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INTRAMOLECULAR NUCLEOPHILIC DISPLACEMENT OF NITRO GROUP IN 2'-NITROBIPHENYL 2-(OR 6) CARBOXYLIC ACIDS. LACTONISATION OF 2,3,4,4'-TETRAMETHOXY 2'-NITROBIPHENYL 6-CARBOXYLIC ACID.

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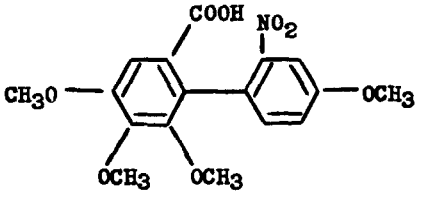
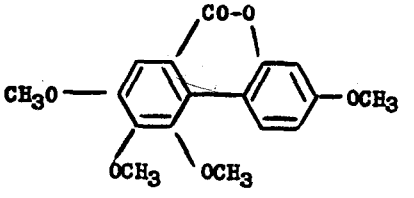
In a recent communication[1], Hey,Leonard and Rees describe the conversion in the presence of base of 2'-Nitrobiphenyl 2-carboxylic acid and its 2',4-dinitro analogue into 3,4,-benzocoumarin and 5'-nitro 3,4-benzocoumarin respectively. These conversions involve the displacement of the 2'-nitro group by the 2-carboxylate anion. We wish to report an additional conversion- that of the acid (I) into the lactone (II), which supports and augments the findings of the above workers with regard to such novel intramolecular nucleophilic displacements.



(I)



(II)

Attempt to decarboxylate 2,3,4,4'-Tetramethoxy 2'-nitrobiphenyl 6-carboxylic acid (I) by heating its (0.2 g.) solution in quinoline (5 ml.) with copper oxide (0.08 g.) for 1 hour gave to us also,instead

of the expected decarboxylated nitrobiphenyl, a new compound m.p. 161-62° (Found: C, 64.07, H,5.7 ; $C_{17}H_{16}O_6$ requires C, 64.55,H,5.06) in 50 percent yield. The same compound could be obtained omitting copper oxide. Its ultraviolet spectrum* in purified dioxane showed λ_{max} 281,301,340 mμ(log ε 4.231,4.185,3.939). This compound gave a hydroxamic test for esters and dissolved in aqueous alkali on heating. Methylation with dimethylsulphate in aqueous alk in the cold followed by 1 hours' refluxing provided an acid m.p. 178° (from benzene). Our compound was thus identical with the lactone (II) of 2,3,4,4'-tetramethoxy 2'-hydroxybiphenyl 6-carboxylic acid m.p. 161° first synthesised by Mayer and Fikentscher[2]. The ultraviolet spectrum (in dioxane) reported by them has λ_{max} 224,256, 282,302,340 mμ(log ε 4.377,4.632,4.287,4.215,3.937). It is stated to be convertible by further methylation with dimethylsulphate to 2,3,4,2',4'-Pentamethoxybiphenyl 6-carboxylic acid, m.p. 176-78°.

The infrared spectrum (in Nujol) of our lactone (II) has the special feature of having in the carbonyl region two split bands near 1730 cm^{-1} and 1710 cm^{-1} for the lactone carbonyl. The appearance of split bands in this region is often met in coumarin type[3] of compounds.

In obtaining the lactone (II), Mayer and Fikentscher[2] had condensed bromotrimethylgallic acid with resorcinol in the presence of sodium in methanol and active copper and obtained in the first instance the hydroxy lactone(II, with 4'-OH). Mild methylation of the latter compound with diazomethane gave finally the lactone (II). The identity of our compound m.p. 161-62° with their lactone thus provides an unequivocal evidence for the 3,4-benzocoumarin

* Absorptions below 262 mμcould not be obtained. The readings were taken in a manually operated Beckmann DU Spectrophotometer.

type of structure for the products that result by heating 2,2' (or 6,2') nitrobiphenyl carboxylic acids in the presence of base.

It is remarkable that the acid(I), which is largely substituted and even carries a blocking substituent in the 2-position, is lactonised to (II) with almost as much ease as the lesser and differently substituted acids. Minor differences in the nature of substituents, their number and position do not seem to modify the change. Obviously, the very favourable steric disposition[1] of the reacting groups in the 2,2' position outweighs other influences.

The 2,3,4,4'-Tetramethoxy 2'-nitrobiphenyl 6-carboxylic acid (I), m.p. 199-200°(from alcohol) (Found: C, 56.5, H, 5.3 ; $C_{17}H_{17}NO_8$ requires C, 56.2, H, 4.7) used in the above displacement reaction was synthesised by us by coupling 2-Nitro 4-methoxy benzene diazonium chloride with Ethyl 3,4,5-trimethoxy benzoate, utilising the Meerwein's Diazo Reaction[4] as adopted by Dickerman and Weiss[5] for the synthesis of biaryls. Its identity was also established by an independent Ullmann type of reaction. The acid (I) had for an aromatic acid carbonyl(dimer) a strong band (KBr) ν_{CO} 1680 cm^{-1}.

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