Abnormal Reaction Product from Condensation of Phloroacetophenone Dimethylether with *p*-Methoxybenzaldehyde

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In the course of our synthetic studies towards some model compounds of thearubigin¹⁾ (one of the black tea pigments), we have encountered an interesting abnormal reaction: condensation²⁾ of phloroacetophenone dimethyl ether(I) with *p*-methoxybenzaldehyde(II) in aqueous-alcoholic sodium hydroxide solution gave mainly an α,β -unsaturated ketone(III), in addition to small amounts of the normal condensation product(IV). Repeated several experiments under slightly different conditions yielded also the similar results.

structure was confirmed by comparison with

authentic specimen (mixed mp, IR), which was prepared³⁾ from *p*-methoxybenzaldehyde and acetone.

The physical properties of the compound(III) are: ν_{max} (Nujol) 1655, 1630, 1600 ($-\text{C}=\text{C}-\text{CO}-$), 980 ($-\text{CH}=\text{CH}-$, *trans*) cm^{-1} ; $\delta(\text{CDCl}_3)$ 3.82 (6H, 2- OCH_3 , singlet), δ_A 7.52, δ_B 6.88

(8H, 2- C_6H_4 -, $J_{AB}=8.5\text{Hz}$, A_2B_2 quartet), δ_A

7.64, δ_B 6.90 (4H, 2 $-\text{HC}=\text{CH}-$, $J_{AB}=16\text{Hz}$, *trans*, AB quartet) ppm; m/e 294 (M^+), 279, 186, 161, 133 and analysis for $\text{C}_{19}\text{H}_{18}\text{O}_3$: Calcd. C, 77.53, H, 6.16, found C, 77.79, H, 6.22%. The interpretation of these data has led us to the structure(III) for this substance. Finally this

On the other hand, the desired chalcone(IV) was obtained with acceptable yields only under the conditions using much larger amounts⁴⁾ of potassium hydroxide.

The mechanism for the abnormal reaction product was postulated as follows.

The extension of this reaction is now under the way.

EXPERIMENTAL⁵⁾

All melting points are uncorrected.

1,5-Di-*p*-methoxyphenyl-1,4-pentadien-3-one(III). To the stirred solution of phloroacetophenone dimethyl

ether (I, 4.0 g) and *p*-methoxybenzaldehyde (II, 3.2 g) in 4.0 ml of 99% ethanol, was added 50% aqueous sodium hydroxide solution (8 ml) and the reaction mixture was kept standing for 4 hr under nitrogen at room temperature. After filtration of the precipitate (III, 0.65 g), the filtrate was extracted with ether.* Evaporation of ether gave the crude products, from which 1.1 g of the crystalline compound(III) was separated by recrystallization (CH_2Cl_2), and the methylene dichloride solution (after concentration) was adsorbed on the silica-gel column, followed by elution with benzene-ethyl acetate. At first the chalcone(IV), 0.25 g (4%), mp 110~111°C, and then 0.55 g of the compound(III) were obtained. Total amounts of (III) were 2.3 g (33% based on *p*-methoxybenzaldehyde). Recrystallization from methylene chloride gave the co-

lorless, leaflet crystals, mp 128~128.5°C. The mixed mp with authentic samples showed no depression.

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* The mother liquor was acidified with dil. hydrochloric acid and extracted with ether. Evaporation of the solvent recovered the starting material(I), 2.3 g (58%).