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BENZODIOXOLE CHEMISTRY. 5.[1] DRAMATIC SUBSTITUENT EFFECT IN THE REACTION OF CARBONYL-BRIDGED CYCLIC CARBONATES WITH METHOXIDE ION

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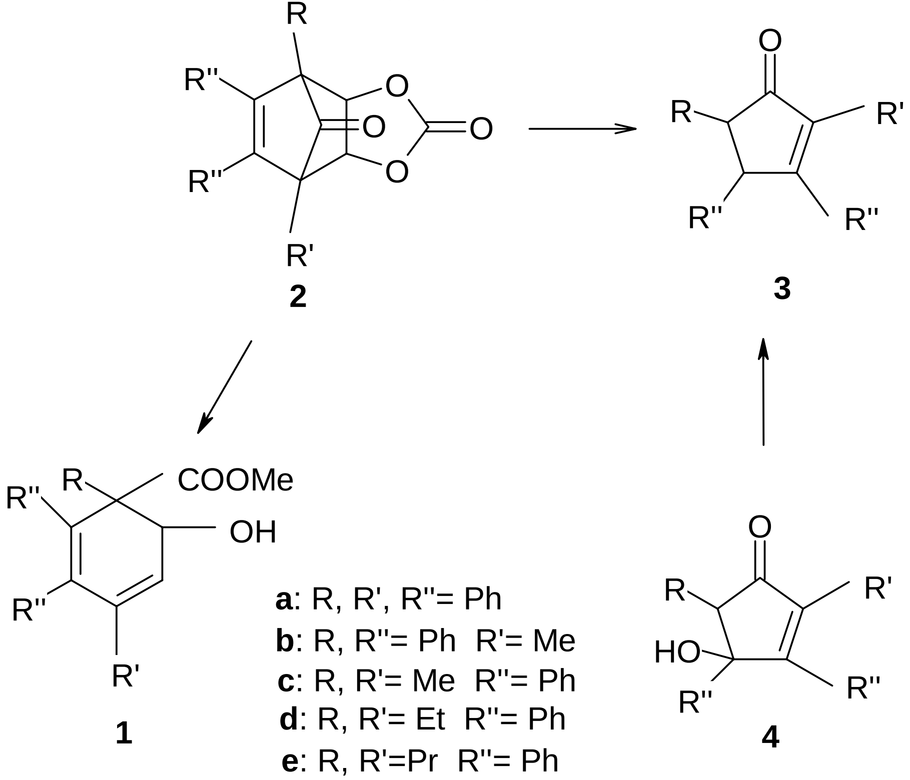
Abstract – Benzodioxolediones (**2c-e**) undergo high-yield conversion to cyclopentenones (**3c-e**) in K_2CO_3/MeOH at room temperature, while analogs (**2a**) and (**2b**) yield exclusively cyclohexadiene carboxylates (**1a** and **1b**) under these conditions. Isolation of intermediate **6(R,R′=Me R″=Ph)** from the reaction of **2c** with K_2CO_3/MeOH at 5-10°C suggests that **3** is formed in a process triggered by attack of $OMe^{(-)}$ at the ester carbonyl of **2**.

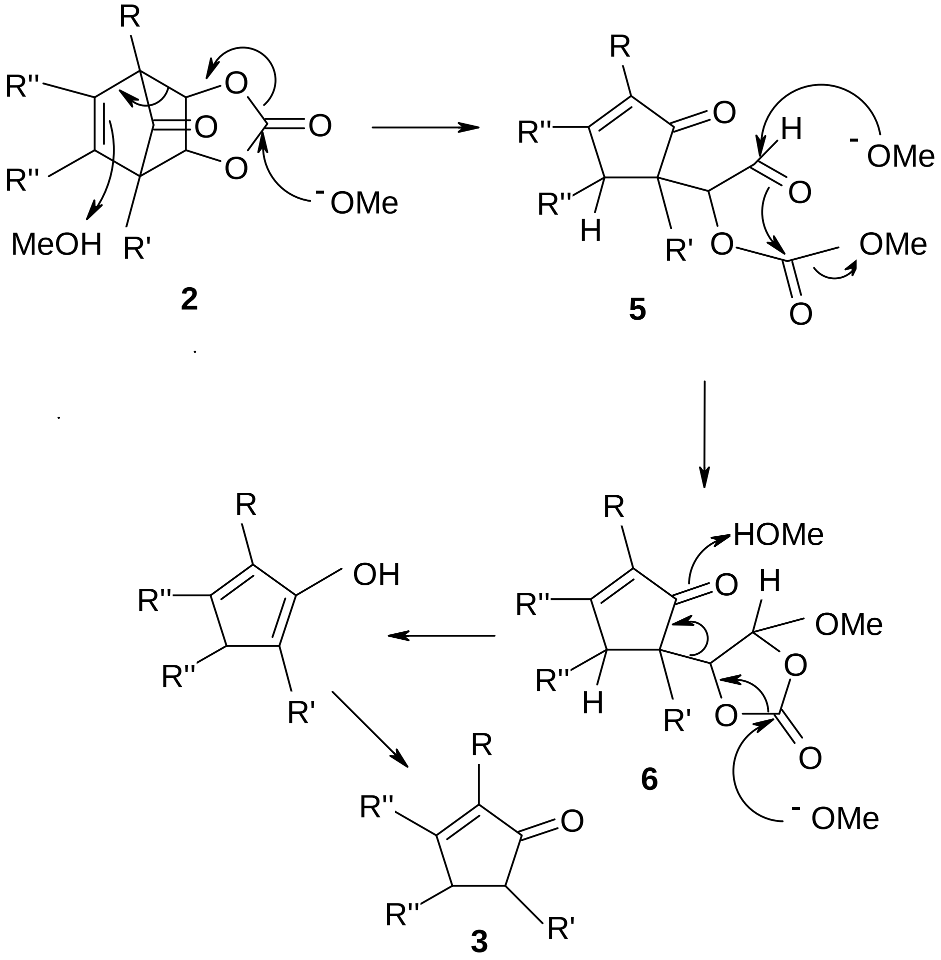
A number of years ago we reported that the tetraphenyl substituted benzodioxoledione **(2a)** reacts with potassium carbonate in methanol to produce methyl 6-hydroxy-1,2,3,4-tetraphenyl-2, 4-cyclohexadiene-1-carboxylate **(1a)** in near-quantitative yield[3] (Scheme 1). At that time we proposed that the reaction is initiated by nucleophilic attack of methoxide ion on the carbonyl bridge of **2a** to produce an anion which then undergoes loss of carbon dioxide (fragmentation) to yield **1a**. In an attempt to gain more information on the scope and mechanism of this reaction, we subjected the mono- and dialkyl substituted analogs $(\mathbf{2b-e})^4$ to the above reaction conditions and found, to our surprise, that only one **(2b)** of these yielded the corresponding dienecarboxylate; the others gave, instead, products previously unobserved under these conditions **(3c-3e)**. In this communication we report on these unexpected but interesting results and we present evidence supporting the view that the formation of **3c-3e** results from a process initiated by attack of methoxide ion on the dioxolone ring carbonyl, rather than on the carbonyl bridge. Treatment of 4-methyl-5,6,7-triphenyl-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxole-2,8-dione **(2b)** with an equimolar amount of anhydrous potassium carbonate in dry methanol at room temperature, Scheme 1



followed by quenching in ice-water yielded a single dienol $(\mathbf{1b})^5$ as a white powder (mp 188-189.5 °C, 86%). By contrast, reaction of the dimethyl **(2c)**, diethyl **(2d)** and dipropyl **(2e)** analogs with methanolic potassium carbonate under the identical conditions gave products identified as 2,5-dimethyl-3,4-diphenyl-2-cyclopenten-1-one[6] (**3c**, mp 117-119 °C, 83% from **2c**), 2,5-diethyl-3,4-diphenyl-2-cyclopenten-1-one[7] (**3d**, mp 83-85 °C, 84% from **2d**) and 2,5-dipropyl-3,4-diphenyl-2-cyclopenten-1-one[8,9] (**3e**, oil, 76% from **2e**) as the only isolated materials. Confirmation of the structure assignments for the reaction products **(3c-e)** was obtained by demonstrating that these compounds were identical in all respects to authentic samples of the three cyclopentenones prepared by reduction of cyclopentenolones (**4c**),[10] (**4d**)[11] and (**4e**),[12] with hydriodic acid and red phosphorus in refluxing acetic acid.

In the course of monitoring (TLC) the low temperature (5-10 °C) reaction of **2c** with potassium carbonate in methanol, we observed that the disappearance of **2c** was accompanied by the appearance of a new substance, non-identical to **3c**, which became the exclusive product after 30 min. This substance was isolated by column chromatography (silica gel, Et_2O:hexanes=1:1) as a white solid, mp 170-172.5 °C (homogeneous on TLC) and identified as the substituted cyclic carbonate ester **(6) (R,R′=Me R″=Ph)** on the basis of HMRS analysis[13] and the following evidence: (i) $M^{+\bullet} = 378$, in addition the MS spectrum showed the expected loss of $C_4H_4O_4$ at m/z 262 (McLafferty Rearrangement of $M^{+\bullet}$); (ii) NMR spectrum [60 MHz, $CDC1_3$] δ 7.37-6.90 (10H, m, aromatic), 6.02 (1H, d, J = 3.4 Hz, $CHOCH_3$), 4.48 (1H, d, J = 3.4 Hz, CHO), 4.60 (1H, q, J = 2.0 Hz, benzylic), 2.08 (3H, d, J = 2.0 Hz, allylic), 3.62 (3H, s, OCH_3), 0.73 (3H, s, CH_3); (iii) υmax (paraffin oil) 1820 (cyclic carbonate C=O),[14] 1695 (conjugated C=O), 750, 690 cm^{-1} (monosub. phenyl).

Scheme 2



The identification of **6** as an intermediate on the reaction pathway of **2c** to **3c** suggests that the conversion $(\mathbf{2c-e} \rightarrow \mathbf{3c-e})$ may well proceed by a series of steps such as those shown in Scheme 2, **with the most likely initiating step being attack of methoxide ion[15] on the dioxolone ring carbonyl** to produce structure **(5)**. Attack of a second methoxide ion on the highly reactive aldehyde carbonyl of **5** followed by ring-closure and accompanying loss of methoxide ion yields the observed intermediate **(6).** The latter molecule can then convert to product **(3)** by reacting with a third methoxide ion in the manner shown. The novel results reported herein are sufficiently intriguing to warrant further investigation. Accordingly, efforts are currently underway in our laboratory to determine the specific factors responsible for the unusual substituent effects observed. Our findings in this regard will be reported in due course.

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