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Construction of a Homonaphthazarin Skeleton and Synthesis of Hydroquinone-annulated Cycloheptatriene Derivatives

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Abstract: 1,4-Dihydroxy-7,8-dihydro-5H-benzo[a]cycloheptene-5,9(6H)-dione (7) was synthesised from hydroquinone and glutaric acid chloride via an acylation reaction. The reaction of dione (7) with bromine followed by treatment with NEt_3 gave homonaphthazarin 8 as well as the brominated derivatives 9 and 10. Reduction of 1,4-dimethoxy-7,8-dihydro-5H-benzo[a]cycloheptene-5,9(6H)-dione (16) with LiAlH_4 gave 2 isomeric alcohols, 17 and 18. Reaction of these alcohols with SOCl_2 followed by HCl elimination with NEt_3 afforded dimethoxybenzocycloheptatriene 19 as the sole product. For the synthesis of the isomeric cycloheptatriene 20, the double bond in 19 was isomerised with KOt-Bu .

Key Words: Naphthazarin, homonaphthazarin, benzocycloheptatriene, acylation, bromination

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