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STIBATRIPTYCENE

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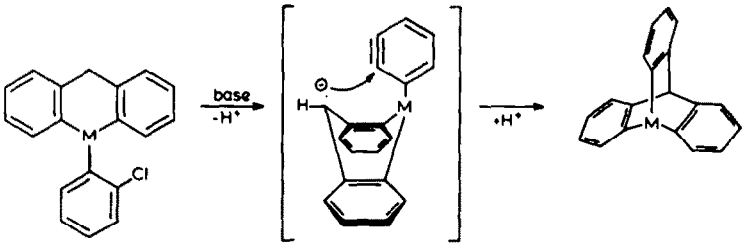
Abstract—Stibatriptycene (**1c**) has been synthesized by cyclization of 9-(o-chlorophenyl)-9,10-dihydro-9-stibaanthracene (**2c**) with an excess of lithium piperidide. The general applicability of this ring closure reaction, first developed for the synthesis of phosphatriptycene (**1a**) and presumed to proceed by nucleophilic attack of a carbanionic centre on a (slowly generated) benzyne, has further been demonstrated by a new synthesis of the known arsatriptycene (**1b**) and by the synthesis of stibatriptycene (**1c**). The structure of **1c** was confirmed by IR, ^{1}H NMR and, in particular, by ^{13}C NMR spectroscopy.

Triptycenes with hetero atoms at bridgehead positions are of interest because of their rigid spatial structure, which is of influence on the bonding situation and the reactivity of the hetero atom. Several hetero triptycenes have been prepared with the use of widely different synthetic approaches.[1-7] We have synthesized phosphatriptycene (**1a**) by cyclization of 9 - (*o* - chlorophenyl) - 9,10 - dihydro - 9 - phosphaanthracene (**2a**) with an excess of lithium diisopropylamide, presumably by attack of the carbanionic centre in **3** on the benzyne.[7]



2a M=P
2b M=As
2c M=Sb

3

1a M=P
1b M=As
1c M=Sb

As it seemed feasible that this approach furnished a general route for the synthesis of triptycenes with both a hetero atom and a C atom in the bridgehead positions, we investigated this reaction for the corresponding arsenic and antimony compounds (**2b** and **2c**, respectively) in order to obtain arsatriptycene (**1b**)[6] and the unknown stibatriptycene (**1c**). The C–M bond length increases from P to Sb, which, according to models, causes a greater distance between the two reacting centers (carbanion and benzyne in **3**). It was therefore to be expected that the ring closure reaction would be more difficult for As and perhaps impossible for Sb, especially as the relatively weak C–Sb bond was more prone to cleavage under the reaction conditions. It was therefore decided to check the applicability of this approach by the synthesis of the known **1b**.[6]

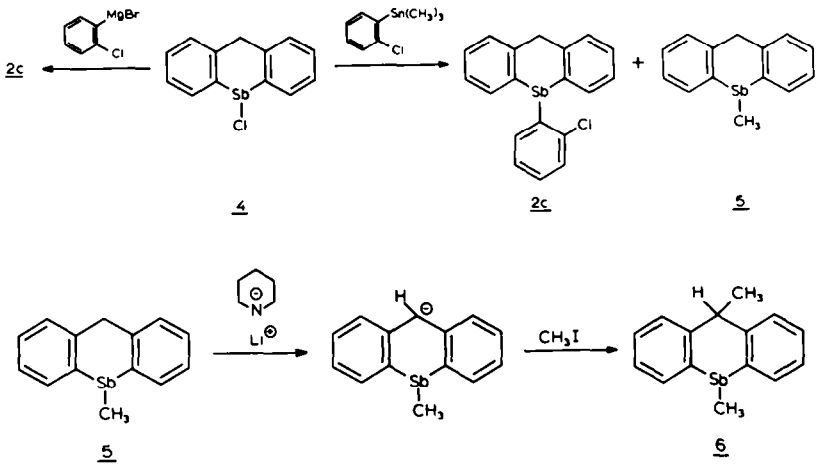
Compound **2b** was synthesized in 75% yield by reaction of 9 - chloro - 9,10 - dihydro - 9 - arsaanthracene with *o*-chlorophenylmagnesium bromide. Indeed, ring closure to **1b** was achieved by treatment of **2b** with excess of lithium diisopropylamide in ether, as described for **1a**,[7] but the yield of 16% was, expectedly, lower than that obtained for **1a** (35%).[7]

It was therefore desirable to improve the yield of this method before applying it to the preparation of the even more evasive **1c**.

As evidenced by the immediate appearance of an intense red colour, the formation of the carbanion with lithium diisopropylamide is very rapid. In contrast, benzyne formation is a rather slow process, and thus the carbanionic centre has a chance to decompose along alternative reaction pathways. If this reasoning is correct, enhancement of the rate of benzyne formation could be expected to improve the yield of the heterotriptycene. The reaction was therefore performed with lithium piperidide as a base, which is known to cause benzyne formation much faster than lithium diisopropylamide.[8] Indeed, the yield of **1b** was found to be 27% under the new conditions, and we now turned our attention to the synthesis of **1c**.

Compound **2c** was prepared by reacting **4**[9] with *o*-chlorophenylmagnesium bromide. However, the yield of **2c** was relatively low (15%) and **2c** was difficult to obtain in pure form. In the reaction of **4** with *o*-chlorophenyltrimethyltin we obtained pure **2c** in a 28% yield, and the main product was **5** (51% yield); the separation of the two products by sublimation posed no problems.

In view of the known instability of antimony phenyl bonds against bases,[10] it was doubtful whether carbanions



such as required in our procedure (*cf* **3**) would be sufficiently stable. For this reason carbanion formation of **5** was studied as a model reaction.

When **5** was reacted with lithium piperidide, the solution immediately turned intense red, indicating the formation of the carbanion. After addition of methyl iodide the solution decolourized and 9,10 - dimethyl - 9,10 - dihydro - 9 - stibaanthracene (**6**) was isolated in 65% yield (one isomer only).

After these preliminary investigations, the stage was set for the synthesis of stibatriptycene (**1c**), which was prepared by the reaction of **2c** with an excess of lithium piperidide in 20% yield; not surprisingly, lithium diisopropylamide as base yielded 8% **1c** only. Recrystallization of **1c** from ethanol gave white crystals. The m.p. (177–178°) of **1c** continues the decreasing line observed in this series (azatriptycene,[2] m.p. 266–267°; triptycene, m.p. 259–260°; **1a**, m.p. 242–243°; **1b**, m.p. 224–226°), which probably largely reflects the decreasing degree of symmetry of the molecules and of their crystal packing.

The UV spectrum of **1c** shows only one shoulder at 273 nm and the IR spectrum has only a few absorptions, as is typical for the other triptycenes, because of the relatively high symmetry of the molecule. The mass spectrum of **1c** shows a molecular ion at *m/e* 362, and doubly and triply charged ions of relatively high intensities. In contrast to other heterotriptycenes **1a** and **1b** where the molecular ion is the base peak, the base peak of **1c** is *m/e* 241, which arises by expulsion of antimony from the molecular ion. This is comprehensible when we consider the weaker antimony-carbon bond compared to the phosphorus- and arsenic-carbon bond, but possibly the greater ring strain in stibatriptycene compared to **1a** and **1b** reinforce this effect.

The ^{1}H NMR spectrum of **1c** is of the $(ABCD)_3X$ type, where X represents the bridgehead proton. It is presented in Fig. 1 together with the simulated spectrum.

Protons 2 and 3 are expected to be at higher field than protons 1 and 4, because the latter give rise to one *ca.* 7 Hz doublet only. In first approximation the ABCD-part of the spectrum may be analyzed as an ABXY-system. As shown in Fig. 2, its AB-part is easily decomposed into four ab-subspectra, the centers of which are given by: $(\nu_2+J_{12}+J_{24},\ \nu_3+J_{13}+J_{34})$, $(\nu_2+J_{12}-J_{24},\ \nu_3+J_{13}-J_{34})$, $(\nu_2-J_{12}+J_{24},\ \nu_3-J_{13}+J_{34})$ and $(\nu_2-J_{12}-J_{24},\ \nu_3-J_{13}+J_{34})$. In Fig. 2 it is assumed that J_{12}, J_{24}, J_{13} and J_{34} have the same sign. If J_{12} and J_{34} had opposite signs the line intensities would have been quite different. The relative signs of J_{13} and J_{24} can only be assessed by a more rigorous analysis. The values of coupling constants and chemical shifts obtained in this way were used as initial values in the simulation program LAOCOON III.[11] The theoretical lines were then attributed to the experimental lines and subsequently the spectral parameters were varied iteratively, until the best fit was obtained. The errors in the experimental line positions were estimated to fall into the range $0.4\ \text{Hz} > \Delta\delta > 0.1\ \text{Hz}$, depending on the line width. In the program, the reciprocal estimated errors were used as relative weights of the line positions. The best fit was obtained with the parameters given in Table 1. Iterations based on theoretical spectra calculated with different relative signs of J_{12}, J_{24}, J_{13} and J_{34}, gave significant

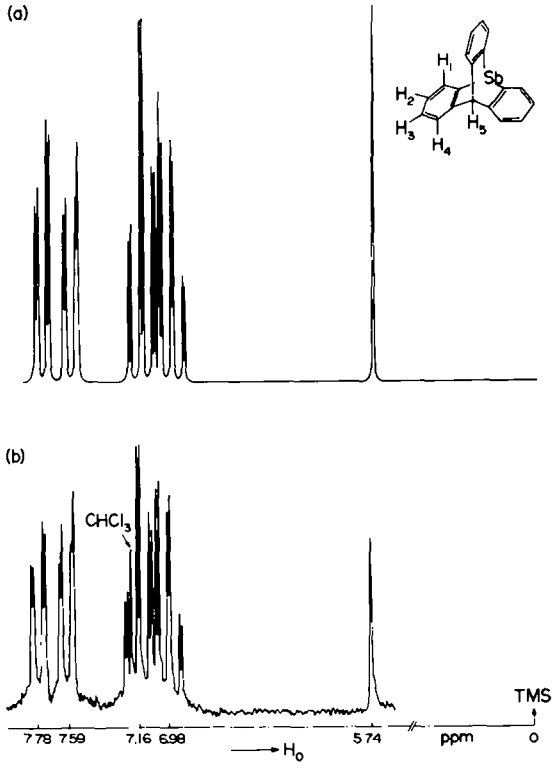


Fig. 1. (a) Simulated proton spectrum of stibatriptycene (**1c**) with the parameters used in Table 1. (b) 100 MHz proton spectrum of **1c** in $CDCl_3$ (δ in ppm, downfield from internal TMS).

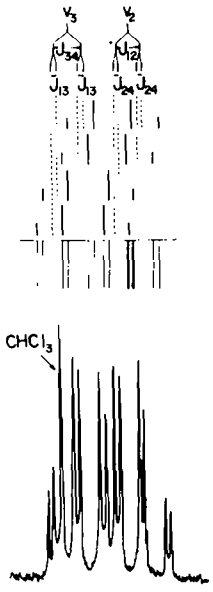


Fig. 2. Subspectral decomposition of the AB-part. Coupling constants J_{12}, J_{24}, J_{13} and J_{34} are assumed to have the same relative signs.

Table 1. Calculated proton chemical shifts (in δ ppm, downfield from internal TMS) and proton-proton coupling constants in stibatriptycene (**1c**)

Chemical shifts		Indirect spin-spin coupling constants
1[a]	7.78	$J_{12} = 7.26 \pm 0.03$[b]
2	6.98	$J_{13} = 1.30 \pm 0.03$
3	7.16	$\lvert J_{14}\rvert = 0.46 \pm 0.07$
4	7.59	$\lvert J_{23}\rvert = 7.43 \pm 0.02$
5	5.74	$J_{24} = 1.06 \pm 0.03$
		$J_{34} = 7.61 \pm 0.03$
		$\lvert J_{45}\rvert = 0.3 \pm 0.1$

[a] See Fig. 1 for proton numbers
[b] Errors are probably errors of the fit. Overall rms error was 0.775 Hz

deviations from the experimental spectrum with respect to the relative line intensities. Thus, we conclude that these couplings must have the same relative sign. It should be noted that the simulations have been based on a five spin ABCDX system, assuming $|J_{CX}| = |J_{45}|$ to be 0.3 Hz. The calculated height of the X-peak was reduced afterwards by a factor of three. It is obvious that the line width of the X-peak, calculated in this way may be substantially too small, as the couplings with the protons of the other two benzene rings give a more complex superposition pattern. The error in the J_{45} value is consequently large and estimated to be 0.1 Hz. J_{45} causes additional line broadening in proton 4 and J_{15} may be neglected; therefore, the sharper resonance at lowest field is assigned to proton 1. It seems that although the electronegativity of the hetero atom undoubtedly influences the chemical shift of proton 1 (expected shift to higher field), the anisotropy of the hetero atom is predominating.

The ^{13}C-NMR spectrum is very characteristic in confirming the structure of **1c**. It shows only seven lines which can be ascribed to the seven types of carbon atoms (Fig. 3).

It was difficult to make the assignment of the different C atoms. In first approximation the assignment of the C atoms was made by comparing the ^{13}C-NMR spectrum of **1c** with that of **1a**, where the assignment of C_7, C_1, C_6 and C_2 had been made on the basis of the off resonance spectrum and the $J_{P\text{-}C}$ coupling constants,[7] but the assignment of C_3, C_4 and C_5 was arbitrary (Table 2). However, the carbon chemical shifts could be calculated to a good approximation in a simple additive fashion.

The following assumptions were made:[12]

(a) The relative ^{13}C chemical shifts of aromatic carbon atoms bearing the substituent (C-X) are mainly influenced by inductive and magnetic anisotropy effects of the substituent.

(b) For *ortho*-C atoms this influences diminishes and resonance effects are predominating.

(c) *Meta* C atoms experience small shifts only and no correlation with the properties of the substituent is possible.

(d) The chemical shifts of *para*-C atoms is influenced only by resonance effects (see Table 3 and Ref. 13).

We concluded from these considerations that if more than a single substituent is present, it might be possible, to calculate the chemical shifts for all benzene ring C atoms, by adding up the separate effects of the individual substituents at the benzene C atoms (Tables 3 and 4). To verify this approach we calculated the carbon chemical shifts for a number of substituted benzene derivatives and compared these with the observed carbon chemical shifts[16] (the values for *o*-cresol are given as an example of the calculation; see Table 4).

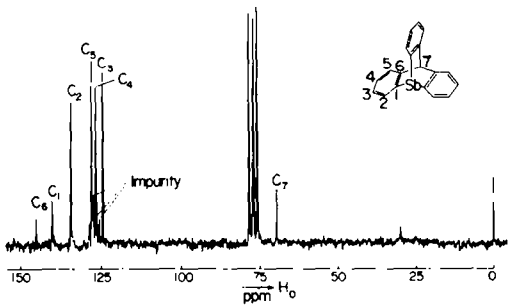


Fig. 3. 25.2 MHz proton noise decoupled natural abundence ^{13}C-FT NMR spectrum (6400 pulses) of stibatriptycene (**1c**) (2% w/w solution in $CDCl_3$, 10 mm tube). Chemical shifts are given in ppm relative to internal TMS.

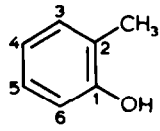
Table 2. Carbon chemical shifts (δ in ppm relative to internal TMS) and assignment of the carbon atoms (see Fig. 3 for carbon numbering) for phosphatriptycene (**1a**) and stibatriptycene (**1c**) and the calculated spectra (with the data from Table 3)

	1a		**1c**	
	Calculated	Observed	Calculated	Observed
C_6	149.6	149.21	152.6	146.27
C_1	137.9	140.79	139.7	141.23
C_2	133.1	132.44	136.1	135.18
C_5	129.0	128.39	129.8	128.57
C_4	128.1	125.56	128.5	127.24
C_3	125.9	125.28	126.7	125.10
C_7		59.74		69.35

Table 3. Aryl ^{13}C chemical shifts in monosubstituted benzene derivatives C_6H_5X

Subst. (X)	δC, ppm from TMS C-1	*ortho*	*meta*	*para*	Δ_x', ppm from C_6H_6 (128.7 ppm) C-1	*ortho*	*meta*	*para*
1 OH	155.6	116.1	130.5	120.8	+26.9	−12.6	−1.8	−7.9[13]
2 CH_3	137.7	129.3	128.5	125.6	+9.0	+0.6	−0.2	−3.1[12]
3 $Sb(C_6H_5)_2$	139.3	136.8	129.4	129.2	+10.6	+8.1	+0.7	+0.5[14]
4 $P(C_6H_5)_2$	137.5	133.8	128.6	128.8	+8.8	+5.1	−0.1	+0.1[15]
5 $CH(C_6H_5)_2$	143.6	129.1	128.0	126.0	+15.8	+0.4	−0.7	−2.7[16]

Table 4. Carbon chemical shifts (δ in ppm relative to internal TMS) and assignment of the carbon atoms for *o*-cresol[12] and the calculated spectrum (with the data from Table 3)



	C_1	C_2	C_3	C_4	C_5	C_6
Δ_{OH}'	+26.9	−12.6	+1.8	−7.9	+1.8	−12.6
Δ_{CH_3}'	+0.6	+9.0	+0.6	−0.2	−3.1	−0.2
$\Delta_X' + 128.7$	+27.5	−3.6	+2.4	−8.1	−1.3	−12.8
calculated	156.2	125.1	131.1	120.6	127.4	115.9
observed[12]	155.9	124.9	130.9	121.4	127.2	115.7

For 15 substituted benzenes the calculated chemical shifts agreed very well with the experimental ones. Using the substituent effects given in Table 3, the carbon chemical shifts of **1a** and **1c** were calculated (Table 2). The good agreement between the calculated and experimental shifts makes the assignments quite reliable; only for C_3, C_4 and C_5 the degree of confidence is somewhat less because of the small differences in chemical shift.

EXPERIMENTAL

M.ps are uncorrected. Mass spectra were recorded on a Varian MAT CH-5 double focussing mass spectrometer with electron impact at 70 eV. ^1H NMR spectra were recorded with a Varian XL-100/12 WG spectrometer. Chemical shifts are given in δ (ppm) from internal TMS. The IR spectra were recorded with a Perkin-Elmer 237 and the UV spectra with a Perkin-Elmer spectrophotometer, model 137. Elemental analysis were performed under supervision of Mr. W. J. Buis at the Microanalytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

9 - (o - *Chlorophenyl*) - 9,10 - *dihydro* - 9 - *arsaanthracene* (**2b**). A soln of the Grignard compound, prepared from *o*-chlorobromobenzene (15.1 mmole) and Mg (18.1 mmole) in dry ether (25 ml) was added at −70° to a soln of 9 - chloro - 9,10 - dihydro - 9 - arsaanthracene (7.25 mmole) in dry ether (50 ml). After stirring overnight at room temp., a few drops of H_2O were added to the red soln, which decolourized immediately; then the soln was evaporated *in vacuo*. Sublimation of the residue (150°/0.1 mm) yielded **2b** (1.89 g, 75%), m.p. 120–122° [Found: C, 64.51; H, 4.16; Cl, 9.70; $C_{19}H_{14}AsCl$ (M = 352.68), requires: C, 64.70; H, 4.00; Cl, 10.05%]. NMR ($CDCl_3$): 7.89–7.62 (m, 2, aryl protons), 7.52–6.67 (m, 10, aryl protons), 3.95 and 3.77 (AB system, 2, methylene protons, J_{AB} = 17 Hz). Mass spectrum *m/e* (%): 354 (10), 353 (7), 352 (32), 241 (34), 240 (41), 188 (6), 186 (18), 166 (73), 165 (100).

9,10 - *Dihydro* - 9,10 - o - *benzeno* - 9 - *arsaanthracene* (*arsatriptycene*, **1b**). n-BuLi (18 mmole) in n-hexane (5 ml) was added at 0° under N_2 to a soln of diisopropylamine (23 mmole) in dry ether (25 ml) and after stirring for 15 min a soln of **2b** (3.8 mmole) in dry THF (5 ml) was added. After stirring for 3 days at room temp. the deep red soln was poured into H_2O (100 ml). The ethereal layer was separated, washed, dried and evaporated to dryness. Sublimation of the residue (180°/0.1 mm) followed by crystallization (EtOH) yielded **1b** (192 mg, 16%), m.p. 207–210°. The NMR spectrum of the product was identical with an authentic sample.[6]

n-BuLi (6.55 mmole) was added at 0° under N_2 to a soln of piperidine (8.40 mmole) in dry ether (20 ml) and after stirring for 15 min a soln of **2b** (1.31 mmole) in dry THF (5 ml) was added. After stirring for 1 day at room temp. the deep red soln was decolourized and the mixture was worked up as described above, yielding **1b** (112.4 mg, 27%), m.p. 219–221°.

9 - *Chloro* - 9,10 - *dihydro* - 9 - *stibaanthracene* (**4**).[9] A mixture of antimony trichloride (24.4 mmole) and 9,9 - dimethyl - 9,10 - dihydro - 9 - stannaanthracene (23.3 mmole) was heated for 5 hr at 140° under N_2. Dimethyltin dichloride was sublimated off (70°/1 mm) and the residue crystallized from n-hexane yielding **4** (6.2 g, 82%), m.p. 101–103° (lit.[9], 105°[9a], 89°[9b], 102°[9c]). NMR ($CDCl_3$): 8.00–7.75 (m, 2, aryl protons), 7.75–7.16 (m, 6, aryl protons), 4.36 (s, 2, methylene protons). Mass spectrum *m/e* (%): 326 (0.5), 324 (1.8), 322 (1.7), 289 (1.9), 288 (4.0), 287 (2.6), 286 (4.9), 167 (14), 166 (100), 165 (54).

o-*Chlorophenyltrimethyltin*[17]. To a filtered Grignard soln, prepared from *o*-chlorobromobenzene (49 mmole) and Mg (75 mmole) in dry ether (70 ml) trimethyltin chloride (38 mmole) in dry ether (25 ml) was added in 1 hr. After stirring overnight the soln was filtered, evaporated to dryness and distilled *in vacuo* yielding *o*-chlorophenyltrimethyltin (8.3 g, 79%), b.p. 60°/1 mm (lit.[17], 47°/0.5 mm). NMR ($CDCl_3$): 7.52–7.03 (m, 4, aryl protons), 0.34 (s, 9, methyl protons, $^2J_{Sn^{117}-H}$ = 27 Hz, $^2J_{Sn^{119}-H}$ = 29 Hz).

9 - (o - *Chlorophenyl*) - 9,10 - *dihydro* - 9 - *stibaanthracene* (**2c**) *and* 9 - *methyl* - 9,10 - *dihydro* - 9 - *stibaanthracene* (**5**). Under N_2 **3** (5.37 mmole) and *o*-chlorophenyltrimethyltin (5.42 mmole) were heated at 180° under stirring for 14 hr. As the reaction proceeded white crystals were formed, which were identified as trimethyltin chloride. After cooling the crude mixture was purified by elution from a basic Al_2O_3-column with CCl_4, followed by sublimation at 85°/0.1 mm, yielding **5** and at 105°/0.1 mm yielding **2c** (600 mg, 28%), m.p. 119–121°. [Found: C, 56.87; H, 3.65; Cl, 8.30. $C_{19}H_{14}ClSb$ (M = 399.50), requires: C, 57.12; H, 3.53; Cl, 8.87%]. NMR ($CDCl_3$): 7.96–7.70 (m, 2, aryl protons), 7.60–7.12 (m, 8, aryl protons), 7.12–6.97 (m, 2, aryl protons), 3.92 and 3.86 (AB system, 2, methylene protons, J_{AB} = 3 Hz). Mass spectrum *m/e* (%): 400 (5), 398 (5), 364 (2), 362 (1), 288 (12), 286 (15), 234 (50), 232 (47), 199 (9), 197 (11), 166 (51), 165 (100). **5** (831 mg, 51%) had the following characteristics: m.p. 84–86° (lit.[9a], 101°, crystallized from CH_2Cl_2/CH_3OH). [Found: C, 55.41; H, 4.41. $C_{14}H_{13}Sb$ (M = 302.99), requires: C, 55.49; H, 4.32%]. NMR ($CDCl_3$): 7.70–7.48 (m, 2, aryl protons), 7.48–6.98 (m, 6, aryl protons), 4.07 and 3.94 (AB system, 2, methylene protons, J_{AB} = 8 Hz), 1.17 (s, 3, methyl protons). Mass spectrum *m/e* (%): 303 (30), 301 (40), 288 (58), 286 (78), 166 (98), 165 (100).

9,10 - *Dimethyl* - 9,10 - *dihydro* - 9 - *stibaanthracene* (**6**). By means of a hypodermic syringe a soln of lithium-piperidide (0.66 mmole), prepared from piperidine (0.75 mmole) and n-BuLi (0.66 mmole) in dry THF (5 ml) was added dropwise under N_2 to a stirred soln of **4** (0.66 mmole) in dry THF (10 ml). The soln turned red immediately and after stirring for 30 min, MeI (1.3 mmole) was added. After the colour had disappeared, a ppt was formed (N-methylpiperidinum iodide), which was filtered off. The filtrate was evaporated *in vacuo* and the residue was sublimed (75°/0.6 mm) yielding **6** (137 mg, 65%), m.p. 95–98°. [Found: C, 56.23; H, 4.57. $C_{15}H_{15}Sb$ (M = 317.02), requires: C, 56.83; H,

4.77%]. NMR ($CDCl_3$): 7.68–7.07 (m, 8, aryl protons), 4.35 (q, 1, methine proton, $^3J_{H-H} = 8$ Hz), 1.41 (d, 3, methyl protons, $^3J_{H-H} = 8$ Hz), 1.12 (s, 3, methyl protons). Mass spectrum *m/e* (%): 318 (5), 316 (6), 303 (8), 301 (10), 288 (5), 286 (5), 225 (17), 223 (23), 179 (80), 165 (100).

9,10 - *Dihydro* - 9,10 - o - *benzeno* - 9 - *stibaanthracene* (*stibatriptycene*, **1c**). Lithium piperidide (3.03 mmole) in THF (5 ml) and n-hexane (1 ml) was added dropwise to a stirred soln of **2c** (1.01 mmole) in dry THF (20 ml) under argon. Gradually, the soln turned dark red and after 3 days of stirring the soln decolourized and MeI (5 mmole) was added in order to remove the piperidine. The ppt (see **6**) was filtered off and the filtrate was evaporated to dryness. Sublimation of the residue (170°/0.01 mm) followed by column chromatography (basic Al_2O_3, $CHCl_3$ as eluent) and crystallization (EtOH) yielded **1c** (75 mg, 20%), m.p. 177–178°. [Found: C, 62.42; H, 3.54. $C_{19}H_{13}Sb$ (M = 363.04), requires: C, 62.85; H, 3.61%]. NMR: see fig. and Tables 1 and 3. IR (KBr) ν_{max} in cm^{-1}: 3050 (m), 2930 (m), 1455 (m), 1440 (s), 1275 (m), 845 (m), 760 (s), 735 (s), 700 (m). UV (96% ethanol) λ_{max} (log ϵ): 273 sh (3.10). Mass spectrum *m/e* (%): 365 (6), 364 (31), 363 (12), 362 (42), M^+ ($C_{19}H_{13}$ ^{121}Sb), 360 (4), 242 (22), 241 (100), 240 (25), 239 (62), 238 (6), 237 (12), 226 (9), 215 (5), 213 (5), 181 (2), M^{2+}, 165 (25), 164 (12), 163 (15), 139 (9), 123 (4), 121 (6), 120 2/3 (0.3), M^{3+}.

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