

BENZODIOXOLE CHEMISTRY. 4.¹ CONCERNING THE AROMATIZATION
OF CARBONYL-BRIDGED CYCLIC CARBONATES EFFECTED BY
POTASSIUM CARBONATE IN AQUEOUS DIMETHYLFORMAMIDE

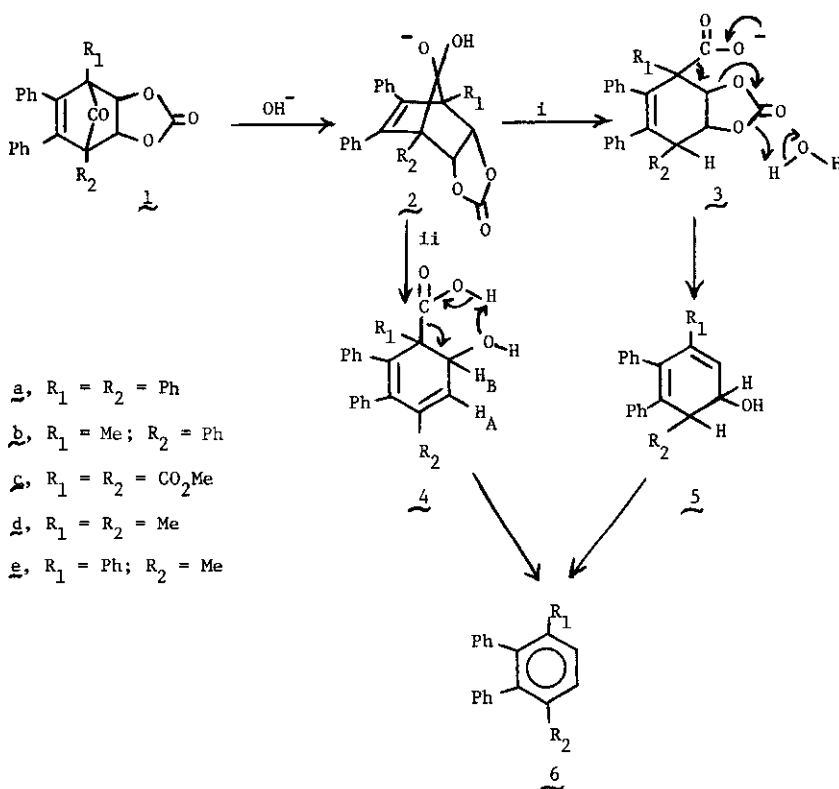
Ernest A. Harrison, Jr.

Department of Chemistry, The Pennsylvania State University
York Campus, York, Pennsylvania 17403

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/H₂O 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.

We¹ 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 unnecessary² 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



The aromatization reactions were carried out on benzodioxolediones 1a-d using the procedure previously described¹, only in the absence of potassium carbonate (see Table 1).

Table 1

Results of the Aromatization 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

^aIsolated yields of nearly pure compound which contained no residual 1 (TLC analysis). ^bThe 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)

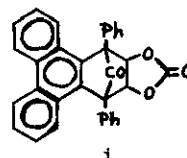
undergo conversion more readily than the one with electron-donating groups in the same positions (1d). Such results are not surprising if one assumes that either of the two mechanisms (Scheme) is still operating even in the absence of appreciable hydroxide ion concentration.

In the course of monitoring (TLC) the aromatization of 1b we observed the formation of a low R_f intermediate³ 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 identified⁴ 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 information⁵ 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, $J_{AB} \sim 4\text{Hz}$, H_B), 5.07 (d, 1H, $J_{AB} \sim 4\text{Hz}$, 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-triphenyl-toluene,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



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.

Received, 17th September, 1979