

Synthesis of 9-Methylene-9,10-dihydroanthracene by Lithium Aluminium Hydride Reduction of (9-Anthrylmethyl)trimethylammonium Chloride

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Treatment of (9-anthrylmethyl)trimethylammonium chloride (2a) with 1 mol equiv. of lithium aluminium hydride (LAH) in refluxing tetrahydrofuran gave predominantly 9-methylene-9,10-dihydroanthracene (3a). However, reaction with 3 mol equiv. of LAH gave a mixture of 9-methyl-9,10-dihydroanthracene (5a) and 9-(9-anthrylmethyl)-9-methyl-9,10-dihydroanthracene (6a), these products being formed by processes involving nucleophilic attack of excess of LAH on compound (3a).

9-Alkylidene-9,10-dihydroanthracene derivatives are generally unstable relative to 9-methylanthracenes: they have been isolated in crowded systems, where the geometry and rigidity of the latter forms are disadvantageous.¹⁻⁵ Consistent with this, semi-empirical SCF- π -molecular orbital studies have revealed that the parent 9-methylene-9,10-dihydroanthracene (3a) is less stable than 9-methylanthracene (4a) by *ca.* 40 kJ mol⁻¹.^{6,†} We were interested in the synthesis of compound (3a) and considered that lithium aluminium hydride (LAH) reduction of (9-anthrylmethyl)trimethylammonium chloride (2a) might be most promising; Jaeger and Kornblum¹ have found that the reaction of the quaternary ammonium chloride (2a) with a stoichiometric amount of the lithium salt of 2-nitropropane gives the corresponding 9-methylene-9,10-dihydroanthracene [equation (1)], this being in marked contrast to the exclusive formation of the anthracene derivative from 9-(chloromethyl)anthracene (1a) [equation (2)]. These results led us to deduce that, in the former reaction, the bulky leaving group with poor leaving ability, trimethylamine, compels the nucleophile to attack the less hindered C-10 atom.

Results and Discussion

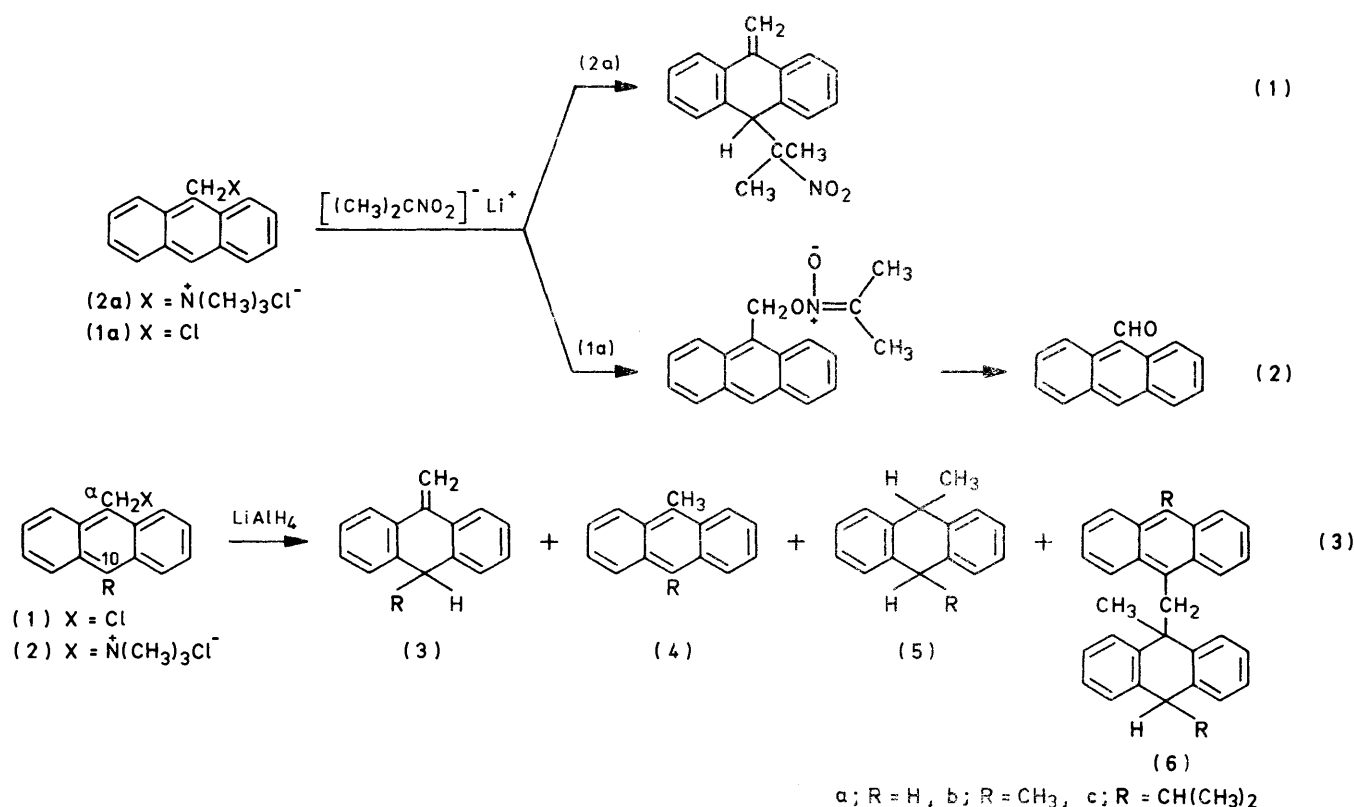
Reaction of equimolar quantities of LAH and the salt (2a) at 70 °C for 1 h under nitrogen, followed by work-up, gave a crude product; n.m.r. analysis of the diethyl ether-soluble products indicated the formation of compounds (3a) and (4a) in the ratio 95 : 5. 9-Methylene-9,10-dihydroanthracene (3a) was isolated by recrystallization from light petroleum. The ¹H n.m.r. assignments (Experimental section) are consistent with the vinylic protons of 9-methylene-1,5,10-trimethyl-9,10-dihydroanthracene and the methylene protons of 9-benzylidene-9,10-dihydroanthracene appearing at δ 5.41² and 3.95,⁴ respectively. The reactions of the salts (2b, c) under the same conditions also gave predominantly the corresponding 9-methylene-9,10-dihydroanthracenes (3b, c), together with lesser amounts of (4b, c), 9-methyl-9,10-dihydroanthracenes (5b, c), and 9-(9-anthrylmethyl)-9-methyl-9,10-dihydroanthracenes (6b, c) [Table 1 and equation (3)]. Reaction of the salts

(2a—c) in refluxing diethyl ether was very slow; the products were a mixture of 9-methylene-9,10-dihydroanthracenes (3a—c) and 9-methylanthracenes (4a—c) (Table 2). In marked contrast, treatment of the 9-(chloromethyl)anthracenes (1a—c) with LAH in THF or diethyl ether at 20 °C gave exclusively the anthracenes (4a—c) [equation (3)].

To obtain an insight into the mechanisms of these reactions, reduction with lithium aluminium deuteride (LAD) was investigated. Treatment of compounds (1a—c) with an equimolar amount of LAD in refluxing THF yielded exclusively compounds (4a—c; α -D), as expected. The reaction of the salt (2a) gave, however, a mixture of compounds (3a; 10-D) and (4a; α -D) in the ratio 98 : 2. These results may be most easily explained by the competitive participation of two reaction processes, *i.e.* S_N2 and S_N2', the proportion of attack at the less hindered C-10 position (S_N2') being increased as the steric bulk at the site of the leaving group (C- α) increases.

The reaction of the salts (2a—c) with 3 mol equiv. of LAH in refluxing THF gave a mixture of compounds (4a—c), (5a—c), and (6a—c); the formation of the methylene anthracenes (3a—c), the major products in the reaction with an equimolar amount of LAH, was not observed (Table 1). In contrast, the 9-methylene-9,10-dihydroanthracenes (3a—c) were again the major products in the reaction in diethyl ether (Table 2); the absence of products (5a, b) and (6a, b) was not due to the relatively low temperature of the reaction in refluxing diethyl ether, since the reaction of compound (2a) in THF at 35 °C gave a mixture of compounds (4a), (5a), and (6a) (Table 1). The following facts suggest that the 9-methyl-9,10-dihydro-9-anthryl carbanions (7a, b) are reasonable intermediates leading to the products (5a, b) and (6a, b) [Scheme and equation (4)]. (a) The reaction of salt (2a) with 3 mol equiv. of LAD provided a mixture of compounds (4a; α -D), (4a; α -, 10-D₂), (5a; α -, 10-D₂), and (6a; D₂-form) in the proportions 1 : 2 : 14 : 3; (b) treatment of salt (2b) with 3 equiv. of LAH, followed by work-up with deuterium oxide, gave a mixture of compounds (4b), (5b; 9-D), and (6b); (c) the ammonium salt (2a) was treated with 1 mol equiv. of LAD in refluxing THF for 1 h; an aliquot was decomposed by water to give a mixture of compounds (3a; α -D) (59%) and (6a; D₂-form) (3%). Then, 2 mol equiv. of LAD was added to the remaining solution and the mixture was stirred for a further 1 h. From the reaction mixture were obtained the products (4a; α -D), (4a; α -, 10-D₂), (5a; α -, 10-D₂), and (6a; D₂-form) in the proportions 1 : 2 : 13 : 4; (d) the reactions of 9-methyl-9,10-dihydroanthryl carbanions, generated *in situ* by treatment of the 9-methyl-9,10-dihydroanthracenes (5a, b) with *n*-butyl-lithium, with the salt (2a, b) gave the expected 9-(9-anthrylmethyl)-9,10-dihydroanthracenes [equation (4)].

† It has been claimed that 9-alkylidene- and 9-arylidene-9,10-dihydroanthracenes, including compound (3a), are synthesized by the reaction of the corresponding phosphonium ylides with 9-anthrone in refluxing benzene (R. S. Tewari, K. C. Gupta, and D. S. Kendurkar, *J. Chem. Eng. Data*, 1977, 22, 351). The reported n.m.r. spectrum of, *e.g.*, 9-benzylidene-9,10-dihydroanthracene [δ 1.30 (2 H, s, CH₂)] is, however, not consistent with the structure, since these hydrogens should appear at *ca.* δ 3.95.⁴ For compound (3a), the literature physical properties except its m.p. (156—158 °C) have not been cited.

Table 1. Reaction of salts (2) with LAH in THF^a

Substrate	Molar proportion of LAH	Reaction temperature (°C)	Isolated yields (%) of products			
			(3)	(4)	(5)	(6)
(2a)	1	70	48	3		4
	3	35		19	38	32
	3	70		17	38	25
(2b)	1	70	48	3	8	14
	3	35		8	34	31
	3	70		8	23	45
(2c)	1	70	35	2	5	33
	3	70		2	12	20

^a The reaction was performed for 1 h under nitrogen.Table 2. Reaction of salts (2) with LAH in diethyl ether^a

Substrate	Molar proportion of LAH	Isolated yields (%) of products	
		(3)	(4)
(2a)	1	32	6
	3	8	5
(2b)	1	40	7
	3	44	8
(2c)	1	33	1
	3	50	10 ^b

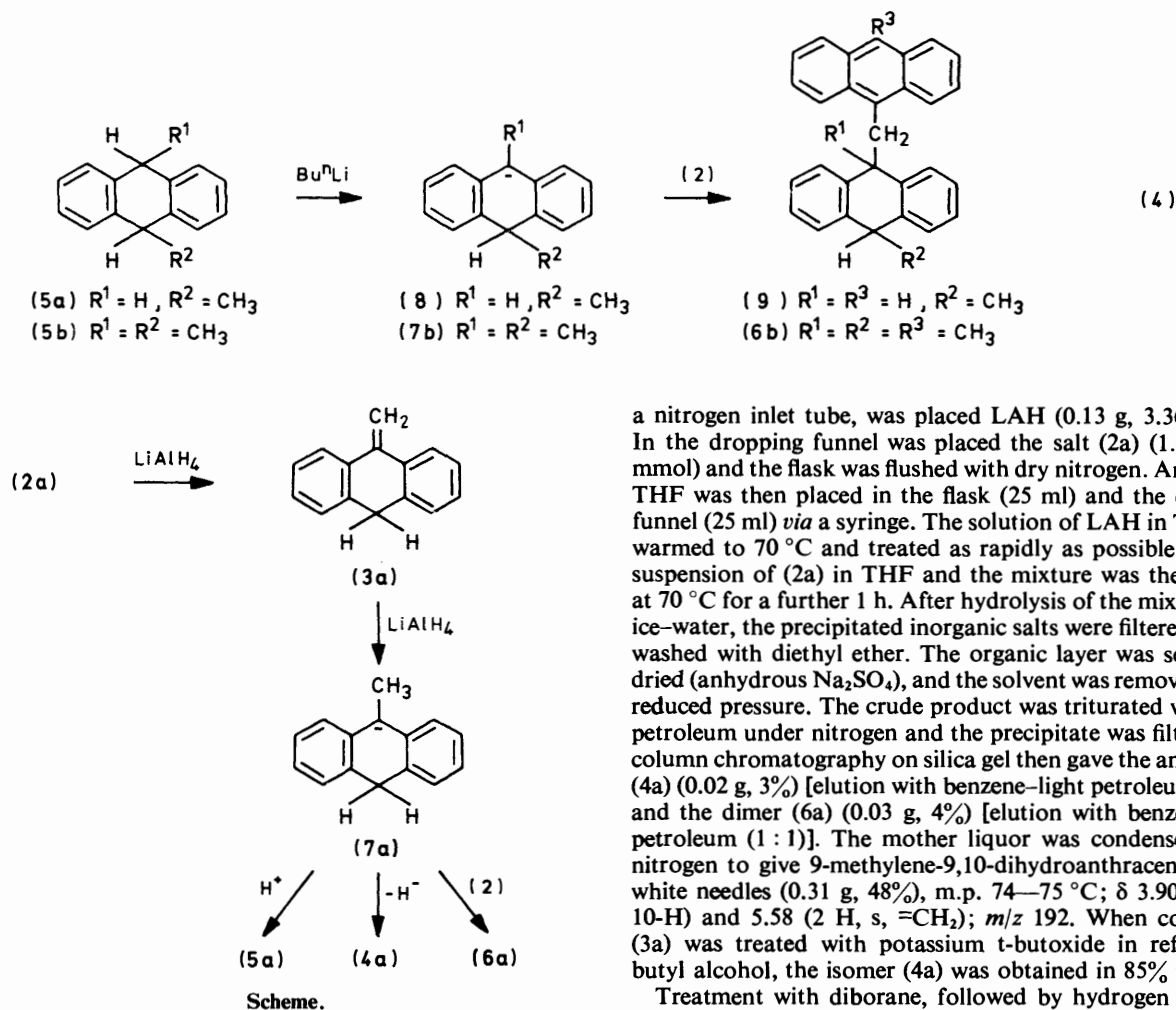
^a The reaction was performed at 35 °C for 5 h under nitrogen.^b Together with compounds (3c) and (4c), (5c) and (6c) were also obtained (in yields of 17 and 14%, respectively).

The mechanism shown in the Scheme seems to illustrate the reaction of the salt (2a) with LAH most reasonably. The first step of the reaction involves nucleophilic attack of LAH on the C-10 atom of the salt (2a) to give compound (3a). In the presence of excess of LAH, attack of this reagent on (3a)

occurs to yield 9-methyl-9,10-dihydro-9-anthryl carbanion (7a); similar attack of LAH on carbon-carbon double bonds has been observed with 9-methylenexanthenes⁷ and 1,1-diphenylethylene.⁸ Protonation of the anion (7a) gives the dihydroanthracene (5a), while loss of hydride ion from (7a) provides the anthracene (4a). The reaction of (7a) with the salt (2a) explains the formation of the dimer (6a). The formation of compounds (5a) and (6a), specifically observed in the reaction in THF, can be interpreted as being due to the increased nucleophilicity of LAH in this solvent, since THF has a higher co-ordinating ability toward lithium cation than does diethyl ether.

Experimental

¹H N.m.r. spectra were obtained with a JEOL LMN 4P100 instrument for CDCl₃ solutions unless otherwise noted, and mass spectra with a Hitachi RMV-6H spectrometer. Tetrahydrofuran and diethyl ether were distilled from lithium aluminium hydride under nitrogen. Light petroleum refers to



that fraction boiling in the range 40–70 °C. 9-(Chloromethyl)-anthracene (1a)⁹ and 9-(chloromethyl)-10-methylanthracene (1b)¹⁰ were prepared by the reported methods. 9-(Chloromethyl)-10-isopropylanthracene (1c) was prepared from 9-isopropylanthracene by the modification of the reported method,⁹ and had m.p. 136–137 °C (from benzene–light petroleum); δ 1.77 (6 H, s), 4.57 (1 H, septet), and 5.43 (2 H, s). LAH was commercial grade and was used without purification.

Preparation of Ammonium Salts (2a–c).—Dry trimethylamine gas was bubbled through a solution of compound (1a) (5.0 g) in dry THF (50 ml) at 20 °C for 5 h, and the reaction mixture was then stirred at 20 °C for a further 12 h. The resulting precipitate was filtered off and dried over CaCl₂ to give the ammonium salt (2a) (90% yield), m.p. 200–202 °C (from ethanol–cyclohexane) (Found: C, 75.75; H, 7.0; N, 4.8. C₁₈H₂₀ClN requires C, 75.65; H, 7.05; N, 4.9%); δ (CD₃OD) 3.10 (9 H, s) and 5.63 (2 H, s). The ammonium salts (2b, c) were similarly prepared: (2b) had m.p. 250–251 °C (decomp.) (from ethanol–cyclohexane); δ (CD₃OD) 2.96 (3 H, s), 3.06 (9 H, s), and 5.55 (2 H, s); (2c) could not be isolated in a pure state, δ (CD₃OD) 1.67 (6 H, d), 3.13 (9 H, s), 4.56 (1 H, septet), and 5.76 (2 H, s).

Reaction of (9-Anthrylmethyl)trimethylammonium Chloride (2a) with an Equimolar Amount of LAH in THF.—In a 100-ml flask, which was equipped with a pressure-equalizing dropping funnel, a mechanical stirrer, and a reflux condenser topped with

a nitrogen inlet tube, was placed LAH (0.13 g, 3.36 mmol). In the dropping funnel was placed the salt (2a) (1.0 g, 3.36 mmol) and the flask was flushed with dry nitrogen. Anhydrous THF was then placed in the flask (25 ml) and the dropping funnel (25 ml) *via* a syringe. The solution of LAH in THF was warmed to 70 °C and treated as rapidly as possible with the suspension of (2a) in THF and the mixture was then stirred at 70 °C for a further 1 h. After hydrolysis of the mixture with ice–water, the precipitated inorganic salts were filtered off and washed with diethyl ether. The organic layer was separated, dried (anhydrous Na₂SO₄), and the solvent was removed under reduced pressure. The crude product was triturated with light petroleum under nitrogen and the precipitate was filtered off; column chromatography on silica gel then gave the anthracene (4a) (0.02 g, 3%) [elution with benzene–light petroleum (1 : 5)] and the dimer (6a) (0.03 g, 4%) [elution with benzene–light petroleum (1 : 1)]. The mother liquor was condensed under nitrogen to give 9-methylene-9,10-dihydroanthracene (3a) as white needles (0.31 g, 48%), m.p. 74–75 °C; δ 3.90 (2 H, s, 10-H) and 5.58 (2 H, s, =CH₂); m/z 192. When compound (3a) was treated with potassium *t*-butoxide in refluxing *t*-butyl alcohol, the isomer (4a) was obtained in 85% yield.

Treatment with diborane, followed by hydrogen peroxide oxidation, converted the salt (2a) into 9-hydroxymethyl-9,10-dihydroanthracene, m.p. 97–98 °C (from benzene–light petroleum); ν_{max} 3 350 and 1 050 cm⁻¹; δ 1.26 (1 H, s, OH), 3.46 (2 H, d, CH₂OH), and 3.46–4.33 (3 H, m, 9-H and 10-H₂).

Reaction of the Salts (2) with LAH in Diethyl Ether.—To a solution of LAH (0.13 g, 3.36 mmol) in anhydrous diethyl ether (25 ml) was added a suspension of the salt (2b) (1.0 g, 3.36 mmol) in diethyl ether (25 ml). The mixture was stirred under reflux for 5 h. After the conventional work-up, the crude product was triturated with light petroleum under nitrogen to give the anthracene (4b). The mother liquor was condensed under nitrogen to provide compound (3b) as white needles, m.p. 121–122 °C (Found: C, 92.65; H, 6.8. C₁₆H₁₄ requires C, 93.15; H, 6.85%); m/z 206; δ (CCl₄) 1.33 (3 H, d, CH₃), 3.67 (1 H, q, 10-H), and 5.33 (2 H, s, =CH₂).

The isopropyl derivative (3c), similarly prepared, was an oil, m/z 234; δ 0.76 (6 H, d), 1.87 (1 H, septet), 3.56 (1 H, d), and 5.53 (2 H, s, =CH₂) (lit.,⁴ δ 0.75, 3.59, and 5.58).

Reaction of the Salts (2) with 3 Mol Equiv. of LAH in THF.—To a solution of LAH (0.6 g, 10.5 mmol) in THF (25 ml) was added a suspension of the salt (2a) (1.0 g, 3.5 mmol) in THF (25 ml) at 70 °C under nitrogen. The mixture was stirred for 1 h. After the conventional work-up, the crude product was separated by column chromatography on silica gel. Elution with benzene–light petroleum (1 : 1) gave a mixture of compounds (4a) and (5a) in the ratio 31 : 69 (0.38 g, 56%). Fractional recrystallizations from methanol gave the di-

hydroanthracene (5a), m.p. 58–59 °C (lit.,¹¹ 59–60 °C); δ 1.36 (3 H, d), 3.79 (1 H, d), 4.00 (1 H, q), and 4.16 (1 H, d). Further elution with benzene–light petroleum (1 : 1) provided compound (6a) (0.16 g, 25%) which was isolated by recrystallization from benzene–light petroleum, m.p. 236–238 °C (Found: C, 93.45; H, 6.25. C₃₀H₂₄ requires C, 93.7; H, 6.3%); δ 1.79 (3 H, s), 3.20 (1 H, d), 3.64 (1 H, d), and 3.97 (2 H, s).

The dihydroanthracene (5b), similarly obtained from the salt (2b), was a mixture of *cis*- and *trans*-isomers; the *cis*-isomer had m.p. 130–131 °C (lit.,¹¹ 130–131 °C), but the *trans*-isomer could not be isolated in a pure state.

The isopropyl derivative (5c), obtained from the salt (2c), was also a mixture of *cis*- and *trans*-isomers; the *cis*-isomer had m.p. 65–66 °C (lit.,¹² 65–66 °C), and the *trans*-isomer had m.p. 75–77 °C (lit.,¹² 76–77 °C).

The dimer (6b) had m.p. 201–203 °C (from benzene–light petroleum) (Found: C, 92.85; H, 6.85. C₃₂H₂₈ requires C, 93.15; H, 6.85%); δ 1.37 (3 H, s), 1.81 (3 H, d), 3.04 (3 H, s), 4.08 (2 H, s), and 4.18 (1 H, q); the dimer (6c) had m.p. 192–194 °C (from benzene–light petroleum); δ 0.57 (6 H, d), 1.75 (6 H, d), 1.92 (3 H, s), 3.52 (2 H, s), and 4.54 (1 H, septet).

Reaction of 9-(Chloromethyl)anthracene (1a) with LAH.—To a solution of compound (1a) (1.0 g, 3.36 mmol) in THF (50 ml) was added LAH (0.39 g, 10.08 mmol) under nitrogen at 20 °C. The mixture was stirred under the same conditions for 1 h. Column chromatography of the crude product on silica gel [elution with benzene–light petroleum (1 : 5)] gave the anthracene (4a) in 84% yield.

Reaction of 9-Methyl-9,10-dihydro-9-anthryl Carbanions (7) with Salts (2).—To a solution of 9,10-dimethyl-9,10-dihydroanthracene (5b) (0.5 g, 2.4 mmol) in THF (25 ml) at 0 °C was added a solution of *n*-butyl-lithium (2.4 mmol) in hexane under nitrogen. The mixture was stirred under the same conditions for a further 4 h. To the resulting green solution was added a suspension of the salt (2a) (0.72 g, 2.4 mmol) in THF (10 ml) in one portion at 0 °C. The colour of the solution immediately disappeared. The products were isolated by column chromatography on silica gel. Elution with benzene–light petroleum (1 : 1) gave the dimer (6b) in a yield of 80%.

When 10-methyl-9,10-dihydro-9-anthryl carbanion (8), prepared from compound (5a) (0.5 g, 2.56 mmol) and *n*-butyl-lithium (2.56 mmol) in THF (25 ml), was treated with the salt (2a) (0.73 g, 2.56 mmol), 9-(9-anthrylmethyl)-10-methyl-9,10-dihydroanthracene (9) was obtained in 75% yield, m.p.

202.0–202.5 °C (from benzene–light petroleum); δ 1.92 (3 H, d), 3.96 (2 H, d), 4.22 (1 H, q), and 4.43 (1 H, t).

Reaction of the Salt (2a) with Lithium Aluminium Deuteride (LAD) in THF.—The reaction of the salt (2a) (0.3 g, 1.05 mmol) with LAD (0.13 g, 3.15 mmol) in THF (25 ml) was performed at 70 °C for 1 h. The product composition and the deuterium content were determined by comparing the areas of the following characteristic peaks in the n.m.r. spectrum of the crude products: (4a) [δ 3.00 (3 H, s) and 8.08–8.28 (3 H, m)]; (5a) [δ 1.36 (3 H, d) and 3.64–4.32 (3 H, m)]; (6a) [δ 1.79 (3 H, s), 3.20 (1 H, d), and 3.64 (1 H, d)].

Reaction of the Salt (2b) with LAH; Work-up with Deuterium Oxide.—The reaction of the salt (2b) (0.3 g, 1.01 mmol) with LAH (0.12 g, 3.03 mmol) in THF (25 ml) was performed at 70 °C for 1 h and the mixture was decomposed by the addition of deuterium oxide (1.0 ml). The product composition and the deuterium content were determined by comparing the areas of the following characteristic peaks in the n.m.r. spectrum of the crude products: (4b) [δ 3.00 (6 H, s) and 8.12–8.28 (2 H, m)]; (5b) [δ 1.49 (3 H, d), 1.56 (3 H, d), and 4.00 (2 H, q)]; (6b) [δ 1.81 (3 H, d), 3.04 (3 H, s), and 4.08 (2 H, s)].

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