# Reaction of 9-α-Chlorobenzylanthracene with Small Nucleophiles at the Ring Position: Differences with the Behaviour of 9-Anthrylbenzyl Hexachloroantimonate

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The reaction of 9-anthrylbenzyl hexachloroantimonate with the nucleophiles H_2O, ^-OH, MeOH, ^-OMe, EtOH, ^-OEt, $^-OPr^i$, and $^-N_3$ gave exclusively products with the anthracene structure by attack of a nucleophile on the central carbon. By contrast, the reaction of 9-α-chlorobenzylanthracene with the same nucleophiles yielded a mixture of anthracene derivatives and compounds with a quinoidal structure. In the reaction of N-(9-benzylidene-9,10-dihydroanthracen-10-yl)-NNN-trimethylammonium chloride with ^-SPh, $^-SC_6H_4NO_2$-p, and $LiAlH_4$, α-substituted benzylanthracenes only were obtained.

WE have found [1] that the reactions of (9-anthryl)-diphenylmethyl hexachloroantimonate (IV) with several nucleophiles give predominantly quinoidal products, which suggests that the central carbon is highly crowded

SbCl$_6^-$
(I)

(II)

(III)

SbCl$_6^-$
(IV)

(V)
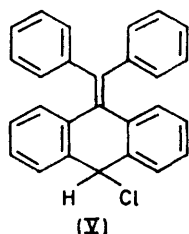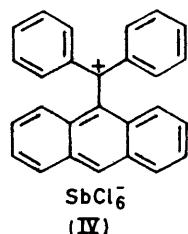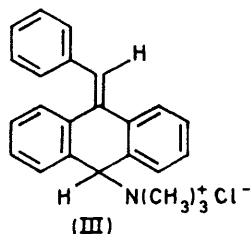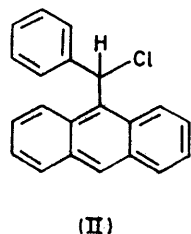
so that approach of a nucleophile to this site is difficult. In the light of these results, we examined the reaction of 9-anthrylbenzyl hexachloroantimonate (I), in which steric hindrance at the central carbon is expected to decrease compared with (IV). The reactions of 9-α-chlorobenzylanthracene (II) and N-(9-benzylidene-9,10-dihydroanthracen-10-yl)-NNN-trimethylammonium chloride (III) have also been investigated.

RESULTS AND DISCUSSION

The salt (I), prepared by the action of $SbCl_5$ on (II) in carbon tetrachloride, was obtained as a dark green solid ($\lambda_{max.}$ 660, 465, and 360 nm) which was unstable even in liquid sulphur dioxide (the colour disappears gradually), and which was able to cleave the C–O bond of tetra-hydrofuran (THF). Therefore, the reactions were performed by adding solid (I) to a solution containing a nucleophile under a slow stream of nitrogen. The reaction was easily monitored by noting the disappearance of the green colour. In reactions with $^-N_3$, ^-SPh, $^-SC_6H_4NO_2$-p, H_2O, ^-OH, ^-OMe, EtOH, ^-OEt, and $^-OPr^i$ in NN-dimethylformamide (DMF) or protic solvents, anthracene derivatives were obtained exclusively. In the conditions used for these reactions (see Experimental section), the isomeric quinoidal compounds are stable, suggesting that the products were formed under kinetically controlled conditions. These results are consistent with the expectation that the central carbon of (I) is not so crowded as that of (IV), permitting attack by a nucleophile to give the thermodynamically

TABLE 1

Reactions of 9-anthrylbenzyl hexachloroantimonate (I) [a]

Nucleophile	Solvent	Reaction time (min)	Product and % yield
LiAlH$_4$	Et$_2$O	10	62 [(1) : (2) 60 : 40] [b]
NaBH$_4$	Et$_2$O	120	40 [(1) : (2) 54 : 46] [b]
CHT [c]	Et$_2$O	120	90 [(1) : (2) 52 : 48] [b]
CHT	SO$_2$	10	90 [(1) : (2) 43 : 57]
NaN$_3$	DMF [d]	5	(3) 60
NaSPh	DMF	10	(7) 37, (28) 34
NaSPh	Et$_2$O	120	(7) 47, (28) 19
H$_2$O	H$_2$O–dioxan	10	(10) 70, (28) 10
KOH	H$_2$O–dioxan	10	(10) 80, (28) 10
NaOMe	MeOH	10	(12) 60
EtOH	EtOH	5	(15) 60, (28) 29
NaOEt	EtOH	5	(15) 96
NaOPr^i	Pr^{i}OH	5	(18) 85
KOBu^t	Bu^{t}OH	5	(21) 29, (22) 8, (28) 33
PhMgBr	Et$_2$O	120	(23) 6, (24) 36, (29) 9

[a] Reactions were performed at 20 °C. [b] Yield of crude products. The ratio of products was calculated from comparison of the peak areas of the n.m.r. spectra of the crude products. [c] Cycloheptatriene. [d] NN-Dimethylformamide.

TABLE 2

Reactions of 9-(α-chlorobenzylanthracene) (II) [a]

Nucleophile	Solvent	Reaction time (min)	Product and % yield
LiAlH₄	Et₂O	120 [b]	72 [(1) : (2) 82 : 18] [d]
NaBH₄	H₂O–diglyme	120 [c]	92 [(1) : (2) 43 : 57] [d]
CHT [e]	SO₂	10	80 [(1) : (2) 50 : 50] [d]
NaN₃	DMF	1440	95 [(3) : (4) 54 : 46] [d]
NaN₃	H₂O–DMF	30	90 [(3) : (4) 33 : 67] [d]
KCN	H₂O–dioxan	5	(5) 56, (6) 28
NaSC₆H₅	DMF	2	(7) 95
NaSC₆H₅	DMF	120	(7) 30, (8) 60
NaSC₆H₄NO₂-p	DMF	10	(9) 93
KOH	H₂O–dioxan	30	(10) 28, (11) 52
MeOH	MeOH	10	(12) 57, (13) 32
NaOMe	MeOH	15	(12) 19, (13) 57
EtOH	EtOH	10	(15) 27, (16) 57
NaOEt	EtOH	10	(15) 18, (16) 70
NaOPrⁱ	PrⁱOH	300	(18) 34, (19) 30
PhMgBr	Et₂O	120	(23) 27, (24) 7
NaCH(CO₂Et)₂	DMF	120 [c]	(25) 36, (10) 22
NaCH(COMe)₂	DMF	120 [c]	(26) 8, (27) 41

[a] Reactions were performed at 20 °C unless otherwise noted. [b] At 38 °C. [c] At 50 °C. [d] Yield of crude products. The ratio of the products was calculated from comparison of the peak areas of the n.m.r. spectra of the crude products. [e] Cycloheptatriene.

TABLE 3

Reactions of N-(9-benzylidene-9,10-dihydroanthracen-10-yl)-NNN-trimethylammonium chloride (III)

Nucleophile	Solvent	Temp. (°C)	Reaction time (h)	Product and % yield
LiAlH₄	Et₂O	38	2	(1) 76
NaSC₆H₅	DMF	20	0.5	(7) 55
NaSC₆H₄NO₂-p	DMF	20	0.5	(9) 58
MeOH	MeOH	65	0.75	(12) 28, (13) 40
NaOMe	MeOH	65	1	(12) 16, (13) 13, (14) 13
EtOH	EtOH	20	96	(15) 13, (16) 13
EtOH	EtOH	78	0.75	(15) 67, (16) 11
NaOEt	EtOH	20	96	38 [(15) : (16) : (17) 48 : 34 : 18] [a]
NaOEt	EtOH	78	1	(15) 39, (16) 29
NaOPrⁱ	PrⁱOH	20	72	(18) 13, (20) 12
NaCH(COMe)₂	DMF	50	6	(26) 14, (27) 33

[a] Yield of crude products. The ratio of products was calculated from comparison of the peak areas of the n.m.r. spectra of the crude products.

more stable 9-α-substituted benzylanthracene.* By contrast, the reaction of (I) with a hydrogen donor (LiAlH₄, NaBH₄, cycloheptatriene) in ether or liquid sulphur dioxide gave a mixture of 9-benzylanthracene (1) and 9-benzylidene-9,10-dihydroanthracene (2). Three explanations are possible for these unexpected results. (a) Hydride ion abstraction proceeds *via* electron donation by a single bond of a hydrogen donor to a two-electron, three-centre bond of a carbonium ion, and so the reaction is subject to considerable steric

hindrance.[2] It is doubtful, however, that LiAlH₄ in ether is a bulkier reagent than sodium isopropoxide in propan-2-ol. (b) Considering the low dielectric constant of ether or liquid sulphur dioxide, and the poor solubility of (I) in these solvents, it is expected to exist as a tight ion pair or solid, in which the carbon centre is blocked by the bulky gegen-anion(s), making approach of
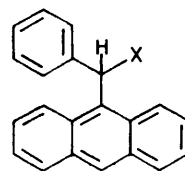
(1) X = H
(3) X = N₃
(5) X = CN
(7) X = SPh
(9) X = SC₆H₄NO₂ -p
(10) X = OH
(12) X = OMe
(15) X = OEt
(18) X = OPrⁱ
(21) X = OBuᵗ
(23) X = C₆H₅
(26) X = CH(COMe)₂
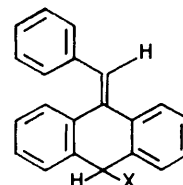
(2) X = H
(4) X = N₃
(11) X = OH
(13) X = OMe
(16) X = OEt
(19) X = OPrⁱ
(22) X = Buᵗ
(24) X = C₆H₅
(25) X = CH(CO₂Et)₂
(27) X = CH(COMe)₂

(6) X = CN
(8) X = SPh
(14) X = OMe
(17) X = OEt
(20) X = OPrⁱ

(28)

a nucleophile difficult. (c) The salt is quite reactive in low nucleophilic solvents, and a nucleophile can be captured both at the carbon centre and the ring position.† It is difficult, however, to decide which is the most probable explanation of the results.

Remarkable differences were observed between (I) and (II) for the sites of capture of nucleophiles. When the reaction of (II) with ⁻SPh was performed for 5 min, the direct substitution product (7) was obtained quanti-

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* 10-Substituted-9-benzylidene-9,10-dihydroanthracenes (2), (4), (11), (13), or (16) rearrange to the isomeric derivatives (1), (3), (10), (12), or (15), respectively, under appropriate conditions (see Experimental section). By contrast, 10-substituted-9-diphenylmethylene-9,10-dihydroanthracene (substituent N₃, OH, OMe, or OEt) is more stable than the isomeric anthracene derivative.[1] However, 9-diphenylmethylene-9,10-dihydroanthracene rearranges to 9-diphenylmethylanthracene in the presence of potassium t-butoxide.
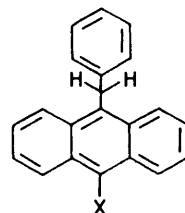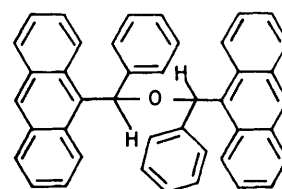
† (9-Anthryl)diphenylmethyl-lithium was found to react with ethanol in ether to afford 9-diphenylmethylanthracene exclusively. In contrast, the reaction with gaseous HCl in the same solvent yielded a mixture of 9-diphenylmethylene-9,10-dihydroanthracene and 9-diphenylmethylanthracene in the ratio 7 : 3.[3]

tatively.* Similar behaviour was observed in the re-
action with $^-SC_6H_4NO_2$-p. In contrast, the reaction
with small nucleophiles ($^-N_3$, ^-CN, ^-OH, ^-OMe, EtOH,
^-OEt, and $^-OPr^i$) in protic solvents gave a mixture of
compounds derived from capture of nucleophiles both at
the central carbon and the ring position. The following
facts suggest that the reactions proceed *via* formation of
cationic species. (a) The reaction of (II) with sodium
azide in anhydrous DMF was complete only after 24 h.
In contrast, (II) disappeared after 30 min when the
reaction was performed in aqueous DMF. Considering
the low nucleophilicity of sodium azide in protic solvents,[4]
ionization of (II) should be rate-determining at least for
the reaction in aqueous DMF. (b) For attack of a weak
nucleophile such as ethanol on the ring position to
occur, considerable charge distribution at this position
is necessary. This can only be accomplished by ioniz-
ation of (II). (c) The similar product compositions
found in the reaction with ethanol and with sodium
ethoxide suggest that S_N2 displacement by sodium
ethoxide is not important. (d) For diphenylmethyl
derivatives, it is now established that during solvolysis,
product formation takes place by nucleophilic attack on
both solvent-separated ion pairs and free carbo-cations.[5]
Similar results for the position of attack have also been
obtained for (IV) and 9-diphenylmethylene-10-chloro-
9,10-dihydroanthracene (V).[1] The reaction of (IV) with
sodium ethoxide gave exclusively 9-diphenylmethylene-
10-ethoxy-9,10-dihydroanthracene. In contrast, when
the reaction of (V) was performed in the same conditions,
9-(p-ethoxydiphenylmethyl)anthracene, together with
the quinoidal compound, was obtained in a yield of 10%.
However, the reaction of (V) with ethanol afforded only
the quinoidal compound. The results obtained by the
reaction of (II) with hydrogen donors are also impressive.
Lithium aluminium hydride reduction in ether, in which
ionization of (II) does not occur, gave (1) predominantly.
In contrast, sodium borohydride reduction in aqueous
diglyme or hydride ion abstraction from cycloheptatriene
in liquid sulphur dioxide, in which ionization of (II)
should be rate-determining, gave a mixture of (1) and (2)
in the molar ratio *ca.* 1 : 1. Thus, rate-determining
ionization of (II) is believed to occur at least for the
reactions in protic solvents, but we can not offer any
conclusive explanation for the unprecedented difference
in the behaviour of the cationoid species from (II) and
the antimonate salt (I).[6] Probably, these results derive
from the very small energy differences for capture of
nucleophiles at two sites.

The bulkier reagents, $^-CH(CO_2Et)_2$ and $^-CH(COMe)_2$,
are prone to attack predominantly the anthracene ring
at the 10-position. The reaction with trimethylamine or
dimethylamine in aqueous THF gave only the corres-
ponding quinoidal compound. This may be explained as
follows; α-substituted benzylanthracenes are expected

to be unstable when the substituent is large. The
ground state of these compounds is considered to be
represented by the conformation in which the α-methine
proton eclipses one of the *peri*-hydrogens of the anthra-
cene ring,[1] and if so, the interaction between the bulkier
substituent and anthracene ring is large. In contrast,
the quinoidal compound, which is known to have a boat
conformation with the bulkier substituent in the pseudo-
axial position,[7] is not subject to such a *peri*-interaction.

As is expected from the fact that trimethylamine is a
poor leaving group,[8] only 38% of the ethoxy compounds
(15)—(17) were isolated in the reaction of the ammonium
chloride (III) with sodium ethoxide in ethanol for 78 h.
However, the reaction with powerful nucleophiles (^-SPh,
$^-SC_6H_4NO_2$-p, and $LiAlH_4$) [9] proceeded smoothly,
giving exclusively the anthracene derivative. Reduc-
tion with $LiAlD_4$ shows that capture of hydride ion only
occurs at the central carbon. These results demonstrate
that the nucleophile attacks a carbon which is not
bonded to the leaving group, clearly opposite to the
behaviour of (II) toward the same nucleophiles.† The
following may be the reasons why strong nucleophiles
attack exclusively the disfavoured site from the view-
point of charge density. The intermediate (A), which
can be derived from capture of a nucleophile at the 10-
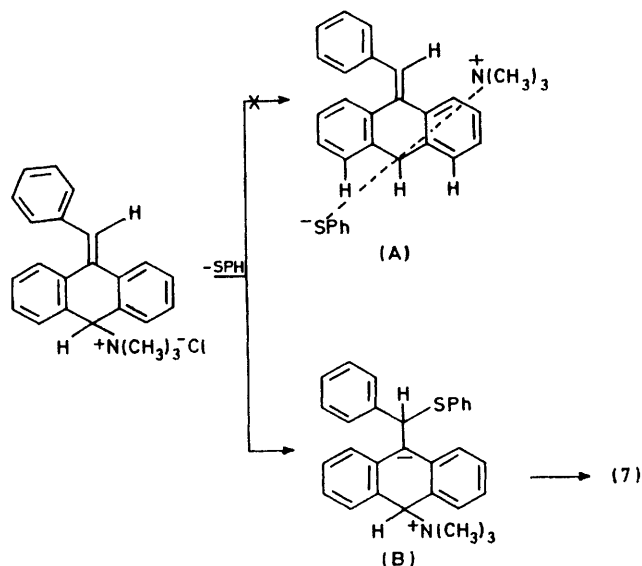
position, is very unstable, because of the severe steric
repulsion between trimethylamine and the anthracene
ring. In contrast, the intermediate (B), which is derived
from attack of a nucleophile on the central carbon, does
not suffer this steric disadvantage. The reaction of (III)
in refluxing ethanol is complete in 45 min, suggesting
that C–N bond fission occurs easily at this temperature.

† A similar discrepancy in sites of attack has also been observed
between 9-chloromethylanthracene and the corresponding
ammonium salt;[10] direct substitution occurs in the reaction of
the chloride. In contrast, the reaction of the ammonium salt
with bulkier reagents like the lithium salt of 2-nitropropane gave
the quinoidal compound exclusively under kinetically controlled
conditions.

* When the reaction was continued for a further 2 h, a mixture
of (7) and (8) was obtained. It is certain that (7) rearranged to
(8) in the system, but the reason is obscure. The reaction of (7)
with ^-SPh in the presence of NaCl in DMF did not yield (8).

More surprisingly, a mixture of (15) and (16) was obtained in 26% yield, when (III) was kept at room temperature for 76 h in ethanol. By comparing the data with those for NaOEt in similar conditions, it may be concluded that ionization is rate-determining even for the reaction of (III) with weak nucleophilic reagents. The starting material was recovered, when the reaction of 9-anthryl-benzyl p-nitrobenzoate or the acetate with sodium thiophenoxide was performed in DMF at room temperature for 2 h.[11]

EXPERIMENTAL

^{1}H N.m.r. were obtained with a JEOL LNM 4P100 instrument, u.v. spectra with a Varian Techron 635 spectrometer, 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 22628 (13 pp.).*

Preparation of 9-α-*Chlorobenzylanthracene* (II).—A solution of 9-α-hydroxybenzylanthracene (8 g, 28 mmol) and thionyl chloride (4 ml) in benzene (20 ml) was refluxed for 3 h. After evaporation of the solvent, the product was triturated with light petroleum to give (II) (70%), m.p. 135—137 °C (from benzene–light petroleum) (Found: C, 83.15; H, 4.85. $C_{21}H_{15}Cl$ requires C, 83.3; H, 5.0%), $\lambda_{max.}$ 393 (log ε 3.78), 373 (3.83), 354 (3.68), and 338 nm (3.39), δ 7.75 (1 H, s).

Preparation of 9-*Anthrylbenzyl Hexachloroantimonte* (I).—To a solution of (II) (1.0 g) in carbon tetrachloride (10 ml) was added a solution of $SbCl_5$ (0.98 g) in carbon tetrachloride (20 ml) at room temperature over 10 min. The solid was filtered off, washed with carbon tetrachloride, and dried ($CaCl_2$) *in vacuo* (yield 76%), m.p. 89—94 °C (Found: C, 44.0; H, 2.7. $C_{21}H_{15}SbCl_6$ requires C, 41.9; H, 2.5%), $\lambda_{max.}$ (SO_2) 660, 465, and 360 nm.

Preparation of N-(9-*Benzylidene*-9,10-*dihydroanthracen*-10-*yl*)-NNN-*trimethylammonium Chloride* (III).—A solution of (I) (5 g, 16.6 mmol) and trimethylamine (*ca.* 30% in water; 10 g) in tetrahydrofuran (100 ml) was stirred at room temperature for 1 h. A crystalline precipitate was filtered off, washed with dry tetrahydrofuran, and dried ($CaCl_2$) (yielded 90%), m.p. 147.0—148.5 °C (Found: C, 75.65; H, 6.65; N, 3.8. $C_{24}H_{24}NCl \cdot H_2O$ requires C, 75.85; H, 6.9; N, 3.7%), $\lambda_{max.}$ 323 (log ε 4.11).

Reaction of (I) *with Lithium Aluminium Hydride*.—To a solution of lithium aluminium hydride (0.75 g, 20 mmol) in ether (50 ml) was added (I) (2 g, 3.3 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 were isolated by column chromatography on silica gel (elution with benzene–light petroleum) (502 mg, 62%). By comparison of the peak areas of the crude products [δ 4.95 for (1) and 3.97 for (2)], the mixture was found to contain 60% (1) and 40% (2).

The crude products were rechromatographed on silica gel. The first fraction contained the crude quinoidal hydrocarbon (2), which was purified by crystallization from ethanol, m.p.

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

134.0—135.5 °C, *m/e* 268, $\lambda_{max.}$ 304 (log ε 3.98) and 243 nm (4.11), δ 3.97 (2 H, s). From the second fraction 9-benzyl-anthracene was isolated, m.p. 134—135 °C (lit.,[12] 133—134 °C), $\lambda_{max.}$ 386 (log ε 4.00), 367 (4.00), 348 (3.83), 332 (3.52), and 249 nm (5.15).

Reaction of (II) *with Sodium Borohydride*.—To a solution of sodium borohydride (0.5 g, 13 mmol), in 70% aqueous diglyme (10 ml) was added (II) (0.5 g, 1.7 mmol), and the mixture was kept at 50 °C for 2 h. After work-up a mixture (0.41 g, 92%) of (1) and (2) was isolated by column chromatography on silica gel.

The reaction of (II) with cycloheptatriene was performed as follows. Into a high-pressure vessel containing (II) (1 g, 3.3 mmol) and cycloheptatriene (1 g), sulphur dioxide (20 ml) was distilled at −70 °C. The vessel was allowed to warm to room temperature, and after 10 min the mixture was cooled, diluted with aqueous potassium hydroxide, and extracted three times with ether. The hydrocarbon mixture (0.71 g, 80%) was isolated by column chromatography.

Reaction of (II) *with Sodium Azide*.—A solution of (II) (1 g, 3.3 mmol) and sodium azide (0.65 g, 10 mmol) in DMF (40 ml) was kept at room temperature for 24 h. After work-up the crude products (0.95 g, 95%) were crystallized from CCl_4–light petroleum to give 10-azido-9-benzylidene-9,10-dihydroanthracene (4), m.p. 129—131 °C, $\lambda_{max.}$ 308 nm (log ε 3.81), δ 5.41 (1 H, s), $\nu_{max.}$ 2 090 cm^{-1}. By column chromatography of the mother-liquors on silica gel, 9-α-azidobenzylanthracene (3) was isolated as a yellow oil, $\lambda_{max.}$ 389 (log ε 3.76), 369 (3.78), 351 (3.60), 335 (3.23), and 263 nm (4.17), δ 8.37 (1 H, s), $\nu_{max.}$ 2 100 cm^{-1}. The n.m.r. and i.r. spectra of the crude products showed the existence of only (3) and (4).

Reaction of (II) *with Potassium Cyanide*.—To a solution of potassium cyanide (1.5 g) in 70% aqueous dioxan was added (II) (1.5 g) in one portion, and stirring was continued for 5 min while a current of nitrogen was bubbled through. A mixture (1.50 g) of (5) and (6) was isolated by column chromatography on silica gel (elution with benzene). Recrystallization from ethanol–light petroleum gave 9-α-cyanobenzylanthracene (5) (0.84 g, 56%), m.p. 163—165 °C (from benzene–ethanol), $\lambda_{max.}$ 388 (log ε 3.83), 369 (3.87), 351 (3.71), and 334 nm (3.38), δ 6.69 (1 H, s), $\nu_{max.}$ 2 240 cm^{-1}. Column chromatography of the mother-liquor on silica gel gave pure 9-benzyl-10-cyanoanthracene, m.p. 160—163 °C (from CCl_4–light petroleum), $\lambda_{max.}$ 410 (log ε 3.72), 388 (3.77), 368 (3.65), and 351 nm (3.39), δ 5.01 (2 H, s), $\nu_{max.}$ 2 220 cm^{-1}. Lithium aluminium hydride reduction of (5) or (6) gave the corresponding primary amine.

Reaction of (II) *with Sodium Thiophenoxide*.—To a solution of sodium thiophenoxide (0.5 g, 3.8 mmol) in DMF (30 ml) was added a solution of (II) (1 g) in DMF (20 ml) over 2 min while a current of nitrogen was bubbled through. The mixture was poured into water and extracted with ether. The crude products were purified by column chromatography on silica gel to give 9-α-phenylthiobenzylanthracene (7) (1.18 g, 95%), a liquid, *m/e* 376, $\lambda_{max.}$ 395 (log ε 3.84), 374 (3.88), 355 (3.69), 338 (3.42), and 268 nm (3.96).

When the reaction was performed under the same conditions for 2 h, a mixture of 9-benzyl-10-phenylthioanthracene (8) and (7) was obtained. Crystallization of the crude products from benzene gave (8), m.p. 206.5—208.5 °C, $\lambda_{max.}$ 406 (log ε 3.83), 385 (3.83), 365 (3.63), 348 (3.33), 330 (3.00), and 264 nm (4.19), δ 5.07 (2 H, s).

The reaction of (II) with sodium *p*-nitrothiophenoxide gave 9-α-(*p*-nitrophenylthio)benzylanthracene (9), m.p. 193—195 °C (from benzene), $\lambda_{max.}$ 396 (log ε 3.94), 377 (4.02), 356 (3.97), and 340 nm (3.95), δ 7.23 (1 H, s).

Reaction of (II) *with Alkoxides.*—To a solution of sodium (4.35 mmol) in ethanol (100 ml) was added (II) (1 g, 3.3 mmol) in one portion, and the mixture was stirred at room temperature for 10 min. The products were isolated by column chromatography on basic alumina. Elution with benzene–light petroleum gave 9-α-ethoxybenzylanthracene (15) (182 mg, 18%), m.p. 135.0—136.5 °C (from ethanol), $\lambda_{max.}$ 387 (log ε 3.86), 367 (3.90), 350 (3.72), 333 (3.41), 318 (3.05), and 257 nm (4.00), δ 1.2 (3 H, t), 3.31 (1 H, dq), and 3.55 (1 H, dq), $\nu_{max.}$ 1 088 cm^{-1}. Elution with benzene gave 9-benzylidene-10-ethoxy-9,10-dihydroanthracene (16); m.p. 98—99 °C (from ethanol), $\lambda_{max.}$ 308 (log ε 4.01) and 242 nm (4.04), δ 1.24 (3 H, t), 3.64 (2 H, q), and 5.24 (1 H, s), $\nu_{max.}$ 1 070 cm^{-1}, *m/e* 312.

The reaction with sodium methoxide gave a mixture of (12) and (13). 9-α-Methoxybenzylanthracene (12) was a solid, m.p. 126—127 °C (from methanol), $\lambda_{max.}$ 388 (log ε 3.79), 378 (3.83), 350 (3.68), and 333 nm (3.41), δ 3.28 (3 H, s) and 6.88 (1 H, s), $\nu_{max.}$ 1 075 cm^{-1}. 9-Benzylidene-10-methoxy-9,10-dihydroanthracene (13) was obtained as a yellow oil, $\lambda_{max.}$ 310 nm, δ 3.37 (3 H, s), and 5.13 (1 H, s), $\nu_{max.}$ 1 068 cm^{-1}.

On treatment of (II) with sodium isopropoxide, (18) and (19) were obtained. 9-α-Isopropoxybenzylanthracene (18) was a solid, m.p. 137—138 °C (from ethanol), $\lambda_{max.}$ 387 (log ε 3.89), 368 (3.94), 351 (3.80), and 332 nm (3.51), δ 0.94 (3 H, d), 1.30 (3 H, d), and 4.88 (1 H), $\nu_{max.}$ 1 060, 1 085, and 1 115 cm^{-1}. 9-Benzylidene-10-isopropoxy-9,10-dihydroanthracene (19) was a yellow oil,[13] $\lambda_{max.}$ 310 nm, δ 1.32 (6 H, d), 3.90 (1 H), and 5.23 (1 H, s), $\nu_{max.}$ 1 060 and 1 115 cm^{-1}.

The reaction of (II) with potassium hydroxide in 70% aqueous dioxan gave the mixture of (10) and (11). 9-α-Hydroxybenzylanthracene (10) was a solid, m.p. 110—112 °C (lit.,[14] 110—112 °C), $\lambda_{max.}$ 388 (log ε 3.87), 367 (3.91), 350 (3.73), 331 (3.42), 318 (3.06), and 260 nm (3.97), δ 2.66 (1 H, d). 9-Benzylidene-10-hydroxy-9,10-dihydroanthracene (11) was a solid, m.p. 119—120 °C (lit.,[15] 120 °C), *m/e* 284, δ 2.32 (1 H, d), 5.60 (1 H, d), 6.70—7.48 (9 H, m), and 7.56—7.84 (4 H, m), $\nu_{max.}$ 3 300 and 1 040 cm^{-1}.

Reaction of (I) *with Potassium t-Butoxide.*—To a solution of potassium t-butoxide (2 g, 17.9 mmol) in t-butyl alcohol (100 ml) was added (I) (2.0 g, 3.3 mmol) in one portion and the mixture was kept at room temperature for 5 min. Crystallization of the crude products from benzene gave bis-9-anthrylbenzyl ether (28); m.p. 287—289 °C, *m/e* 550, $\lambda_{max.}$ 391 (log ε 4.1), 370 (4.13), 352 (3.96), 336 (3.67), and 268 nm, δ 6.6 (2 H, s), $\nu_{max.}$ 1 060 and 1 010 cm^{-1}. Column chromatography of the mother-liquor on basic alumina gave (21) and (22). 9-α-t-Butoxybenzylanthracene (21) was a solid, m.p. 175—178 °C (from benzene–light petroleum), $\lambda_{max.}$ 387 (log ε 3.55), 368 (3.58), 351 (3.47), and 332 nm (3.17), δ 1.15 (9 H, s), *m/e* 340. 9-Benzylidene-10-t-butoxy-9,10-dihydroanthracene (22) was a liquid, $\lambda_{max.}$ 310 nm, δ 1.42 (9 H, s) and 5.45 (1 H, s).

Reaction of (I) *with Phenylmagnesium Bromide*—The reaction of (I) (2 g, 3.3 mmol) and phenylmagnesium bromide (6.6 mmol) in ether (100 ml) was performed at room temperature for 2 h. The column chromatography of the products on neutral alumina gave 9-benzylidene-10-phenyl-9,10-dihydroanthracene (24), and also 9-diphenylmethylanthracene (23) (36%),[1] m.p. 131—133 °C (from benzene–

ethanol), *m/e* 344, $\lambda_{max.}$ 309 (log ε 3.96) and 249 nm (4.09), δ 5.18 (1 H, s).

Reaction of (II) *with Diethyl Sodiomalonate.* To a solution of diethyl sodiomalonate prepared from NaH (50%) (0.47 g, 11 mmol) and diethyl malonate (1.6 g, 9.9 mmol) in DMF (30 ml) was added (II) (3.0 g, 9.9 mmol) in benzene (15 ml) during 10 min, and the mixture was stirred at 50 °C for 2 h. The products were isolated by column chromatography on neutral alumina. Elution with benzene gave diethyl 9-diphenylmethylene-9,10-dihydroanthracen-10-ylmalonate (25), a yellow oil, *m/e* 426, $\lambda_{max.}$ 308 (log ε 3.88), 257 (1.61), and 252 nm (1.60), δ 1.06 (6 H, t), 3.68 (1 H, d), 3.98 (4 H, q), and 4.70 (1 H, d), $\nu_{max.}$ 1 755 and 1 740 cm^{-1}. When a solution of (25) (500 mg, 1.17 mmol) and potassium t-butoxide (500 mg, 5.2 mmol) in t-butyl alcohol (30 ml) was kept under reflux for 2 h, 9-α-carboxymethyl-10-benzylanthracene was isolated (78%), m.p. 261—265 °C (from ethanol) (Found: C, 84.3; H, 5.45. $C_{23}H_{18}O_2$ requires C, 84.65; H, 5.55%), $\lambda_{max.}$ 398, 377, 357, 340, 324, and 263 nm, δ (in CDCl$_3$–Et$_3$N) 4.56 (2 H, s) and 4.95 (2 H, s), $\nu_{max.}$ 1 705 cm^{-1}.

Reaction of (II) *with Sodiodiacetylmethane.*—To a solution of sodiodiacetylmethane, prepared from sodium hydride (50% dispersion in mineral oil; 700 mg; 15 mmol) and acetylacetone (1.5 g, 15 mmol) in DMF (45 ml), was added a solution of (II) (1.5 g, 5 mmol) in benzene (15 ml), and the mixture was stirred at 50 °C for 2 h. The products were isolated by column chromatography on silica gel (elution with ether). The first fraction contained 9-α-(diacetylmethyl)benzylanthracene (26) (145 mg, 8%), m.p. 232—234 °C (from ether–light petroleum), $\lambda_{max.}$ 391 (log ε 3.77), 370 (3.81), 352 (3.66), and 335 nm (3.39), δ 1.34 (3 H, s), 2.43 (3 H, s), 5.50 (1 H, d), and 6.65 (1 H, d), $\nu_{max.}$ 1 692 cm^{-1}. From the second fraction was obtained 9-benzylidene-10-diacetylmethyl-9,10-dihydroanthracene (27) (745 mg, 41%), m.p. 98.0—99.5 °C (from ether–light petroleum), $\lambda_{max.}$ 310 nm (log ε 4.05), δ 1.81 (3 H, s), 2.06 (3 H, s), 4.21 (1 H, d), and 4.78 (1 H, d), $\nu_{max.}$ 1 733 and 1 700 cm^{-1}.

Reaction of (III) *with Alkoxide.*—To a solution of sodium (0.5 g, 22 mmol) in ethanol (100 ml) was added (III) (0.5 g, 1.53 mmol), and the mixture was refluxed for 1 h. By column chromatography on basic alumina, 9-benzyl-10-ethoxyanthracene (17), with (15) and (16), was isolated as a yellow oil, $\lambda_{max.}$ 402 (log ε 3.70), 381 (3.74), 361 (3.56), and 345 nm (3.30), δ 1.65 (3 H, t), 4.28 (2 H, q), and 4.88 (2 H, s), $\nu_{max.}$ 1 280 and 1 090 cm^{-1}.

9-Benzyl-10-methoxyanthracene (14) was a liquid, $\lambda_{max.}$ 402 (log ε 3.77), 380 (3.82), 361 (3.65), and 343 nm (3.40), δ 4.09 (3 H, s) and 4.87 (2 H, s), $\lambda_{max.}$ 1 280 and 1 075 cm^{-1}. 9-Benzyl-10-isopropoxyanthracene (20) was a solid, m.p. 96—97 °C (from ether–light petroleum), $\lambda_{max.}$ 404 (log ε 3.91), 383 (3.96), 365 (3.82), and 351 nm (3.58), δ 1.43 (6 H, d), 4.63 (1 H), and 4.91 (2 H, s), $\nu_{max.}$ 1 280 and 1 090 cm^{-1}.

Thermodynamic Stabilities of Compounds with Anthracene Structure and with Quinoidal Structure.—When a mixture of (2) (330 mg, 1.23 mmol) and potassium t-butoxide (300 mg, 2.8 mmol) in t-butyl alcohol (15 ml) was heated under reflux for 4 h, the u.v. absorption of (2) disappeared completely. From the reaction mixture (1) was isolated in 70% yield.

A solution of (4) and sodium azide (3 mol. equiv.) in aqueous DMF was kept at 80 °C for 6 h, and after conventional work-up (3) was isolated in 85% yield by column chromatography on silica gel.

When a solution of (16) in ethanol in the presence of small

amounts of sulphuric acid was kept at room temperature for 4 h, (15) was obtained quantitatively. Under similar conditions, (11) and (13) rearranged completely to (10) and (12), respectively.

[9/515   *Received, 2nd April,* 1979]

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