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CHEMISTRY OF LACTONES:
A ONE STEP SYNTHESIS OF α-PHENYL-γ-BENZYLIDENE-$\Delta^{\alpha,\beta}$-BUTENOLIDE

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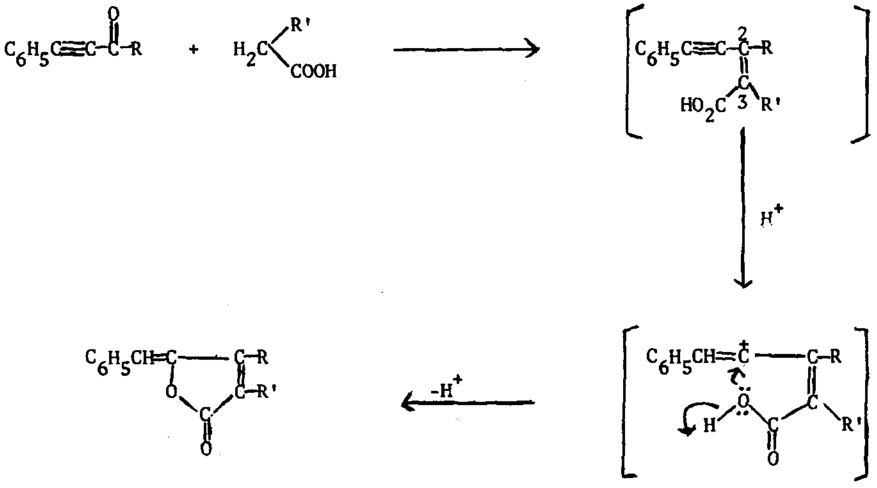
α-Arylidene-γ-aryl-$\Delta^{\beta,\gamma}$ butenolides [2-(3H)-furanones]$^{\neq}$ are readily prepared from β-aroylpropionic acids under Perkin-Erlenmeyer conditions and their chemistry has been investigated extensively.[1] A similar general method is not available for the synthesis of the isomeric α-aryl-γ-benzylidene-$\Delta^{\alpha,\beta}$ butenolides and not much is known about these compounds. γ-Arylidene (or alkylidene)-butenolides have been prepared from substituted maleic anhydrides[2], azido- and hydroxyquinones[3], from the ylides of butenolides[4], from γ-benzoylbutryic acid[5], by condensation of α-aryl-β-methyl-$\Delta^{\alpha,\beta}$ butenolide with aldehydes[6] and by the thermal- or silver ion catalyzed-isomerization of phenylpropargylidenemalonic acids.[7]

Compound I (R = H, R' = C_6H_5) was first reported by Spiegel[8] as one of the reduction products of pulvinic acid and was named "Cornicularlactone". It was subsequently synthesized by Thiele and Rossner[9] by the dehydrobromination of the dibromide of 2,5-diphenylpenta-2,4-dienoic acid. More recently, this compound has been prepared by the DMSO-acetic anhydride oxidation of 2,5-diphenyl-3-hydroxy-1,4-benzoquinone.[3(e,f)]

We report here a simple one step synthesis of these compounds. When phenylpropargylaldehyde (or a similar acetylenic ketone) is condensed with phenylacetic and substituted phenylacetic acids in the presence of acetic anhydride and triethylamine at 150° for 18 hours, compound I is obtained in 25% yield. The intermediate acid II, which is not isolated possesses the cis configuration around carbons 2 and 3[10] and readily undergoes acid-catalyzed ring closure to the isomeric lactone. That this method is general has been demonstrated by the synthesis of several analogs (I) - Table I.

Compound I (R = H; R' = C_6H_5, m.p. 141°) shows $>C=O$ absorption at 1790 cm^{-1} and 1750 cm^{-1}, characteristic of such conjugated lactones. Its mass spectrum exhibited parent peak at 248. Alkaline hydrolysis gave an acid melting at 122° (cornicularic acid, m.p. 121-122°)[9]. It may be pointed out that Wiley and coworkers[11] had prepared 2,5-diphenylpentene-2-yne-4-oic acid (II, R = H, R_1 = C_6H_5), which cyclized to 3,6-diphenyl-2-pyrone in the presence of mercuric sulfate and dilute sulfuric acid, a reagent that normally hydrates an acetylenic bond. However, these authors[12] also reported the isolation of $\Delta^{\alpha,\beta}$-butenolides from acetylenic acids similar to II. It is well known that acetylenic acids containing six carbon atoms cyclize to give either γ-lactones or δ-lactones, depending on the reaction conditions.[13]



I

TABLE I

R	R'	m.p.	% Yield	lit m.p.
H	C_6H_5	141°	80	142° (8,9)
H	p-$NO_2C_6H_4$	208°	85	- * *
CH_3	C_6H_5	97°	70	- * *
CH_3	p-$NO_2C_6H_4$	232°	75	231° (6)
C_6H_5	C_6H_5	173°	40	174°

(**Satisfactory analyses have been obtained for these compounds.)

Since a general method is now available for the synthesis of substituted phenylpropargyl aldehydes,[7(d)] a simple straight forward route to these $\Delta^{\alpha,\beta}$-butenolides is now in hand. It is interesting to note that only one isomer I (R = H, R' = C_6H_5), in which the exocyclic hydrogen and ring hydrogen are cis to each other is obtained.

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