Studies in [3,4] Sigmatropic Rearrangements:[1] A Novel Synthesis of 9-Allenyl-10-Substituted Anthracenes from 10,10-Disubstituted 9-Anthrols

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A series of 10,10-disubstituted anthrones (**3a–f**) have been prepared from anthrone (**1**) and 10-prop-2-ynylanthrone (**2**) by both phase-transfer catalysed alkylation and classical alkylation. Reduction of these compounds with sodium borohydride in methanol gave a series of 10,10-disubstituted anthrols (**6a–f**). These when heated in acetic acid underwent smooth rearrangement to give 9-allenyl-10-alkyl (and related alkenyl and alkynyl) anthracenes (**7a, b, e, f**) except for 10,10-dibut-2-ynyl (**6c**) and 10,10-dibut-2-enyl-9-anthrol (**6d**) where the corresponding acetates (**8c, d**) were obtained. This reaction was also studied in the presence of a small amount of trifluoroacetic acid (TFA) and toluene-*p*-sulphonic acid (TPSA). In the presence of the former in carbon tetrachloride the reaction was complete in 5 min at 0–5 °C. The migratory aptitude of groups and the mechanism of the reaction is commented on.

There has been continued interest in the synthesis[2] and reactions[3] of substituted allenes and their use in the synthesis of complex molecules. Different aspects of allene chemistry have also been recently reviewed[4–7] extensively. Available routes to the synthesis of allenes include base-catalysed isomerisation of acetylenes,[8] rearrangement of prop-2-ynyl derivatives,[9,10] reduction of prop-2-ynyl halides,[11] addition of Grignard reagents to propynyl derivatives,[12,13] addition of Wittig reagents to ketenes and acid chlorides,[14,15] oxidation of intermediate pyrazolones with thallium(III) nitrate,[16] reaction of cuprates and prop-2-ynyl derivatives[17,18] and from ethynyl-alkanol acetates *via* organoboranes.[19,20] To our knowledge almost no work on allenylanthracenes has been reported.

During our work[21] on the alkylation of anthrone, an efficient phase-transfer catalysed procedure[22] for the synthesis of a number of 10,10-dialkenyl- and 10,10-dialkynyl-anthrones was developed. We considered the possibility of synthesising 9-allenylanthracene derivatives utilising transannular migration of the propynyl function in some of these compounds. This is more significant in view of the renewed interest in the synthesis[23] of 9-vinyl- and 9-isopropenyl-anthracene systems because of their fascinating polymer chemistry.[24,25]

The starting materials for this study, 10,10-disubstituted anthrones (**3**), were prepared either by phase-transfer catalysed alkylation of anthrone (**1**) or 10-prop-2-ynylanthrone (**2**) or by classical alkylation of 10-prop-2-ynylanthrone (**2**). 10,10-Diprop-2-ynylanthrone (**3a**) was prepared in almost quantitative yield from the reaction of anthrone or 10-propynylanthrone (**2**) and prop-2-ynyl bromide using benzyltriethyl-ammonium chloride (BTEAC) as catalyst. Alkylation of 10-prop-2-ynylanthrone (**2**) with 3-bromobut-1-yne in a similar fashion gave the 10,10-alkylated product (**3b**) (Scheme 1). 10,10-Dibut-2-ynylanthrone (**3c**) and 10,10-dibut-2-enylanthrone (**3d**) were prepared according to our earlier published procedure.[22] Unlike acetylenic halides, allyl and benzyl halides gave *O*-alkylated products when treated with 10-prop-2-ynylanthrone (**2**) by a PTC technique.[22] However, 10-prop-2-ynylanthrone[21] (**2**) was further *C*-alkylated in refluxing ethanolic potassium hydroxide with allyl and benzyl bromides respectively to give 10-allyl-10-prop-2-ynylanthrone (**3e**) (55%) and 10-benzyl-10-prop-2-ynylanthrone (**3f**) (60%) (Scheme 1). Our attempt to prepare 10-methyl-10-prop-2-ynylanthrone (**4a**) from 10-prop-2-ynylanthrone (**2**) by reaction with MeI/Me₂SO₄ using

(3e) R² = CH₂CH=CH₂   (3a) R² = CH₂C≡CH
(3f) R² = CH₂Ph   (3b) R² = CH(Me)C≡CH
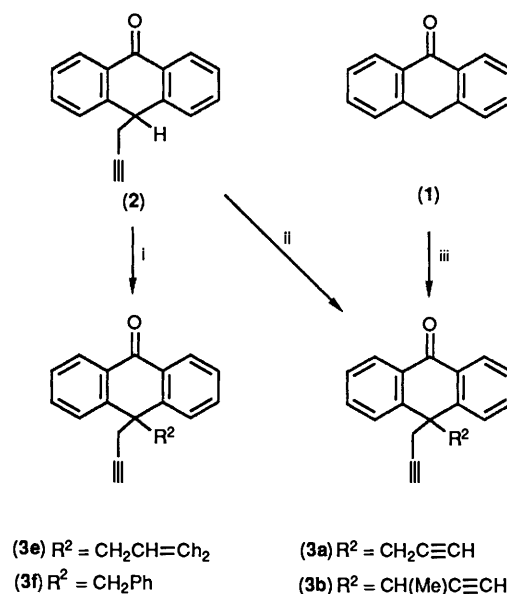
Scheme 1. *Reagents:* i, R₂X, KOH, EtOH; ii, R₂X, BTEAC, CH₂Cl₂, Aq. NaOH; iii, BrCH₂C≡CH, BTEAC, CH₂Cl₂, Aq. NaOH.

either a phase-transfer catalysed[22] or classical alkylation procedure were of no avail. In both the cases we obtained 10-prop-2-ynyl-9-methoxyanthracene (**5a**) resulting from *O*-alkylation.[22] Recently Branz *et al.* reported[26] the thermal rearrangement of 9-allyloxy-10-phenylanthracene to 10-allyl-10-phenylanthrone. An attempt by this procedure to obtain 10-methyl-10-prop-2-ynylanthrone (**4a**) by heating 9-methoxy-10-prop-2-ynylanthracene (**5a**) gave recovery of unchanged starting material. Our attempt to prepare 10-(2-methylbut-3-ynyl)-10-prop-2-ynylanthrone (**4b**) by treating 10-prop-2-ynyl-anthrone and 2-bromo-2-methylbut-3-yne under classical and PTC alkylation conditions also failed, only the 9-(2-methylbut-3-ynyloxy)-10-prop-2-ynylanthracene (**5b**) being obtained as a result of *O*-alkylation (Scheme 2).
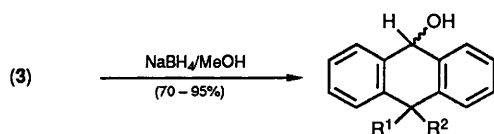
The nature of alkylation, *viz.* *C*-alkylation [formation of 10,10-dialkylated anthrone, (**3**)] or *O*-alkylation [formation of 10-alkyl-9-alkoxyanthracene, (**5**)] was determined from the presence or absence of IR carbonyl absorption and the
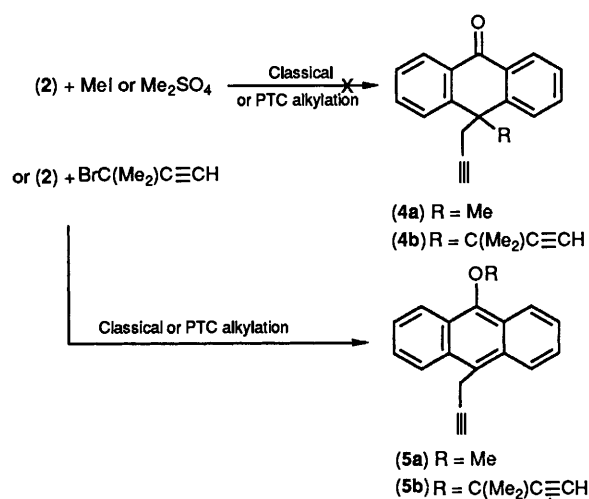
Scheme 2.

absence of a dibenzylic proton on their ^{1}H NMR spectra. The 10,10-dialkylated anthrones (**3a, b, e, f**), crystalline solids, were characterised from their elemental analyses, UV, IR, ^{1}H NMR and MS data. The dialkylated products (**3**) showed strong IR carbonyl absorption at v_{max} 1 650 cm^{-1} and no dibenzylic proton in their ^{1}H NMR spectra. The position of two aromatic protons (at C-1 and C-8) in the lowfield region at δ 8.12–8.56 is also characteristic of a C-alkylated product. The O-alkylated products (**5a, b**) showed neither carbonyl absorption in their IR spectra nor a dibenzylic proton in their ^{1}H NMR spectra.

The 10,10-disubstituted anthrones (**3a–f**) were successfully reduced with sodium borohydride in methanol (30–48 h) to give the corresponding anthrols (**6a–f**) in 70–95% yield
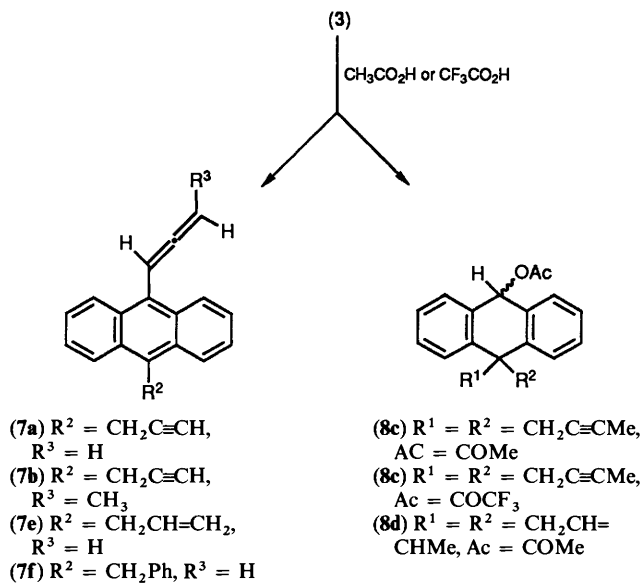

Comp.	Reaction time (h)	
(**3a**)	48	(**6a**) R^1 = R^2 = CH$_2$C≡CH
(**3b**)	30	(**6b**) R^1 = CH$_2$C≡CH, R^2 =
(**3c**)	36	CH(Me)C≡CH
(**3d**)	40	(**6c**) R^1 = R^2 = CH$_2$C≡CMe
(**3e**)	45	(**6d**) R^1 = R^2 = CH$_2$CH=
(**3f**)	38	CHMe
		(**6e**) R^1 = CH$_2$C≡CH, R^2 =
		CH$_2$CH=CH$_2$
		(**6f**) R^1 = CH$_2$C≡CH, R^2 =
		CH$_2$Ph

Scheme 3.

(Scheme 3). The 10,10-disubstituted anthrols (**6a–f**) were either crystalline solids or viscous liquids, characterised on the basis of elemental analyses and UV, IR, and ^{1}H NMR spectral data. The conversion of the anthrones (**3**) into the anthrols (**6**) were convincingly indicated by the disappearance of carbonyl absorption (v_{max} 1 650 cm^{-1}) and appearance of IR hydroxy absorption (v_{max} 3 300–3 520 cm^{-1}); they also showed UV absorption (λ_{max} 235–240 and 260–265 nm).

When refluxed in acetic acid (1.5 h), 10,10-diprop-2-ynyl-9-anthrol (**3a**) underwent facile conversion into 9-allenyl-10-prop-2-ynylanthracene (**7a**) (90%), whereas the 10-(3-but-2-

ynyl)-10-prop-2-ynyl-9-anthrol (**3b**) rearranged in acetic acid (0.5 h) to give the corresponding allene (**7b**) by a transannular migration of the 3-but-2-ynyl group in preference to the prop-2-ynyl group. On investigating similar rearrangements, we found that 10-allyl-10-prop-2-ynyl-9-anthrol (**6e**) and 10-benzyl-10-prop-2-ynyl-9-anthrol (**6f**) on treatment with acetic acid also rearranged smoothly to give the corresponding allenes (**7e**) (75%) and (**7f**) (80%) respectively by prop-2-ynyl migration (Scheme 4). The allenylanthracenes (**7a, b, e, f**), all crystalline solids, were characterised on the basis of their elemental analyses, UV, IR, ^{1}H NMR, ^{13}C NMR, and MS data:

(**7a**) R^2 = CH$_2$C≡CH, R^3 = H	(**8c**) R^1 = R^2 = CH$_2$C≡CMe, AC = COMe
(**7b**) R^2 = CH$_2$C≡CH, R^3 = CH$_3$	(**8c**) R^1 = R^2 = CH$_2$C≡CMe, Ac = COCF$_3$
(**7e**) R^2 = CH$_2$CH=CH$_2$, R^3 = H	(**8d**) R^1 = R^2 = CH$_2$CH= CHMe, Ac = COMe
(**7f**) R^2 = CH$_2$Ph, R^3 = H	

| Compound	Reaction time (h)	Compound	Reaction time (h)
(**6a**)	1.5	(**6d**)	6.0
(**6b**)	0.5	(**6e**)	1.0
(**6c**)	6.0	(**6f**)	1.5

Scheme 4.

Attempted rearrangement of 10,10-dibut-2-ynyl-9-anthrol (**6c**) in refluxing acetic acid gave only the acetate (**8c**) (m.p. 162 °C, 85%), replacement of the acetylenic proton by a methyl group surprisingly hindering the rearrangement. 10,10-Dibut-2-enyl-9-anthrol (**6d**) reacted similarly to give the acetate (**8d**). Both acetates were characterised on the basis of their elemental analyses and spectral data. Schmid et al.[27] also isolated the acetate (**10**) by treatment of 4-allyl-4-methylcyclohex-2-enol
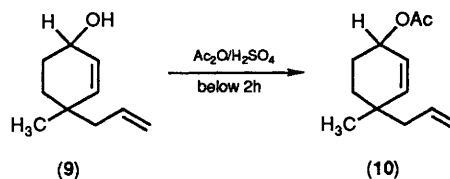
(**9**) with acetic anhydride and sulphuric acid (reaction time <2 h); the former rearranged with a longer reaction time. Attempted conversion of the acetates (**8c, d**) with longer reaction times were unsuccessful.

The conversion of the anthrols (**6a, b, e, f**) into the corresponding allenylanthracenes (**7a, b, e, f**) was also achieved under less energetic condition within shorter reaction times (TFA, 5 min, 0–5 °C). The anthranol (**6c**), however, did not rearrange even in TFA. The trifluoroacetate derivative (**8c**) was obtained quantitatively. This rearrangement was also studied in ether in the presence of a catalytic amount of TPSA

Scheme 5.
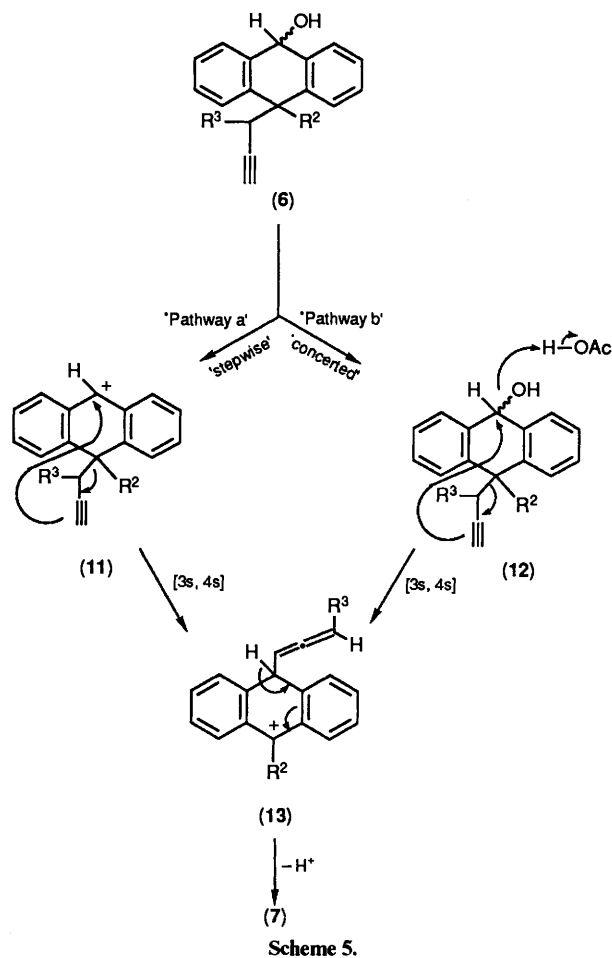
at 35 °C, anthranol (6a) rearranged to the corresponding allenylanthracene (7a) within 3 h.

The rearrangement may be regarded as a modified dienol–benzene rearrangement[28–33] and involves a transannular migration of the propynyl (or 1-methylprop-2-ynyl) group from C-10 to C-9. From crossover experiments Beckwith et al.[34] have established the intramolecular nature of the rearrangement and proposed a series of consecutive 1,2-shifts of the benzyl group in the conversion of 10,10-dibenzyl-9-anthrol into 9,10-dibenzylanthracene. During the recent past the course of the rearrangement was extensively studied in cyclohexadienol system by Schmid et al.[35] It was established that three competing processes viz. [1s, 2s], [3s, 3s], and [3s, 4s] during the migration of the allyl group in dienol–benzene rearrangement to form a mixture of products. It was also shown by ^{14}C-labelling experiment that the inversion of the allyl group took place during the rearrangement. They also studied[36,37] the rearrangement of methyl substituted o- and p-prop-2-ynyl cyclohexadienol and observed [1s, 2s], [3s, 3s], and [3s, 4s] shifts in each case and mixtures of products were obtained. However, in the present study the formation of the allenylanthracenes (7a, b, e, f) from the anthrols (6a, b, e, f) may easily be explained by the exclusive [3s, 4s] shift of the propynyl (1-methylprop-2-ynyl) group from C-10 to C-9 (Scheme 5). In this case a labelling experiment is unnecessary to show the inversion of the migrating group since conversion of the propynyl group in the reactant into the allenyl group in the product itself is indicative of this.

This arrangement may take place either via a stepwise mechanism (pathway a) or via a concerted mechanism (path-

way b). Given the intrinsic stability of the intermediate diarylmethyl cation (11), it is possible that 'pathway a' is preferred and consequently it is suggested that the migratory aptitude of the 3-but-2-ynyl group is greater than that of prop-2-ynyl, allyl, and benzyl groups whereas the prop-2-ynyl group has greater migratory aptitude than that of allyl and benzyl groups. However, if 'pathway b' is operative then the choice of migrating group [C(R^3)HC≡CH or R^2 where R^3 = H or Me and R^2 = CH$_2$CH=CH$_2$, or CH$_2$Ph or CH$_2$C≡CH] will be dictated by the stereochemistry of the anthrol (6) rather than by the relative migratory aptitude, of the C(R^3)HC≡CH and R^2 groups.

Experimental

M.p.s were determined in a sulphuric acid bath and are uncorrected. UV absorption spectra were recorded on a Hitachi 200–20 spectrometer for solution in chloroform and ethanol. IR spectra were run for KBr discs on a Perkin-Elmer 1330 apparatus. ^{1}H NMR spectra were determined for solutions in deuteriochloroform with SiMe$_4$ as internal standard on JEOL FX-100 (100 MHz) at the Indian Institute of Chemical Biology, Calcutta. Elemental analyses and recording of mass spectra were carried out by RSIC (CDRI), Lucknow. Silica gel (60–120 mesh) was obtained from BDH and SRL, India. Ether refers to diethyl ether. Light petroleum and petroleum refer to the fractions of b.p. 40–60 and 60–80 °C respectively.

Preparation of 10,10-*Diprop-2-ynyl* (3a) *and* 10-(2-*But*-3-*ynyl*)-10-*prop-2-ynyl-anthrone* (3b).—To a mixture of anthrone (1) (1.0 g, 5 mmol) or 10-prop-2-ynylanthrone (2) (1.2 g, 5 mmol), and prop-2-ynyl bromide (1.8 g, 15 mmol) in dichloromethane (25 ml) was added a solution of BTEAC (0.25 g) in 30% NaOH (25 ml) and the mixture was stirred at room temperature for 1 h. It was then diluted with water (100 ml) and extracted with CH$_2$Cl$_2$ (3 × 25 ml). The combined extracts were washed successively with 2M HCl (3 × 25 ml), 5% aq. NaHCO (3 × 25 ml), and brine (3 × 25 ml) and dried (Na$_2$SO$_4$). The solvent was removed under reduced pressure and the residue recrystallised from CHCl$_3$–petroleum to give a white crystalline solid (95%), m.p. 210 °C. This was found to be identical (UV, IR ^{1}H NMR, Co-TLC and mixed m.p.) with 10,10-diprop-2-ynylanthrone[38] (3a).

Compound (3b), similarly prepared from 10-prop-2-ynyl-anthrone (2) and 2-bromobut-3-yne, isolated and purified by column chromatography over silica gel (60–120 mesh, SRL), eluting with benzene–petroleum (1:1), and recrystallisation from chloroform–petroleum.

Compound (3b) (60%), m.p. 152 °C; λ$_{max}$ 270 nm; ν$_{max}$ 2 140 (C≡C) and 1 650 cm^{-1} (C=O); δ$_H$ 0.6 (d, 3 H, J 8.0 Hz, CH$_3$), 1.50 (t, 1 H, J 2.5 Hz, CH$_2$C≡CH), 2.32 [d, 1 H, J 2.5 Hz, CH(Me)C≡CH], 3.00–3.28 [m, 1 H, CH(Me)C≡CH], 3.40 (d, 2 H, J 2.5 Hz, CH$_2$C≡CH), 7.40–7.80 (m, 6 H, ArH), and 8.28–8.48 (m, 2 H, ArH) (Found: C, 88.6; H, 5.7. C$_{21}$H$_{16}$O requires C, 88.73; H, 5.63%).

Compounds (3c) and (3d) were prepared according to our earlier published procedure.[22]

Preparation of 10-*Allyl*-10-*prop-2-ynylanthrone* (3e) *and* 10-*Benzyl*-10-*prop-2-ynylanthrone* (3f).—10-Prop-2-ynylanthrone (2) (1.2 g, 5 mmol) in ethanol (90%; 50 ml) and potassium hydroxide (0.28 g, 5 mmol) was refluxed for 0.5 h. The corresponding alkyl bromide (7.5 mmol) was then added to the above solution and stirred for 4 h. Ethanol was removed from the reaction mixture and the residue was extracted with chloroform (3 × 50 ml). The chloroform extract was washed with brine (3 × 50 ml), dried (Na$_2$SO$_4$), and evaporated to give an oil which was chromatographed over silica gel (60–120

mesh, BDH). Compound (3e) was eluted with benzene–petroleum (1:1) and compound (3f) was eluted with benzene–petroleum (1:3). Both were recrystallised from chloroform–petroleum.

Compound (3e) (55%), m.p. 140 °C; λ_{max} 270 nm; ν_{max} 1 650 cm^{-1} (C=O); δ_H 1.62 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 2.96–3.24 (m, 4 H, $CH_2C{\equiv}CH$ and $CH_2CH{=}CH_2$), 4.52–5.28 (m, 3 H, olefinic H), 7.36–7.88 (m, 6 H, ArH), and 8.28–8.56 (m, 2 H, ArH) (Found: C, 88.05; H, 5.75. $C_{20}H_{16}O$ requires C, 88.23; H, 5.88%).

Compound (3f) (60%), m.p. 164 °C; λ_{max} 270 nm; ν_{max} 2 135 (C≡C) and 1 650 cm^{-1} (C=O); δ_H 1.62 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 3.28–3.56 (m, CH_2Ph and $CH_2C{\equiv}CH$), 6.04–6.36 (m, 2 H, ArH), 6.68–7.08 (m, 3 H, ArH), 7.36–8.00 (m, 6 H, ArH), and 8.12–8.44 (m, 2 H, ArH) (Found: C, 89.25; H, 5.65. $C_{24}H_{18}O$ requires C, 89.44; H, 5.59%).

Attempted Preparation of Compounds (4a) *and* (4b).—Treatment of 10-prop-2-ynyl anthrone (2) with MeI or Me_2SO_4 by the classical alkylation procedure described in an earlier experiment gave a yellow crystalline solid (70%), m.p. 148 °C, identical (UV, IR, ^1H NMR, and mixed m.p.) with 9-methoxy-10-prop-2-ynylanthracene.[22]

The reaction of 10-prop-2-ynylanthrone (2) with 2-bromo-2-methylbut-3-yne both by the classical alkylation and PTC alkylation procedures as described earlier gave a yellow crystalline solid.

Compound (5b) (40%), m.p. 110 °C; λ_{max} 258 and 358 nm; ν_{max} 2 135 (C≡C), and 1 285 cm^{-1} (ether linkage); δ_H 1.80 (s, 3 H, CH_3), 1.82 (s, 3 H, CH_3) 2.10 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 2.14 (s, 1 H, $CC{\equiv}CH$), 4.45 (d, 2 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 7.40–7.64 (m, 4 H, ArH), and 8.20–8.36 (m, 4 H, ArH) (Found: C, 88.4; H, 6.1. $C_{22}H_{18}O$ requires C, 88.59; H, 6.04%).

Reduction of Compounds (3a–f) *with Sodium Borohydride.*—To 10,10-dialkenyl- or 10,10-dialkynyl- or 10-alkenyl-10-alkynyl-anthrone (3) (20 mmol) in methanol (25 ml) was added sodium borohydride (0.2 g, 5 mmol) and the mixture was stirred for 30–48 h with a magnetic stirrer at room temp. Methanol was removed and the residue extracted with ether (4 × 50 ml). The extract was washed with brine (3 × 50 ml) and water (50 ml), dried (Na_2SO_4), and evaporated to give a viscous liquid. Chromatography of this over silica gel (60–120 mesh) with benzene as eluant gave the products (6a–f).

Compound (6a) (95%), m.p. 95 °C; λ_{max} 240 and 262 nm; ν_{max} 3 300 (OH) and 2 135 cm^{-1} (C≡C); δ_H 1.67 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 1.87 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 2.13 (d, 1 H, J 8.0 Hz, OH, D_2O exchangeable), 3.03 (d, 2 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 3.09 (d, 2 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 5.68 (d, 1 H, J 8.0 Hz, 9-H), and 7.36–7.44 (m, 8 H, ArH) (Found: C, 88.2; H, 6.05. $C_{20}H_{16}O$ requires C, 88.23; H, 5.88%).

Compound (6b) (70%), m.p. 122 °C; λ_{max} 240 and 262 nm, ν_{max} 3 300 (OH) and 2 140 cm^{-1} (C≡C); δ_H 0.64–0.96 (dd, 3 H, J 6.0, 14.0 Hz, CH_3), 1.48–1.60 [m, 1 H, CH(Me)C≡CH], 2.14 (d, 1 H, J 8.0 Hz, OH, D_2O exchangeable), 2.24 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 2.80–3.16 (m, 1 H, CH(Me)C≡CH), 3.40 (d, 2 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 5.56 (d, 1 H, J 8.0 Hz, 9-H), and 7.28–7.88 (m, 8 H, ArH) (Found: C, 88.0; H, 6.2. $C_{21}H_{18}O$ requires C, 88.11; H, 6.29%).

Compound (6c) (90%), m.p. 167 °C; λ_{max} 240 and 262 nm, ν_{max} 3 520 cm^{-1} (OH); δ_H 1.38 (t, 6 H, J 2.5 Hz, C≡CCH_3), 2.10 (d, 1 H, J 8.0 Hz, OH, D_2O exchangeable), 2.64 (d, 2 H, J 2.5 Hz, $CH_2C{\equiv}C$), 2.72 (d, 2 H, J 2.5 Hz, $CH_2C{\equiv}C$), 5.10 (d, 1 H, J 8.0 Hz, 9-H), and 6.60–7.02 (m, 8 H, ArH) (Found: C, 87.95; H, 6.75. $C_{22}H_{20}O$ requires C, 88.00; H, 6.67%).

Compound (6d) (70%), viscous liquid; λ_{max} 240 and 262 nm; ν_{max} 3 400 cm^{-1} (OH); δ_H 1.42–1.80 (m, 6 H, CH=CHCH_3),

2.10 (d, 1 H, J 8.0 Hz, OH, D_2O exchangeable), 2.40–2.50 (m, 2 H, $CH_2CH{=}CH$), 3.08–3.28 (m, 2 H, $CH_2CH{=}CH$), 4.12–4.60 (m, 2 H, olefinic H), 5.40–5.96 (m, 3 H, olefinic H and 9-H), and 7.00–8.40 (m, 8 H, ArH) (Found: C, 86.95; H, 7.8. $C_{22}H_{24}O$ requires C, 86.84; H, 7.89%).

Compound (6e) (85%), m.p. 92 °C; λ_{max} 240 and 265 nm; ν_{max} 3 300 (OH) and 2 140 cm^{-1} (C≡C); δ_H 1.67 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 2.00 (d, 1 H, J 8.0 Hz, OH), 2.80–3.48 (m, 4 H, $CH_2CH{=}CH_2$ and $CH_2C{\equiv}CH$), 4.60–5.00 (m, 2 H, $CH_2CH{=}CH_2$), 5.08–5.40 (m, 1 H, $CH_2CH{=}CH_2$), 5.68 (d, 1 H, J 8.0 Hz, 9-H), and 7.28–7.80 (m, 8 H, ArH) (Found: C, 87.35; H, 6.55. $C_{20}H_{18}O$ requires C, 87.59; H, 6.57%).

Compound (6f) (75%), viscous liquid; λ_{max} 235 and 260 nm; ν_{max} 3 520 (OH) and 2 135 cm^{-1} (C≡C); δ_H 1.58–1.68 (m, 2 H, $CH_2C{\equiv}CH$ and OH) 3.20–3.40 (m, 4 H, CH_2Ph and $CH_2C{\equiv}CH$), 5.68 (d, 1 H, J 8.0 Hz, 9-H), 6.64–6.28 (m, 2 H, ArH), 6.72–7.08 (m, 3 H, ArH), and 7.28–7.80 (m, 8 H, ArH) (Found: C, 88.95; H, 6.05. $C_{24}H_{20}O$ requires C, 88.88; H, 6.17%).

Rearrangement of Compound (6a–f) *in Acetic Acid.*—10,10-Dialkenyl- or 10-alkenyl-10-alkynyl-, or 10,10-dialkynyl-9-anthrol (6) (1 mmol) in acetic acid (2 ml) was refluxed on an oil-bath for 0.5–6 h. The reaction mixture was neutralised with 10% aqueous sodium hydrogen carbonate and extracted with ether (3 × 50 ml). The extract was washed with brine (3 × 25 ml), dried (Na_2SO_4), and evaporated to give a viscous liquid which was chromatographed over silica gel (60–120 mesh, BDH). All the rearranged products (7) were eluted with petroleum and the acetates (8) were eluted with benzene–petroleum (1:1). The rearranged products (7) were recrystallised from chloroform–hexane.

Compound (7a) (90%), m.p. 168 °C, λ_{max} 265 nm; ν_{max} 2 130 (C≡C) and 1 950 cm^{-1} (CH=C=CH_2); δ_H 2.08 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 4.48 (d, 2 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 5.04 (d, 2 H, J 7.0, Hz, CH=C=CH_2), 6.98 (t, 1 H, J 7.0 Hz, CH=C=CH_2), 7.48–7.76 (m, 4 H, ArH), and 8.24–8.68 (m, 4 H, ArH); m/z 255 (M^+ + 1), 254 (M^+), and 215 (base peak) (Found: C, 94.6; H, 5.45. $C_{20}H_{14}$ requires C, 94.49; H, 5.51%).

Compound (7b) (70%), m.p. 138 °C, λ_{max} 265 nm; ν_{max} 2 140 (C≡C) and 1 950 cm^{-1} [CH=C=CH(Me)]; δ_H 1.68–1.88 (dd, 3 H, J 3.0, 4.0 Hz, CH_3), 2.04 (t, 1 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 3.42 (d, 2 H, J 2.5 Hz, $CH_2C{\equiv}CH$), 5.24–5.52 [m, 1 H, CH=C=CH(Me)], 6.80–7.00 [m, 1 H, CH=C=CH(Me)], 7.40–7.68 (m, 4 H, ArH), and 8.20–8.60 (m, 4 H, ArH) (Found: C, 93.9; H, 5.9. $C_{21}H_{16}$ requires C, 94.03; H, 5.97%).

Compound (7e) (75%), m.p. 85 °C; λ_{max} 262 nm; ν_{max} 1 950 cm^{-1} (CH=C=CH_2); δ_H 4.32–4.56 (m, 2 H, $CH_2CH{=}CH_2$), 4.68–5.20 (m, 4 H, $CH_2CH{=}CH_2$ and CH=C=CH_2), 6.08–6.40 (m, 1 H, $CH_2CH{=}CH_2$), 7.00 (t, 1 H, J 7.0 Hz, CH=C=CH_2), 7.44–7.76 (m, 4 H, ArH), and 8.12–8.60 (m, 4 H, ArH); m/z 256 (M^+) and 215 (base peak) (Found: C, 94.0; H, 6.1. $C_{20}H_{16}$ requires C, 93.75; H, 6.25%).

Compound (7f) (80%), m.p. 115 °C; λ_{max} 264 nm; ν_{max} 1 950 cm^{-1} (CH=C=CH_2); δ_H 4.98 (s, 2 H, CH_2Ph), 5.08 (d, 2 H, J 7.0 Hz, CH=C=CH_2), 6.98 (t, 1 H, J 7.0 Hz, CH=C=CH_2), 7.12–7.32 (m, 5 H, ArH), 7.40–7.68 (m, 4 H, ArH), and 8.12–8.68 (m, 4 H, ArH) (Found: C, 93.8; H, 6.05. $C_{24}H_{18}$ requires C, 94.12; H, 5.88%).

Compound (8c) (80%), m.p. 162 °C; λ_{max} 242, 268, and 275 nm; ν_{max} 1 750 cm^{-1} (C=O); δ_H 1.62 (s 3 H, C≡CCH_3), 1.86 (s, 3 H, $COCH_3$), 1.92 (s, 3 H, C≡CCH_3), 2.10 (s, 2 H, $CH_2C{\equiv}C$), 3.00 (s, 2 H, $CH_2C{\equiv}C$), 4.38 (s, 1 H, 9-H), and 6.36–6.90 (m, 8 H, ArH); m/z 343 (M^+ + 1), 342 (M^+), 299 (M^+ + 1 − $COCH_3$), 283 (M^+ − $OCOCH_3$), 2.30 (base peak, M^+ − $OCOCH_3$ − C_4H_5) (Found: C, 84.35; H, 6.4. $C_{24}H_{22}O_2$ requires C, 84.21; H, 6.43%).

Compound (8d) (60%), viscous liquid; λ_{max} 240, 268, and

272 nm; ν_{max} 1 750 cm^{-1} (C=O); δ_H 1.20–1.40 (m, 3 H, CH=CHCH_3), 1.68–1.96 (m, 3 H, CH=CHCH_3), 1.80 (s, 3 H, COCH_3), 2.08–2.20 (m, 2 H, CH_2CH=CH), 3.08–3.28 (m, 2 H, CH_2CH=CH) 4.00–4.60 (m, 2 H, olefinic H), 4.38 (s, 1 H, 9-H), 5.80–6.00 (m, 2 H, olefinic H), and 7.00–7.60 (m, 8 H, ArH) (Found: C, 83.3; H, 7.4. $C_{24}H_{26}O_2$ requires C, 83.23; H, 7.51%).

Rearrangement of Compound (**6a–c**) *and* (**6e–f**) *in Trifluoroacetic Acid.*—To 10-alkenyl-10-alkynyl or 10,10-dialkynyl-9-anthrol (**6**) (1 mmol) in carbon tetrachloride (10 ml) was added TFA (0.75 ml) in carbon tetrachloride (4.25 ml) and the mixture stirred magnetically at 0–5 °C; TLC monitoring showed that the reaction was complete within 5 min. The reaction mixture was then neutralised with 10% aqueous NaHCO$_3$ and extracted with carbon tetrachloride (100 ml). The extract was washed with brine (3 × 25 ml), dried (Na$_2$SO$_4$), and evaporated to give a viscous liquid which was chromatographed over silica gel. The anthranols (**6a, b, e, f**) furnished the corresponding allenes (**7a, b, e, f**). Compound (**6c**), however, gave the trifluoroacetate (**8c'**). Compound (**8c'**) was eluted in benzene–petroleum (3:1) and recrystallised from chloroform–petroleum.

Compound (**8c'**) (60%), m.p. 130 °C; λ_{max} 242, 270, and 278 nm; ν_{max} 1 750 cm^{-1} (C=O); δ_H 1.80 (t, 3 H, J 2.5 Hz, CH$_2$C≡CCH_3), 1.98 (q, 2 H, J 2.5 Hz, CH_2C≡CMe), 2.08 (t, 3 H, J 2.5 Hz, CH$_2$C≡CMe), 3.28 (q, 2 H, J 2.5 Hz, CH$_2$C≡C), 4.60 (s, 1 H, 9-H), and 7.40–7.60 (m, 8 H, ArH) (Found: C, 72.6; H, 4.6. $C_{24}H_{19}F_3O_2$ requires C, 72.22; H, 4.79%).

Rearrangement of 10,10-*Diprop-2-ynyl-9-anthrol* (**6a**) *in Toluene-*p-*sulphonic Acid.*—To 10,10-diprop-2-ynyl-9-anthrol (**6a**) (0.27 g, 1 mmol) taken in ether (10 ml) was added TPSA (0.01 g) and the mixture refluxed on a water-bath at 35 °C. The reaction was complete within 3 h (monitored by TLC). The reaction mixture was then neutralised with 10% aqueous NaHCO$_3$ and extracted with ether (3 × 50 ml). The extract was washed with brine (3 × 25 ml), dried (Na$_2$SO$_4$), and evaporated to give viscous liquid which was chromatographed over silica gel (60–120 mesh). The rearranged product (**7a**) was eluted in petroleum to yield the product (0.18 g, 67%), m.p. 168 °C.

Acknowledgements

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