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# INDIRECT HYDROQUINONE SUCCINOYLATION VIA A PHOTO-FRIES REARRANGEMENT APPLICATION TO THE SYNTHESIS OF ENOL LACTONES.

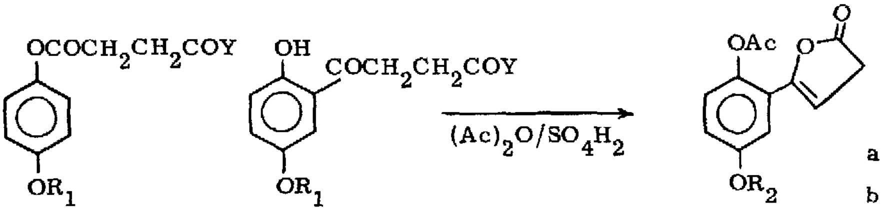
Roberto Martínez-Utrilla* and Miguel Angel Miranda

Instituto de Química Orgánica General (C S.I.C.), Juan de la Cierva, 3. Madrid-6, Spain.

Summary A photo-Fries rearrangement of hydroquinone succinates is the key step that allows the preparation of some γ-aryl enol lactones by dehydration of the corresponding aroyl propionic acids.

In the course of a series of studies[1] concerning the photochemistry of five membered enol lactones, it became necessary to synthesize 5-(2-acetoxy-5-methoxyphenyl)- and 5-(2,5-diacetoxyphenyl)-2(3H)-furanone (**3**a and **3**b). A classical synthetic approach to these compounds would involve the Friedel-Crafts direct succinoylation of the corresponding hydroquinone derivatives, following a general and well established procedure[2]. Subsequent lactonization of the resulting substituted benzoylpropionic acids would afford the required enol lactones. Unfortunately the Friedel-Crafts reaction between aromatic substrates and succinic anhydride suffers from serious disadvantages with free phenols and, particularly, fails completely with hydroquinone or with its monomethyl ether[3]. In general, the partial dealkylation of phenyl ethers is frequently a side effect accompanying the main reaction[4, 5].

In order to circumvent this difficulty, an indirect succinoylation process has been achieved by the intermediacy of a photo-Fries rearrangement, the enol lactones being obtained according to the following sequence



**1** a,b,c **2** a,b,c **3** a,b

a $R_1=R_2=Me$, Y=OH
b $R_1=H$, $R_2=Ac$, Y=OH
c $R_1=Me$, Y=OMe

A facile preparation[6] of the aryl succinates **1** is followed by a photo—Fries rearrangement[7] to give the o-hydroxyketones **2**. The cyclization step affording the desired lactones **3** is also readily attained by use of acetic anhydride containing a trace of sulfuric acid[8]. Yields and most significant physical data are listed in the Table[9]

| | Yield % | m.p. °C | IR, $\bar{\nu}_{max}$ (cm$^{-1}$) nujol | | $^1$Hnmr, $\delta$(ppm), CDCl$_3$ | | | |
|---|---|---|---|---|---|---|---|---|
| **1a**[6]<br>**1b**<br>**1c** | 97<br>90<br>100 | 116-7<br>171-3<br>oil | 1760<br>1750<br>1755 | C = O<br>ester | | | | |
| **2a**<br>**2b**<br>**2c** | 60<br>55<br>58 | 142 5 - 3.5<br>183 5 - 4.5<br>oil | 1640<br>1640<br>1645 | C= O<br>ketone | 11.7<br>11 6<br>11 7 | chelated<br>OH | | |
| **3a**<br>**3b** | 100<br>100 | 93<br>110 | 1780<br>1800 | C = O<br>lactone | 5.80 (t)<br>5.92 (t) | H(C-3) | 3.38 (d)<br>3.42 (t) | H (C-4) |

In connection with the photochemical step, it must be said that the analogous Lewis-acid catalyzed rearrangement carried out on the same substrates did not work in spite of being attempted under a wide range of experimental conditions[10]. Also worth mentioning is the reported[11] abnormal photo-Fries rearrangement of aryl phthalates. As far as we are aware, this was the first time in which such a photoreaction was attempted with aryl esters of a dicarboxylic acid The formation of a product with an orthoanhydride structure was rationalized by the authors assuming that the normal homolysis of the carbonyl-aryloxy bond was followed by the bonding of the acyl radical to the adjacent carbonyl oxygen, this step being made possible by the formation of a delocalized benzyl radical. The results reported here are in accord with those assumptions. In our case there is no possibility of forming the benzylic analog and therefore the photo-Fries pathway is preferred.

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