Synthesis of 10-Alkyl-9-allenylanthracenes involving [3,4]Sigmatropic Rearrangement†

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A synthesis of 10-alkynyl-9-allenylanthracenes (and related 10-alkenyl and 10-benzyl analogues) *via* acid catalysed [3,4]sigmatropic rearrangement of *e.g.* 10,10-dialkynyl-9-anthranols is reported; the migratory aptitudes of allyl, benzyl, and prop-2-ynyl groups is discussed.

There has been continued interest in the synthesis^{1a} and reactions^{1b} of substituted allenes including their use in the synthesis of complex molecules. Other aspects of allene chemistry have also been recently reviewed.² However, to our knowledge there have been few reports on the synthesis of allenylanthracenes. This is significant in view of the renewed interest in the synthesis³ of 9-vinyl and 9-isopropenyl anthracene systems because of their interesting polymer chemistry.⁴

During our work⁵ on the alkylation of anthrone, an efficient phase-transfer catalysed procedure^{5b} 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 this type of compound. 10,10-Diprop-2-ynylanthrone^{5c} (1a) (m.p. 212 °C, yield 95%) was prepared from the reaction of anthrone and prop-2-ynyl bromide using benzyltriethylammonium chloride as catalyst. \ddagger On reduction with sodium borohydride in ethanol (48 h) this

[†] Earlier parts, K. C. Majumdar, R. N. De, A. T. Khan, S. K. Chattopadhyay, K. De, and A. Patra, J. Chem. Soc., Chem. Commun., 1988, 777; K. C. Majumdar and S. K. Chattopadhyay, *ibid.*, 1987, 524.

[‡] All new compounds reported in this study gave satisfactory elemental analyses and exhibited the correct u.v., i.r., ¹H n.m.r., and mass spectra.



a;	$R = CH_2C \equiv CH$
b;	$R = CH_2CH=CH$
c;	$R = CH_2Ph$

Scheme 1. Reagents and conditions: i, NaBH₄, MeOH; ii, MeCO₂H, heat.

gave 10,10-diprop-2-ynylanthran-9-ol (2) (m.p. 95°C, yield 95%). When refluxed in acetic acid (2a) underwent facile conversion (<1.5 h) to 9-allenyl-10-prop-2-ynyl-anthracene (3a), obtained as yellow crystals following chromatography over silica gel [m.p. 168 °C, yield 90%. $C_{20}H_{14}$ from elemental analyses); u.v. λ_{max} . (CHCl₃) 265 nm; i.r. 2135 (C=C), 1950 cm⁻¹ (C=C=C); n.m.r. δ_H 2.04-2.12 (1H, t, J 3Hz), 4.44-4.52 (2H, d, J 3Hz), 5.08-5.10 (2H, d, J 7Hz), 6.88-7.10 (1H, t, J 7 Hz), 7.48–7.76 (4H, m), and 8.24–8.68 (4H, m); δ_{C} 211 $(C=C=C); m/z 254 (M^+).$

We then concentrated on the rearrangement of mixed substrates such as 10-allyl- (1b) and 10-benzyl-10-prop-2-

ynylanthrone (1c). These could not be prepared from 10-prop-2-ynylanthrone by phase-transfer catalysis (p.t.c.) as *O*-alkylation has been reported to occur under these conditions.^{5b} However, 10-prop-2-ynylanthrone^{5a} was further *C*-alkylated by refluxing in ethanolic potassium hydroxide with allyl and benzyl bromide respectively to give (1b) (m.p. 140 °C, yield 55%) and (1c) (m.p. 164 °C, yield 60%). Reduction with sodium borohydride produced the corresponding alcohols (2b) (m.p. 92 °C, yield 85%) and (2c) (gum, yield 75%), both of which rearranged smoothly to the corresponding allenes (3b) (m.p. 85 °C, yield 75%) and (3c) (m.p. 115 °C, yield 80%) (Scheme 1).

The rearrangement may be regarded as a modified version of the well-known dienol-benzene rearrangement and involves a transannular migration of the propynyl group. Beckwith et al. 6a have established the intramolecular nature of the rearrangement and proposed a number of consecutive 1,2-shifts of the benzyl group in the conversion of 10,10dibenzylanthran-9-ol to 9,10-dibenzylanthracene. Later, the course of this rearrangement was explored^{6b-c} in cyclohexadienol systems by Schmid et al. and was found to involve competitive [1,2], [1,4], [3,3], and [3,4] migrations to form a mixture of products. However, in the present study, the formation of (3) from (2) is explicable by the exclusive [3,4]shift of the propynyl group from C(10). This shift may take place either via a stepwise mechanism (pathway a) or via a concerted mechanism (pathway b). Given the intrinsic stability of the intermediate diarylmethyl cation (4), it is possible that 'pathway a' is preferred and consequently it is suggested that the migratory aptitude of the propynyl group is greater than that of the benzyl and allyl groups in this rearrangement. However, if 'pathway b' is operative then the choice of migrating group (CH₂C \equiv CH or R, where R = CH₂C \equiv CH, CH₂CH=CH₂, or CH₂Ph) will be dictated by the stereochemistry of the anthranol rather than by the relative migratory aptitudes of the CH₂C=CH and R groups. We are currently working on this and the results will be reported later.

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