The Hydroxide Ion-induced Aromatization of a Norbornenone Derivative

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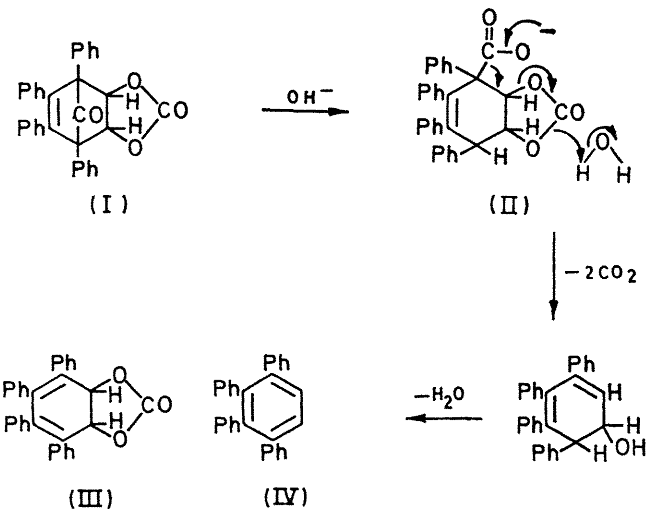
Summary The carbonate ester of 5,6-dihydroxy-1,2,3,4-tetraphenylnorbornen-7-one (I) is converted exclusively into 1,2,3,4-tetraphenylbenzene under mild alkaline conditions, the near quantitative conversion, unlike others of this type, does not appear to involve decarbonylation

WHEN 5,6-dihydroxy-1,2,3,4-tetraphenylnorbornen-7-one (I)[1] was exposed to various acidic conditions that normally foster hydrolysis [*e g* boiling 0 3M hydrochloric acid (24 h), boiling conc acetic acid (3 h) or conc hydrochloric acid (up to 5 days)], quantitative recovery of starting material was realized in all cases Yet, when a solution of (I) in aqueous dimethylformamide (DMF) containing potassium carbonate was stirred at room temperature for 2 h and then poured over ice a light pink solid (IV) was the only product isolated After crystallization from benzene–methanol it was identified as 1,2,3,4-tetraphenylbenzene by direct comparison with an authentic sample [2]

There was no evidence of carbon monoxide evolution during conversion of (I) into (IV) † Control studies‡ indicate that the hydroxide ion, *specifically*, is necessary for the production of (IV) This suggests that the overall process is triggered by initial attack by hydroxide ion at the carbonyl bridge of (I) to produce a structure such as (II),§ rather than initial decarbonylation to the diene (III) Conversion of (II) into (IV) could then conceivably proceed (Scheme) by loss of carbon dioxide (2 mols) and water (1 mol), and formation of these stable species with the final aromatic system of (IV) providing the driving force for the transformation



SCHEME

The *chemical* conversion of a norbornenone derivative into an aromatic compound by a mild, one-step procedure not involving decarbonylation has not previously been reported although analogous *photochemical* transformations are known [6–8] If this reaction is a general one, as work in progress indicates, it provides a simple, efficient route to aromatic structures, especially those containing acid and/or heat-sensitive substituents

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† At the conclusion of the reaction time the flask was swept with argon gas The effluent, bubbled into PdCl$_2$ solution,[8] produced no palladium black

‡ No reaction occurs when (I) is stirred with DMF–H$_2$O or DMF alone at room temperature and products different from (IV) are obtained if other base–solvent combinations are used

§ The generation of (II) by hydroxide ion attack at the bridge carbonyl of (I) followed by ring-opening to a carbanion and proton transfer is supported by several precedents[4,5] in the literature

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