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BENZODIOXOLE CHEMISTRY. 4.[1] CONCERNING THE AROMATIZATION *OF CARBONYL-BRIDGED CYCLIC CARBONATES* EFFECTED BY POTASSIUM CARBONATE IN AQUEOUS DIMETHYLFORMAMIDE

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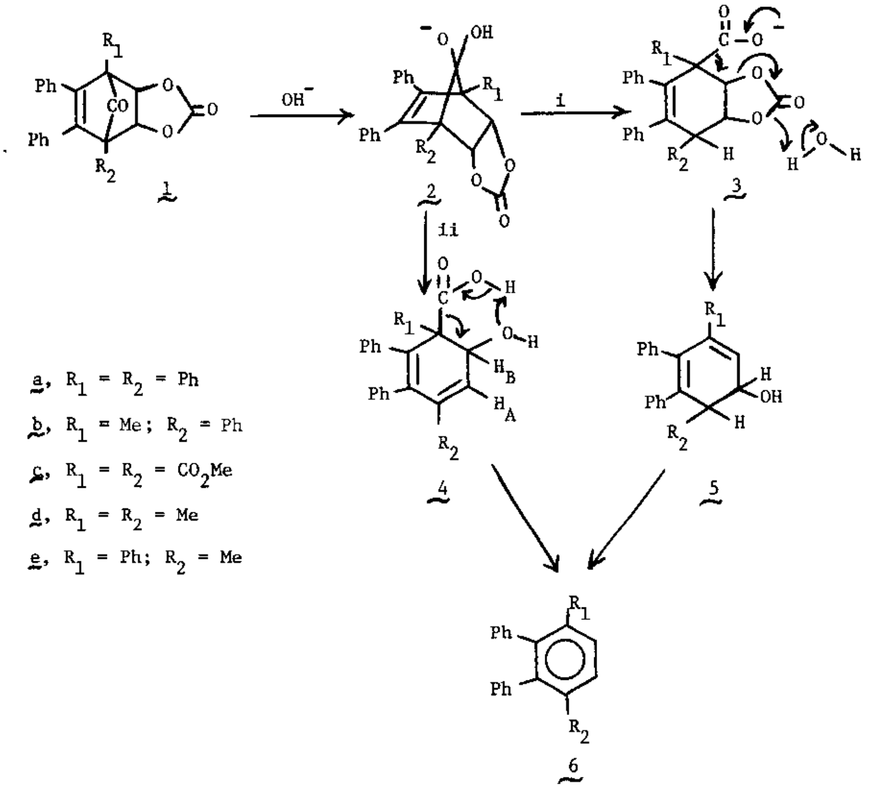
Three 4,5,6,7-tetrasubstituted 3a,4,7,7a-Tetrahydro-4,7-methano-1,3,-benzodioxole-2,8-diones (**1a**-**c**) containing electron-withdrawing groups in the 4- and 7-positions undergo clean, high-yield conversion to aromatic products **6a**-**c** in 4% aqueous dimethylformamide containing no added potassium carbonate. By comparison, one benzodioxoledione (**1d**) containing electron-donating groups in the same positions yields no aromatic product under these conditions. By allowing the reaction of **1b** with DMF/H_2O to proceed for only 24 h good yields of hydroxyacid **4b** (36%) and hydrocarbon **6b** (40%) are obtained. Taken in conjunction with the substituent-dependent reactivity, isolation of **4b** lends strong support to a previous mechanistic proposal; while discovery of the fact that the aromatization reaction can proceed without added base broadens the scope of its synthetic potential.

We[1] recently reported a facile aromatization of the carbonyl-bridged cyclic carbonates **1** in excellent yields by potassium carbonate in aqueous dimethylformamide at room temperature. At that time mechanisms were proposed (Scheme) which involved nucleophilic attack of hydroxide ion at the carbonyl bridge followed by conversion to the aromatic product **6** via either the carboxylate anion **3** or hydroxyacid **4**. We now wish to report that the presence of potassium carbonate is unnecessary[2] to effect chemical reaction for several reactive substrates and, in addition, we present evidence which bears on the mechanism by which **1** is converted into **6**.

SCHEME



a, $R_1 = R_2 = Ph$

b, $R_1 = Me$; $R_2 = Ph$

c, $R_1 = R_2 = CO_2Me$

d, $R_1 = R_2 = Me$

e, $R_1 = Ph$; $R_2 = Me$

The aromatization reactions were carried out on benzodioxolediones **1a**-**d** using the procedure previously described[1], *only in the absence of potassium carbonate* (see Table 1).

Table 1

Results of the Aromatication Reaction in the Absence of Potassium Carbonate

Substrate	Product	Yield %	Duration of Reaction
1a	6a	83[a]	24 h
1b	6b	90[a]	72 h
1c	6c	74[a]	24 h
1d	6d	0[b]	7 da

[a] Isolated yields of nearly pure compound which contained no residual **1** (TLC analysis). [b] The majority (78%) of **1d** was recovered unchanged and there was no **6d** in evidence (TLC analysis).

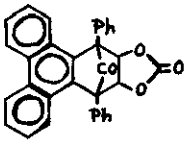
On examination of the data found in the Table an interesting trend emerges: namely, those benzodioxolediones with electron-withdrawing groups in the 4- and 7- positions (**1a** and **1c**) undergo conversion more readily than the one with electron-donating groups in the same positions (**1d**). Such results are not surprising if one assumes that either of the two mechanisms (Scheme) is still operating even in the absence of appreciable hydroxide ion concentration.

In the course of monitoring (TLC) the aromatization of **1b** we observed the formation of a low R_f intermediate[3] which gradually built up at the expense of **1b** and then subsequently disappeared as **6b** was formed. On quenching the reaction in ice-water after 24 h we obtained a mixture of **6b** and this low R_f intermediate. Chromatographic separation (silica gel column) yielded **6b** (40%) and a white solid (36%) of mp 139° (gas evolution) *tentatively* identified[4] as 6-hydroxy-1-methyl-2,3,4-triphenyl-2,4-cyclohexadiene-1-carboxylic acid (**4b**). The hydroxyacid structure (**4b**) was assigned on the basis of high-resolution mass spectral information[5] and the following evidence: (i) M^+ = 382, in addition the mass spectrum showed the expected losses of CO_2 at m/e 338 and $CO_2 + H_2O$ at m/e 320 (base peak); (ii) nmr spectrum [60MHz, CD_3COCD_3] δ 6.91 (d, 10H, aromatic), 6.67 (s, 7H, aromatic, OH, CO_2H),[6] 5.93 (d, 1H, $J_{AB}\sim 4$Hz, H_B), 5.07 (d, 1H, $J_{AB}\sim 4$Hz, H_A), 1.40 (s, 3H, CH_3); (iii) ν_{max} (paraffin oil) 2800-2500 (OH), 1710 cm^{-1} (carboxylic acid C=O); (iv) on heating above 140° the compound is converted cleanly and efficiently (89%) into 2,3,4-triphenyltoluene,[1] carbon dioxide being evolved in the process. The isolation of this intermediate lends strong support to the proposal that route ii (SCHEME) is a likely route by which **1** is converted into **6**.

Discovery of the fact that the aromatization reaction proceeds under still milder conditions than it was previously thought extends the synthetic utility of the reaction to include the preparation of aromatic compounds containing heat-, acid-, *or base-sensitive substituents*. Further research in this area is in progress and will be reported at a later date.

References and Footnotes

1. For Part 3, see: E. A. Harrison, Jr., *J. Org. Chem.*, 1979, **44**, 1807.
2. In our original communication describing the aromatization reaction we reported that no reaction occurred between **1a** and DMF/H_2O (E. A. Harrison, Jr., *Chem Commun.*, 1090 (1971)). Our later inability to reproduce this result prompted the initiation of an expanded study the results of which are described herein.
3. We have also observed the formation of a similar low R_f intermediate on monitoring the reaction of i with DMF/H_2O. In the cases of **1a** and **1c**, however, no such intermediates were detected by periodic analysis (e.g. only varying amounts of **6a** and **1a** were observed). Presumably, in these cases the rate of the decarboxylation-dehydration step is competitive



i

with the hydroxyacid formation,

4. The isomeric structure **4e** cannot be excluded as a possibility on the basis of the present evidence.

5. The molecular ion peak was of too low an intensity to permit accurate mass measurement; however, the observed value for the $M^{+}-CO_2$ peak was within 4 ppm of the value calculated for $C_{25}H_{22}O$.

6. Two of the seven protons are D_2O-exchangeable.

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