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TRANSANNULAR REARRANGEMENT IN 9,10-DIHYDROANTHRACENE DERIVATIVES[1]

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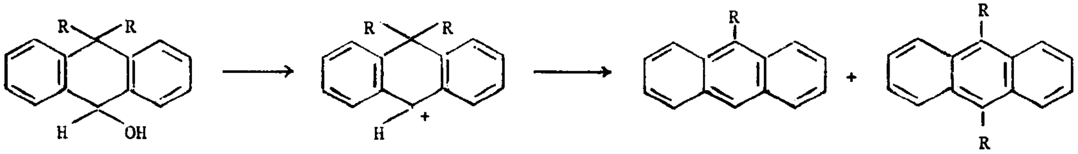
Attention has recently been focused on reactions of carbonium ions formed from derivatives of 9,10-dihydroanthracene.[4,5] We now wish to report that carbonium ions of the general type (II) containing substituents of high migratory aptitude, when generated under conditions of thermodynamic control, undergo aromatization by transannular migration of one of the substituents.

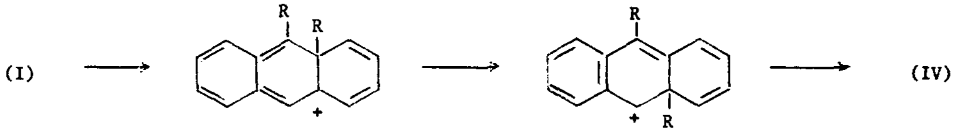
Thus, 9,9-dibenzyl-9,10-dihydro-10-hydroxyanthracene[6] (I; R = $PhCH_2$), m.p. 175-177°, when refluxed in acetic acid for 12 hours, afforded 9,10-dibenzylanthracene (IV; R = $PhCH_2$) in 60% yield together with a smaller amount (19%) of the monobenzyl compound (III; R = $PhCH_2$). 10,10-Di-*p*-chlorobenzylanthrone,[7] m.p. 203°, prepared by treatment of anthrone with *p*-chlorobenzyl chloride,[6] when reduced with lithium aluminium hydride in tetrahydrofuran afforded the appropriate alcohol[7] (I; R = *p*-$ClC_6H_4CH_2$), m.p. 152-153°, which was similarly converted by treatment with hot acetic acid into 9,10-di-*p*-chlorobenzylanthracene (IV; R = *p*-$ClC_6H_4CH_2$), m.p. 268-270°, in 58% yield and *p*-chlorobenzylanthracene (III; R = *p*-$ClC_6H_4CH_2$), m.p. 129-130°, in 23% yield. Alkylation of anthrone with potassium hydroxide and allyl bromide in methanol gave 10,10-diallylanthrone,[8] m.p. 85-86°, which was converted to the alcohol[7] (IV; R = $CH_2{=}CH{-}CH_2$), m.p. 67-68° by reduction with lithium aluminium hydride. When refluxed in acetic acid for 2 hours diallylanthranol (IV; R = $CH_2{=}CH{-}CH_2$) was converted solely (86%) into 9,10-diallylanthracene,[9] m.p. 133-134°.



(I) (II) (III) (IV)

These unusual rearrangement reactions appear to be truly intramolecular. When a mxiture of the dibenzylanthranol (I; R = $PhCH_2$) and its p-chlorobenzyl analogue (I; R = $p\text{-}ClC_6H_4CH_2$) was heated in acetic acid there were obtained the same products in similar yields to those isolated when the two compounds were each treated separately. No 9-benzyl-10-p-chlorobenzylanthracene was formed. Furthermore, both anthracene and 9,10-dibenzylanthracene were each quantitatively recovered after treatment with benzyl acetate in refluxing acetic acid.

This rearrangement, which may be regarded as a variation of the well known dienol-benzene transformation, is most easily visualised as proceeding by a series of consecutive 1,2-shifts.[10]



However, the course of the reaction is also consistent with an intramolecular π complex mechanism.[11]

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7 All new compounds had ultraviolet, infrared, n.m.r., and mass spectra consistent with the assigned structures and gave acceptable microanalytical results.

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11 See M. J. S. Dewar, "Molecular Rearrangements" ed. P. de Mayo, Interscience, New York, N.Y., 1963, pp. 295-344.