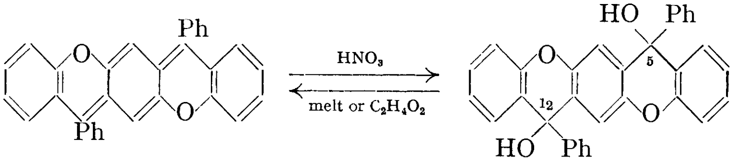
336. *Studies in Pyrolysis.* Elimination of Two Hydroxyl Groups from a Glycol.*

By Alexander Schönberg and Robert Michaelis.

The following communication deals with the remarkable property of a glycol which loses both hydroxyl groups on heating or on treatment with glacial acetic acid.

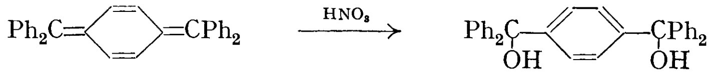
Liebermann and Barrollier (*Annalen*, 1934, **509**, 40) stated that the deep red chromanorufen (I) is converted by oxidising agents, such as nitric acid in acetic acid, into a colourless compound of unknown structure. As a result of our investigations we regard the colourless compound as 5 : 12-*dihydroxychromanorufan* (II). We have confirmed the observation of Liebermann and Barrollier that it is easily reconverted into chromanorufen, but do not share the view that it contains two loosely bound oxygen atoms and is the analogue of rubrene dioxide (VIII) (cf. Dissert., Jean Barrollier, Berlin, 1932, p. 14). We consider the oxidation of chromanorufen involves the addition of the elements of hydrogen peroxide and is analogous to the formation of $\omega\omega\omega'\omega'$-tetraphenyl-*p*-xylylene glycol (IV) from 1 : 4-bisdiphenylmethylene-$\Delta^{2:5}$-*cyclo*hexadiene (III), a fact observed by us.

(I.)



(II.)

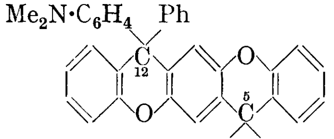
(III.)

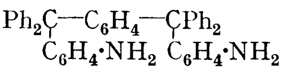


(IV.)

Formula (II) accounts satisfactorily for the properties of the oxidation product of chromanorufen, *e.g.*, its lack of colour and the fact that it gives a colour reaction with concentrated sulphuric acid; this is typical of phenylxanthydrol and its derivatives. The presence of the two hydroxyl groups is shown by the formation of 5 : 12-*bis*-p-*dimethylaminophenylchromanorufan* (V) by the action of dimethylaniline in glacial acetic acid on (II). Under the same conditions, 4-dimethylaminodiphenylxanthen (VII) is formed from phenylxanthydrol (Ullmann and Engi, *Ber.*, 1904, **37**, 2374). Reference may also be made to the formation of 4 : 4′-diaminohexaphenyl-*p*-xylene (VI) from (IV) and aniline hydrochloride in glacial acetic acid (Ullmann and Schlaepfer, *Ber.*, 1904, **37**, 2004).

(V.)

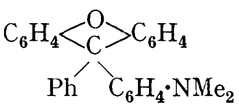




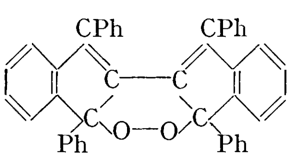
$\underset{C_6H_4\cdot NH_2}{Ph_2C}-C_6H_4-\underset{C_6H_4\cdot NH_2}{CPh_2}$

(VI.)

(VII.)



$\underset{Ph\quad C_6H_4\cdot NMe_2}{C_6H_4{<}\substack{O\\C}{>}C_6H_4}$



(VIII.)

Contrary to the statement of Liebermann and Barrollier that tetra-*p*-xylylene glycol (IV) melts without decomposition or discoloration at 169°, we find that it melts with evolution of gas, becoming yellow and acquiring a fluorescence similar to that of a solution

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* For earlier papers on pyrolysis by A. Schönberg and co-workers, see *Ber.*, 1925, **58**, 580; *Annalen*, 1927, **454**, 47; *Ber.*, 1927, **60**, 2344; 1928, **61**, 478, 2175; 1929, **62**, 2322, 2550; 1930, **63**, 178; *Annalen*, 1930, **483**, 90, 107, 177; *Ber.*, 1931, **64**, 2578, 2582.

of 1 : 4-bisdiphenylmethylene-$\Delta^{2:5}$-*cyclo*hexadiene (III) : possibly it is converted into (III) by losing the elements of hydrogen peroxide.

EXPERIMENTAL.

1 : 4-*Bisdiphenylmethylene*-$\Delta^{2:5}$-cyclo*hexadiene* (III).—In an atmosphere of carbon dioxide, with exclusion of light, 6·9 g. of ωωω′ω′-tetraphenyl-*p*-xylylene dichloride (Ullmann and Schlaepfer, *Ber.*, 1904, **37**, 2003) were boiled under reflux in absolute benzene (340 c.c.) with copper–bronze (Kahlbaum) (13·6 g.) for 2 hours, more copper–bronze (6 g.) being added after the first 10 hours. The liquid was filtered hot and cooled to 0°. Orange-yellow crystals were obtained of a compound which after recrystallisation from ligroin was identical with that described by Thiele and Balhorn (*Ber.*, 1904, **37**, 1469).

Action of Concentrated Nitric Acid on 1 : 4-*Bisdiphenylmethylene*-$\Delta^{2:5}$-cyclo*hexadiene*.—0·2 G. of (III) was treated with a mixture of 5 c.c. of nitric acid (*d* 1·42) and 5 c.c. of glacial acetic acid, and the deep orange product heated for 10 minutes on the water-bath. The clear solution was poured into 100 c.c. of water and the colourless precipitate immediately obtained was washed with cold water till neutral, dried over sodium hydroxide in a vacuum desiccator (yield 0·15 g.), and crystallised successively from ligroin, benzene, and ligroin. The colourless compound obtained was identical with ωωω′ω′-tetraphenyl-*p*-xylylene glycol (IV) (Ullmann and Schlaepfer, *loc. cit.*); its intense brown-bordeaux solution in concentrated sulphuric acid became yellow on addition of water (Found : C, 86·7; H, 6·2. Calc. for $C_{32}H_{26}O_2$: C, 86·9; H, 5·9%).

5 : 12-*Dihydroxychromanorufan* (II).—This was obtained by the action of glacial acetic acid and nitric acid on chromanorufen (cf. Liebermann and Barrollier, *loc. cit.*). Its deep green solution in concentrated sulphuric acid became deep red on addition of water. It separated from ligroin in colourless crystals, decomp. about 260° with reddening (Found : C, 81·9; H, 5·2. $C_{32}H_{22}O_4$ requires C, 81·7; H, 4·7%).

Effect of heat. Carbon dioxide dried by sulphuric acid was passed through a flask, containing 0·2 g. of (II), immersed in a bath at 290°. The temperature was increased to 310° during 25 minutes, the colourless compound (II) melting and turning red with evolution of a gas. After 25 minutes, the mixture was allowed to cool and the crystalline mass obtained was boiled for 10 minutes with benzene (10 c.c.), leaving a residue of chromanorufen (0·09 g.). This was washed with methyl alcohol, dried in a vacuum desiccator, and sublimed in a high vacuum (temp. of bath 290—360°; the sublimation process occupied 45 minutes). Only a small residue was left. The sublimate was shown to be pure chromanorufen by its properties and by absorption spectra measurements carried out in bromobenzene solution at room temperature, air and light being excluded during the preparation of the solution.

Removal of the two hydroxyl groups by glacial acetic acid. 0·1 G. of (II) was slowly heated with glacial acetic acid (5 c.c.) with frequent shaking and finally the solution was boiled under reflux for 45 minutes. Characteristic crystals of chromanorufen were isolated from the hot solution by filtration and were washed with methyl alcohol. The purity of the product (0·06 g.) was shown by absorption spectra determinations.

Separate experiments showed that 5 minutes' boiling of (II) with glacial acetic acid is sufficient to form red crystals of chromanorufen.

Action of dimethylaniline. 0·6 G. of (II) was suspended in glacial acetic acid (15 c.c.), dimethylaniline (1·5 g.) added in the cold, and the mixture heated for 4 hours on a gently boiling water-bath. After standing over-night in the cold, the faintly greyish-yellow precipitate was collected and repeatedly washed with glacial acetic acid, and then with benzene. Yield, 0·7 g. Crystallisation from boiling bromobenzene gave 5 : 12-*bis*-p-*dimethylaminophenylchromanorufan* (V) as pale yellow crystals, decomp. about 340°, very slightly soluble in acetone but soluble in hot nitrobenzene (Found : C, 84·5; H, 6·0; N, 4·2. $C_{48}H_{40}O_2N_2$ requires C, 85·2; H, 6·0; N, 4·1%).

The formation of (V) is not due to the intermediate production of chromanorufen, for this compound (0·3 g.), after being heated in glacial acetic acid (7 c.c.) with dimethylaniline (1·5 g.) for 11 hours, was recovered in almost theoretical yield.

We thank Mr. Neil Campbell for his assistance in the translation of the manuscript and acknowledge our profound gratitude to Prof. G. Barger, F.R.S., for his hospitality.

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[*Received, July* 1*st*, 1935.]