

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

Shinsaburo Oka

(Nodzu Laboratory)

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)

Keiiti Sisido and Hiroshi Kuyama

(Sisido Laboratory)

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. $144\text{--}145^\circ$.

2,5-Dimethoxyallylbenzene was isomerized to 2,5-dimethoxypropenylbenzene by potassium hydroxide and the hydrobromide addition compound was condensed by reduced iron powder to 3,4-bis-(2,5-dimethoxyphenyl)-hexane* (yellow oil, b.p. 215–280°/5 mm.) The meso compound* which crystallized (yield 11%) melted at 118–119°. The demethylation gave 3,4-bis-(2,5-dihydroxyphenyl)-hexane,*m.p. 219–220°; tetraacetate,*m.p. 149–150°.

α -Diisosaftrole was treated with phosphorus pentachloride in refluxing toluene and decomposed with iced aqueous sodium carbonate solution yielding white crystals of carbonyldioxy derivative of diisosaftrole,*m.p. 152.5–153°, yield, 37%.

Demethylation of metanethole with methylmagnesium iodide gave 1-ethyl-1-(p-hydroxyphenyl)-2-methyl-6-indanol* in colorless needles, m.p. 158–159°.

The antioxidative property and the toxicity of these compounds together with 3,4-bis-(m, p-dihydroxyphenyl)-hexane* and 3,4-bis-(m, p-carbonyldioxyphenyl)-hexane* (Sisido, Nozaki and Kuyama, J. Org. Chem., **14**, 1124 (1949)) were tested in the laboratory of Prof. Takata. The results will be published elsewhere.

30. The Study on the Reaction of Acetylene under High Pressure. (III)

Synthesis of N-Vinyl Phthalimide

Junji Furukawa and Akira Onishi

(Oda Laboratory)

N-vinyl phthalimide is now prepared by pyrolysis of β -acetoxyethylphthalimide (over-all yield 50%) and the polymer is a new source of polyvinylamine. It is claimed in one patent that the compound was also obtained by the reaction of C_2H_2 and phthalimide at high pressure and temperature with Hg salt as catalyst. (C.A. **35**, 32667 (1941)). But our repetition of this method disclosed that no vinyl phthalimide could be obtained and metallic Hg was liberated.

Attempts were then made to accomplish this reaction by means of various catalysts, including $(CH_3COO)_2Zn$, Zinc stearate and $(CH_3COO)_2Cd$. $(CH_3COO)_2Cd$ has proved successful. The others were less effective. Phthalimide potassium was also used, but without success. The results are shown in the following table.

Catalyst (g)	Reactn. Temp.	Reactn. time	vinyl P.I.	Resin
Zn Stearate 3	220°C	9 hrs.	0.5g (10%)	5.3g
$(CH_3COO)_2Cd$ 5	200	2	3.0g (50%)	6.0
HgCl ₂ 6	190	3	0	2.0

P.I. = phthalimide. P.I. 20g and xylene 40g are used in all cases. Yields are calculated allowing for recovered P.I.