

A NEW METHOD FOR THE PREPARATION OF NAPHTAZARINS

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AMONG quinone pigments, the derivatives of naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) present a special interest, not only because they are important natural products, the structure of which has not been elucidated in many cases, but also because they have been employed as colouring matter for industrial application.

The methods of synthesis of naphthazarin derivatives are not, however, very satisfactory. Roussin¹ obtained naphthazarin for the first time by the action of fuming sulphuric acid and a reducing agent on the 1,5-dinitronaphthalene, but the method was not applied to the homologues until Bruce and Thomson,² who obtained in low yield 2-methylnaphthazarin, 2,6-dimethylnaphthazarin and 2,6-dichloronaphthazarin starting with the

¹ Z. Roussin, C. R. Acad. Sci., Paris 52, 1033 (1861).

² D. B. Bruce and R. H. Thomson, J. Chem. Soc. 1089 (1955).

appropriate dinitronaphthalenes. Zahn and Ochwat³ developed a method of synthesis of naphazarins by condensing hydroquinones with maleic anhydride, or derivatives, in fused sodium chloride-zinc or aluminium chloride. This method has been applied, for example, to the preparation of hydroxydrosone⁴ from maleic anhydride and 2-methyl-3-methoxyhydroquinone and of echinochrome A⁵ using 2-ethyl-1,3,4-trimethoxybenzene and dibenzoyloxymaleic anhydride, although in this case the yield is only 1.5 - 2 per cent.

In our study on diene synthesis with quinones, we experimented with the preparation of naphazarins from the adducts of butadiene, or derivatives, with p-benzoquinones, which are usually obtained readily and in good yields. We tried in this way to develop a more satisfactory method of synthesis of the natural products in question, especially the spinochromes and echinochromes.

The butadiene-p-benzoquinone adduct (I) by acetylation with acetic anhydride was transformed in the acetate of the diphenolic form (II). The oxidation in α of this product could lead to the naphazarin diacetate (III). However, if it is carried out with selenium dioxide only the aromatized product, the naphthohydroquinone diacetate (IV), is obtained, while by oxidation with chromic anhydride at 0°C the naphazarin diacetate (III) is formed, and this by alkaline hydrolysis yields naphazarin (V).

³ K. Zahn and P. Ochwat, Ann. 462, 72 (1928).

⁴ A. K. Macbeth, J. R. Price and F. L. Winzor, J. Chem. Soc. 334 (1935).

⁵ K. Wallenfels and A. Gauhe, Ber. 76, 325 (1943).

case the same methylnaphtazarin is obtained from the butadiene-toluquinone or 2-metilbutadiene-p-benzoquinone adduct. This allows the use of the dienes or quinones most suitable in each case.

The new process seems to be of general application and the preparation of several substituted naphtazarins from the corresponding Diels - Alder adducts (butadiene-quinone; butadiene-toluquinone; isoprene-quinone; 2,3-dimethylbutadiene-quinone; 2,3-dimethylbutadiene-toluquinone; 2,3-dimethylbutadiene-methoxyquinone) has been studied.

In all cases the acetyl derivative of the adduct has been obtained by refluxing with acetic anhydride for 2 or 3 hr. As an example of the experimental conditions the details for the last steps of the obtention of methylnaphtazarin are given below:

To 36 g of chromic anhydride dissolved in the smallest possible quantity of 80 per cent aqueous acetic acid, a solution of 24 g of 1,4-dihydroxy-5,8-dihydro-7-methylnaphtalene diacetate (from the isoprene-p-benzoquinone adduct) in glacial acetic acid is added, drop by drop and with constant stirring, keeping the temperature under 5°C. The stirring is continued for several hours and the greenish solution formed is poured over 500 ml of ice water. The yellow precipitate of methylnaphtazarin diacetate formed is filtered, washed with water and recrystallized from alcohol, m.p. 169,5°C. Yield 75 per cent.

The methylnaphtazarin diacetate is hydrolysed by heating in a water bath with 5 per cent aqueous sodium hydroxide. The solution of an intense blue colour is filtered and acidified with hydrochloric acid, the red precipitate of methylnaphtazarin being collected. Red-brown needles are

obtained by sublimation. Recrystallization from alcohol gives needles, m.p. 175° C.

Studies are in progress on the preparation of oxyderivatives of the type of echinochromes and spinochromes and of higher condensed systems from adducts with naphtoquinone.