149. *The Action of Grignard Reagents on Dianthron-9-ylidene and Dianthron-9-yl.*

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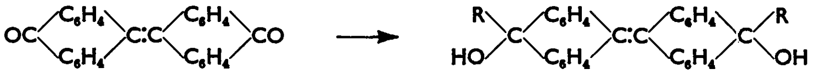
Dianthron-9-yl (V) is converted by Grignard reagents into diols (VI), except that benzylmagnesium chloride affords only the monoalcohol. These alcohols with acetic anhydride and acetic acid give acetates, but the di-α-naphthyl diol (VI) is thereby dehydrated to the hydrocarbon (IV; R = α-$C_{10}H_7$). Dianthron-9-ylidene (I) is reduced by lithium aluminium hydride to 10 : 10′-dihydrodianthr-9-ylidene.

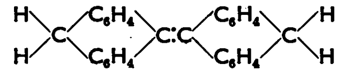
Schönberg and Ismail [1] prepared dianthron-9-ylidene * (I) from dianthron-9-yl (V) by enolisation followed by oxidation with *p*-benzoquinone. They showed [2] that with Grignard reagents it gave, after hydrolysis, *inter alia* the diols (II; R = Ph, *o*-C_6H_4Cl, and α-$C_{10}H_7$). We have now prepared the parent compound (III) by the action of lithium aluminium hydride on dianthron-9-ylidene (I).

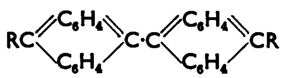
(I)



(II)

(III)

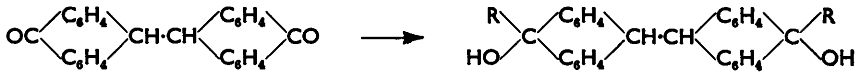




(IV)

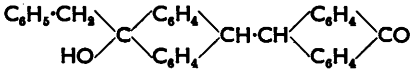
On treatment with glacial acetic acid in presence of acetic anhydride, the diols (II) gave the corresponding dianthr-9-yl derivatives (IV) by the elimination of two hydroxyl groups.[2] We have found that dianthron-9-yl (V), like dianthron-9-ylidene, reacts normally with Grignard reagents, giving on hydrolysis, the tetrahydrodihydroxydianthr-9-yls (VI;

(V)



(VI)

R = Ph, *p*-C_6H_4Cl, and α-$C_{10}H_7$). However, benzylmagnesium chloride, under different conditions, gives only the monohydroxy-compound (VII); it is known that benzylmagnesium chloride behaves similarly in many cases, *e.g.*, it reacts with anthraquinone



(VII)

under different conditions giving mainly the monohydroxy-derivative.[3] No similar products were isolated when *o*-chlorophenylmagnesium bromide reacted with dianthron-9-yl, probably owing to steric effects. Repeating Schönberg and Ismail's work,[2] we have found their product (II; R reputed to be *o*-C_6H_4Cl) is the *p*- and not the *o*-isomer.

Treating the compounds (VI; R = Ph) and (VII) with glacial acetic acid and acetic anhydride gave the acetyl derivatives, but the diol (VI; R = α-$C_{10}H_7$) was dehydrated to di-(10-α-naphthylanthr-9-yl), thus affording an easier method for its preparation.[2] The ultraviolet absorption spectrum of this compound (see Figure) was identical with that previously obtained by Schönberg and Ismail [2]—the m. p. (above 330°) was too high to be of value for characterisation. The curve shows pronounced vibrational fine structure, as for polycyclic benzenoid hydrocarbons of the linear series, *e.g.*, naphthalene and

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* For nomenclature see *J.*, 1950, 3702.

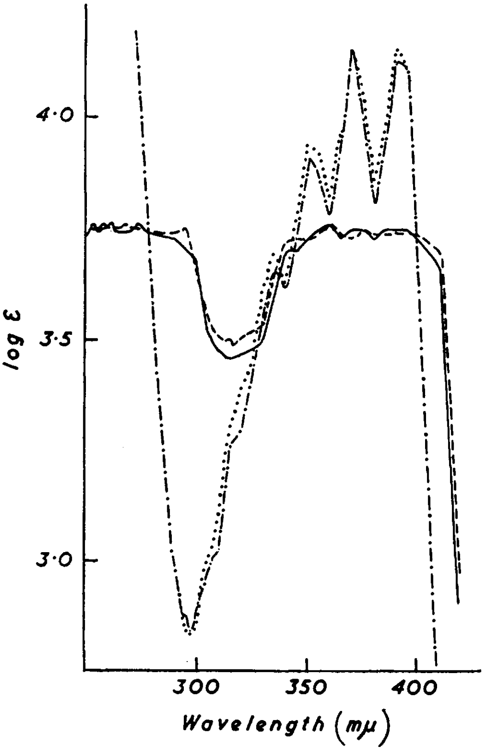
[1] Schönberg and Ismail, *J.*, 1944, 307.

[2] *Idem*, *J.*, 1945, 201.

[3] Scholl and Meyer, *Annalen*, 1934, **512**, 112.

anthracene.[4] The absorption spectrum of the parent substance dianthr-9-yl (IV; R = H) (see Figure) shows the relation between the two structures.

The present work (Experimental section) had clarified that of Barnett and Matthews [5] on the preparation of dianthr-9-yl, which was later criticised by Barnett and others.[6]



Absorption spectra of: *di*-(10-α-*naphthylanthr*-9-*yl*), (i) (———) *as prepared by Schönberg* et al.[2] *and* (ii) (– – – –) *prepared from dianthron*-9-*yl*; *and dianthr*-9-*yl*, (i) (— · — · —) *as prepared by Clar* (*Ber.*, 1932, **65**, 503) *and Bell* et al.,[7] *and* (ii) (. . . .) *prepared from anthrone.*

The compound obtained was identical (see Figure) with that prepared by Bell and Waring's method.[7]

EXPERIMENTAL

Absorption spectra were determined in $CHCl_3$ with a Unicam SP. 500 spectrophotometer.

Di-(9 : 10-*dihydro*-10-*hydroxy*-10-*phenyl*-9-*anthryl*) (VI; R = Ph).—To a solution of phenylmagnesium bromide (magnesium, 1·1 g.; bromobenzene, 7·2 g.; ether, 25 c.c.), dry benzene (50 c.c.) was added and the mixture treated gradually with powdered dianthron-9-yl [5] (V) (5 g.), then refluxed with stirring for 4 hr., the ether being allowed to evaporate slowly; a deep green colour appeared. The cooled mixture was poured into ice-cold water acidified with hydrochloric acid, the curdy white precipitate (A) was filtered off, and the benzene layer separated from the filtrate, washed, dried, and evaporated. The residue was added to (A) and the whole material (5·2 g.) crystallised from ethyl acetate in colourless prismatic crystals, m. p. 285° (decomp.). The *diol* gave a deep green colour with concentrated sulphuric acid, was sparingly soluble in acetone, benzene, toluene, and xylene, but almost insoluble in alcohol (Found: C, 87·9; H, 5·4. $C_{40}H_{30}O_2$ requires C, 88·5; H, 5·5%).

This product (1 g.) was refluxed with acetic acid (40 c.c.) and acetic anhydride (5 c.c.) for 4 hr., the solution becoming pale yellow. On cooling, the mixture was diluted with water whereby a yellow solid separated, and the whole was extracted with ether. The ethereal layer

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[4] Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," E. Arnold, London, 1954, p. 121.

[5] Barnett and Matthews, *J.*, 1923, 380.

[6] Schlenk and Bergmann, *Annalen*, 1928, **463**, 98; Barnett and Goodway, *J.*, 1929, 813; Bergmann and Schuchardt, *Annalen*, 1931, **487**, 225; Clar, *Ber.*, 1932, **65**, 503; Bell and Waring, *J.*, 1949, 1579.

[7] Bell and Waring, *J.*, 1949, 267.

was washed, dried, then evaporated, and the residue (0·85 g.) crystallised from toluene in yellowish-green prismatic crystals, m. p. 140°. This *diacetate* gave a deep green colour with concentrated sulphuric acid and was soluble in hot benzene, toluene, and xylene, but less soluble in alcohol (Found: C, 84·6; H, 5·2. $C_{44}H_{34}O_4$ requires C, 84·3; H, 5·4%). The diacetate (0·5 g.) was refluxed with 10% aqueous sodium hydroxide solution (20 c.c.) for 1 hr., cooled, and acidified with dilute hydrochloric acid, and the curdy white precipitate filtered off, washed, and dried. The diol crystallised from ethyl acetate in colourless prismatic crystals, m. p. 285° (decomp.) alone or when mixed with the product (VI; R = Ph).

The following reactions were carried out by methods substantially the same as those described above.

10-*Benzyl*-9 : 9′ : 10 : 10′-*tetrahydro*-10-*hydroxy*-10′-*oxodi*(*anthr*-9-*yl*) (VII) (*reaction in hot solution*).—The precipitate (5 g.) corresponding to (A) crystallised from toluene–light petroleum (b. p. 80—100°) in colourless prismatic crystals, m. p. 178°, moderately soluble in benzene, acetone, and xylene, less so in alcohol, giving a deep green colour with concentrated sulphuric acid, changing slowly to a pale yellow (Found: C, 88·2; H, 6·0; active H, 0·42. $C_{35}H_{26}O_2$ requires C, 87·9; H, 5·4; active H, 0·41%). In this experiment, the molar ratio of benzylmagnesium chloride to dianthronyl was 3 : 1, but a 6 : 1 ratio gave the same *product*. The *monoacetate*, crystallised once from alcohol, then repeatedly from methyl alcohol, formed pale yellow crystals, m. p. 170°, giving a deep green colour in concentrated sulphuric acid, and very soluble in benzene, toluene, and xylene (Found: C, 85·4; H, 5·7. $C_{37}H_{28}O_3$ requires C, 85·4; 5·4%); hydrolysis regenerated the alcohol.

Di-(10-p-*chlorophenyl*-9 : 10-*dihydro*-10-*hydroxyanthr*-9-*yl*) (VI; R = p-C_6H_4Cl) (*reaction in hot solution*).—The precipitate (6 g.) corresponding to (A) crystallised from toluene in pearly leaflets, m. p. 298° (decomp.). This *diol* gave green colour with concentrated sulphuric acid, sparingly soluble in benzene, toluene, and xylene, and almost insoluble in alcohol (Found: C, 79·2; H, 4·9; Cl, 11·2. $C_{40}H_{28}O_2Cl_2$ requires C, 78·6; H, 4·6; Cl, 11·6%).

Di-(9 : 10-*dihydro*-10-*hydroxy*-10-α-*naphthylanthr*-9-*yl*) (VI; R = α-$C_{10}H_7$) (*reaction in hot solution*). The precipitate (6·2 g.) corresponding to (A) was very sparingly soluble in benzene, toluene, or xylene and crystallisation therefrom seemed to be accompanied by decomposition, since the solutions gave on concentration a deep blue-violet fluorescence characteristic of the corresponding hydrocarbon (IV; R = α-$C_{10}H_7$). The product (0·7 g.), m. p. >300°, which gave a green-blue colour with concentrated sulphuric acid, was refluxed with acetic acid (40 c.c.) and acetic anhydride (2 c.c.) for 3 hr., then no longer giving the green-blue colour in concentrated sulphuric acid. The mixture was cooled and the solid (0·5 g.) crystallised from toluene in pale yellow crystals, identical with authentic di-(10-α-naphthylanthr-9-yl)[2] (IV; R = α-$C_{10}H_7$). Both samples, separately or mixed, did not melt below 330°. They had the same crystalline shape and the same green fluorescence in ultraviolet light, gave no colour in concentrated sulphuric acid, and were very sparingly soluble in boiling ether and benzene, but moderately soluble in chloroform (Found: C, 94·7; H, 5·2. Calc. for $C_{48}H_{30}$: C, 95·0; H, 5·0%).

Reaction of p-*Chlorophenylmagnesium Bromide with Di*(*anthron*-9-*yl*).—The sample of *o*-chlorobromobenzene (Schering-Kahlbaum, Berlin) previously used by one of us[2] for this reaction was found to be the *p*-isomer, and so that experiment was repeated. *Di*-(10-p-*chlorophenyl*-10-*hydroxyanthr*-9-*ylidene*) (II; R = p-C_6H_4Cl) was obtained, on reaction in hot solution, from the precipitate (6 g.) corresponding to (A) and crystallised from toluene in colourless prismatic crystals, m. p. >300° (decomp.), giving a deep greenish-blue colour in concentrated sulphuric acid, and moderately soluble in hot benzene, toluene, and xylene, but almost insoluble in methyl and ethyl alcohol (Found: C, 78·8; H, 4·7; Cl, 11·5. $C_{40}H_{26}O_2Cl_2$ requires C, 78·8; H, 4·3; Cl, 11·6%).

10 : 10′-*Dihydrodianthr*-9-*ylidene* (III).—To pulverised lithium aluminium hydride (1·2 g.) in ether (100 c.c.), dianthron-9-ylidene (3 g.) in benzene (100 c.c.) was added gradually. The reddish-brown mixture was refluxed for 3 hr. with stirring, then set aside overnight at room temperature, and poured into ice-cold water acidified with hydrochloric acid, the precipitate (B) was collected, and the benzene layer separated, washed, dried, and evaporated. The residual *hydrocarbon* was added to (B), and the whole material (2·5 g.) crystallised once from toluene, then repeatedly from benzene, forming colourless prismatic needles, m. p. 328° (depressed to *ca.* 298° on admixture with dianthr-9-yl), moderately soluble in benzene, toluene, and xylene, sparingly soluble in methyl and ethyl alcohol (Found: C, 94·2; H, 5·8. $C_{28}H_{20}$ requires C, 94·4; H, 5·6%).

Dianthr-9-yl (IV; R = H).—Anthrone (20 g.), reduced by zinc and hydrochloric acid,[5] gave a product crystallising from acetic acid in pale yellow prismatic needles (10 g.), m. p. 310—312° alone or mixed with authentic dianthr-9-yl[7] (Found: C, 94·7; H, 5·3. Calc. for $C_{28}H_{18}$: C, 94·9; H, 5·1%).

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