

Reaction of 9- α -Chloronaphthylmethylanthracene and Its Homologues with Nucleophiles under Solvolytic Conditions. Effect of the Increase of Bulk at C- α on the Reaction Site

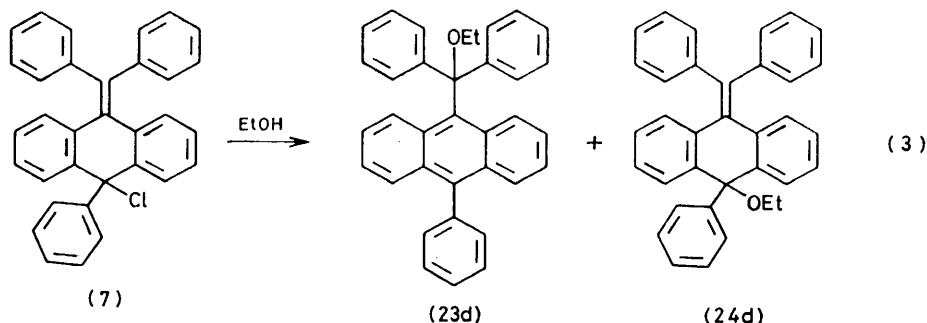
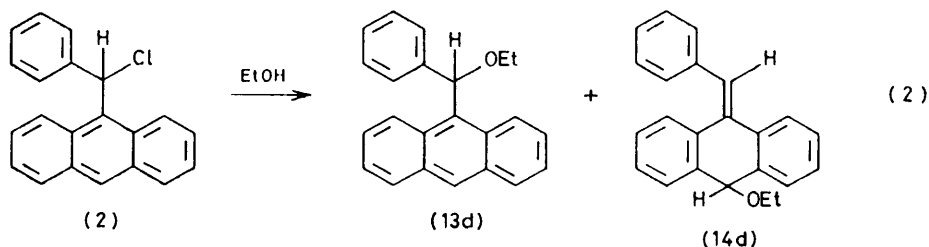
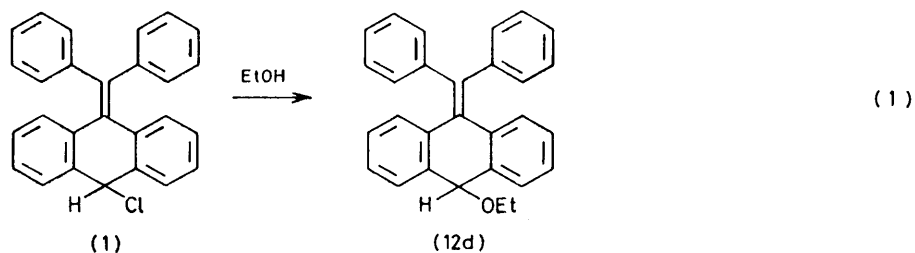
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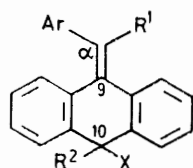
The reaction of 9- α -chloronaphthylmethylanthracene and its homologues with (a) sodium ethoxide in ethanol, (b) ethanol in the presence of triethylamine, (c) sodium borohydride in aqueous diglyme, and (d) sodium azide in aqueous *NN*-dimethylformamide has given a mixture of substituted anthracenes and 9,10-dihydroanthracenes. The yield of the latter increases as the aryl group at C- α becomes larger. The phenyl ring of a chloride at C-10 causes the reaction at this position to be retarded. The relative thermodynamic stabilities between the anthracenes and the 9,10-dihydroanthracenes have been investigated.

RECENTLY we reported that under solvolytic conditions 9-diphenylmethylene-10-chloro-9,10-dihydroanthracene (1) undergoes nucleophilic attack to give predominantly the expected substitution product (12d) [equation (1)].¹ The reaction of 9- α -chlorobenzylanthracene (2) with the same nucleophile also affords the expected substitution product (13d) but this is accompanied by the 9,10-dihydroanthracene derivative (14d) in which the substituent had entered the less hindered 10-position in (2) [equation (2)].^{2,3} This effect of steric hindrance at the site of the α -chloro-group is further illustrated in equation (3).¹ Thus, as is well known,⁴⁻⁸ an increase in steric bulk at the site of the leaving group in a conjugated

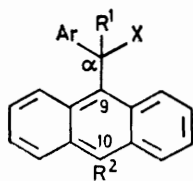
allylic system leads to substitution with rearrangement. Consistent with this, Applequist and Sward⁹ have found that the reaction of bis(anthracenyl)methanol (19c) with ethanol in the presence of 1 mol equiv. of zinc chloride gives only the 9,10-dihydro-ether (20d): again there is a change in reaction type from S_N to S_N' .

In the light of these results, we have investigated the reactions of 9- α -chloronaphthylmethylanthracene (3) and its homologues, (4)–(6) and (9)–(10), with several nucleophiles under solvolytic conditions to determine the effect of a gradual increase of bulk at C- α . The relative thermodynamic stabilities of the isomeric anthracene and 9,10-dihydroanthracene derivatives have





- (5) Ar = 9-anthryl, R¹ = R² = H, X = Cl
 (6) Ar = 10-phenyl-9-anthryl, R¹ = R² = H, X = Cl
 (10) Ar = 10-phenyl-9-anthryl, R¹ = H, R² = Ph, X = Cl
 (12)a; Ar = R¹ = Ph, R² = X = H
 b; Ar = R¹ = Ph, R² = H, X = N₃
 d; Ar = R¹ = Ph, R² = H, X = OEt
 (14)a; Ar = Ph, R¹ = R² = X = H
 b; Ar = Ph, R¹ = R² = H, X = N₃
 d; Ar = Ph, R¹ = R² = H, X = OEt
 (16)a; Ar = 1-naphthyl, R¹ = R² = X = H
 b; Ar = 1-naphthyl, R¹ = R² = H, X = N₃
 d; Ar = 1-naphthyl, R¹ = R² = H, X = OEt
 (18)a; Ar = 9-phenanthryl, R¹ = R² = X = H
 b; Ar = 9-phenanthryl, R¹ = R² = H, X = N₃
 d; Ar = 9-phenanthryl, R¹ = R² = H, X = OEt
 e; Ar = 9-phenanthryl, R¹ = R² = H,
 X = NHPO(OCH₂CH₂Cl)₂
 (20)a; Ar = 9-anthryl, R¹ = R² = X = H
 b; Ar = 9-anthryl, R¹ = R² = H, X = N₃
 c; Ar = 9-anthryl, R¹ = R² = H, X = OH
 d; Ar = 9-anthryl, R¹ = R² = H, X = OEt
 e; Ar = 9-anthryl, R¹ = R² = H,
 X = NHPO(OCH₂CH₂Cl)₂
 (22)a; Ar = 10-phenyl-9-anthryl, R¹ = R² = X = H
 b; Ar = 10-phenyl-9-anthryl, R¹ = R² = H, X = N₃
 c; Ar = 10-phenyl-9-anthryl, R¹ = R² = H, X = OH
 d; Ar = 10-phenyl-9-anthryl, R¹ = R² = H, X = OEt
 e; Ar = 10-phenyl-9-anthryl, R¹ = R² = H,
 X = NHPO(OEt)₂
 (24)d; Ar = R¹ = R² = Ph, X = OEt
 (26)a; Ar = R² = Ph, R¹ = X = H
 b; Ar = R² = Ph, R¹ = H, X = N₃
 (28)a; Ar = 1-naphthyl, R² = Ph, R¹ = X = H
 b; Ar = 1-naphthyl, R² = Ph, R¹ = H, X = N₃
 c; Ar = 1-naphthyl, R² = Ph, R¹ = H,
 X = NHPO(OCH₂CH₂Cl)₂
 (30)a; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = X = H
 b; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = H, X = N₃
 c; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = H, X = OH
 d; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = H, X = OEt
 e; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = H,
 X = NHPO(OEt)₂



- (3) Ar = 1-naphthyl, R¹ = R² = H, X = Cl
 (4) Ar = 9-phenanthryl, R¹ = R² = H, X = Cl
 (8) Ar = R² = Ph, R¹ = H, X = Cl
 (9) Ar = 1-naphthyl, R¹ = H, R² = Ph, X = Cl
 (11)a; Ar = R¹ = Ph, R² = X = H
 b; Ar = R¹ = Ph, R² = H, X = N₃
 (13)a; Ar = Ph, R¹ = R² = X = H
 b; Ar = Ph, R¹ = R² = H, X = N₃
 d; Ar = Ph, R¹ = R² = H, X = OEt
 (15)a; Ar = 1-naphthyl, R¹ = R² = X = H
 b; Ar = 1-naphthyl, R¹ = R² = H, X = N₃
 c; Ar = 1-naphthyl, R¹ = R² = H, X = OH
 d; Ar = 1-naphthyl, R¹ = R² = H, X = OEt
 (17)a; Ar = 9-phenanthryl, R¹ = R² = X = H
 b; Ar = 9-phenanthryl, R¹ = R² = H, X = N₃
 c; Ar = 9-phenanthryl, R¹ = R² = H, X = OH
 d; Ar = 9-phenanthryl, R¹ = R² = H, X = OEt
 (19)a; Ar = 9-anthryl, R¹ = R² = X = H
 c; Ar = 9-anthryl, R¹ = R² = H, X = OH
 (21)a; Ar = 9-anthryl, R² = Ph, R¹ = X = H
 b; Ar = 9-anthryl, R² = Ph, R¹ = H, X = N₃
 c; Ar = 9-anthryl, R² = Ph, R¹ = H, X = OH
 e; Ar = 9-anthryl, R² = Ph, R¹ = H, X = NHPO(OEt)₂
 (23)a; Ar = R¹ = R² = Ph, X = H
 b; Ar = R¹ = R² = Ph, X = N₃
 d; Ar = R¹ = R² = Ph, X = OEt
 (25)a; Ar = R² = Ph, R¹ = X = H
 b; Ar = R² = Ph, R¹ = H, X = N₃
 d; Ar = R² = Ph, R¹ = H, X = OEt
 (27)a; Ar = 1-naphthyl, R² = Ph, R¹ = X = H
 b; Ar = 1-naphthyl, R² = Ph, R¹ = H, X = N₃
 d; Ar = 1-naphthyl, R² = Ph, R¹ = H, X = OEt
 e; Ar = 1-naphthyl, R² = Ph, R¹ = H,
 X = NHPO(OCH₂CH₂Cl)₂
 (29)a; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = X = H
 b; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = H, X = N₃
 c; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = H, X = OH
 d; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = H, X = OEt
 e; Ar = 10-phenyl-9-anthryl, R² = Ph, R¹ = H,
 X = NHPO(OEt)₂
 (31) Ar = Ph, R¹ = *p*-ethoxyphenyl, R² = X = H
 (32) Ar = Ph, R¹ = *p*-ethoxyphenyl, R² = Ph, X = H

been investigated. These data add to our knowledge of anionotropic systems.¹⁰⁻¹²

RESULTS AND DISCUSSION

Reaction of 9- α -Chloronaphthylmethylanthracene and its Homologues.—We have examined the reactions of the chlorides (3)—(6) with (a) sodium ethoxide in ethanol, (b) ethanol in the presence of triethylamine, (c) sodium borohydride in aqueous diglyme, and (d) sodium azide in

aqueous *NN*-dimethylformamide (DMF). Treatment of (3) with sodium ethoxide gave a mixture of the anthracene (15d) and 9,10-dihydroanthracene (16d): the ratio of (15d) to (16d) (9 : 91) is much smaller than that of (13d) to (14d) (3 : 7) observed in the reaction of (2) with the same nucleophile. These results support the suggestion that an increase in steric hindrance at the site of the leaving group compels the nucleophile to attack at the alternative less hindered site. The product composition observed for ethanolysis of the chlorides (3)—(6) is very similar to that found for the reaction with sodium

TABLE 1

Reaction of (3) and its homologues with nucleophiles ^a

Substrate	Nucleophile	Product [% yield] ^b
(2)	NaOEt ^c	88 [(13d) : (14d) = 30 : 70] ^h
(3)	NaOEt ^c	92 [(15d) : (16d) = 9 : 91]
(4)	NaOEt ^c	(18d) [95]
(5)	NaOEt ^c	(20d) [98]
(6)	NaOEt ^c	(22d) [91]
(1)	NaOEt ^c	(12d) [80], (31) [5] ⁱ
(2)	EtOH ^d	84 [(13d) : (14d) = 33 : 67] ^h
(3)	EtOH ^d	86 [(15d) : (16d) = 12 : 88]
(4)	EtOH ^d	(18d) [96]
(5)	EtOH ^d	(20d) [93]
(6)	EtOH ^d	(22d) [94]
(1)	EtOH ^d	(12d) [85] ⁱ
(2)	NaBH ₄ ^e	96 [(13a) : (14a) = 40 : 60] ^h
(3)	NaBH ₄ ^e	81 [(15a) : (16a) = 25 : 75]
(4)	NaBH ₄ ^e	86 [(17a) : (18a) = 33 : 67]
(5)	NaBH ₄ ^e	75 [(19a) : (20a) = 9 : 91]
(6)	NaBH ₄ ^e	90 [(21a) : (22a) = 19 : 81]
(1)	NaBH ₄ ^{e, g}	95 [(11a) : (12a) = 40 : 60] ⁱ
(2)	NaN ₃ ^f	90 [(13b) : (14b) = 54 : 46] ^h
(3)	NaN ₃ ^f	85 [(15b) : (16b) = 28 : 72]
(4)	NaN ₃ ^f	90 [(17b) : (18b) = 32 : 68]
(5)	NaN ₃ ^f	(20b) [95]
(6)	NaN ₃ ^f	92 [(21b) : (22b) = 17 : 83]
(1)	NaN ₃ ^f	90 [(11b) : (12b) = 50 : 50] ⁱ

^a Reaction performed at 20 °C. ^b Isolated yield. The ratio of products was calculated from the comparison of the peak areas of the n.m.r. spectra of the crude products. ^c For 10 min. ^d Reaction in the presence of triethylamine (3 mol equiv.) for 10 min. ^e Reaction performed in aqueous diglyme for 30 min. ^f A solution in aqueous DMF was allowed to react for 30 min. ^g Reaction performed for 1 h. ^h Data taken from ref. 4. ⁱ Data taken from the ref. 1.

ethoxide, suggesting that nucleophilicity does not affect the product composition.*

The reaction of (3) with sodium borohydride in aqueous diglyme gave a mixture of (15a) and (16a). As is expected from the increased steric crowding at C- α in (3) compared with (2), the (15a) : (16a) ratio (1 : 3) is lower than the (13a) : (14a) ratio (2 : 3). However, treatment of (4) with the same nucleophile gave a mixture of (17a) and (18a) in a molar ratio of 1 : 2, in spite of the fact that the benzylic site of (4) must be more crowded than the same site in (3): the reason is obscure. A similar reverse-product composition was also found in the reactions of (3) and (4) with sodium azide. Small nucleophiles, sodium borohydride and sodium azide, attack both the benzylic sites and the ring sites of (4)—(6) [the exception is the reaction of (5) with sodium azide, in which the 9,10-dihydroanthracene azide (20b) was the sole product]. In the cases of (5) and 10-chloro-9-(10'-phenylanthracen-9'-ylidene)-9,10-dihydroanthracene (6) the nucleophile may attack C-10' as well as C- α and C-10. However, the reaction of (6) did not give a product derived from attack on C-10'. In the case of (5), however, C-10' seems to be a possible reaction site. Consistently, the proportion of nucleophilic attack at C- α is higher in the reaction of (6) compared with (5).

* However, the nucleophilicity of a reagent can affect the reaction site in (10): the reaction with ethanol, a weak nucleophile, gives only a 9,10-dihydro-compound (30d), while sodium ethoxide attacks both the benzylic and ring sites to give a mixture of (29d) and (30d) (Table 2). A similar dependence of reaction site on the nucleophilicity of a reagent has been observed in the reactions of (1) and (7) (Tables 1 and 2).¹

A phenyl substituent on the allylic methylene group (C-10) hinders direct displacement of chloride so that substitution occurs at the less hindered conjugated sites (S_N' reaction) [compare the reactions of the chlorides (2), (3), and (6) with those of (8), (9), and (10), respectively] (Table 2). The dihedral angle between the phenyl ring and the anthracene ring of 9-phenylanthracene is known to be *ca.* 67°. ¹³ Thus, the approach of a nucleophile to the position of attachment of a phenyl ring must be highly hindered to all but the smallest nucleophiles. Hence, there is relatively more direct displacement of chloride by sodium azide and sodium borohydride, compared with sodium ethoxide.

TABLE 2

Reaction of (9) and its homologues with nucleophiles ^a

Substrate	Nucleophile	Product [% yield] ^b
(7)	NaOEt	(32 [74] ^c
(8)	NaOEt	(25d) [90] ^d
(9)	NaOEt	(27d) [91]
(10)	NaOEt	85 [(29d) : (30d) = 20 : 80]
(7)	EtOH	99 [(23d) : (24d) = 48 : 52] ^c
(8)	EtOH	(25d) [93] ^d
(9)	EtOH	(27d) [89]
(10)	EtOH	(30d) [96]
(7)	NaBH ₄ ^e	(23a) [87] ^c
(8)	NaBH ₄ ^e	(25a) [90] ^d
(9)	NaBH ₄ ^e	82 [(27a) : (28a) = 72 : 28]
(10)	NaBH ₄ ^e	87 [(29a) : (30a) = 48 : 52]
(7)	NaN ₃ ^c	(23b) [85] ^c
(8)	NaN ₃ ^c	85 [(25b) : (26b) = 65 : 35] ^d
(9)	NaN ₃ ^c	89 [(27b) : (28b) = 54 : 46]
(10)	NaN ₃ ^c	82 [(29b) : (30b) = 20 : 80]

^a Reaction conditions are described in the footnote of Table 1. ^b Ratio of the products was calculated from comparison of the peak areas of the n.m.r. spectra of the crude products. ^c Data taken from ref. 1. ^d Data taken from ref. 4. ^e Reaction performed for 1 h.

Relative Thermodynamic Stabilities of the Isomeric Anthracene and 9,10-Dihydroanthracene Derivatives.—Because of the resonance of anthracene, usually 9,10-dihydroanthracenes rearrange to the isomeric anthracenes under appropriate conditions (anionotropic and prototropic isomerizations).^{2,10-12} Consistent with this, treatment of the 9,10-dihydroanthracenes (aryl = phenyl, 1-naphthyl, and 9-phenanthryl; substituent = H, OH, N₃, and OEt) under the conditions cited in the footnote of Table 3 gave the isomeric anthracenes. The 9,10-dihydroanthracene hydrocarbons (20a), (22a), and (30a) also rearrange to the anthracenes (19a), (21a), and (29a), respectively. However, an increase in steric bulk at C- α leads to an increase in the relative stability of the 9,10-dihydroanthracenes, because destabilization by the steric hindrance overcomes stabilization by aromatization in the corresponding anthracene isomers.^{14,15} Consistent with this, the α -substituted 9-(9-anthrylmethyl)anthracene (the substituent OH, N₃, and OEt) rearrange to the isomeric 10-substituted 9,10-dihydroanthracenes. The phenyl ring on C-10 did not affect the relative stabilities of the isomeric anthracene and 9,10-dihydroanthracene derivatives (Table 3).

TABLE 3

Relative thermodynamic stabilities of the isomeric products

Substrate	Conditions ^a	Product [% yield ^b]
(16a)	i	(15a) [97]
(16b)	ii	(15b) [85]
(16d)	v	(15d) [90]
(18a)	i	(17a) [96]
(18b)	ii	(17b) [87]
(18d)	v	(17d) [90]
(19c)	iv	(20c) [74]
(20a)	i	(19a) [90]
(21c)	iv	(22c) [70]
(22a)	i	(21a) [87]
(28a)	i	(27a) [97]
(28b)	iii	(27b) [87]
(29b)	ii	(30b) [95]
(29c)	iv	(30c) [91]
(30a)	i	(29a) [90]f

^a A solution of a hydrocarbon and *t*-butoxide (10 mol equiv.) in *t*-butyl alcohol was heated under reflux for 2 h (condition i). An azide was isomerized by column chromatography on silica gel (condition ii) or on treatment with sodium azide (10 mol equiv.) in aqueous DMF (condition iii). A solution of an alcohol and catalytic amounts of sulphuric acid in aqueous dioxan was kept at 70 °C for 2 h (condition iv). Treatment of an ether with sulphuric acid in ethanol at 70 °C for 2 h gave the isomeric product (condition v). ^b Isolated yield.

EXPERIMENTAL

¹H N.m.r. spectra were obtained for solutions in CDCl₃ with a JEOL LMN 4P 100 instrument, u.v. spectra for solutions in dioxan with a Varian Techtron 635 spectrometer unless otherwise noted, and i.r. spectra with a Hitachi 215 spectrometer.

Di-(9-anthracenyl)methanol (19c) was prepared by the reported method.¹⁶ (1-Naphthyl)-(9-anthryl)methanol (15c), (9-phenanthryl)-(9-anthryl)methanol (17c), (10-phenyl-9-anthryl)-(9-anthryl)methanol (21c), (1-naphthyl)-(10-phenyl-9-anthryl)methanol (27c), and bis-(10-phenyl-9-anthryl)methanol (29c) were prepared by similar methods.

The alcohol (15c) had m.p. 180–181 °C (from benzene–light petroleum), λ_{\max} 389 (log ϵ 3.75), 366 (3.78), 350 (3.61), and 333 nm (3.25), ν_{\max} 3450 and 1050 cm⁻¹; (17c) had m.p. 226–229 °C (from benzene–light petroleum), λ_{\max} 389 (4.02), 369 (4.04), 351 (3.89), and 333 nm (3.60), ν_{\max} 3550 and 1060 cm⁻¹; (21c) had m.p. 221–222 °C (from benzene–light petroleum), λ_{\max} 399 (4.18), 378 (4.14), and 358 nm (3.94), ν_{\max} 3550, 3400, and 1030 cm⁻¹; (27c) had m.p. 155–157 °C (from benzene–light petroleum), λ_{\max} 396 (4.19), 376 (4.21), 357 (3.99), 340 (3.64), and 324 nm (3.24), ν_{\max} 3550, 3350, and 1025 cm⁻¹; (29c) had m.p. 151 °C (from benzene–light petroleum), λ_{\max} 402 (4.29), 382 (4.28), 360 (4.05), 355 (3.76), 336 (3.44), and 264 nm (4.33), ν_{\max} 3550 and 1040 cm⁻¹.

Preparation of Chlorides.—Through a solution of the alcohol (15 mmol) and anhydrous CaCl₂ (15 mmol) in CH₂Cl₂ was bubbled dry HCl gas at 20 °C for 20 min. After removal of the CaCl₂ by filtration, the solvent was evaporated off *in vacuo*. The crude products were triturated with light petroleum. The solid was collected and purified by recrystallization from appropriate solvents. The chlorides (3), (4), and (9) were prepared as above: (3) had m.p. 141–144 °C (from benzene–light petroleum), λ_{\max} 393 (log ϵ 3.88), 372 (3.94), 351 (3.81), and 337 nm (3.59); (4) had m.p. 217–220 °C (from benzene–light petroleum), λ_{\max} 394 (3.86), 374 (3.95), 354 (3.78), and 338

n.m. (3.53); (9) had m.p. 188–193 °C (from CH₂Cl₂–light petroleum), λ_{\max} 402 (3.95), 381 (4.00), 361 (3.80), and 342 nm (3.48). 9-(9-Anthrylmethylidene)-10-chloro-9,10-dihydroanthracene (5) was prepared by the reported method.³ In a similar manner, (6) and (10) were prepared from the corresponding alcohols: (6) had m.p. 193–196 °C (from CH₂Cl₂–light petroleum), λ_{\max} 400 (log ϵ 4.15), 382 (4.10), and 363 nm (3.91); (10) had m.p. 162–163 °C (from benzene–light petroleum), λ_{\max} 400 (4.29), 381 (4.24), and 362 nm (4.02).

Reaction with Sodium Ethoxide.—To a solution of sodium ethoxide (10 mmol) in ethanol (50 ml) was added a solution of (9-anthryl)-(1-naphthyl)chloromethane (3) (1.0 g, 2.83 mmol) in benzene (50 ml), and the mixture was stirred at 20 °C for 10 min. U.v. and n.m.r. spectroscopy indicated that the crude products contained (9-anthryl)-(1-naphthyl)-methyl ethyl ether (15d) and 9-(1-naphthylmethylidene)-10-ethoxy-9,10-dihydroanthracene (16d) in the molar ratio 9:91. Column chromatography on basic alumina (elution with 1:10 benzene–light petroleum) afforded first (16d) (0.65 g, 83%); m.p. 165–166 °C (from benzene–light petroleum), λ_{\max} 325 nm (log ϵ 2.99), ν_{\max} 1070 cm⁻¹, δ 1.28 (3 H, t), 3.67 (2 H, q), and 5.32 (1 H, s). From the second fraction (15d) was isolated (0.09 g, 9%); m.p. 176–177 °C (from benzene–light petroleum), λ_{\max} 389 (log ϵ 4.02), 369 (4.05), 350 (3.87), 334 (3.53), and 318 nm (3.22), ν_{\max} 1080 cm⁻¹, δ 1.20 (3 H, t) and 3.65 (2 H, q).

The ether (17d) had m.p. 194–195 °C (from benzene–light petroleum), λ_{\max} 389 (log ϵ 3.94), 369 (3.98), 351 (3.81), and 334 nm (3.48), ν_{\max} 1062 cm⁻¹, δ 1.16 (3 H, t) and 3.16–3.84 (2 H, m); (18d) had m.p. 137–140 °C (from benzene–light petroleum), λ_{\max} 321 nm (4.19), ν_{\max} 1070 cm⁻¹, δ 1.35 (3 H, t), 3.75 (2 H, q), and 5.37 (1 H, s); (22d) had m.p. 216–218 °C (from benzene–light petroleum), λ_{\max} 400 (4.15), 380 (4.11), and 363 nm (3.90), ν_{\max} 1070 cm⁻¹, δ 1.34 (3 H, t), 3.66 (2 H, q), and 5.30 (1 H, s); (27d) had m.p. 122–125 °C (from benzene–light petroleum) λ_{\max} 397 (4.11), 376 (4.14), 357 (3.93), 338 (3.60), and 322 (3.24), ν_{\max} 1180 cm⁻¹, 1.20 (3 H, t) and 3.20–3.90 (2 H, m); (29d) had m.p. 264–266 °C (from benzene–light petroleum), λ_{\max} 403 (4.42), 381 (4.35), 361 (4.09), and 343 nm (3.79), ν_{\max} 1082 and 1065 cm⁻¹, δ 1.30 (3 H, t) and 3.74 (2 H, q); (30d) had m.p. 204–205 °C (from ether), λ_{\max} 400 (4.31), 381 (4.27), and 362 nm (4.04), ν_{\max} 1060 cm⁻¹, δ 1.25 (3 H, t) and 3.23 (2 H, q).

Reaction with Ethanol in the Presence of Triethylamine.—The chloride (3) (1.0 g, 2.83 mmol) was added to a mixture of ethanol (50 ml) and triethylamine (1 ml), and the mixture was kept at 20 °C for 10 min. After work-up the crude products were separated by column chromatography on basic alumina to give first (16d) (0.77 g, 75%) and then (15d) (0.11 g, 11%).

Reaction with Sodium Borohydride.—To a solution of sodium borohydride (0.5 g, 13.2 mmol) in aqueous 70% (v/v) diglyme (60 ml), was added (3) (1.0 g, 2.83 mmol) at 20 °C during 10 min. The reaction was continued for a further 20 min. By column chromatography on alumina (elution with 1:10 benzene–light petroleum) afforded first 9-(1-naphthylmethylidene)-9,10-dihydroanthracene (16a); m.p. 155–156 °C (from benzene–ethanol), λ_{\max} 324 (log ϵ 4.08), δ 4.89 (2 H, s). The second fraction contained 9-(1-naphthyl)methylanthracene (15a) (0.18 g, 20%); m.p. 186–187 °C (from benzene–ethanol), λ_{\max} 390 (log ϵ 3.90), 367 (4.05), 332 (3.37), and 316 nm (3.10), δ 5.41 (2 H, s).

The hydrocarbon (17a) had m.p. 255–257 °C (from

benzene-ethanol), λ_{max} 389 (log ϵ 4.07), 367 (4.09), 348 (3.93), 330 (3.63), and 312 nm (3.35), δ 5.40 (2 H, s); (18a) had m.p. 172—173 °C (from benzene-ethanol), λ_{max} 318 nm (4.09), δ 4.12 (2 H, s); (21a) had m.p. 234—236 °C (from benzene-light petroleum), λ_{max} 402 (4.28), 379 (4.22), and 359 nm (4.01), δ 6.00 (2 H, s); (22a) had m.p. 200 °C (decomp.) (from benzene-light petroleum), λ_{max} 399 (4.06), 381 (4.05), 361 (3.83), and 341 nm (3.82), δ 4.19 (2 H, s); (27a) had m.p. 227—229 °C (from benzene-ethanol), λ_{max} 396 (4.09), 375 (4.10), 357 (3.90), 340 (3.53), and 323 nm (3.12), δ 5.47 (2 H, s); (28a) had m.p. 179—181 °C (from benzene-ethanol), λ_{max} 324 nm (4.06), δ 5.30 (1 H, s); (29a) had m.p. >300 °C, λ_{max} 404 (4.36), 382 (4.31), 362 (4.06), 343 (3.76), and 327 nm (3.43), δ 6.07 (2 H, s); (30a) had m.p. 155 °C (from benzene-ethanol), λ_{max} 400 (4.14), 380 (4.10), 361 (3.87), and 343 nm (3.62), δ 5.40 (1 H, s).

Reaction with Sodium Azide.—To a solution of (3) (1.0 g, 2.83 mmol) in dimethylformamide (DMF) (30 ml) was added a solution of sodium azide (0.56 g, 8.5 mmol) in 40% (v/v) aqueous DMF (30 ml) at 20 °C, and stirring was continued for a further 30 min. The quinoidal product (16b), isolated by triturating with CCl₄-methanol, was purified by fractional recrystallizations: m.p. 125—127 °C (from CCl₄-methanol), λ_{max} 330 nm (log ϵ 4.17), ν_{max} 2 080 and 1 220 cm⁻¹, δ 5.48 (1 H, s). Column chromatography of the mother-liquor on silica gel gave (15b); m.p. 140—142 °C (from CCl₄-methanol), λ_{max} 389 (log ϵ 3.90), 370 (3.93), 352 (3.80), 335 (3.55), and 318 nm (3.38), ν_{max} 2 070 and 1 230 cm⁻¹. The reaction of (4) gave the quinoidal azide (18b) [δ 5.52 (1 H, s), λ_{max} 324 nm], but the pure compound could not be isolated because of lability during column chromatography on silica-gel or alumina. To characterize (18b), the crude products were treated with 1 mol equiv. of tris-(2-chloroethyl) phosphite in refluxing benzene for 12 h to yield the amidophosphate (18e) which was isolated by column chromatography on silica gel (elution with 1 : 19 methanol-ether); m.p. 132—135 °C (from ether-light petroleum), λ_{max} 320 nm (log ϵ 3.94), ν_{max} 1 250, 1 060, and 1 010 cm⁻¹, δ 3.24 (1 H, d, *J* 11 Hz), 3.71 (4 H, t, *J* 5 Hz), 4.10—4.44 (4 H, m), and 5.50 (1 H, t, *J* 11 Hz). Similarly, (27b) and (28b) were treated with tris-(2-chloroethyl) phosphite to give the corresponding amidophosphates (27e) and (28e) respectively: (27e) had m.p. 186—188 °C (from ether-light petroleum), λ_{max} 397 (log ϵ 4.05), 376 (4.07), 358 (3.86), 340 (3.53), and 325 nm (3.28), ν_{max} 1 240, 1 065, and 1 010 cm⁻¹, δ 3.00—3.60 (5 H, m), and 3.80—4.28 (4 H, m); (28e) had m.p. 205—206 °C (from ether-light petroleum), λ_{max} 327 nm (4.08), ν_{max} 1 230, 1 065, and 1 020 cm⁻¹, δ 3.40—3.64 (4 H, q, *J* 6 Hz), 3.80 (1 H, d, *J* 7

Hz), and 3.90—4.20 (4 H, m). The amidophosphates (20e), (29e), and (30e) were obtained by the reactions of (20b), (29b), and (30b), respectively, with triethyl phosphite; (20e) had m.p. 188—190 °C (from ether-light petroleum), λ_{max} 391 (log ϵ 3.89), 372 (3.85), and 356 nm (3.67), ν_{max} 1 240, 1 055, and 1 035 cm⁻¹, δ 1.34 (6 H, t, *J* 7 Hz), 3.22 (1 H, t, *J* 11 Hz), 4.00—4.40 (4 H, m), and 5.50 (1 H, t, *J* 8 Hz); (29e) had m.p. 264—267 °C (from ether-light petroleum), λ_{max} 404 (4.49), 382 (4.45), 360 (4.20), and 344 nm (3.90), ν_{max} 1 230 and 1 030 cm⁻¹, δ 0.95 (6 H, t, *J* 7 Hz) and 3.05—4.00 (5 H, m); (30e) had m.p. 237—239 °C (from ether), λ_{max} 400 (4.11), 380 (4.07), 384 (3.61), 342 (3.48), and 359 nm (4.60), ν_{max} 1 230 and 1 040 cm⁻¹, δ 1.00—1.36 (6 H, t, *J* 6 Hz), 3.60 (1 H, d, *J* 8 Hz), and 3.91 (4 H, q).

The azide (17b) had m.p. 210—212 °C (decomp.) (from benzene), λ_{max} 392 (log ϵ 3.89), 370 (3.92), 352 (3.78), and 333 nm (3.57), ν_{max} 2 080 and 1 260 cm⁻¹; (27b) had m.p. 134—137 °C, λ_{max} 398 (4.26), 376 (4.26), 358 (4.67), and 339 nm (3.83), ν_{max} 2 090 and 1 235 cm⁻¹.

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