53. *Studies in the Anthracene Series. Part II.* The Action of Grignard Reagents on Dianthraquinone. New Derivatives of* 9 : 9′-*Dianthranyl.*

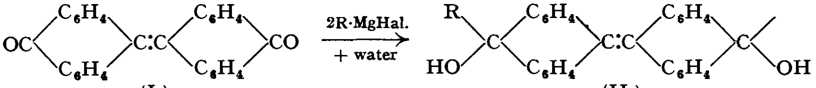
By Alexander Schönberg and Abdel Fattah Aly Ismail.

Dianthraquinone (I) reacts with Grignard reagents; the products on hydrolysis give *inter alia* compounds of type (II). (II; R = Ph, o-C_6H_4Cl, or α-$C_{10}H_7$), on pyrolysis or on reaction with glacial acetic acid in presence of acetic anhydride, loses two hydroxyl groups and gives (III; R = Ph, o-C_6H_4Cl, or α-$C_{10}H_7$), but with the same reagent (II; R = CH_2Ph) loses two molecules of water and gives (V).

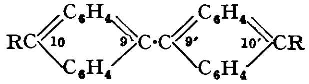
Comparatively little is known about the chemistry of 9 : 9′-dianthranyl derivatives (III) and derivatives of dianthranene (II †) in spite of the possibility of their showing carcinogenic activity.

Barnett and Cook (J., 1923, **123**, 2631) prepared 10 : 10′-diphenyl-9 : 9′-dianthranyl (III; R = Ph) from 9-phenylanthrone, but the method is not of general application because homologues of the latter compound could not be obtained.

By the reaction of dianthraquinone (I), now easily available, with Grignard reagents, followed by hydrolysis, we have obtained 10 : 10′-*diphenyl-*, 10 : 10′-*di-*(o-*chlorophenyl*)-, 10 : 10′-*di-*(α-*naphthyl*)-, and 10 : 10′-*dibenzyl*-10 : 10′-*dihydroxydianthranene*. The first three compounds, on pyrolysis or on treatment with glacial acetic acid in presence of acetic anhydride, gave 10 : 10′-diphenyl-9 : 9′-dianthranyl, 10 : 10′-*di-*(o-*chlorophenyl*)- and 10 : 10′-*di-*(α-*naphthyl*)-9 : 9′-*dianthranyl* respectively.



(I.) (II.)



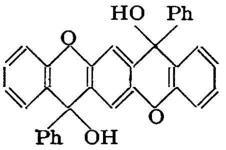
(III.)

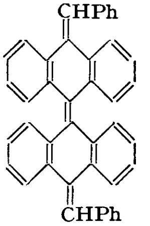
The elimination of two hydroxyl groups from a glycol by the action of glacial acetic acid has already been effected by Schönberg and Michaelis (J., 1935, 1403) in the case of (IV).

Substance (II; R = Ph, o-C_6H_4Cl, or α-$C_{10}H_7$) simulates (IV) in so far as (IV) also loses two hydroxyl groups on pyrolysis (Schönberg and Michaelis, *loc. cit.*).

10 : 10′-Dihydroxy-10 : 10′-dibenzyldianthranene (II; R = CH_2Ph) behaves somewhat differently from the other three compounds of type (II), since by the action of glacial acetic acid in presence of acetic anhydride two molecules of water are eliminated [compare the similar behaviour (elimination of water by hydrogen chloride) of benzyloxanthranol (Haller and Padova, *Compt. rend.*, 1905, **141**, 857)]; the compound produced, unlike the 9 : 9′-dianthranyl derivatives mentioned above, shows no fluorescence in benzene solution and is formulated as 10 : 10′-*dibenzylidenedianthranene* (V).

(IV.)





(V.)

Experimental.

10 : 10′-*Dihydroxy*-10 : 10′-*diphenyldianthranene* (II, R = Ph).—To a solution of phenylmagnesium bromide (magnesium, 1·1 g.; bromobenzene, 7·2 g.; dry ether, 25 c.c.), dry benzene (50 c.c.) was added, and the mixture treated gradually with powdered dianthraquinone (I) (4 g.) (Schönberg and Ismail, *loc. cit.*). The solution immediately became olive-green, but after 4 hours' refluxing (with stirring), the ether being allowed to evaporate slowly, it had become orange-red and a yellow precipitate had formed. The cooled reaction mixture was poured into ammonium chloride–ice, the precipitate (A) collected, the benzene layer separated, washed, and dried, and the benzene evaporated. The residue was added to (A), and the whole material (3·6 g.) crystallised from ethyl acetate. It then separated from toluene in colourless prismatic crystals, m. p. above 300° (decomp.). It gave a blue-green coloration with concentrated sulphuric acid (Found: C, 88·9; H, 5·5. $C_{40}H_{28}O_2$ requires C, 88·9; H, 5·2%).

10 : 10′-*Diphenyl*-9 : 9′-*dianthranyl* (III, R = Ph) *from* (II, R = Ph).—(a) *By the action of glacial acetic acid in presence of acetic anhydride.* (II, R = Ph) (0·5 g.) was refluxed with glacial acetic acid (50 c.c.) and acetic anhydride (1 c.c.) for 2 hours (calcium chloride guard-tube). The end of the reaction was attained when a sample of the solid no longer gave the blue-green coloration with concentrated sulphuric acid given by the original material. The mixture was cooled, and the yellow solid collected (0·35 g.).

(b) *By pyrolysis.* (II, R = Ph) (1 g.) was heated in a vacuum in a boiling mercury bath for 2 hours. A small amount of the hydrocarbon sublimed and an additional quantity was obtained from the dark residue by extraction with boiling benzene, filtration, and evaporation (yield, 0·2 g.).

The products from (a) and (b) separated from benzene or toluene in pale yellow crystals identical with each other

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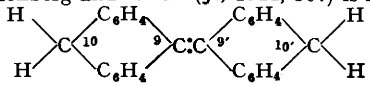
* The publication of Schönberg and Ismail (J., 1944, 307) is regarded as Part I of this series.

† For the ring system :  we propose the name " dianthranene."

and with authentic 10 : 10′-diphenyl-9 : 9′-dianthranyl (Barnett and Cook, *loc. cit.*). The samples, separately or mixed, did not melt below 300°. The crystals prepared by the three methods had the same crystalline shape, the same green fluorescence in ultra-violet light (mercury vapour lamp), and the same blue-violet fluorescence in benzene or toluene solution; they gave no coloration with concentrated sulphuric acid, were very sparingly soluble in boiling ether and soluble in boiling toluene [Found for a sample prepared by method (a) : C, 94·6; H, 5·5. Calc. for $C_{40}H_{26}$: C, 94·8; H, 5·2%].

The following compounds were prepared by methods substantially the same as those described above. 10 : 10′-*Dihydroxy*-10 : 10′-*di*-(o-*chlorophenyl*)*dianthranene* (reaction in hot solution) : The precipitate corresponding to (A) was washed repeatedly with small quantities of acetone (4·5 g.) and then extracted twice with boiling xylene (250 c.c. each time). The xylene solution was filtered and cooled and the almost colourless, prismatic crystals formed were recrystallised from toluene; m. p. above 300° (decomp.). They gave a deep blue-green coloration with concentrated sulphuric acid (Found : C, 79·0; H, 4·6; Cl, 11·0. $C_{40}H_{26}O_2Cl_2$ requires C, 78·8; H, 4·3; Cl, 11·6%).

10 : 10′-*Di*-(o-*chlorophenyl*)-9 : 9′-*dianthranyl* separated from benzene in yellow crystals, m. p. above 300°, showing a deep green fluorescence in ultra-violet light and giving no coloration with concentrated sulphuric acid. Solutions in benzene or toluene showed a blue fluorescence [Found for a sample prepared by method (b) : C, 82·9; H, 4·3; Cl, 12·3. $C_{40}H_{24}Cl_2$ requires C, 83·5; H, 4·2; Cl, 12·3%].

10 : 10′-*Dihydroxy*-10 : 10′-*di*-(α-*naphthyl*)*dianthranene* (reaction in hot solution) : the final mixture of pale yellow deposit and deep red liquid was left overnight and then decomposed with ammonium chloride–ice. The precipitate formed was very sparingly soluble in acetone, 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 (III, $R = \alpha\text{-}C_{10}H_7$). The product gave a green-blue coloration with concentrated sulphuric acid and its m. p. was above 300°. It was used without further purification for the preparation of 10 : 10′-*di*-(α-*naphthyl*)-9 : 9′-*dianthranyl.* This separated from toluene (to which it imparted a blue-violet fluorescence) in small yellow crystals, m. p. above 300°, which gave a bright green fluorescence in ultra-violet light, no coloration with concentrated sulphuric acid, and were very sparingly soluble in boiling ether and boiling benzene [Found for a sample prepared by method (a) : C, 94·4; H, 5·5. $C_{48}H_{30}$ requires C, 95·0; H, 5·0%].

10 : 10′-*Dihydroxy*-10 : 10′-*dibenzyldianthranene* (reaction in hot solution; more benzene was added after ½ hour's refluxing) : the precipitate corresponding to (A), after being washed twice with small quantities of acetone, separated from benzene in pale yellow crystals, m. p. about 300° (decomp. and evolution of gas). It gave a bright green coloration with concentrated sulphuric acid (Found : C, 88·6; H, 5·7. $C_{42}H_{32}O_2$ requires C, 88·7; H, 5·6%).

10 : 10′-*Dibenzylidene*-9 : 9′-*dianthranene* (V).—(II, $R = CH_2Ph$) (1 g.) was refluxed with glacial acetic acid (25 c.c.) and acetic anhydride (25 c.c.). The material dissolved on boiling, but after about 15 minutes reprecipitation occurred. Refluxing was continued for 2 hours, the mixture cooled, and the deep yellow product filtered off (0·45 g.). An additional quantity was obtained from the mother-liquor. Recrystallised from benzene, it formed yellow crystals which darkened (decomp.?) at about 230° and were sparingly soluble in ether (Found : C, 94·2; H, 5·5. $C_{42}H_{28}$ requires C, 94·7; H, 5·3%).

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