

28. Alkylation of Dioxybenzenes by p-Toluenesulfonic Acid Ester. (II)

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In the previous paper it was reported about the alkylation (C_1 , C_2 , C_4 , C_6) of pyrocatechin, resorcin, hydroquinone by p-toluenesulfonic acid ester. Now we prepared 70~80% in yield p-toluenesulfonic acid ester (C_8 , C_{10} , C_{12} , C_{14} , C_{16}) from the corresponding alcohols and p-toluenesulfonyl chloride by using picolin (B.P. $130^{\circ}\sim 150^{\circ}$) as the condensation reagent.

The alkylation of the dioxybenzene by these higher esters was performed as easily as in the cases of the lower esters. But in these cases, separation of the monoalkyl ether from the dialkyl ether was not enable by means of aq. NaOH. The separation was attained by fractional distillation or fractional recrystallisation from methanol, in which the dialkyl ether is nearly insoluble.

Monoalkyl ether was refined by redistillation or recrystallisation from benzene or petroleum ether, if it is crystalline. Dialkyl ether was purified by recrystallisation from a mixture of methanol and benzene.

The yields of monoalkyl and dialkyl ethers were about 50~60% and 20~25%, respectively, using 0.2 mol dioxybenzene and 0.1 mol sodium for 0.1 mol ester.

29. Syntheses of Antioxidants for Fats and Oils. (I)

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In view of the recent development of an antioxidant, nordihydroguaiaretic acid or NDGA, several dinuclear phenols with the analogous structure were synthesized. The product indicated with an asterisk (*) is a new compound.

Hydroquinone methyl allyl ether was rearranged to 2-allyl-4-methoxyphenol which was then methylated to 2,5-dimethoxyallylbenzene and the Grignard reagent of its hydrobromide, 1-(2,5-dimethoxyphenyl)-2-bromopropane* (yellow oil, b.p. $142\text{--}152^{\circ}/5\text{--}7\text{ mm.}$) was treated with iodine, giving a meso and racemic mixture of 1,4-bis-(2,5-dimethoxyphenyl)-2,3-dimethylbutane* (yellow oil, b.p. $240\text{--}250^{\circ}/5\text{--}6\text{ mm.}$, yield 27%). On demethylation by hydrobromic acid and recrystallizations from benzene a mixture of meso and racemic free phenols, 1,4-bis-(2,6-dihydroxyphenyl)-2,3-dimethylbutane,* was obtained in white powder. meso-Tetraacetate,* m.p. $144\text{--}145^{\circ}$.