEPT-NMR. This signal had to be assigned to three peripheral bridgehead C-atoms, as in some cases a triplet splitting with a ^2J(C,H) = 8 Hz was observed.

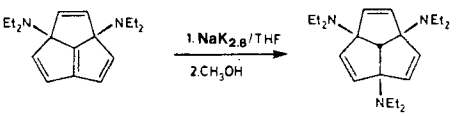
Although these findings were consistent with the formation of the C_3-symmetrical dianion $\mathbf{3}^{2-}$, two control experiments gave contradicting evidence. Firstly, the reaction of Na with Et_2NH (D_8)THF gave a solution of $NaN(CH_2CH_3)_2$, the ^{1}H-NMR signals of which differed from those of the Et_2N groups in the reduction product fo **12i**. Secondly, in one experiment, in which **12i** had been reacted with $NaK_{2.8}$ [27] at room temperature for 24 h and then quenched at −78° with MeOH, 1,4,7-tris(diethylamino)triquinacene (**9i**) was isolated in 53% yield and identified by its MS *(Scheme 6)*. Although the signal of H–C(10) could not be assigned, the chemical shift of the signal at 5.55 ppm was almost identical to that of the alledged $\mathbf{3}^{2-}$.

[3]) The change of the chemical shift relative to benzene is 10.7 ppm per unit charge at the C-atoms bearing H-atoms. The charge excess of C(2,3,5,6,8,9) in $\mathbf{3}^{2-}$ is calculated to be −0.144 (see *Table 7*). 7.27–0.144 × 10.7 ppm = 5.73 ppm.

Table 8. *^{13}C-NMR Data of the Na-Reduction Products of* **12**. Spectra of the reaction mixtures after complete reaction; Obs. = observable; SEFT: Spin-echo-FT; DEPT: Distortionless enhancement by polarization transfer; chemical shift δ_{TMS} in ppm in (D_8)THF; P = phase, + = positive, – = negative; Mult. = multiplicity; coupling constants J in Hz.

Educt	ν [MHz]	Pulse sequ.	Obs. signals							
12e	100.62	SEFT	δ	26.0	27.7	50.5	89.0	133.1		
			P	–	–	–	–	+		
			Mult.	*t*	*t*	*t*	*t*	*d*		
			^1J(C,H)	126	127	130	–	162		
			^2J(C,H)	–	–	–	8	–		
12f	67.93	SEFT	δ	49.2	50.0	58.3	68.1	88.6	133.2	
			P	–	–	+	–	–	+	
12i	100.62	SEFT	δ	16.1	44.2	65.3	87.4	132.9		
			P	+	–	+	–	+		
			Mult.	*q*	*tq*	*d*	*t*	*d*		
			^1J(C,H)	125	131	130	–	161		
			^2J(C,H)	–	5	–	8	–		
	50.13	SEFT	δ	16.5	44.6	45.2	65.5	87.6	133.1	133.3
			P	+	+	–	+	–	+	+
	50.13	DEPT	δ	16.5	44.6	45.2	65.5		133.1	133.3
			P	+	+	–	+		+	+

Scheme 6

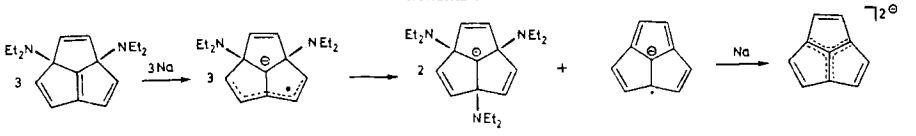


12i **9i**

As no D was incorporated upon quenching with (D_1) methanol, **9i** had apparently been formed before the addition of MeOH by proton transfer from one of the Et_2N groups or undeuterated THF. Compound **9i** cannot have arisen from an addition of diethylamide ions to starting material **12i**, since corresponding control experiments did not yield any **9i**. Direct reaction of the tribromide **8b** with diethylamide also did not lead to **9i**, but only to **12i** (82%). All experimental observations are compatible with some sort of reduction/disproportionation reaction, which overall transforms three molecules **12i** probably *via* $\mathbf{12}^{\cdot-}$ and **15** into two molecules **9i**. In addition, one molecule of **3**, $\mathbf{3}^{\cdot-}$, or $\mathbf{3}^{2-}$ must have been formed, which subsequently suffered from polymerization *(Scheme 7)*. Without further experiments, it can only be speculated that the additional signal near 130 ppm in some ^{13}C-NMR spectra of reduction products belonged to $\mathbf{3}^{2-}$.

It is reasonable to assume that **12i** is reduced to $\mathbf{12}^{\cdot-}$ by Na in the first step. As $\mathbf{12}^{\cdot-}$ would be less planar than **12i**, it might be more easily attacked by a diethylamide anion or

Scheme 7



12i $\mathbf{12i}^{\cdot-}$ **15** $\mathbf{3}^{\cdot-}$ $\mathbf{3}^{2-}$

an aminyl radical [28]. This implies a maximum yield of 66% for **9i**, which is in accord with the 53% isolated yield. An intermediate anion of type **15** should be a very strong base.

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Experimental Part

General. Gas chromatography GC: Anal., *Siemens L402 (GC 402), Hewlett-Packard 5710 A (GC 5710)*; prep., *Varian Aerograph 920 (GC 920)*. Column chromatography was performed with silica gel *60* of *E. Merck*. UV spectra [$\lambda_{max}(\log\varepsilon)$]: *Perkin-Elmer-Hitachi 200* in spectroscopic grade hexane. IR ($\bar{\nu}$ in cm^{-1}): *Perkin-Elmer 297* and *399*. ^{1}H-NMR (δ_{TMS} in ppm, *J* in Hz): *Varian T 60* (60 MHz), *Bruker WP 80* (80 MHz), *WH 270* (270 MHz), and *WM 400* (400 MHz). ^{13}C-NMR (δ_{TMS} in ppm, *J* in Hz): *Bruker WP 80* (20.17 MHz), *WH 270* (67.91–67.93 MHz), *WM 400* (100.62 MHz), and *Varian XL 200* (50.31 MHz). Positive (CH or CH_3) and negative (C or CH_2) phases for SEFT (spin-echo *Fourier* transform) and DEPT (distortionsless enhancement by polarization transfer) spectra are indicated by + and −, resp. MS (EI) and MS (CI) (*m/z*): *Varian CH7, MAT 311, MAT 311A*, and high-resolution MS (HR-MS): *MAT 311* and *MAT 731*.

1,4,7-Tris(dimethylamino)tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (**9d**). *1,4,7-trichlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene* (**8a**; 130 mg, 0.56 mmol) in Me_2NH (3 ml) were kept at 25° in a thick-wall screw-cap bottle, wrapped in aluminum foil. After 4 d, the anal. GC (*GC 402*, 1.5 m 3% *SE 30*, 150°) of the mixture showed one main product, which was purified by prep. GC (*GC 920*, 1.0 m 10% *SE 30*, 150°): 62.4 mg (0.24 mmol, 43.0%) of **9d**. t_R 3.60 (rel. to **8a**), colorless cryst. M.p. 74°, purity 100% (NMR). IR (KBr): 3040, 2980, 2930, 2810, 2770, 1450, 1330, 1110, 1010, 790, 760. ^{1}H-NMR (270 MHz, $CDCl_3$): 2.45 (*s*, 3 $(CH_3)_2N$); 3.21 (*s*, H–C(10)); 5.57 (*s*, H–C(2(3,5,6,8,9))). MS (70 eV): 260 (M^+ + 1,5), 259 (M^+, 27), 215 ($M^+ - (CH_3)_2N$, 35), 214 ($M^+ - H - (CH_3)_2N$, 77), 200 ($M^+ - CH_3 - (CH_3)_2N$, 90), 185 ($M^+ - 2CH_3 - (CH_3)_2N$, 25), 171 ($M^+ - 2(CH_3)_2N$, 87), 156 ($M^+ - 2(CH_3)_2N - CH_3$, 100), 128 ($M^+ - 3(CH_3)_2N + H$, 33), 127 ($M^+ - 3(CH_3)_2N$, 18). HR-MS ($C_{16}H_{25}N_3$): calc. 259.204838; found 259.20497.

1,4,7-Tris(dimethylamino)[10-^{2}H]tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (**11d**). Compound **8a** (102.0 mg, 0.44 mmol) was reacted with Me_2ND (3 ml) as described for **9d**. The anal. GC (*GC 402*, 1.5 m 3% *SE 30*, 150°) showed one main product with the same t_R as **9d**. The product was purified by prep. GC (*GC 920*, 1.0 mg 10% *SE 30*, 150°): 32.3 mg (0.12 mmol, 28.3%) of **12d**. IR (KBr): as for **9d**. ^{1}H-NMR (270 MHz, $CDCl_3$): 2.45 (*s*, 3 $(CH_3)_2N$); 3.31 (*s*, 0.35H, H–C(10)); 5.57 (*s*, H–C(2(3,5,6,8,9))). MS (80 eV): 261 (M^+ + 1,4), 260 (M^+, 18), 259 (M^+ − H, 9); 65% D incorporation (det. by ^{1}H-NMR and MS).

Tetraenes **12**. – *General Procedure.* – The 1,4,7-trihalotriquinacene **8** is stirred with the freshly distilled secondary amine at 25°. After a sufficiently long reaction time, the secondary amine is evaporated in a rotary evaporator. The residue is dissolved in pentane (30 ml), and solid ammonium halide is filtered off. The soln. is extracted with H_2O (3 × 30 ml). Each aq. phase is extracted with pentane (30 ml). The combined org. phases are dried ($MgSO_4$). The solvent is evaporated in a rotary evaporator, the residue dissolved in *t*-BuOMe and chromatographed at −30° through 50 g of silica gel ((*t*-Bu)OMe/Me_3N 10:1, column 40 × 2 cm).

4,7-Bis(dimethylamino)tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene (**12d**). *1,4,7-Tribromotriquinacene* (**8b**) (215 mg, 0.59 mmol) [4] [6] in Me_2NH (5 ml) was kept at 25° in a thick-wall screw-cap bottle. After 5 min, crystals of Me_2NH_2Br started to precipitate. After 14 d, the bottle was carefully opened and the Me_2NH allowed to evaporate. The residue was dissolved in pentane (30 ml). Solid ammonium salt was filtered off, and the soln. was extracted with water (3 × 30 ml). Each aq. phase was extracted with pentane (30 ml). The combined org. phases were dried ($MgSO_4$) and concentrated in a rotary evaporator to about 2 ml. The anal. GC (*GC 5710*, 1.5 m 5% *SE 30*, 150°) showed that two main products had been formed. The solvent was completely evaporated, and the remaining colorless syrup was dried *in vacuo* for 30 min at 0.1 Torr. The mixture (108 mg), was analyzed by ^{1}H-NMR and GC/MS without separation. *Component I* (rel. t_R 1.00): 48 mg (0.19 mmol, 31%) of **9d**. *Component II* (t_R 1.28): 60 mg (0.28 mmol, 47%) of **12d**. IR (film): **9d** and **12d**: 3055, 2950, 2865, 2840, 2780, 1450, 1270, 1020, 800. ^{1}H-NMR (270 MHz, $CDCl_3$): **12d**: 2.34 (*s*, $(CH_3)_2N$); 2.41 (*s*, $(CH_3)_2N$); 5.68 (*s*, H–C(5(6))); 6.21 (*d*, ^3J(2(9),3(8)) = 5.0, H–C(3(8))); 6.75 (*d*, H–C(2(9))). MS (70 eV): **12d**: 215 (M^+ + H, 100), 200 (M^+ + H–CH_3, 14), 199 ($M^+ - CH_3$, 14), 185 (M^+ + H − $2CH_3$, 11), 171 (M^+ + H − $(CH_3)_2N$, 31), 170 ($M^+ - (CH_3)_2N$, 43), 127 (M^+ + H − $2(CH_3)_2N$, 29), 126 ($M^+ - 2(CH_3)_2N$, 17).

4,7-Dipiperidinotricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene (**12e**). *a)* Compound **8a** [7] (41 mg, 0.18 mmol) was reacted with piperidine (5 ml) for 14 d (see *General Procedure*). 40 mg (0.14 mmol, 86%) **12e**, bright yellow oil, which rapidly becomes dark under the influence of air.

b) Compound **8b** (360 mg, 0.98 mmol) [4] [6] was reacted with piperidine (5 ml) for 1 d. Yield 227 mg (0.84 mmol, 86%) of **12e**, purity ~95% (NMR). IR (film): 3075, 2960, 2880, 2850, 2770, 1460, 1325, 1190, 1130, 795. ^{1}H-NMR (270 MHz, C_6D_6): 1.25–1.70 (*m*, 12H, 2H–C(3'), 2H–C(4'), 2H–C(5')); 2.70–2.95 (*m*, 8H, 2H–C(2'), 2H–C(6')); 5.50 (*s*, H–C(5(6))); 6.20 (*d*, ^3J(2(9),3(8) = 5.0, H–C(3(8))); 6.72 (*d*, H–C(2(9))). ^{13}C-NMR (67.91 MHz, C_6D_6) 25.5 (*t*, ^1J(C,H) = 128.0, C(4')); 27.1 (*t*, ^1J(C,H) = 128.0, C(3')); 50.6 (*t*, ^1J(C,H) = 131.9, C(2')); 82.1 (br. *s*, C(4(7))); 129.6 (*d*, ^1J(C,H) = 165.4, C(5(6))); 135.9 (*d*, ^1J(C,H) = 165.4, C(2(9))); 147.8 (*d*, ^1J(C,H) = 165.4, C(3(8))); 163.2 (*s*, C(1)); 163.4 (*s*, C(10)). MS (70 eV): 294 (M^+, 1), 211 ($M^+ + H - C_5H_{10}N$, 70), 210 ($M^+ - C_5H_{10}N$, 29), 209 ($M^+ - C_5H_{11}N$, 100), 128 ($M^+ + 2H - 2C_5H_{10}N$, 23), 127 ($M^+ + H - 2C_5H_{10}N$, 22), 126 ($M^+ - 2C_5H_{10}N$, 54), 115 (12), 84 ($C_5H_{10}N$, 60). MS (isobutane-CI): 295 ($M^+ + H$, 72), 294 ($M^+ + H - H$, 13), 293 ($M^+ + H - 2H$, 23), 213 ($M^+ + H - C_5H_8N$, 20), 212 ($M^+ + H - C_5H_9N$, 72), 211 ($M^+ + H - C_5H_{10}N$, 33), 210 ($M^+ + H - C_5H_{11}N$, 100), 129 ($M^+ + H - 2C_5H_9N$, 20), 128 ($M^+ + H - C_5H_{10}N - C_5H_9N$, 20), 127 ($M^+ + H - 2C_5H_{10}N$, 24), 116 (13). HR-MS ($C_{15}H_{15}N$, $M^+ - C_5H_{11}N$): calc. 209.1204; found 209.1202.

4,7-Dimorpholinotricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene (**12f**). Compound **8b** (300 mg, 0.82 mmol) was reacted with morpholine (5 ml) for 1 d: 208 mg (0.70 mmol, 86%) of **12f**, bright yellow oil, which becomes brown under the influence of air, purity ~90% (NMR). IR (film): 3080, 2955, 2855, 2820, 1660, 1620, 1450, 1270, 1115, 790. ^{1}H-NMR (270 MHz, C_6D_6): 2.57–2.79 (*m*, 8H, 2H–C(3'), 2H–C(5')); 3.67 (*t*, ^3J(2',3') = 4.7, 8H, 2H–C(2'), 2H–C(6')); 5.41 (*s*, H–C(5(6))); 6.27 (*d*, ^3J(2(9),3(8) = 5.0, H–C(3(8))); 6.56 (*d*, H–C(2(9))). ^{13}C-NMR (67.91 MHz, C_6D_6): 50.0 (C(3')); 67.6 (C(2')); 81.6 (C(4(7))); 130.8 (C(5(6))); 135.6 (C(2(9))); 147.3 (C(3(8))); 161.5 (C(1)); 164.9 (C(10)). MS (70 eV): 300 ($M^+ + 2H$, 13), 299 ($M^+ + H$, 47), 298 (M^+, 14), 214 ($M^+ + 2H - C_4H_8NO$, 72), 213 ($M^+ + H - C_4H_8NO$, 86), 212 ($M^+ - C_4H_8NO$, 35), 211 ($M^+ - C_4H_9NO$, 92), 128 ($M^+ + 2H - 2C_4H_8NO$, 100), 127 ($M^+ + H - 2C_4H_8NO$, 65), 126 ($M^+ - 2C_4H_8NO$, 90), 115 (36), 87 (C_4H_9NO, 38), 86 (C_4H_8NO, 38). HR-MS ($C_{18}H_{23}N_2O_2$, $M^+ + H$): calc. 299.175953; found 299.1759 ± 0.0002.

4,7-Bis(3',5'-dimethylpiperidino)tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene (**12g**). Compound **8b** (115 mg, 0.31 mmol) was reacted with 3,5-dimethylpiperidine (5 ml; *cis/trans* mixture) for 1 d: 40 mg (0.11 mmol, 36%) of **12g**, yellow oil, which rapidly becomes dark under the influence of air, purity ~90% (NMR). IR (film): 3040, 2940, 2900, 2780, 1450, 1360, 1320, 1190, 1120, 860, 790, 765. ^{1}H-NMR (270 MHz, C_6D_6): 0.80–0.87 (2*d*, $4CH_3$); 1.50–2.14 (*m*, 8H, H–C(3'(5')), 2H–C(4')); 3.04–3.45 (*dm*, 8H, 2H–C(2'), 2H–C(6')); 5.60 (*s*, H–C(5(6))); 6.21 (*d*, ^3J(2(9),3(8) = 5.0, H–C(3(8))); 6.72 (*d*, H–C(2(9))). MS (70 eV): 351 ($M^+ + H$, 8), 350 (M^+, 4), 239 ($M^+ + H - C_7H_{14}N$, 38), 238 ($M^+ + H - C_7H_{14}N$, 20), 237 ($M^+ + H - C_7H_{14}N$, 62), 126 ($M^+ - 2C_7H_{14}N$, 88), 58 (100). HR-MS ($C_{24}H_{35}N_2$, $M^+ + H$): calc. 351.280010; found (I) 351.28062 (II) 351.2797.

4,7-Bis(diethylamino)tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene (**12i**). Compound **8b** (1135 mg, 3.09 mmol) was reacted with Et_2NH (8 ml) for 4 d according to the *General Procedure*. In addition, the product was purified by *Kugelrohr* distillation (100°/0.1 Torr): 645 mg (2.39 mmol, 77%) of **12i**, colorless oil, which rapidly becomes brown under the influence of air, purity 100% (NMR). IR (film): 3060, 2980, 2940, 2880, 2830, 1460, 1450, 1375, 1205, 1105, 1070, 790. UV (hexane) 215 (*sh*, 4.012), 235 (3.644), 285 (3.584). ^{1}H-NMR (270 MHz, C_6D_6): 1.09 (*t*, ^3J(1',2') = 7.2, $4CH_3$)); 2.66–2.93 (*m*, ^2J(1',1') = –13.0, $4CH_3CH_2$)); 5.47 (*s*, H–C(5(6))); 6.14 (*d*, ^3J(2(9),3(8)) = 5.0, H–C(3(8))); 6.61 (*d*, H–C(2(9))). ^{13}C-NMR (100.63 MHz, C_6D_6): 15.88 (*qt*, ^1J(C,H) = 125.2, ^2J(C,H) = 2, C(2')); 45,6 (*tq*, ^1J(C,H) = 131.6, ^2J(C,H) = 4.3, C(1')); 82.0 (*t*, ^2J(C,H) ≈ 6, C(4(7))); 128.8 (*dd*, ^1J(C,H) = 164.2, ^2J(C,H) = 5, C(5(6))); 136.2 (*dd*, ^1J(C,H) = 166.2, ^2J(C,H) = 2.5, C(2(9))); 148.5 (*dd*, ^1J(C,H) = 165.5, ^2J(C,H) = 3, C(3(8))); 162.2 (*tt*, ^2J(C,H) = 11, ^3J(C,H) = 5, C(1)); 165.2 (*t*, ^3J(C,H) = 4, C(10)). MS (70 eV): 272 ($M^+ + 2H$, 10), 271 ($M^+ + H$, 46), 270 (M^+, 8), 242 ($M^+ + H - C_2H_5$, 13), 241 ($M^+ - C_2H_5$, 32), 199 ($M^+ + H - (C_2H_5)_2N$, 99), 198 ($M^+ - (C_2H_5)_2N$, 48), 197 ($M^+ - (C_2H_5)_2NH$, 100), 184 ($M^+ + H - (C_2H_5)_2N - CH_3$, 68), 182 ($M^+ - (C_2H_5)_2NH - CH_3$, 26), 128 ($M^+ + 2H - 2(C_2H_5)_2N$, 82), 127 ($M^+ + H - 2(C_2H_5)_2N$, 71), 126 ($M^+ - 2(C_2H_5)_2N$, 91), 115 (51). HR-MS ($C_{18}H_{27}N_2$, $M^+ + H$): calc. 271.21741; found 271.21715.

Reaction of **8b** *with Pyrrolidine.* Compound **8b** (200 mg 0.55 mmol) was reacted with dist. pyrrolidine (5 ml) for 1 d. Workup without column chromatography gave 110 mg of a viscous brown syrup, probably predominantly *1,4,7-tripyrrolidinocyclo[5.2.1.0^{4,10}]deca-2,5,8-triene* (**9h**). ^{1}H-NMR (60 MHz, $CDCl_3$): 5.70 (br. *s*), and non-resolved signals between 1 and 3 ppm.

Reaction of **8b** *with 2,6-Dimethylpiperidine.* Compound **8b** (20 mg 0.05 mmol) was stirred for 5 d in 2,6-dimethylpiperidine (3 ml) at 25°. The amine was distilled off in rotary evaporator and the residue dried *in vacuo* for 30 min at 0.1 Torr. The ^{1}H-NMR spectrum indicated, that no reaction had taken place.

Reaction of **8b** *with 2,2,6,6-Tetramethylpiperidine.* Compound **8b** (20 mg, 0.05 mmol) was stirred for 14 d in 2,2,6,6-tetramethylpiperidine (3 ml) at 25°. The amine was distilled off in a rotary evaporator, and the residue was dried *in vacuo* for 2 h at 40°/0.1 Torr. The ^{1}H-NMR spectrum indicated, that no reaction had taken place.

Attempted Quaternization of **12**. *a)* Compound **12i** (150 mg 0.55 mmol) was stirred with MeI (1.0 ml, 15.20 mmol) in anh. Et_2O (20 ml) for 2 d, worked up by standard procedures, and dried *in vacuo* for 30 min at 25°/0.1 Torr. Yield: 120 mg brown syrup, tending to polymerization. Most likely some different quaternization products had been formed. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.00 (*t*); 2.50-2.85 (*m*); 3.00–3.85 (*m*); 5.94 (*s*); 6.30 (*d*, ^3J = 5); 7.25 (*d*, ^3J = 5).

b) Compound **12e** (120 mg, 0.41 mmol) was stirred with Me_2SO_4 (51 mg, 0.41 mmol) in anh. Et_2O (10 ml) for 1 d at 25°. Standard workup yielded a brown syrup tending to polymerization. All purification attempts failed.

Reaction of **12i** *with Na under NMR Control. a)* Compound **12i** (70 mg, 0.26 mmol) was reacted with Na at 25° according to [25]. After 6 h, the color became dark red-brown. The NMR signals of **12i** decreased, signals of a reaction product showed up. After 31 h, only traces of **12i** were left, after 55 h the reaction was complete. ^{1}H-NMR (270 MHz, (D_8)THF): 1.03 (*t*, CH_3, ^3J = 7.2); 2.71 (*q*, CH_2N); 5.55 (*s*). ^{13}C-NMR (100.63 MHz, (D_8)THF, SEFT): 16.1 (+, *q*, ^1J (C,H) = 125); 44.2 (–, *tq*, ^1J(C,H) = 131, ^2J(C,H) = 5); 65.3 (+, *d*, ^1J(C,H) = 130), 87.4 (–, *t*, ^2J(C,H) = 8), 132.9 (+, *d*, ^1J(C,H) = 161).

b) Compound **12i** (110 mg, 0.41 mmol) was reacted with Na at –30° according to the [25]. After 6 h, the mixture became dark red-brown. The NMR signals of **12i** decreased, the signals of the product obtained under *a* showed up. The reaction was complete after 66 h. ^{1}H-NMR (270 MHz, (D_8)THF): as under *a*. ^{13}C-NMR (50.31 MHz, (D_8)THF, SEFT): 16.5 (+); 44.6 (–); 45.2 (–); 65.5 (+); 87.6 (–); 133.1 (+); 133.3 (+). ^{13}C-NMR (50.31 MHz, (D_8)THF, DEPT): 16.5 (+); 44.6 (–); 45.2 (–); 65.5 (+); 133.1 (+); 133.3 (+). The signals at 133.1 and 133.3 ppm have the same intensity.

Reaction of **12e** *with Na under NMR Control.* Compound **12e** (30 mg, 0.10 mmol) was reacted with Na at 25° according to [25]. After 8 h, the mixture became dark red-brown. The NMR signals of **12e** decreased, the signals of a reaction product showed up. The reaction was complete after 107 h. Quenching experiment with MeOH *vide infra*. ^{1}H-NMR (270 MHz, (D_8)THF): 1.48 (*m*, CH_2); 2.34–2.63 (*m*, CH_2N); 3.30 (*s*); 5.31 (*s*). ^{13}C-NMR (100.62) MHz, (D_8)THF, SEFT): 26.0 (–, *t*, ^1J(C,H) = 126); 27.7 (–, *t*, ^1J(C,H) = 127); 50.5 (–, *t*, ^1J(C,H) = 130); 89.0 (–, *t*, ^2J(C,H) = 8); 133.1 (+, *d*, ^1J(C,H) = 162). Within several months, the intensity ratio of the ^{1}H-NMR signals at 5.31 and 3.30 ppm changed from 6:1 to 2.5:1.

Reaction of **12f** *with Na under NMR Control.* Compound **12f** (50 mg, 0.17 mmol) was reacted with Na under NMR control at 25° according to [25]. The mixture became dark red-brown after 6 h. The NMR signals of **12f** decreased, and the signals of a reaction product showed up. The reaction was complete after 107 h. ^{1}H-NMR (270 MHz, (D_8)THF): 2.37–2.76 (*m*, CH_2N); 3.63 (*m*, CH_2O); 5.45 (*s*). ^{13}C-NMR (67.93 MHz, (D_8) THF, SEFT): 49.2 (–, CH_2N); 50.0 (–, CH_2N); 58.3 (+); 68.1 (–, CH_2O); 88.6 (–); 133.2 (+).

Reaction of **12i** *with Na-K Alloy. a)* Compound **12i** (40 mg, 0.15 mmol) in anh. THF (5 ml) was stirred under Ar with Na-K alloy (0.3 ml, $NaK_{2.8}$) [27] for 24 h at 25°. The mixture became dark brown. The soln. was decanted under Ar into MeOH (10 ml) at –78°; the mixture was stirred for 12 h, allowing it to slowly warm up to 25°, and then was poured into H_2O (30 ml). The resulting mixture was extracted with *t*-BuOMe (3 × 30 ml). The combined org. phases were dried $MeSO_4$, filtered, and the solvent was distilled off in a rotary evaporator. The residue was chromatographed through 20 g of silica gel ($(t$-Bu$)_2O$/Et_3N 10:1, column 20 × 1 cm): 25 mg (0.07 mmol, 53%) *1,4,7-tris(diethylamino)tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene* (**9i**), colorless oil, which turns brown under the influence of air, purity ~95% (NMR). IR (film): 3050, 2970, 2930, 2870, 2800, 1470, 1450, 1370, 1340, 1210, 1100, 1030, 800, 750. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.01 (*t*, ^3J(1′,2′) = 7.2, 6 CH_3); 2.65 (*quint.*, 6CH_3CH_2); 2.77 (*s*, H–C(10)?); 5.55 (*s*, H–C(2(3,5,6,8,9))). ^{13}C-NMR (20.17 MHz, $CDCl_3$): 15.8 (*q*, C(2′)); 43.8 (*t*, C(1′)); 87.3 (*s*, C(1(4,7))); 132.8 (*d*, C(2(3,5,6,8,9))). MS (70 eV): 344 (M^+ + 1,2), 343 (M^+, 7), 272 (M^+ + H – $(C_2H_5)_2N$, 42), 271 (M^+ – $(C_2H_5)_2N$, 45), 242 (M^+ – $(C_2H_5)_2N$ – C_2H_5, 60), 227 (M^+ – $(C_2H_5)_2N$ – C_2H_5 – CH_3, 38), 199 (M^+ + H – $(C_2H_5)_2N$ – $2C_2H_5$ – CH_3, 50), 184 (M^+ – $(C_2H_5)_2N$ – $3C_2H_5$, 36), 170 (M^+ – $2(C_2H_5)_2N$ – C_2H_5, 100), 128 (M^+ + H – $3(C_2H_5)_2N$, 41), 127 (M^+ – $3(C_2H_5)_2N$, 18), 115 (18).

b) Compound **12i** (30 mg, 0.11 mmol) was reacted as described under *a*. MeOH was replaced by CH_3OD. 19 mg (0.05 mmol, 45%) of **9i**, no D incorporation (MS).

Trapping of the Reaction Product of **12e** *and Na.* Compound **12e** (30 mg, 0.10 mmol) was reacted with Na under NMR control at 25° according to [25]. After 60 d, the NMR tube was opened, and the content was poured into MeOH (10 ml) at –78° under Ar. After stirring for 2 h at –78°, the mixture was allowed to warm up to 25°, and was then poured into H_2O (30 ml). The mixture was extracted three times with $(t$-Bu$)_2O$. The combined org. phases were dried $MgSO_4$, filtered, and concentrated in a rotary evaporator to about 2 ml. Polymeric components were

removed by column chromatography through 10 g silica gel (*t*-BuOMe/Et_3N 10:1, column 10 × 1 cm) to give 44 mg of a dark brown, viscous syrup. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.4–1.8 (*m*); 2.2–2.6 (*m*); 3.36 (*s*); 5.44 (*s*). MS (70 eV): 592 (12), 508 (592 – $C_5H_{10}N$, 21), 424 (592 – $2C_5H_{10}N$, 8), 296 (592 – $2C_5H_{10}N$ – $C_{10}H_8$, 72), 212 (296 – $C_5H_{10}N$, 84), 211 (296 – $C_5H_{11}N$, 100), 128 (296 – $2C_5H_{10}N$, 79).

Reaction of **12i** *with Diethylamide.* Et_2NH (575 mg, 7.88 mmol) was stirred under Ar in anh. THF (8 ml) at 25° with Na-K alloy (0.3 ml; $NaK_{2.8}$) [27] for 6 h. The soln. was decanted under Ar into 35 mg (0.13 mmol) of **12i**, which previously had been dried for 2 h at 25°/0.1 Torr. The mixture was stirred for 20 h at 25°, poured into H_2O (50 ml) and then extracted with *t*-BuOMe (3 × 50 ml). The combined org. phases were dried ($MgSO_4$), filtered, the solvent was removed in a rotary evaporator, and the residue was dried *in vacuo* for 30 min at 25°/0.1 Torr. Yield 30 mg (0.11 mmol), 85%) of unreacted **12i**, identified by its ^{1}H-NMR spectrum.

Reaction of **8b** *with Diethylamide.* Et_2NH (1.0 g, 13.7 mmol) was stirred in anh. THF (10 ml) with Na-K alloy (0.5 ml; $NaK_{2.8}$) under Ar for 6 h at 25°. The soln. was cooled to –78°, and a soln. of **8b** (50 mg, 0.14 mmol) in anh. THF (3 ml) was added within 5 min. The mixture was warmed to 25° over a period of 1 h, then stirred for 2 d and decanted into H_2O (30 ml). The mixture was extracted with *t*-BuOMe (3 × 30 ml). The combined org. phases were dried ($MgSO_4$), filtered, and the solvent was removed in a rotary evaporator. The residue was dried for 30 min at 25°/0.1 Torr. Yield 30 mg (0.11 mmol), 82%) of **12i**, identified by its ^{1}H-NMR spectrum.

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