Along these lines the supposed antithesis between homopolar and heteropolar reactions disappears. A more detailed discussion of these aspects of the theory of organic reactions will be submitted elsewhere.

R. ROBINSON

Dyson Perrins Laboratory,
South Parks Road,
Oxford.
Jan. 18.

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A New Synthesis of isoFlavones

EIGHTEEN different iso flavones are known to occur in plants either in the free state or as glycosides; 5:7-dihydroxy-4'-methoxyiso flavone (I) (biochanin-A) may be taken as a typical example.

Two main methods have been developed for their synthesis. In the first, a deoxybenzoin, for example (II), is converted into a 2-styryliso flavone, either by direct cinnamoylation¹ or by acetylation to a 2-methyliso flavone followed by the condensation of the reactive methyl group with benzaldehyde², and, after protecting any free phenolic groups, oxidation by permanganate gives a 2-carboxyiso flavone, which is decarboxylated and the protecting groups removed. The yields at the oxidation stage are poor, and the method is not well suited for the preparation of partially alkylated iso flavones; it has been used for the preparation of genistein, daidzein and ψ -baptigenin.

In the second, a deoxybenzoin (II) is directly converted into an iso flavone by treatment with ethyl formate and sodium. In the early experiments³, the mixture was heated and the yields were poor; but Venkataraman and others showed⁴ that much better results were obtained at 0°. The chief drawback to this synthesis is that it only proceeds satisfactorily if all phenolic groups in the deoxybenzoin, except that involved in the cyclization, are protected by methylation or benzylation, though it has been claimed⁵ that the deoxybenzoin (II) is directly converted into the iso flavone (I) by this method. We have, however, been unable to prepare (I) in this way, and related reactions involving formylation of deoxybenzoins containing three free phenolic groups have also failed⁶. A modification of this formylation method⁷ using ethyl orthoformate in pyridine proceeds satisfactorily in the cases of a 2-hydroxy- and

of 2:4-dihydroxy-deoxybenzoin, but failed to give an iso flavone with 2:4:6-trihydroxydeoxybenzoin.

We have now developed a new simple iso flavone synthesis starting from a deoxybenzoin (II) which gives good yields at all stages, even when several free phenolic groups are present. It is particularly suited for the preparation of partially alkylated iso flavones without the necessity of employing devices such as partial protection by benzyl groups, partial methylation or partial demethylation. The new method may be illustrated by the preparation of the iso flavone (I). The deoxybenzoin (II), when treated at room temperature with ethyl oxalyl chloride in pyridine, gives directly 2-carbethoxy-5:7-dihydroxy-4'-methoxyiso flavone (III; melting point, 189-190°; 60 per cent yield). Mild alkaline hydrolysis then gives the corresponding acid (yield, 98 per cent), which loses carbon dioxide at its melting point, giving the iso flavone (I), best purified as its diacetyl derivative (yield, 81 per cent). Alkaline hydrolysis then gives biochanin-A. The generality of the method has been established by the preparation of a number of other iso flavones, including genistein and ψ -baptigenin.

W. BAKER

W. D. OLLIS

(with P. J. L. BINNS, J. CHADDERTON, I. DUNSTAN, J. B. HARBORNE and D. WEIGHT).

University, Bristol.

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Separation of the 3,5-Dinitrobenzoates of Volatile Alcohols by Paper Chromatography

Few methods for the separation of derivatives of volatile alcohols by paper chromatography have been reported. Rice, Keller and Kirchner¹ have separated a number of 3,5-dinitrobenzoates by using various solvent systems and filter papers. They quote no R_F values, however. Kariyone, Hashimoto and Kimura² have separated the potassium xanthogenates of a number of alcohols, using alkaline butanol as solvent.

The following method for the separation of 3,5-dinitrobenzoates has been of use in the detection of volatile aliphatic alcohols dissolved in benzene or petroleum ether, in quantities greater than 10⁻⁷ gm. mole. The non-aqueous two-phase solvent system methanol-heptane was used—methanol (commercial absolute), heptane ('fraction from petroleum'). A method of revealing the derivatives, previously used in column separations³, was adapted for the paper technique. Whatman No. 1 paper, soaked in a methanolic solution of Rhodamine 6 GBN.500 (I.C.I., Ltd.), 20 mgm.