Novel Reactivity of (9-Anthryl)diphenylmethyl Hexachloroantimonate and Related Compounds with Nucleophiles at the Ring Position

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The reactions of (9-anthryl)diphenylmethyl hexachloroantimonate (1) with nucleophiles gave mainly the quinoidal products by attack on the 10-position of the anthracene ring, suggesting the existence of a strong interaction of the two phenyl rings with the hydrogens at the 1- and 8-positions of the anthracene ring. Compound (1) is propellor-shaped, and thus approach by the nucleophile to the benzylic site is difficult. For the reactions of 9-diphenylmethylene-10-chloro-9,10-dihydroanthracene, data were obtained which suggest that the approach of the nucleophile to the 10-position of anthracene ring is more hindered than the case of (1). By substituting the 10-hydrogen of (1) with a phenyl group, a remarkable retardation of attack by nucleophiles on position 10 was observed.

It is generally agreed that the triphenylmethylium ion is propellor-shaped with considerable positive charge delocalized onto the three rings giving rise to resonance forms. Reaction with bulkier reagents gives *para*-coupling products.[1] 1,8-Bis(phenylthio)anthracen-9-ylmethylium ion, in which the *peri*-interaction of the central carbon with the phenylthio-groups is extremely large, was found to react with methanol at the ring position.[2]

Recently we reported the formation of quinoidal compounds by the reaction of (9-anthryl)diphenylmethylium and (10-phenylanthracen-9-yl)diphenylmethylium ions, derived from oxidation of the corresponding neutral radicals with liquid sulphur dioxide, with ethanol.[3] In the light of these results, we examined the reactions of (9-anthryl)diphenylmethyl hexachloroantimonate and its homologues with several nucleophiles to obtain further insight into the reactivity of the ring positions of triphenylmethylium ion.

RESULTS AND DISCUSSION

The reaction of (9-anthryl)diphenylmethyl hexachloroantimonate (1), 10-chloro-9-diphenylmethylene-9,10-dihydroanthracene (2), *N*-(9-diphenylmethylene-9,10-dihydroanthracen-10-yl)-*NNN*-trimethylammonium chloride (3), (10-phenylanthracen-9-yl)diphenylmethyl hexachloroantimonate (4), and 10-chloro-9-diphenylmethylene-10-phenyl-9,10-dihydroanthracene (5) with several nucleophiles were performed under a slow stream of nitrogen.

Reactions of (9-Anthryl)diphenylmethyl Hexachloroantimonate (1).—The reaction of (1) with hydrogen donors afforded a mixture of hydrocarbons (6) and (7). In the reaction of triphenylmethylium ion, attack by hydrogen donors on the phenyl ring has also been observed, and the reaction was regarded as proceeding *via* electron donation by the single bond of the hydrogen donor to the two-electron, three-centre bond of the carbonium ion.[4] When (1) was treated with sodium azide in *NN*-dimethylformamide (DMF), a mixture of (8) and (9) was obtained in the molar ratio of 7 : 3, *i.e.*, azide ion attacks both the aromatic and the benzylic site. However, the other nucleophiles we examined only attacked position 10 of the anthracene ring (Table 1). These results lead to the following conclusion: because of the strong interaction of the two phenyl rings with the hydrogens at the 1- and 8-positions of the anthracene ring, compound (1) is propellor-shaped, and approach by nucleophiles to the benzylic site is difficult.

Although (7) is known to be more stable than (6),[5] other (9-anthryl)diphenylmethyl derivatives were found to be unstable relative to the isomeric quinoidal compounds; (9) rearranges completely to (8) when kept at room temperature for 6 h in the presence of sodium azide in aqueous DMF. From both (16) and (17), an equilibrium mixture of (16) and (17) in the ratio 9 : 1 was obtained in the presence of acid catalyst. These results may be explained as follows. Not all the substituents in the (9-anthryl)diphenylmethyl derivatives are able to occupy favourable positions in which *peri*-interactions with hydrogens at the 1- and 8-positions are absent. The same conclusion is obtained from a comparison of the chemical shift of the α-proton of (9-anthryl)diphenylmethane with that of triphenylmethane. Table 2 lists the chemical shifts for the side-chain protons of toluene, 9-methylanthracene, and their derivatives. The remark-

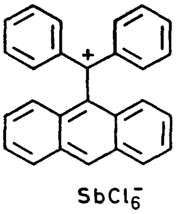
TABLE 1

Reaction of (9-anthryl)diphenylmethyl hexachloroantimonate (1) [a]

Nucleophile	Solvent	Reaction time (min)	Product and % yield
$LiAlH_4$	Et_2O	10	77 [(6) : (7) = 33 : 67] [d]
$NaBH_4$	THF [c]	10	74 [(6) : (7) = 50 : 50] [d]
CHT [b]	THF [c]	60	65 [(6) : (7) = 35 : 65] [d]
CHT [b]	SO_2	60	80 [(6) : (7) = 12 : 88] [d]
CHT [b]	$MeNO_2$	60	76 [(6) : (7) = 12 : 88] [d]
NaN_3	DMF	10	70 [(8) : (9) = 70 : 30] [d]
NaSCN	DMF	10	(10) 80
NaSPh	DMF	10	(14) 70
KOH	H_2O–dioxan	10	(16) 92
MeOH	MeOH	10	(18) 70
NaOMe	MeOH	10	(18) 80
EtOH	EtOH	10	(20) 93
NaOEt	EtOH	10	(20) 80
MeMgI	Et_2O	60	(22) 46
PhMgBr	Et_2O	60	(23) 44

[a] The reaction was performed at 20 °C. [b] Cycloheptatriene. [c] Tetrahydrofuran. [d] The yield of the crude products. The ratio of the products was calculated by the comparison of the peak areas of the n.m.r. spectra of the crude products.

able constancy of the $\Delta\delta$ values in the monosubstituted methylanthracenes has been explained as follows.[6,7] The steric environment at the ring position results in a higher population of the conformer in which the dihedral angle between the substituent and the aromatic ring is 90°. The large values of $\Delta\delta$ (1.5—1.7 p.p.m.) found in



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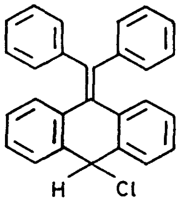

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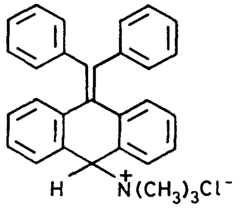

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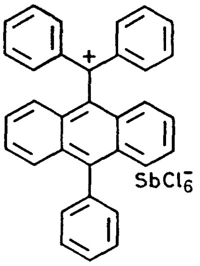

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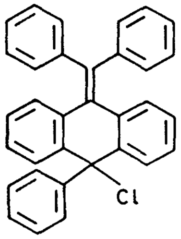

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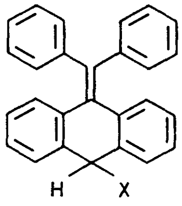


(6) X = H

(8) X = N_3

(10) X = NCS

(13) X = OCOMe

(14) X = SPh

(16) X = OH

(18) X = OMe

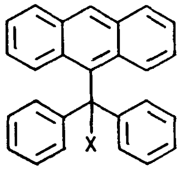
(20) X = OEt

(22) X = Me

(23) X = Ph

(24) X = $CH(CO_2Et)_2$

(26) X = $CH(COMe)_2$

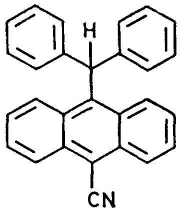


(7) X = H

(9) X = N_3

(12) X = CN

(17) X = OH



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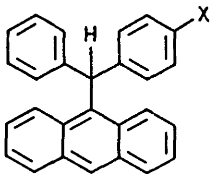
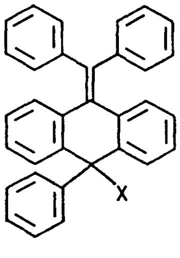


(15) X = SPh

(19) X = OMe

(21) X = OEt

(25) X = $CH(CO_2Et)_2$



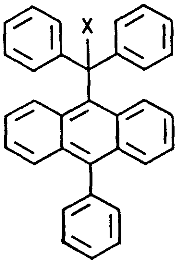
(28) X = N_3

(30) X = NCS

(32) X = OH

(34) X = OMe

(37) X = OEt



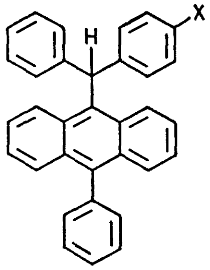
(27) X = H

(29) X = N_3

(33) X = OH

(35) X = OMe

(38) X = OEt



(31) X = SPh

(36) X = OMe

(39) X = OEt

Table 2

Chemical shifts [a] of side-chain protons in ArCHXY systems

X	Y	Chemical shift (δ) Ar = Phenyl	Chemical shift (δ) Ar = 9-Anthryl	Δδ [b]
H	H	2.36	3.00	0.64
H	Ph	4.00	4.95	0.95
H	OH	4.63	5.63	1.00
H	Cl	4.55	5.58	1.08
H	OCH_3	4.36	5.37	1.01
Ph	Ph	5.37	7.08	1.51
Ph	OH	5.70	7.20	1.50
Ph	CN	5.10	6.71	1.61
Ph	Cl	6.13	7.75	1.62
Ph	OCH_3	5.15	6.88	1.73

[a] Chemical shifts relative to Me_4Si; concentration 30 mg per 0.3 ml $CDCl_3$. [b] The chemical shift of the side-chain protons of the 9-anthrylmethyl derivatives relative to the toluene derivatives.

the disubstituted derivatives suggest that hydrogen, the smallest substituent, exists on the same plane as the anthracene ring. Semi-empirical calculations for 1,3,5-trimethylisopropylbenzene also suggest that the ground state of this compound is represented by a conformation in which the α-methine proton eclipses one of the methyl groups.[8] These results lead to the conclusion that one of the substituents in ααα-trisubstituted 9-anthrylmethanes and a hydrogen of the anthracene ring at the 1- or 8-position are eclipsed. In contrast, the quinoidal compound, which is known to have a boat conformation with the bulkier substituent in the pseudo-axial position,[9] is not subject to such a *peri*-interaction. Additionally, 9-anthrylbenzyl derivatives (substituents H, OH, OEt, and N_3) are thermodynamically more stable than the isomeric quinoidal compounds.[10]

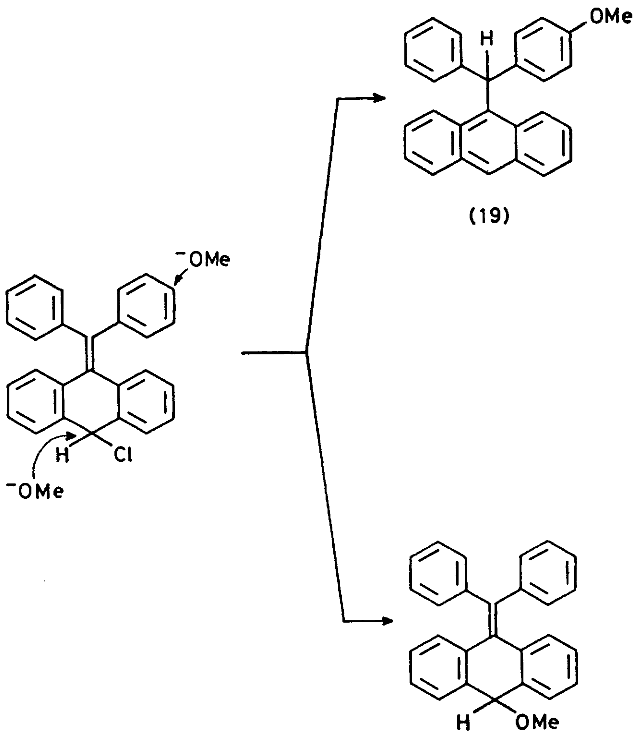
Table 3

Reaction of 10-chloro-9-diphenylmethylene-9,10-dihydroanthracene (2) [a]

Nucleophile	Solvent	Reaction time (min)	Product and % yield
$LiAlH_4$	Et_2O	60	95 [(6) : (7) = 62 : 38] [e]
$NaBH_4$	H_2O–	60 [c]	95 [(6) : (7) = 60 : 40] [e]
$NaBH_4$	THF [b] dioxan	60 [d]	No reaction
NaN_3	DMF	10	90 [(8) : (9) = 50 : 50] [e]
NaSCN	DMF	10	(10) 95
KCN	H_2O–dioxan	10	(11) 52, (12) 27
NaOCOMe	DMF	10	(13) 85
NaSPh	DMF	10	(14) 80, (15) 15
KOH	H_2O–dioxan	10	(16) 76, (17) 3
MeOH	MeOH	10	(18) 85
NaOMe	MeOH	10	(18) 85, (19) 5
EtOH	EtOH	10	(20) 85
NaOEt	EtOH	10	(20) 80, (21) 5
MeMgI	Et_2O	60	(22) 45
PhMgBr	Et_2O	60	(23) 75
$NaCH(CO_2Et)_2$	DMF	60 [c]	(24) 53, (25) 20, (7) 13
$NaCH(COMe)_2$	DMF	60 [c]	(26) 30, (7) 8

[a] The reaction was performed at 20 °C unless otherwise noted. [b] Tetrahydrofuran. [c] At 50 °C. [d] At 68 °C. [e] Yield of crude products. The ratio of the products was calculated by comparison of the peak areas of the n.m.r. spectra of the crude products.

Reactions of 10-*Chloro*-9-*diphenylmethylene*-9,10-*dihydroanthracene* (2).—Notable differences were observed in the reactions of (2) with some nucleophiles compared with those of (1) (Table 3). In contrast to (1), the reaction of (2) with sodium azide gave a mixture of (8) and (9) in 1 : 1 ratio, which suggests that steric hindrance at the 10-position of the anthracene ring increases in the reaction of (2). Cyanide ion, which is a small nucleophile like azide ion, attacks both the benzylic and the ring site. More surprisingly, the reaction of sodium methoxide takes place not only at the 10-position of the anthracene ring, but also at the *para*-position of one of the phenyl rings to afford (19). The physical properties of (19) are consistent with those of an authentic sample prepared by sodium borohydride reduction of 10-hydroxy-9-(*p*-methoxydiphenylmethylene)-9,10-dihydroanthracene in trifluoroacetic acid. Attack on the *para*-position of the phenyl ring was also observed for reactions with sodium ethoxide, sodium thiophenoxide, and diethyl sodiomalonate. In contrast, hydroxide ion and ethanol gave only (16) and (20), respectively, which suggests that high reactivity of a nucleophile is a necessary requirement for reaction to occur at a phenyl ring with low charge density.



(19)

(18)

It seems that ionization of (2) is rate-determining at least for the reactions in protic solvents,[10,11] but we cannot offer any explanation for the differences in behaviour between the cationoid species from (2) and the antimonate salt (1). In connection with this, the reaction of (1) with sodium thiophenoxide or sodium acetate in the presence of oxygen gave only an un-

TABLE 4

Reaction of *N*-(9-diphenylmethylene-9,10-dihydroanthracen-10-yl)-*NNN*-trimethylammonium chloride (3)

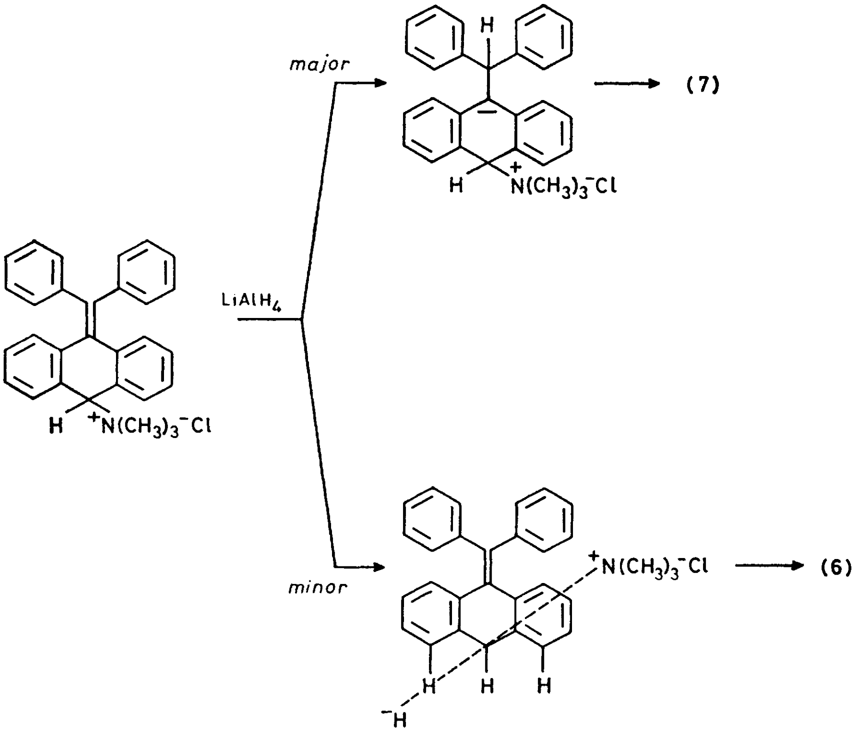
Nucleophile	Solvent	Temp. (°C)	Reaction time (h)	Product and % yield
$LiAlH_4$	Et_2O	38	2	75 [(6) : (7) = 5 : 95] [b]
$NaBH_4$	THF [a]	70	4	60 [(6) : (7) = 64 : 36] [b]
NaSCN	DMF	20	8	(10) 33 [c]
NaOCOMe	DMF	70	1	(13) 80
NaSPh	DMF	40	2	(14) 80, (15) 10
KOH	H_2O–dioxan	20	18	(16) 30 [c]
EtOH	EtOH	78	0.2	(20) 90
NaOEt	EtOH	20	18	(20) 80
MeMgI	Et_2O	20	3	(22) 31 [c]
PhMgBr	Et_2O	38	2	(23) 60
$NaCH(CO_2Et)_2$	DMF	50	2	(24) 30, (25) 5

[a] Tetrahydrofuran. [b] Yield of crude products. The ratio of the products was calculated by comparison of the peak areas of the n.m.r. spectra of the crude products. [c] Starting material was recovered.

identified peroxide, which suggests that the reaction proceeds *via* electron transfer between (1) and a nucleophile.[12,13] The reaction with cyanide ion or diethyl sodiomalonate even under nitrogen gave a complex mixture. However the reactions with alcohols, hydroxide, ethoxide, and azide ions, in which electron transfer does not seem to occur, gave the expected products of aerial conditions, suggesting that whether or not electron transfer occurs is not the key factor deciding the different behaviour of (2) and (1). In the reaction of (2) this remarkable effect of oxygen could not be observed.

Reaction of N-(9-*Diphenylmethylene*-9,10-*dihydroanthracen*-10-*yl*)-NNN-*trimethylammonium Chloride* (3).—As expected from the poor leaving ability of the trimethylamino-group, (3) reacted slowly with nucleophiles (Table 4). Lithium aluminium hydride attacks the benzylic site predominantly to give (7) (reduction with lithium aluminium deuteride confirms selective attack on this position). This may be attributable to the fact that the transition state of an S_N2 reaction is highly disfavoured because of the strong interaction of the trimethylamino-group with the anthracene ring, and the relatively small nucleophile attacks the benzylic site with elimination of trimethylamine by an 'S_N2' or rather a stepwise mechanism.[14] In the reaction with sodium azide, a mixture of (8) and (9) was obtained, but (9) rearranges to (8) even in DMF, and so the precise ratio of products could not be obtained. Other reagents, which are not able to approach the benzylic site, reacted at the 10-position of the anthracene ring. However a small amount of (15) was obtained in the reaction with thiophenoxide ion. At 70 °C (3) decomposes in solution to the methylium ion and trimethylamine, and even with ethanol it reacted in 10 min to give (20). In the solid state (3) decomposes at *ca.* 120 °C with evolution of trimethylamine.

Reactions of (10-*Phenylanthracen*-9-*yl*)*diphenylmethyl Hexachloroantimonate* (4) *and* 10-*Chloro*-9-*diphenylmethylene*-10-*phenyl*-9,10-*dihydroanthracene* (5).—Upon substituting the hydrogen at the 10-position of (1) by a phenyl group, a remarkable retardation of attack by nucleophiles on the anthracene ring was observed. Not only hydride and azide ions but also hydroxide ion, which reacted only at the ring position of (1), reacted selectively at the benzylic site of (4). Thiophenoxide and ethoxide ions were captured by (4) selectively at the *para*-position of a phenyl ring, giving (31) and (39),



respectively. In contrast, reaction with ethanol gave (37) and (38), suggesting that this weakly nucleophilic reagent does not attack the phenyl ring which has low charge density but rather the sterically hindered benzylic site and the 10-position of the anthracene ring. Sodium methoxide, a moderately nucleophilic reagent, reacted at three positions, *i.e.*, the benzylic site, the 10-position of anthracene ring, and the *para*-position of one of the phenyl rings. Compound (40), obtained by attack on the *para*-position of the phenyl ring attached to the 10-position of anthracene, could not be observed. In contrast to the above results, the relative thermodynamic stabilities of quinoidal compounds and those with the anthracene structure are the same as those for diphenylmethylanthracene derivatives and their quinoidal isomers. The hydrocarbon (27) is more stable than (23), but (29), (33), (35), and (38) rearrange under thermodynamically controlled conditions to (28), (32), (34), and (37), respectively. The notable retardation of the reaction at the 10-position of the anthracene ring is explained as follows. The phenyl ring attached to the 10-position is not on the same plane as the anthracene ring, and approach of nucleophile to the 10-position is difficult. The reaction of (5) gave the same results as (4). It is likely that the presence of the phenyl group determines which positions are attacked.

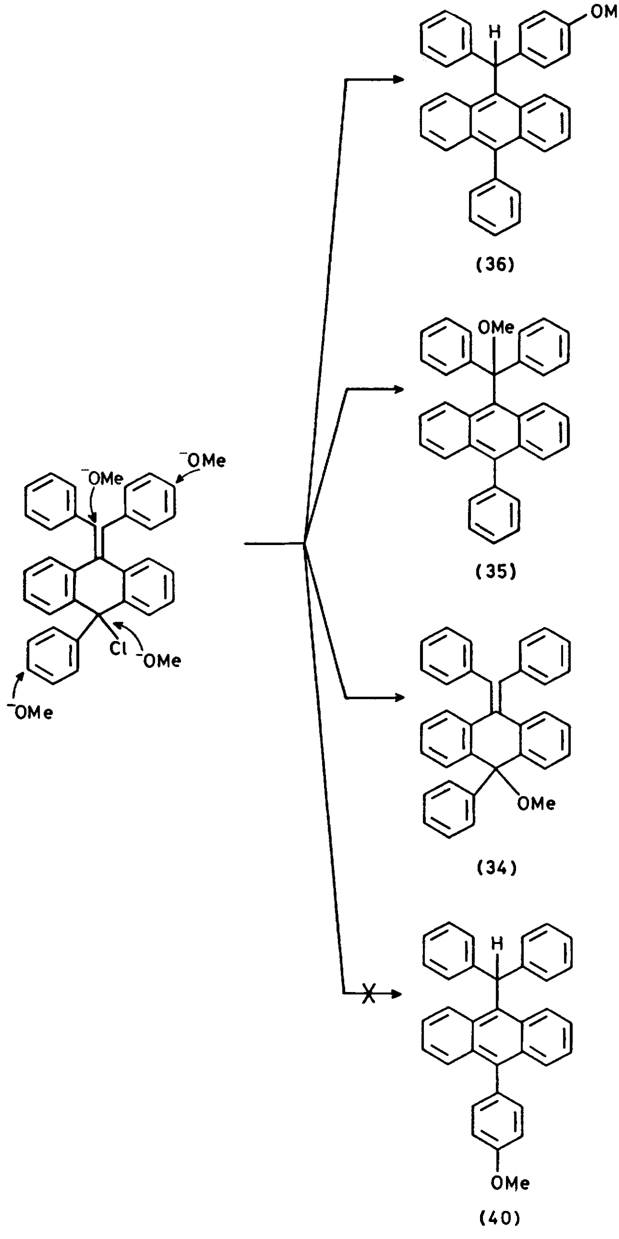


TABLE 5

Reaction of (10-phenylanthracen-9-yl)diphenylmethyl hexachloroantimonate (4) and 10-chloro-9-diphenylmethylene-10-phenyl-9,10-dihydroanthracene (5) [a]

Substrate	Nucleophile	Solvent	Product and % yield
(4)	$LiAlH_4$	Et_2O	(27) 90
(5) [b]	$LiAlH_4$	Et_2O	(27) 90
(4)	$NaBH_4$	Et_2O	(27) 85
(5) [b]	$NaBH_4$	Et_2O	(27) 87
(4)	NaN_3	DMF	(29) 70
(5)	NaN_3	DMF	(29) 85
(5)	NaSCN	DMF	(30) 75
(4)	NaSPh	DMF	(31) 70
(5)	NaSPh	DMF	(31) 85
(5)	H_2O	H_2O–dioxan	(33) 93
(4)	KOH	H_2O–dioxan	(33) 80
(5)	KOH	H_2O–dioxan	(33) 80
(5)	MeOH	MeOH	(34) 70, (35) 28
(5)	NaOMe	MeOH	(34) 45, (35) 20, (36) 12
(5)	EtOH	EtOH	(37) 51, (38) 48
(4)	NaOEt	EtOH	(39) 95
(5)	NaOEt	EtOH	(39) 74

[a] The reaction was performed at 20 °C for 10 min unless otherwise noted. [b] The reaction was performed for 1 h.

EXPERIMENTAL

^1H N.m.r. spectra were obtained with a JEOL LNM 4P100 instrument, ^{13}C n.m.r. with a JEOL FX-60 instrument at 15.03 MHz in $CDCl_3$ at 21 °C using the pulsed Fourier-transform technique, u.v. spectra with a Varian Techron 635 spectrometer in dioxan unless otherwise noted, mass spectra with a Hitachi RMU-6H spectrometer, and i.r. spectra with a Hitachi 215 spectrometer. Analytical data for new compounds are given in Supplementary Publication No. SUP 22627 (4 pp.) *

10-Chloro-9-diphenylmethylene-9,10-dihydroanthracene (2) and 10-chloro-10-phenyl-9-diphenylmethylene-9,10-dihydroanthracene (5) were prepared by reported methods.[3]

Preparation of (9-*Anthryl*)*diphenylmethyl Hexachloroantimonate* (1).—To a solution of (2) (1 g) in carbon tetrachloride (10 ml) was added a solution of antimony pentachloride (0.8 g) in carbon tetrachloride (20 ml) at room temperature over 10 min. The solid formed was filtered off, washed with carbon tetrachloride, and dried ($CaCl_2$) *in vacuo*, m.p. 132—134 °C (from methylene chloride–light petroleum), $\lambda_{max.}$ (liquid SO_2) 785, 450, and 400 nm.

From (5) (10-phenylanthracen-9-yl)diphenylmethyl hexachloroantimonate (4) was obtained in 85% yield, m.p.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index Issue.

117—120 °C (from methylene chloride–light petroleum), $\lambda_{max.}$ (liquid SO_2) 820 nm.

Preparation of N-(9-*Diphenylmethylene*-9,10-*dihydroanthracen*-10-*yl*)-NNN-*trimethylammonium Chloride* (3).—Through a solution of (2) (3.0 g) in tetrahydrofuran (200 ml) was bubbled a current of dry trimethylamine at room temperature for 30 min. The solid was filtered off, washed with tetrahydrofuran, and dried *in vacuo*, m.p. 120 °C (decomp.), $\lambda_{max.}$ 306 nm, δ 3.57 (9 H, s), *m/e* 402.

Reaction of (1) *with Lithium Aluminium Hydride.*—To a solution of lithium aluminium hydride (0.8 g, 21 mmol) in ether (50 ml) was added (1) (2 g, 3 mmol) during 10 min at room temperature, while a current of nitrogen was bubbled through. The mixture was poured into ice-cold aqueous potassium hydroxide, and extracted with three portions of ether. The combined extracts were dried (Na_2SO_4) and evaporated. The hydrocarbon products (798 mg, 77%) were isolated by column chromatography on silica gel (elution with benzene–light petroleum). By comparison of the peak areas of the crude product [δ 3.96 for (6) and 8.42 for (7)], the mixture was found to contain 33% (6) and 67% (7).

Recrystallization of the product from benzene–light petroleum gave pure (7), m.p. 205.5—208 °C (lit.,[5] 204—205 °C). From the mother-liquor (6) was isolated by recrystallization, m.p. 264—266 °C (lit.,[5] 258 °C).

Reaction of (1) *with Cycloheptatriene.*—To a solution of cycloheptatriene (0.5 g, 5.4 mmol) in nitromethane (20 ml) was added a solution of (1) (1.5 mmol) in nitromethane (10 ml) during 10 min, and stirring was continued for 1 h. By column chromatography on silica gel, a mixture of (6) and (7) was isolated in 76% yield.

Reaction of (1) *with Sodium Azide.*—A mixture of (1) and sodium azide (3 mol. equiv.) in DMF was kept at room temperature for 10 min. After conventional work-up, the crude product was triturated with light petroleum to give (9), m.p. 137 °C (decomp.) (from benzene–light petroleum), $\nu_{max.}$ 2 080 and 1 243 cm^{-1}, $\lambda_{max.}$ 398, 378, 358, and 342 nm, δ 8.50 (1 H, s).

By column chromatography of the mother-liquor on silica gel pure (8) was obtained, m.p. 188—189 °C (from benzene–light petroleum), $\nu_{max.}$ 2 095 and 1 223 cm^{-1}, $\lambda_{max.}$ 298 nm, δ 5.46 (1 H, s).

The reaction with sodium thiocyanate was performed under similar conditions. The isothiocyanate (10) was a solid, m.p. 205—208 °C (decomp.) (from chloroform–light petroleum), $\nu_{max.}$ 2 110br and 2 048sh cm^{-1}, $\lambda_{max.}$ 293 nm, δ 5.76 (1 H, s).

Reaction of (1) *with Sodium Thiophenoxide.*—To a solution of sodium thiophenoxide (1 g, 7.6 mmol) in DMF (50 ml), through which was bubbled nitrogen for 30 min, was added (1) (2 g, 3 mmol) in 10 min. After conventional work-up, (14) was isolated in 70%, m.p. 200—202 °C (decomp.) (from benzene–light petroleum), *m/e* 452, $\lambda_{max.}$ 292 nm, δ 5.20 (1 H, s).

In aerial conditions, a solid, which was not soluble in hot benzene or chloroform, was obtained in good yield, m.p. >300 °C, $\lambda_{max.}$ 297 nm, $\nu_{max.}$ 1 480, 1 440, 1 080, 1 020, and 740 cm^{-1}, which did not contain sulphur.

Reaction of (1) *with Potassium Hydroxide.*—To a mixture of dioxan (30 ml) and water (10 ml) was added (1) (0.5 g, 0.7 mmol) over 10 min, while nitrogen was bubbled through. By column chromatography on alumina (elution with ether) the quinoidal compound (16) was obtained in 92% yield, m.p. 192—193 °C (lit.,[15] 195 °C).

The reaction of (1) with sodium methoxide (3 mol. equiv.) in methanol gave (18), m.p. 179—181 °C (from ethanol), $\lambda_{max.}$ 295 nm, δ 3.49 (3 H, s) and 5.08 (1 H, s). By reaction of (1) with sodium ethoxide (3 mol. equiv.) in ethanol (20) was obtained, m.p. 165—166 °C (from ethanol), *m/e* 388, $\nu_{max.}$ 1 070 cm^{-1}, $\lambda_{max.}$ 297 and 242 nm, δ 1.35 (3 H, t), 3.70 (2 H, q), and 5.17 (1 H, s).

Reaction of (1) *with Phenylmagnesium Bromide.*—To a solution of phenylmagnesium bromide, prepared from bromobenzene (3 g, 19 mmol) and magnesium (0.45 g, 19 mmol) in ether, was added (1) (1.8 g, 2.7 mmol) at room temperature over 10 min, while a current of nitrogen was bubbled through. After a further 1 h, the mixture was poured into ice-cold hydrochloric acid. The products were extracted with ether, and separated by column chromatography on silica gel. Elution with benzene afforded (23), m.p. 224—225 °C (from benzene–ethanol), *m/e* 420, $\lambda_{max.}$ 288 and 252 nm, δ 5.20 (1 H, s). By elution with ether (16) was isolated in 24%.

The reaction of (1) with methylmagnesium iodide (7 mol. equiv.) gave (22), m.p. 225—227 °C (from ethanol), $\lambda_{max.}$ 285 nm, δ 1.70 (3 H, d) and 4.00 (1 H, q).

Reaction of (2) *with Sodium Borohydride.*—To a solution of sodium borohydride (0.6 g, 15.8 mmol) in aqueous 70% (v/v) diglyme, was added (2) (0.8 g, 2.1 mmol) at room temperature over 10 min. The mixture was then warmed up 50 °C, and the reaction was continued for a further 1 h under nitrogen. By column chromatography on silica gel a mixture of hydrocarbons (6) and (7) was isolated in 95% yield.

Reaction of (2) *with Potassium Cyanide.*—To a solution of (2) (1.0 g, 2.5 mmol) in aqueous 75% (v/v) dioxan was added potassium cyanide (1 g, 15 mmol), while a current of nitrogen was bubbled through. The products were isolated by column chromatography on silica gel. Elution with benzene–ether gave (11), m.p. 211—214 °C (from benzene–light petroleum), $\nu_{max.}$ 2 218 cm^{-1}, $\lambda_{max.}$ 412, 390, 370, and 351 nm. Elution with ether afforded (12), $\lambda_{max.}$ 393, 375, 359, and 342 nm, δ_C 57.540 (1 C, s).

Reaction of (2) *with Thiophenoxide.*—To a solution of sodium thiophenoxide (0.35 g, 2.6 mmol) in DMF (20 ml) was added (2) (1 g, 2.6 mmol). After conventional work-up the products were crystallized from methylene chloride–light petroleum to give (14). The mother-liquor was chromatographed on silica gel. Elution with benzene–light petroleum gave (15) in pure form, an amorphous solid, $\lambda_{max.}$ 391, 370, 351, and 334 nm, δ 8.34 (1 H, s), δ_C 50.557 (1 C, d).

Reaction of (2) *with Sodium Methoxide.*—The reaction of (2) with sodium methoxide gave a mixture of (18) and (19). Compound (19) was a solid, m.p. 166—168 °C (from ethanol), δ 3.67 (3 H, s), 6.64 (2 H, d), and 6.96 (2 H, d).

From the reaction of (2) with sodium ethoxide was obtained, along with (20), compound (21), an amorphous solid, $\nu_{max.}$ 1 240 and 1 040 cm^{-1}, $\lambda_{max.}$ 391, 370, 351, and 334 nm, δ 1.34 (3 H, t), 3.89 (2 H, q), 6.70 (2 H, d), and 8.35 (1 H, s), δ_C 49.786 (1 C, d).

Reaction of (2) *with Diethyl Sodiomalonate.*—Sodium hydride (0.2 g; 50% dispersion in mineral oil) was washed by centrifugation with light petroleum. With the aid of dry DMF (20 ml) it was then washed into a 100-ml three-necked flask fitted with a nitrogen inlet, drying tube, thermometer, and dropping funnel. Dry nitrogen was passed through the magnetically stirred suspension for 30 min, then, at room temperature, a solution of diethyl malonate (0.5 g) in dry benzene (15 ml) was added over 10 min while the temperature rose to 40 °C. Nitrogen was passed through the solution for 1 h more. Then (2) (1 g) was added in one portion, the mixture was warmed to 50 °C, and stirring under nitrogen was continued for 1 h. After conventional work-up, the products were isolated by column chromatography on silica gel. Elution with light petroleum gave the hydrocarbon (7). Elution with benzene–light petroleum produced a mixture of (24) and (25), which was triturated with light petroleum to afford (24), m.p. 183—185 °C (from benzene–light petroleum), $\nu_{max.}$ 1 746 and 1 721 cm^{-1}, $\lambda_{max.}$ 290 nm, δ 1.08 (6 H, t), 3.93—4.20 (5 H, m), and 4.67 (1 H, s).

From the mother-liquor (25) was isolated by column chromatography on silica gel (twice), an amorphous solid, $\nu_{max.}$ 1 760 and 1 735 cm^{-1}, $\lambda_{max.}$ 391, 380, 371, and 344 nm, δ 1.21 (6 H, t), 4.15 (4 H, q), 4.51 (1 H, s), and 7.03 (1 H, s), δ_C 50.148 (d).

The reaction with sodium acetylacetonate was performed as above. After column chromatography on silica gel, the isolated products were triturated with light petroleum to give (26), m.p. 220—223 °C (from benzene–light petroleum), $\nu_{max.}$ 1 690 (br) cm^{-1}, $\lambda_{max.}$ 290 nm, δ 2.08 (6 H, s), 4.55 (1 H, d), and 4.70 (1 H, d).

Reaction of (5) *with Lithium Aluminium Hydride.*—A mixture of (5) and lithium aluminium hydride (10 mol. equiv.) in ether was kept at 20 °C for 10 min. By column chromatography on silica gel, hydrocarbon (27) was isolated in 90% yield, m.p. 150 °C.[3]

Reaction of (5) *with Sodium Azide.*—The reaction of (5) with sodium azide was performed at 20 °C for 10 min. After conventional work-up the product was triturated with light petroleum to give (29), m.p. 95 °C (decomp.), $\nu_{max.}$ 2 090 and 1 257 cm^{-1}, $\lambda_{max.}$ 405, 383, 364, and 342 nm. This compound did not give a satisfactory elemental analysis, but the fact that it rearranged to the isomeric quinoidal compound (28) quantitatively suggests that it was almost pure. The azide (28) was a solid, m.p. 191 °C (decomp.) (from benzene–light petroleum), $\lambda_{max.}$ 285 nm, $\nu_{max.}$ 2 100 and 1 260 cm^{-1}.

By reaction of (5) with sodium thiocyanate, (30) was obtained, m.p. 208 °C (decomp.) (from chloroform–light petroleum), $\nu_{max.}$ 2 050(br) cm^{-1}, $\lambda_{max.}$ 298 nm.

The product from the reaction of (5) with sodium thiophenoxide was purified by column chromatography on silica gel. Compound (31) was isolated, m.p. 92—95 °C, 528, $\lambda_{max.}$ 400, 380, 361, and 342 nm, δ_C 50.354 (d).

Reaction of (5) *with Sodium Methoxide.*—The reaction of (5) with sodium methoxide (10 mol. equiv.) was performed at 20 °C for 10 min in benzene–methanol (1 : 1 v/v) as solvent. By column chromatography on silica gel, (34)—(36) were isolated. Compound (34) was a solid, m.p. 206—208 °C (from ethanol), $\nu_{max.}$ 1 061 cm^{-1}, $\lambda_{max.}$ 288 nm, δ 3.23 (3 H, s); (35) was a solid, m.p. 204—206 °C (from ethanol), $\nu_{max.}$ 1 070 cm^{-1}, $\lambda_{max.}$ 404, 382, and 362 nm, δ 3.26 (3 H, s); and (36) was a solid, m.p. 106—109 °C (from ethanol), $\nu_{max.}$ 1 241 and 1 020 cm^{-1}, $\lambda_{max.}$ 399, 378, and 358 nm, δ 3.76 (3 H, s).

9-Diphenylmethyl-10-*p*-methoxyphenylanthracene (40), prepared by sodium borohydride reduction of 9-diphenylmethyl-10-*p*-methoxyphenyl-10-hydroxy-9,10-dihydroanthracene in trifluoroacetic acid,[16] had m.p. 216—218 °C (from carbon tetrachloride), $\nu_{max.}$ 1 240 and 1 021 cm^{-1}, $\lambda_{max.}$ 399, 378, and 358 nm, δ 3.95 (3 H, s).

The reaction of (5) with sodium ethoxide in ethanol afforded (39), m.p. 108—112 °C (from ethanol), $\nu_{max.}$ 1 240 cm^{-1}, $\lambda_{max.}$ 399, 378, 359, and 341 nm, δ 1.36 (3 H, t), 3.98 (2 H, q), and 6.76 (2 H, d).

On treatment of (5) with ethanol, a mixture of (37) and (38) was obtained; (37) was a solid, m.p. 243.5—244.5 °C (from benzene–light petroleum), $\nu_{max.}$ 1 065 cm^{-1}, $\lambda_{max.}$ 290 nm, δ 1.34 (3 H, t), 3.31 (2 H, q), and 7.62 (2 H, d); and (38) was a solid, m.p. 190—192 °C (from ethanol), $\nu_{max.}$ 1 062 cm^{-1}, $\lambda_{max.}$ 406, 384, 364, and 345 nm, δ 1.24 (3 H, t) and 3.45 (2 H, q).

Relative Thermodynamic Stabilities of Compounds with Anthracene and Quinoidal Structures.—When a mixture of (23) and potassium t-butoxide in t-butyl alcohol was heated under reflux for 4 h, the u.v. absorption of (23) disappeared completely. From the reaction mixture (27) was isolated in 75% yield. A solution of (9) and sodium azide (3 mol. equiv.) in aqueous DMF was stirred at room temperature, and after conventional work-up, (8) was isolated in 90% yield. The same behaviour was observed for the reaction of (29). Compounds (9) and (29) rearrange to (8) and (28), respectively, even upon column chromatography on silica gel. A mixture of (17) and small amounts of concentrated sulphuric acid in aqueous dioxan was kept at room temperature for 24 h. The u.v. and n.m.r. spectra of the crude products showed that they contained 10% (17) and 90% (16). The reaction of (16) under the same conditions gave the same mixture. The reaction of (33) under these conditions gave an equilibrium mixture of (32) and (33) (95 : 5). When a solution of (38) in ethanol in the presence of small amounts of sulphuric acid was heated under reflux for 1 h, (37) was obtained quantitatively.

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