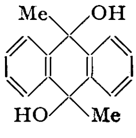
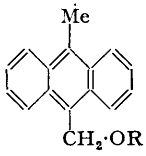
207. *Substituted Anthracene Derivatives. Part VI.** 9-n-*Prop*-1′-*enyl*-10-n-*propylanthracene.*

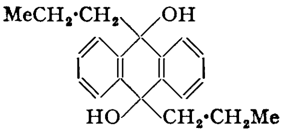
By G. M. BADGER.

9-*n*-Prop-1′-enyl-10-*n*-propylanthracene has been obtained by the addition of a little hydrochloric acid to a boiling alcoholic solution of 9 : 10-dihydro-9 : 10-dihydroxy-9 : 10-di-*n*-propylanthracene. The structure of the product has been confirmed by an independent synthesis, and the mechanism of the reaction is discussed.

IN Part III (Badger and Pearce, *J.*, 1950, 2314) it was shown that the acid-catalysed dehydration of 9 : 10-dihydro-9 : 10-dihydroxy-9 : 10-dimethylanthracene (I) leads to the formation of 9-alkoxymethyl-10-methylanthracene (II) the nature of the alkoxy-group depending on the alcohol used as solvent. A mechanism involving a 1 : 5-anionotropic shift of the initial product of dehydration was suggested to account for this observation.


(I)


(II)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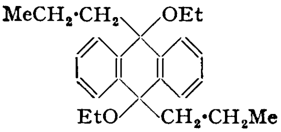
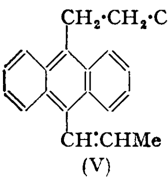

(IV)


(V)

In order to examine the reaction further, however, it seemed desirable to study the acid-catalysed dehydration of some other diols, particularly those having alkyl groups other than methyl.

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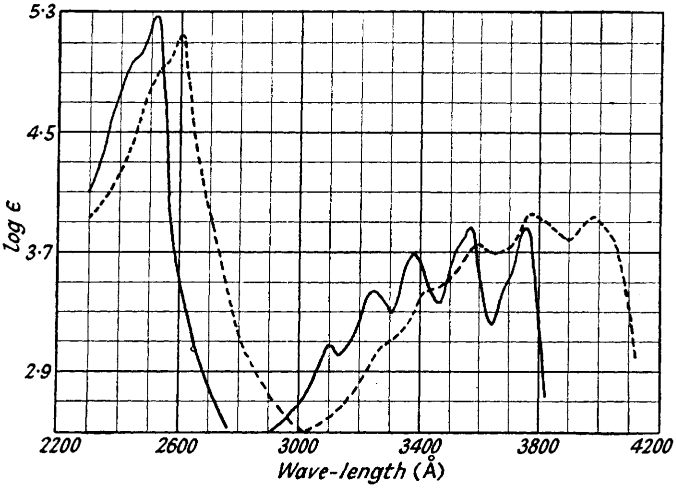
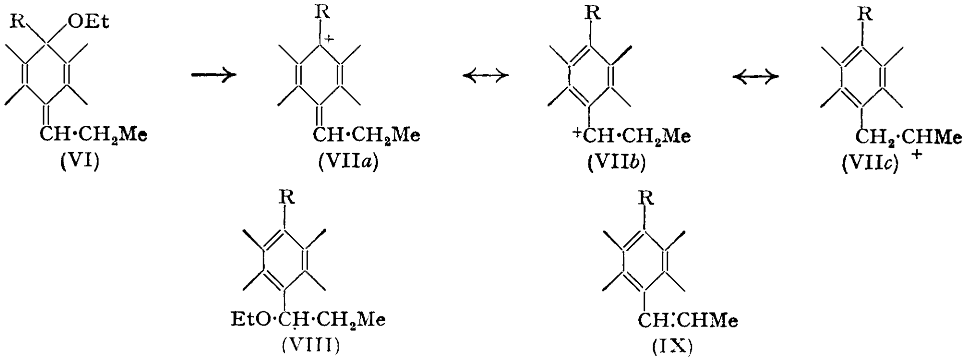
* Part V, *J.*, 1952, 1112.

It has now been found that when a boiling alcoholic solution of either 9 : 10-dihydro-9 : 10-dihydroxy-9 : 10-di-*n*-propylanthracene (III) or its diethyl ether (IV) is treated with a little hydrochloric acid, both oxygen atoms are lost and 9-*n*-prop-1′-enyl-10-*n*-propylanthracene (V) results.

The diethyl ether (IV) was prepared from the diol (III) by use of cold ethanol and a little mineral acid, and it seems likely that the initial effect of adding acid to a boiling alcoholic solution of the diol is also to form the ether. Removal of one molecule of ethanol would then give the intermediate (VI), and the transformation of this into the final product (IX) might be expected to proceed in two ways. For example, the elimination of a second ethoxy-group from (VI) would give the mesomeric ion (VII), and removal of a proton from (VII*b*) would give (IX) directly. Alternatively, the intermediate (VI) would be expected to undergo 1 : 5-anionotropic rearrangement (*via* VII) to give the ether (VIII). This compound could not be isolated from the reaction mixture even after runs carried out under somewhat milder conditions than usual. Nevertheless, it may be an intermediate, for further heating with acid would be expected to remove the ethoxy-group and again give the ion (VII*b*). In either case, the driving force of the reaction is clearly the tendency towards increased conjugation and increased resonance stabilisation.



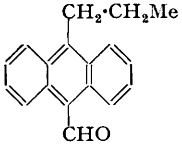
Ultra-violet absorption spectra of anthracene (——) *and of* 9-n-*prop*-1′-*enyl*-10-n-*propylanthracene* (– – –), *in ethanol. The latter has maxima (and log* ε) *at* 2605 (5·13), 3595 (3·76), 3775 (3·96), *and* 3930 Å, 3·93); *and points of inflexion at* 3250 (3·02), *and* 3400 Å (3·42).

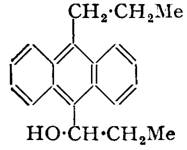


(VI) (VII*a*) (VII*b*) (VII*c*)

(VIII) (IX)

This mechanism is also supported by the nature of the independent synthesis of the product. 9-*n*-Propylanthracene was prepared by Sieglitz and Marx's method (*Ber.*, 1923, **56**, 1619) and was converted into 10-*n*-propyl-9-anthraldehyde (X) by Fieser's formanilide aldehyde synthesis (*Org. Synth.*, 1940, **20**, 11). After treatment of (X) with ethylmagnesium bromide, the crude alcohol (XI) was obtained. This could not be obtained pure, and was accordingly treated with boiling ethanol containing a little hydrochloric acid. The 9-*n*-prop-1′-enyl-10-*n*-propylanthracene (V) obtained in this way was shown to be identical with that obtained by the first method.


(X)


(XI)

The structure of the product is also supported by its ultra-violet absorption spectrum (see figure) which is of the anthracene type. The very large bathochromic shift, however, is noteworthy; such a large shift would be expected from an anthracene derivative having a substituent (such as a propenyl group) capable of strong conjugation with the ring system.

EXPERIMENTAL

9 : 10-*Dihydro*-9 : 10-*dihydroxy*-9 : 10-*di*-n-*propylanthracene*.—The following method proved more convenient than that given in the literature. A mixture of anthraquinone (10 g.), magnesium (5 g.), anhydrous ether (60 c.c.), and anhydrous, thiophen-free benzene (60 c.c.) was treated with excess of *n*-propyl bromide (20 c.c.). After the reaction had abated somewhat, the mixture was refluxed for an hour, then cooled and decomposed with ice and ammonium chloride. The product was isolated in the usual way and freed from unchanged anthraquinone with alkaline dithionite. The yield of diol was 3·9 g.

9 : 10-*Diethoxy*-9 : 10-*dihydro*-9 : 10-*di*-n-*propylanthracene*.—A solution of the above diol (0·25 g.) in absolute ethanol, was treated (below 15°) with 2 drops of concentrated sulphuric acid in a little ethanol. After 1 hour the crystals (0·25 g.) were collected and recrystallised from ethanol. 9 : 10-*Diethoxy*-9 : 10-*dihydro*-9 : 10-*di*-n-*propylanthracene* formed prisms, m. p. 211—213° (Found : C, 82·0; H, 9·1. $C_{24}H_{32}O_2$ requires C, 81·8; H, 9·1%).

10-n-*Propyl*-9-*anthraldehyde* (X).—A mixture of 9-*n*-propylanthracene (10 g.), methylformanilide (10 c.c.), phosphorus oxychloride (10 c.c.), and chlorobenzene (10 c.c.) was heated on the water-bath for 1½ hours. After the red solution had cooled, sodium acetate (30 g.) in water (100 c.c.) was added. The solvents were removed by rapid steam-distillation, and the product (8·6 g.) was recrystallised from alcohol (charcoal). 10-n-*Propyl*-9-*anthraldehyde* formed golden plates, m. p. 102—104° (Found : C, 87·2; H, 6·4. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%).

9-n-*Prop*-1′-*enyl*-10-n-*propylanthracene* (V).—(i) A solution of the diol (5·0 g.) in boiling absolute ethanol (150 c.c.) was treated with dilute hydrochloric acid (10 c.c.). A white precipitate formed almost at once and this gradually dissolved on further heating. After two hours, water was added, and the mixture set aside overnight. The gummy precipitate was then dissolved in benzene, the benzene solution washed and dried, and the solution evaporated on the steam-bath. After being set aside overnight in the refrigerator, the product was mostly crystallised; it was purified by recrystallisation from alcohol and sublimation at 140°/0·5 mm. 9-n-*Prop*-1′-*enyl*-10-n-*propylanthracene* (1·6 g.) formed yellow blades (from alcohol), m. p. 125—126° (Found : C, 92·3; H, 7·7. $C_{20}H_{20}$ requires C, 92·2; H, 7·8%).

Similar results were obtained by using the diethyl ether instead of the diol.

The *s*-trinitrobenzene *complex* was prepared in alcohol and recrystallised from the same solvent; it formed shining red needles, m. p. 131° after slight sintering (Found : C, 66·25; H, 5·0. $C_{20}H_{20},C_6H_3O_6N_3$ requires C, 65·95; H, 4·9%). The hydrocarbon could not be recovered from the complex by chromatography on alumina; but the following method proved satisfactory. The complex was dissolved in boiling alcohol, and a warm solution of stannous chloride in concentrated hydrochloric acid was gradually added until the red colour was completely discharged. Water was then added to the cooled mixture, and the hydrocarbon was collected, washed, and recrystallised.

(ii) 10-*n*-Propyl-9-anthraldehyde (8·3 g.) was gradually added, at room temperature, to a Grignard solution prepared from ethyl bromide (15 c.c.), magnesium (2·5 g.), anhydrous ether (70 c.c.), and anhydrous, thiophen-free benzene (70 c.c.). After 3 hours the mixture was warmed for ½ hour on the steam-bath. The cooled reaction mixture was then decomposed with ice and ammonium chloride. The organic layer was washed with water, dried, and evaporated, but the resulting gum could not be induced to crystallise. The crude product was therefore dissolved in boiling ethanol, and dilute hydrochloric acid (10 c.c.) added. After being boiled for 2 hours and then cooled, water was added, and the product extracted with benzene. Evaporation of the solvent gave crystalline 9-*n*-prop-1′-enyl-10-*n*-propylanthracene (3·6 g.). After crystallisation from alcohol, it formed yellow blades, m. p. 125—126° not depressed by admixture with a specimen prepared as above. Furthermore, it gave a red *s*-trinitrobenzene complex, m. p. 131° either alone or mixed with a specimen of the complex prepared from the hydrocarbon above.

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