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NEW PHOTOCHEMICAL APPROACHES TO THE SYNTHESIS OF CHROMONES

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Abstract - Irradiation of the p-methoxyphenyl and p-methylphenyl esters of 2-butynoic, propynoic, 3-(ethylenedioxy)butanoic, 3,3-dimethoxypropanoic and 3-oxobutanoic acids (**1-3**) affords the corresponding photo-Fries products **4-6**. Compound **5a** is converted in part into the acetophenone **7a**, by way of a Norrish type II photo-reaction, while compound **6a** is reluctant to undergo this process, in spite of the fact that it also possess γ-carbonyl hydrogen atoms. From the preparative point of view, the photorearrangement of the esters **1a-d** and **2a,c-d** is exploitable, while that of **3a** proceeds with a lower yield. The differences found in the photochemical behaviour of **2a** and **3a** show the sharp influence of the acetal group on the course of the reaction. Compounds **4-6** are representative model compounds valuable as direct chromone precursors; in fact, they can be readily cyclized to the chromones **10** under basic or acidic conditions.

INTRODUCTION

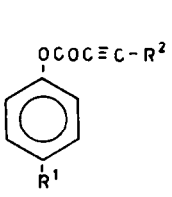
The synthesis, chemistry, occurrence in nature and biological activity of chromones have been the subject of several comprehensive reviews.[1-3] As a part of our continuing studies on the applications of the photo-Fries rearrangement to the synthesis of heterocyclic compounds,[4-6] we were interested in exploring the photolysis of the three types of aryl esters **1**, **2** and **3**, which could in principle afford representative model compounds valuable as direct chromone precursors.

The results of these studies are reported in the present paper.

RESULTS AND DISCUSSION

First of all, we decided to investigate the p-methoxyphenyl esters **1a**, **2a** and **3a**. The preparation of these substrates resulted to be less trivial than initially assumed, but, after several unsuccessful attempts, we found that the esterification of p-methoxyphenol with 2-butynoic acid[7] and

3-(ethylenedioxy)butanoic acid was efficiently promoted by N,N´-dicyclohexylcarbodiimide,[8] in the presence of 4-dimethylaminopyridine.[9] The best procedure for the preparation of p-methoxyphenyl 3-oxobutanoate **3a** was found to be the silica gel-induced deacetalization of **2a**.[10]



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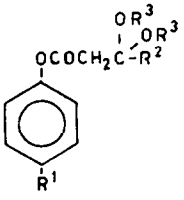

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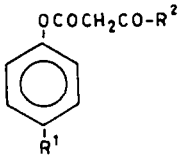

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a	$R^1 = OCH_3$	$R^2 = CH_3$	$R^3, R^3 = CH_2\text{-}CH_2$
b	$R^1 = CH_3$	$R^2 = CH_3$	
c	$R^1 = OCH_3$	$R^2 = H$	$R^3 = OCH_3$
d	$R^1 = CH_3$	$R^2 = H$	$R^3 = OCH_3$

The irradiation of **1a**, **2a** and **3a** gave rise to the corresponding photo-Fries products **4a**, **5a** and **6a**, with yields of 52, 55 and 25%, respectively. Additionally, in the case of **2a** was isolated 2-hydroxy-5-methoxyacetophenone **7a** (34%), whose formation can be explained as occurring from **5a**, by way of a Norrish type II photoreaction. This secondary process involves the abstraction of a γ-hydrogen by the carbonyl group, and must compete with the intramolecular proton transfer classically undergone by the o-hydroxyphenones, wich usually provides an efficient energy wasting channel, responsible for their ability to act as UV-stabilizers.[11]

It is noticeable that no significant amount of the acetophenone **7a** was isolated in the photolysis of the ketoester **3a**, in spite of the fact that the resulting photo-Fries product **6a** also posses γ-carbonyl hydrogen atoms. This observation is in accordance with the well-studied photoreactivity of β-diketones, whose irradiation has been reported to affect solely to the keto-enol ratio, favouring the keto form.[12]

In this context, the fraction corresponding to the photorearranged product, as obtained by chromatography of the crude photomixture from **3a**, was shown by ^{1}H-nmr to initially contain a considerable amount of the diketone **6a**, the chromanone **8a** and the enol **9a** also being present.[13]

From the preparative point of view, the photo-Fries rearrangement of the esters **1a** and **2a** can be considered exploitable; however, in the case of **3a**, the efficiency of the reaction is considerably lower. This constitutes a new interesting example of the suitability of acetals as carbonyl blocking groups in certain photochemical processes.[14]

The possibility of obtaining a chromone by cyclization of the photoproducts **5a** and **6a** had been anticipated in view of the existing literature precedents. Thus, the most frequently used methods of preparing chromones involve the acidic treatment of 1,3-dioxophenols of the type **6**, obtained in turn by the Claisen condensation of o-hydroxyaryl alkyl ketones with carboxylic esters, or also by the Baker-Venkataraman rearrangement of o-acyloxyaryl alkyl ketones.[1] Likewise, although less substantiated in the literature, the formation of chromones from acetals of 1,3-dioxophenols such as **5** is admitted to occur during the synthesis of benzopyrylium salts by treatment of o-hydroxyaryl alkyl ketones with triethyl orthoformate and a strong acid.[15]

As expected, the cyclization of **6a** in acetic acid, in the presence of a small amount of sulfuric acid, afforded the chromone **10a** with a very high yield. The same product was obtained from **5a** by means of a quantitative deacetalyzation with wet silica gel, followed by cyclization as before.

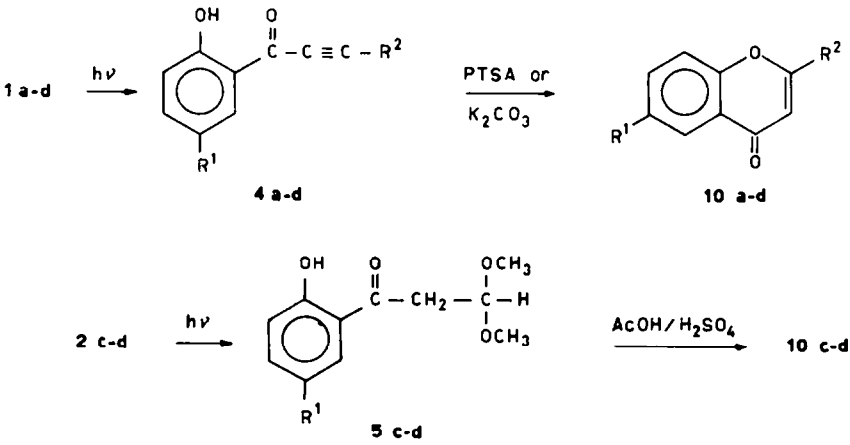
The acetylenic ketone **4a** was also considered potential precursor of the chromone **10a**, through a conjugate intramolecular addition of the phenolic hydroxy group to the activated triple bond. Concerning this point, it is not easy to predict the direction of ring closures involving nucleophilic attacks at triple bonds. Thus, the Baldwin's rules[16] postulated an acute approach angle in digonal systems, and stated that the 6-endo-dig cyclizations are preferred over the 5-exo-dig ones; however, more recent work[17] supports the proposal of obtuse approach angles for the same geometric arrangement, based on **ab initio** calculations, and hence favour the 5-exo-dig cyclization mode. The existing experimental data, although few and far between, confirm that both types of ring closure are allowed processes.[18,19]

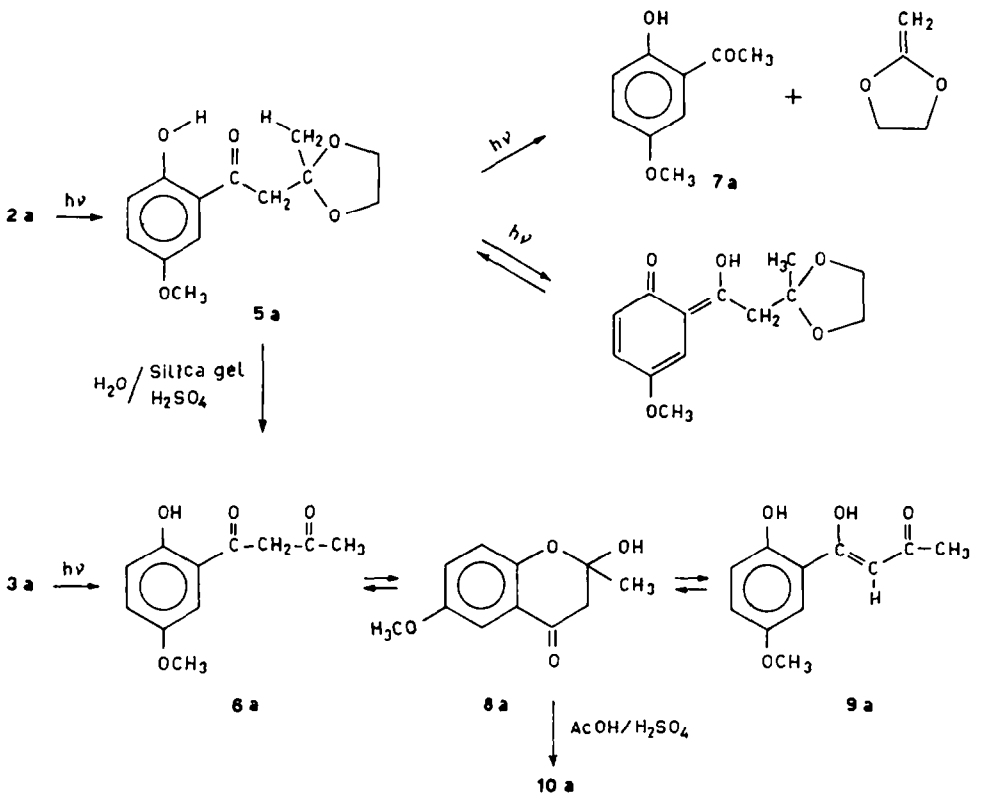
As a matter of fact, compound **4a** easily cyclized by means of potassium carbonate in acetone or p-toluenesulphonic acid in dichloromethane, affording the expected chromone **10a** with almost quantitative yields. In this case, it is probable that the polarization of the triple bond, due to conjugation with the ketone carbonyl group, determines the occurrence of the nucleophilic attack exclusively at the β-carbon, in accordance with the usual reactivity of α,β-acetylenic carbonyl compounds.[20]

Of the three new approachs for the synthesis of chromones explored, the most promising one appeared to be that based on the photo-Fries rearrangement of aryl esters of substituted propynoic acids, followed by cyclization in acidic or basic media, as it has been exemplified for the p-methoxyphenyl ester of 2-butynoic acid (**1a**) as model compound.

In order to disclose the scope and limitations of this synthetic route to chromones we changed the nature of the substituent attached to the phenolic ring, as well as the lenght of the acyl rest. Thus, we decided to irradiate the esters **1b**, **1c**, **1d**, **2c** and **2d**. The studies of the esters from propynoic acid **1c** and **1d** could be particularly interesting, since these compounds could afford chromones without any substituent at the pyrone ring. The presence of a substituent at the para position with respect to the phenolic oxygen was mantained in order to avoid an undesired 1,5 migration of the acyl group.

As expected, the photo-Fries products **4b**, **4c** and **4d** were obtained with yields close to 50 %, and their cyclization was easily accomplished using the same conditions as those employed in that of **4a**.





Turning to the irradiation of acetals of β-oxoesters of the type **3**, it remained to investigate the photochemical behaviour of substrates uncapable of undergoing a competitive Norrish II process. The esters **2c** and **2d** would meet this requeriment and, on the other hand, lead to the same chromones as obtained from the aryl propynoates **1c** and **1d**. The synthesis of the compounds **2c** and **2d** was carried out by direct esterification of 3,3-dimethoxypropanoic acid with p-methoxyphenol or p-cresol respectively, using N,N´-dicyclohexylcarbodiimide and catalytic amounts of 4-dimethylaminopyridine. The photo-Fries rearrangement of **2c** and **2d** was the only photoreaction observed, giving rise to the corresponding o-hydroxyketones **5c** and **5d** with appreciably higher yields (72 and 67 %, respectively). Subsequent cyclization with acetic acid gave the chromones **10c** and **10d**.

In conclusion, the present work illustrates the advantages of two new approaches to the synthesis of chromones, based on the photo-Fries rearrangement of aryl propynoates and/or acetals of the related β-oxoesters, followed by cyclization under standard conditions.

EXPERIMENTAL

General. M.ps were determined with a Büchi 510 apparatus and are uncorrected. Ir spectra were obtained in CCl_4 solns with a Perkin-Elmer 781 spectrophotometer; $\bar{\nu}_{max}$ (cm^{-1}) is given only for the main bands. ^{1}H-nmr spectra were measured in CCl_4 with a 60-MHz Varian 360 EM instrument; chemical shifts are reported in δ (ppm) values, using TMS as internal standard. The combustion analyses were performed at the Instituto de Química Bio-Orgánica of C.S.I.C. in Barcelona. Isolation and purification were done by flash column chromatography on silica gel Merck 60, 70-230 mesh, using hexane as eluent and a Waters isocratic h.p.l.c. equipment provided of a semipreparative microporasil™ column, using hexane-ethyl acetate as eluent.

Preparation of the aryl esters 1, 2 and 3.
Preparation of **1a-d.** To a soln of the acetylenic acid (12 mmol), the corresponding phenol (12

mmol) and 4-(N,N-dimethylamino)pyridine, **DMAP**, (100 mg) in 25 ml of $CHCl_3$ was added dropwise N,N´-dicyclohexylcarbodiimide, **DCC**, (2.4 g, 11.7 mmol) in 5 ml of $CHCl_3$; the mixture was stirred for 15 min at room temperature, then filtered to remove the precipitated N,N´-dicyclohexylurea, concentrated in vacuo and purified by chromatography. The yields obtained were: **1a**, 84% (1.9 g, 10 mmol); **1b**, 81% (1.7 g, 9.7 mmol); **1c**, 76% (1.6 g, 9.1 mmol); **1d** 67% (1.3 g, 8.0 mmol).

Preparation of 4-methoxyphenyl 3-(ethylenedioxy)butanoate **2a**. 10 g (76.9 mmol) of ethyl acetoacetate, with 5 g (80.6 mmol) of 1,2-ethanediol and 0.5 g of 4-toluenesulphonic acid were heated in 100 ml of benzene using a Dean-Stark system, until no more water was formed. Then the crude soln was washed with water, concentrated in vacuo and submitted to saponification with 50 ml of 10% aqueous NaOH. After heating 1 h, the mixture was neutralized and thoroughly extracted with ethyl ether, giving 5.3 g (36.3 mmol, 47%) of 3-(ethylenedioxy)butanoic acid. 1 g (6.8 mmol) of this acid, 0.9 g (7.2 mmol) of 4-methoxyphenol, **DMAP** (100 mg) and **DCC** (1.4 g, 6.8 mmol) were treated as the above mentioned procedure for the preparation of the esters **1**, to give 1.3 g (5.2 mmol, 76%) of **2a**.

Preparation of aryl 3,3-dimethoxypropanoates **2c** and **2d**. The methyl 3,3-dimethoxypropanoate was prepared following the method described in reference 21. Saponification of this methyl ester (10 g, 67.6 mmol) was accomplished heating 1 h with 50 ml of 10% aqueous NaOH. After this time, the mixture was neutralized and submitted to continuous liquid-liquid extraction with ethyl ether, giving 6.9 g (51.5 mmol, 76%) of 3,3-dimethoxypropanoic acid. Esterifications of this acid (1 g, 7.5 mmol) with 4-methoxyphenol (0.9 g, 7.5 mmol) or 4-methylphenol (0.8 g, 7.5 mmol) using the procedure employed in the preparation of the esters **1** (**DCC**, 1.5 g, 7.5 mmol; **DMAP** 100 mg) gave rise to **2c** (1.4 g, 5.8 mmol, 78%) and **2d** (1.2 g, 5.4 mmol, 71%) respectively.

Preparation of 4-methoxyphenyl 3-oxobutanoate **3a**. 20% H_2SO_4 (0.2 ml) was added with continuous magnetic stirring to a slurry of silica gel Merck 60, 70-230 mesh (3 g) in CH_2Cl_2 (10 ml). After disappearing the aqueous phase, **2a** (1 g, 4 mmol) was added and stirring continued at r. t. for 6 h. Then, the solid phase was filtered and washed with CH_2Cl_2. Evaporation of the solvent and purification gave the ester **3a** (700 mg, 85%).

Irradiations

General procedure. A soln of 500 mg of aryl ester in 450 ml of freshly distilled hexane was irradiated for 6 h at r. t. with a 125 W medium pressure mercury lamp inside a quartz immersion well. The photorearranged products were isolated, after removal of the solvent, with silica gel flash-column chromatography using hexane as eluent.

Irradiation of **1a**. The only photoproduct isolated was **4a** (260 mg, 52%).

Irradiation of **1b**. The only photoproduct isolated was **4b** (265 mg, 53%).

Irradiation of **1c**. The only photoproduct isolated was **4c** (240 mg, 48%).

Irradiation of **1d**. The only photoproduct isolated was **4d** (225 mg, 45%).

Irradiation of **2a**. The following products were isolated: 2-hydroxy-5-methoxyacetophenone[13] **7a** (110 mg, 34%), **5a** (275 mg, 55%).

Irradiation of **2c**. The only photoproduct isolated was **5c** (360 mg, 72%).

Irradiation of **2d**. The only photoproduct isolated was **5d** (335 mg, 67%).

Irradiation of **3a**. After the chromatographic workup, a fraction containing a mixture of tautomers **6a**, **8a** and **9a** was isolated. The most characteristic ^{1}H-nmr signals of each tautomer were: **6a**: 4.05 (s, CH_2), 2.32 (s, CH_3). **8a**: 2.90 (s, CH_2), 1.76 (s, CH_3). **9a**: 14.96 (s, enolic OH), 6.11 (s, =CH), 2.20 (s, CH_3). From the relative intensities the ratio **6a**:**8a**:**9a** was established as 1:1:2.

Cyclizations

Cyclization of the hydroxyaryl ethynyl ketones **4a-d**. Acid-catalyzed cyclization. A soln of **4** (250 mg) and 4-toluenesulphonic acid (50 mg) in CH_2Cl_2 (10 ml) was refluxed for 30 min. Then, the mixture was washed with 5% aqueous $HNaCO_3$, dried over anhydrous Na_2SO_4 and the solvent removed, leading in all cases quantitatively to the corresponding chromone **10**. Base-catalyzed cyclization. Anhydrous K_2CO_3 (50 mg) was added to a soln of **4** (250 mg) in acetone (10 ml). The resulting suspension was heated at reflux 30 min, then filtered and the solvent removed to give quantitatively **10**.

Cyclization of **5a**. Deacetalization of **5a** (0.5 g, mmol) was accomplished by the procedure described for the preparation of **3a**, giving a complex mixture (370 mg, 89%) of the tautomers **6a**, **8a** and **9a**, which was cyclized by the method described in the sequel.

Cyclization of **5c-d** and **6a**. To a soln of the starting compound (250 mg) in glacial acetic acid (10 ml) was added conc H_2SO_4 (0.1 ml). The mixture was refluxed 30 min, then cooled and finally poored into ice-water (25 ml). The resulting suspension was filtered in vacuo and the solid washed with water and dried to give almost quantitatively the chromones **10a,c-d**.

Spectral and analytical data of the new compounds

4-Methoxyphenyl 2-butynoate **1a**. M.p 58-60 °C; analysis: C 69.25 H 5.28 % (Calcd. for $C_{11}H_{10}O_3$: C 69.47 H 5.30 %); ir: 2230 (C≡C) 1735 (ester); ^{1}H-nmr: 7.14-6.67 (m, 4H, ar H), 3.79 (s, 3H, OCH_3), 2.06 (s, 3H, C≡C-CH_3).

4-Methylphenyl 2-butynoate **1b**. M.p 47-48 °C; analysis: C 75.83 H 5.87 % (Calcd. for $C_{11}H_{10}O_2$: C 75.84 H 5.78 %); ir: 2235 (C≡C) 1730 (ester); ^{1}H-nmr: 7.32-6.86 (m, 4H, ar H), 2.34 (s, 3H, Ar-CH_3), 2.09 (s, 3H, C≡C-CH_3).

4-Methoxyphenyl propynoate **1c**. Oil; analysis: C 68.05 H 4.84 % (Calcd. for $C_{10}H_8O_3$: C 68.18 H 4.58 %); ir 2110 (C≡C) 1730 (ester); ^{1}H-nmr: 7.19-6.69 (m, 4H, ar H), 3.77 (s, 3H, CH_3), 2.94 (s, 1H, C≡C-H).

4-Methylphenyl propynoate **1d**. Oil; analysis: C 74.91 H 5.21 % (Calcd. for $C_{10}H_8O_2$: C 74.98 H 5.03 %); ir: 2140 (C≡C) 1735 (ester); ^{1}H-nmr: 7.29-6.91 (m,4H, ar H), 2.94 (s, 1H, C≡C-H), 2.37 (s, 3H, CH_3).

4-Methoxyphenyl 3-(ethylenedioxy)butanoate **2a**. Oil; analysis: C 61.58 H 6.12 % (Calcd. for $C_{13}H_{16}O_5$: C 61.90 H.6.39 %); ir: 1755 (ester); ^{1}H-nmr: 7.09-6.62 (m, 4H, ar H), 3.96 (s, 4H, -O-CH_2-CH_2-O-), 3.75 (s, 3H, OCH_3), 2.73 (s, 2H, $COCH_2$), 1.54 (s, 3H ,CCH_3).

4-Methoxyphenyl 3,3-dimethoxypropanoate **2c.** Oil; analysis: C 59.61 H 6.77 % (Calcd. for $C_{12}H_{16}O_5$: C 59.99 H 6.71 %); ir: 1760 (ester); ^{1}H-nmr: 7.09-6.61 (m, 4H, ar H), 4.85 (t, J=5 Hz, 1H, CH), 3.74 (s, 3H, Ar-OCH_3), 3.43 (s, 6H, $C(OCH_3)_2$), 2.73 (d, J=5 Hz, 2H, CH_2).
4-Methylphenyl 3,3-dimethoxypropanoate **2d.** Oil; analysis: C 64.21 H 7.44 % (Calcd. for $C_{12}H_{16}O_4$: C 64.27 H 7.19 %); ir: 1760 (ester); ^{1}H-nmr: 7.23-6.79 (m, 4H, ar H), 4.87 (t, J=5 Hz, 1H, CH), 3.33 (s, 6H, $C(OCH_3)_2$), 2.75 (d, J=5 Hz, 2H, CH_2), 2.31 (s, 3H, Ar-CH_3).
4-Methoxyphenyl 3-oxobutanoate **3a.** Oil; analysis: C 63.59 H 5.71 % (Calcd. for $C_{11}H_{12}O_4$: C 63.46 H 5.81 %); ir: 1750 (ester) 1720 (ketone); ^{1}H-nmr: 7.15-6.60 (m, 4H, ar H), 3.70 (s, 3H, OCH_3), 3.50 (s, 2H, CH_2), 2.19 (s, 3H, $COCH_3$).
1-(2-Hydroxy-5-methoxyphenyl)-2-butynone **4a.** M.p 65-67 °C; analysis: C 69.55 H 5.36 % (Calcd. for $C_{11}H_{10}O_3$: C 69.47 H 5.30 %); ir: 2220 (C≡C) 1610 (C=O); ^{1}H-nmr: 11.08 (s, 1H, OH), 7.33-6.58 (m, 3H, ar H), 3.72 (s, 3H, OCH_3), 2.13 (s, 3H, C≡C-CH_3).
1-(2-Hydroxy-5-methylphenyl)-2-butynone **4b.** M.p 61-62 °C; analysis C 75.84 H 5.82 % (Calcd. for $C_{11}H_{10}O_2$: C 75.84 H 5.78 %); ir: 2220 (C≡C) 1630 (C=O); ^{1}H-nmr: 11.30 (s, 1H, OH), 7.85-6.60 (m, 3H, ar H), 2.35 (s, 3H, Ar-CH_3), 2.25 (s, 3H, C≡C-CH_3).

1-(2-Hydroxy-5-methoxyphenyl)propynone **4c.** Oil; analysis C 67.94 H 4.52 % (Calcd. for $C_{10}H_8O_3$: C 68.18 H 4.58 %); ir: 2100 (C≡C) 1630 (C=O); ^{1}H-nmr: 10.99 (s, 1H, OH), 7.51-6.62 (m, 3H, ar H), 3.79 (s, 3H, OCH_3), 3.47 (s, 1H, C≡C-H).
1-(2-Hydroxy-5-methylphenyl)propynone **4d.** Oil; analysis C 74.41 H 5.47 % (Calcd. for $C_{10}H_8O_2$: C 74.98 H 5.03 %); ir: 2100 (C≡C) 1630 (C=O); ^{1}H-nmr: 11.30 (s, 1H, OH), 7.90-6.71 (m, 3H, ar H), 3.50 (s, 1H, C≡C-H), 2.39 (s, 3H, CH_3).
3-(Ethylenedioxy)-1-(2-hydroxy-5-methoxyphenyl)-1-butanone **5a.** Oil; analysis: C 62.07 H 6.54 % (Calcd. for $C_{13}H_{16}O_5$: C 61.90 H 6.39 %); ir: 1640 (C=O); ^{1}H-nmr: 11.76 (s, 1H, OH), 7.24-6.63 (m, 3H, ar H), 3.86 (s, 4H, -O-CH_2-CH_2-O-), 3.73 (s, 3H, OCH_3), 3.16 (s, 2H, $COCH_2$), 1.42 (s, 3H, C-CH_3).
1-(2-Hydroxy-5-methoxyphenyl)-3,3-dimethoxy-1-propanone **5c.** Oil; analysis C 60.20 H 6.80 % (Calcd. for $C_{12}H_{16}O_5$: C 59.99 H 6.71 %); ir: 1645 (C=O); ^{1}H-nmr: 11.69 (s, 1H, OH), 7.15-6.75 (m, 3H, ar H), 4.89 (t, J=5 Hz, 1H, CH), 3.79 (s, 3H, Ar-OCH_3), 3.39 (s, 6H, $C(OCH_3)_2$), 3.17 (d, J=5 Hz, 2H, CH_2).
1-(2-Hydroxy-5-methylphenyl)-3,3-dimethoxy-1-propanone **5d.** Oil; analysis C 64.54 H 7.17 % (Calcd. for $C_{12}H_{16}O_4$: C 64.27 H 7.19 %); ir: 1640 (C=O); ^{1}H-nmr: 11.88 (s, 1H, OH), 7.59-6.72 (m, 3H, ar H), 4.91 (t, J=5 Hz, 1H, CH), 3.39 (s, 6H, $C(OCH_3)_2$), 3.19 (d, J=5 Hz, 2H, CH_2), 2.29 (s, 3H, Ar-CH_3).

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