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Fries rearrangement of 2-, 3- and 4-methoxyphenyl 3-methylbut-2-enoates **3-5** in methanesulfonic acid, polyphosphoric acid, aluminum chloride and under photochemical conditions have been studied. The outcome of the reactions was determined by the substitution pattern in the starting products and the reaction conditions used. Under Lewis acid catalysis, acylation accounted for the major components of the reaction mixtures, leading to the formation of indanones and 2,3-dihydro-4*H*-1-benzopyran-4-ones respectively in the case of *o*- and *m*-esters **3** and **5**, whereas alkylation to afford dihydrocoumarins was the favored path for *p*-ester **5**. On the other hand, *o*-acylation was in all cases the major reaction course in the photochemical rearrangement.

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Introduction.

Several procedures have been described in the literature for the preparation of precocenes (**1** and **2**, Figure 1) [1], the potent insect antijuvénile hormone agents with a 2,2-dimethyl-3-chromene structure, isolated from *Ageratum houstonianum* [2]. One of the most straightforward of these procedures consists in the condensation of phenols with 3-methylbut-2-enoic acid in the presence of the appropriate acid catalysts, to afford 2,3-dihydro-2,2-dimethyl-4*H*-1-benzopyran-4-ones, which by reduction and concomitant dehydration are easily transformed into the desired structures [3]. This one pot preparation of the required 4-chromanones implies a three step sequence, namely, esterification, Fries rearrangement and cyclization. However, in many cases, depending on the substitution pattern of the aromatic ring in the starting compounds and on the reaction conditions, this multistep procedure afforded mixtures of products. Apparently, this result might be attributed to the non-specificity of the Fries rearrangement, as it has been previously reported for methylphenols [4].

In this context, we describe herein a systematic study of the photochemically induced and acid catalyzed Fries rearrangements of methoxyphenyl 3-methylbut-2-enoates **3-5** (Figure 1), for preparations of precursors of precocene I and its isomers.

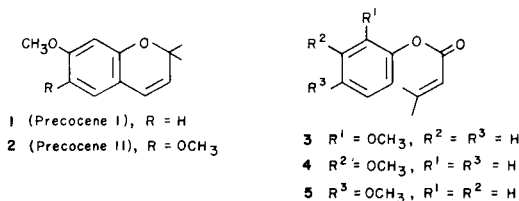


Figure 1

As shown in Table 1 and Figure 2, rearrangement of the 2-methoxyester **3** afforded different products, according to the reaction conditions. These products, after separation in acid and neutral fractions, were identified by spectral and chromatographic means, and by comparison with authentic samples, prepared by independent synthesis. In some cases, very minor components were only detected by gc/ms techniques.

Table 1

Fries Rearrangement Reactions of 2-Methoxyphenyl But-2-enoate (**3**)

Solvent and catalyst	Temperature	Time (Hours)	Products (%)
CH_3SO_3H	70	1.5	6 (6), 9 (50), 7 (6), 10 (18), 12 (3)
CH_3SO_3H	25	4	6 (4), 7 (4), 8 (70), 9 (3), 10 (3), 12 (13)
PPA	100	1	9 (51)
$CH_3NO_2/AlCl_3$	70	3	12 (48)
$CH_3OH/h\nu$ (254 nm)	50	69	8 (54), 12 (21), 13 (22)
hexane/ $h\nu$ (254 nm)	50	56	8 (12), 12 (5), 13 (6)

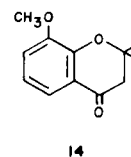
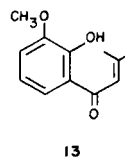
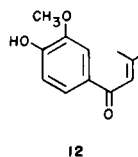
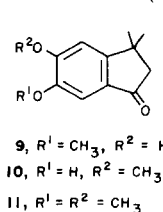
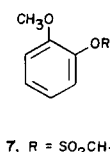
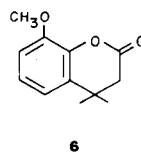


Figure 2

Results and Discussion.

a) Reactions of 2-methoxyphenyl 3-methylbut-2-enoate (**3**).

In the experiments using methanesulfonic acid as solvent and catalyst, the temperature was important for the outcome of the reaction; while at 25° hydrolysis of starting ester **3** was predominant, at 70° indanones **9** and **10** were the major products of the reaction. These compounds were isolated as a 70:30 isomeric mixture, respectively, in 50 and 18% yields.

Although this mixture could not be resolved by conventional procedures, its methylation with methyl iodide in dimethylformamide in the presence of potassium carbonate yielded quantitatively a single product, dimethoxyindanone **11**. On the other hand, compounds **9** and **10** were clearly differentiated by recording the ¹H nmr spectra of the above isomeric mixture in acetone-d₆ and acetone-d₆-NaOD. Under these conditions, absorption of H-4 in **9** shifted upfield from 7.00 to 6.46 ppm, whereas in **10** a strong shielding effect was observed for H-7 (7.18 to 6.69 ppm). Moreover, indanone **9** was independently prepared by heating *p*-acylphenyl **12** in methanesulfonic acid at 70°.

As shown in Table 1, this acylphenol was another component of the acid fraction of the resulting mixtures of the Fries rearrangement of **3**, being the amount isolated of **12** higher at 25° than at 70°, probably due to its cyclization to **9** when the temperature was raised.

Likewise, reaction at 70° afforded minor amounts of compounds **6** and **7**. Dihydrocoumarin **6** was identified by its ir carbonyl absorption (1777 cm⁻¹) and the signals corresponding to three aromatic protons and one CH₂-CO moiety in the ¹H nmr. Formation of this compound can be envisaged by an attack of the aromatic ring to the softer part of the α,β-unsaturated ester. On the other hand, methanesulfonate ester **7** was identified by comparison with an authentic sample, prepared by an independent synthesis.

When polyphosphoric acid at 100° was used instead of methanesulfonic acid, indanone **9** (51%) was the only compound isolated. In this case a high selectivity for acylation at the *para*-position to the hydroxyl group was observed, although total yield of acylated derivatives was lower than with methanesulfonic acid. This decrease might be explained by the lability of some of the reaction products at the high temperature required to overcome the practical drawbacks inherent to the viscosity of polyphosphoric acid.

On the other hand, to clarify the formation pathway of indanone **10**, in which the presence of an appropriate substituent in the aromatic ring would be required to direct the acylation at the *meta* position with respect to the hydroxyl group in **3**, reaction of methanesulfonate ester **7** with 3-methylbut-2-enoic acid for 6 hours at 70° in methanesulfonic acid was carried out. However, under these conditions the presence of indanone **10** was not detected

and only the formation of decomposition products arising from the unsaturated acid and of *t*-butylated aromatic compounds was observed.

The influence of the temperature on the outcome of the reaction was confirmed by the results from treatment of **3** with aluminum trichloride in nitromethane. Formation of *p*-acylphenol **12** (48%) was observed at 70°, whereas a lower conversion to this product was achieved at 40° and extensive resinification occurred at 100°.

Finally, the photo-Fries rearrangement of ester **3** was studied by irradiation at 254 nm in different solvents, using a Rayonet reactor. Best results were obtained by irradiation in methanol solution, which afforded practically equal amounts of *p*-acylphenol **12** (21%) and *o*-acylphenol **13** (22%), whereas in hexane lower yields of both isomers were formed. In addition, other reaction conditions assayed, such as irradiation with a sun lamp in the presence of sensitizers in the above solvents or irradiation at 254 nm in a benzene/10% sodium hydroxide two phase system [5], proved to be ineffective in the present case.

In conclusion, the *o*-methoxy ester **3** exhibits a preference for acylation at the *para* position to the formal hydroxyl group in the acid catalyzed Fries rearrangement. It is worthy of note that formation of *o*-isomer **13**, easily transformed into the desired 2,3-dihydro-8-methoxy-2,2-dimethyl-4*H*-1-benzopyran-4-one (**14**) by acid treatment, was only observed in the photochemical reaction. These results can be contrasted with those reported by Colonge and Chambard in the rearrangement of *o*-methylphenyl esters in aluminum chloride where the corresponding dihydrocoumarin was the predominant product [4].

b) Reactions of 3-Methoxyphenyl 3-Methylbut-2-enoate (**4**).

Products isolated from reaction of the ester **4** are depicted in Figure 3. Treatment of **4** with methanesulfonic acid at 70° afforded 4-chromanone **15** in 79% yield, in agreement with our previous results in the reaction of the corresponding acid and phenol under the same conditions [6]. Furthermore, from the acid fraction of the crude reaction mixture *p*-acylphenol **16** (13%) was also isolated.

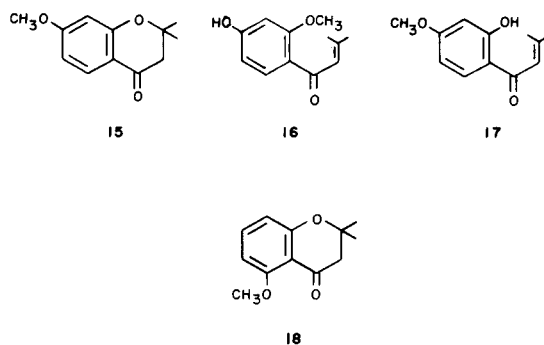


Figure 3

In this case, treatment of ester **4** with polyphosphoric acid gave similar results to those obtained with methanesulfonic acid.

On the other hand, when **4** was reacted with aluminum chloride in nitromethane, the predominant product formed was *o*-acylphenyl **17** (42%), accompanied by the corresponding 4-chromanone **15** (37%) and *p*-acylphenol **16** (10%). Likewise, in this case remarkable differences were also observed with the results reported in the rearrangement of *m*-cresol esters under these conditions which afforded the corresponding dihydrocoumarin (10%) and 4-chromanone (18%) as major products [4].

Finally, photochemical irradiation of **4** at 254 nm in methanol afforded low conversions to **17** (25%) and **16** (7%). However, under these conditions, a small amount (7%) of a new compound, identified as 4-chromanone **18**, was also isolated.

c) Reactions of 4-Methoxyphenyl 3-Methylbut-2-enoate (**5**).

In Table 2 and Figure 4 are shown the products obtained from neutral and acid fractions of the Fries rearrangement reactions performed with *p*-methoxyphenyl ester **5**.

In methanesulfonic acid at 70°, dihydrocoumarin **19** was formed predominantly (52%), along with minor amounts of 4-chromanone **20** (13%) and hydroxyindanone **21** (9%). However, in this case, the use of polyphosphoric acid led to lower combined yields of dihydrocoumarin **19** (12%) and 4-chromanone **20** (10%) and also to the formation of a new compound, identified by its spectral and analytical data as pyrone **22** [7,8].

As it was anticipated from its structure, the formation of **22** could be rationalized by a dimerization of 3-methylbut-2-enoyl moiety under the particular conditions of the reaction medium. In fact, treatment of 3-methylbut-2-enoic acid in polyphosphoric acid at 100° afforded pyrone **22** in 49% yield. This yield could be improved up to 83% when methanesulfonic acid saturated with phosphorus pentoxide was used as solvent and catalyst.

Table 2

Fries Rearrangement Reactions of 4-Methoxyphenyl 3-Methylbut-2-enoate (**5**)

Solvent and catalyst	Temperature	Time (hours)	Products (%)
CH ₃ SO ₃ H	70	0.5	19 (52), 20 (13), 21 (9), 25 (21)
PPA	100	1	19 (10), 20 (12), 22 (18),
CH ₃ NO ₂ /AlCl ₃	70	2	19 (20), 20 (5), 21 (5), 24 (25), 23 (6), 25 (18), 26 (21)
CH ₃ NO ₂ /AlCl ₃	40	4	19 (43), 21 (2), 24 (10), 23 (6), 25 (16), 26 (21)
CH ₃ OH/hν (254 nm)	50	15	23 (37), 25 (57)
1N NaOH/C ₆ H ₆ /hν (254 nm)	50	48	20 (55), 25 (41)

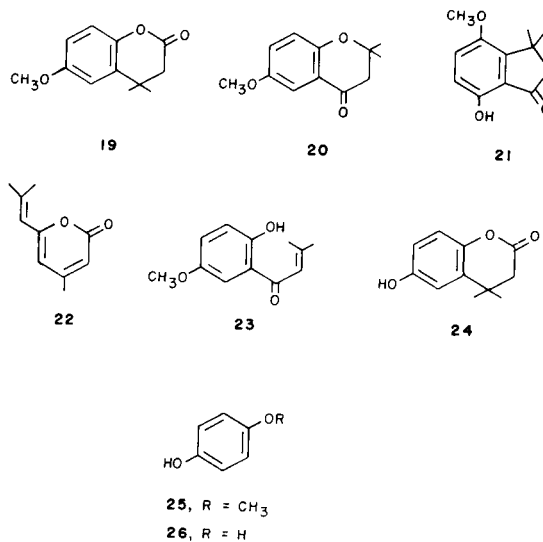


Figure 4

On the other hand, dihydrocoumarin **19** and its demethylated analog **24** were the main products formed in the reaction of **5** with aluminum chloride in nitromethane, but the amount of demethylated analog increased sharply at the expense of **19** by temperature raise. Similar results to those summarized in Table 2 were obtained when nitrobenzene was used as solvent. Predominance of dihydrocoumarin formation had also been observed for the rearrangement of the corresponding *p*-methylphenyl ester under these conditions [4].

Photo-Fries rearrangement of ester **5** has been recently described, by using a two-phase system (benzene/10% sodium hydroxide solution) irradiated by a medium pressure mercury lamp, to afford 82% yield of 4-chromanone **20** [5]. These results have also been confirmed in our laboratory although conversion was somewhat lower. In a complementary assay by irradiation of a methanolic solution of **5** at 254 nm, *ortho* acylation was also the sole rearrangement pathway observed, but yields of *o*-acylphenyl **23**, the precursor of 4-chromanone **20** were reduced to 37%.

In conclusion, the results of the Fries rearrangement of esters **3-5** were determined by the relative position of substituents in the aromatic ring in the starting compounds and by the specific reaction conditions used in each case.

Esters with activated free positions towards electrophilic substitution (*i.e.* **3** and **4**) yielded mostly acylated compounds arising from formal Fries rearrangements. In particular, acylation at *para* position with respect to the initial ester moiety was preferred in ester **3**, whereas in ester **4** substitution at *ortho* position was significantly favored. On the other hand, acylation pathways appeared to be restricted for ester **5** and alkylation was predominant. However, photochemical rearrangement in all cases favored the *ortho* acylation process.

Among the Lewis acids tested, methanesulfonic acid and polyphosphoric acid exhibited greater differences than those expected in advance. Polyphosphoric acid operated as strong acid as anticipated, but also as strong dehydrating (*cf.* ester **5**) and demethylating agent, due to the high temperature of application needed for practical reasons. On the other hand, methanesulfonic acid allowed to work under milder conditions which minimize dealkylations, and, in addition, it showed a capability to interact with free phenols with the concomitant alteration of the activated positons for preferred acylations (*cf.* ester **3**), leading to the isolation of Fries rearranged derivatives which were not formed in the reaction mixture resulting from polyphosphoric acid or aluminum chloride treatments.

EXPERIMENTAL

Melting points were determined with a Kofler apparatus and are uncorrected. The uv spectra were recorded on a Kontron Uvikon 720 spectrometer. The ir spectra were obtained with a Perkin Elmer 399B instrument. The ¹H nmr spectra were recorded on a Bruker WP-80 SY spectrometer operating at 80.13 MHz in the Fourier transform mode; all chemical shifts are given in ppm downfield from internal tetramethylsilane for solutions in deuteriochloroform at normal probe temperature (32°). Gas chromatography-mass spectra were determined on a Hewlett-Packard 5995 B apparatus, using a 25 m OV-101 capillary column. Irradiation assays were performed with a Rayonet reactor (1100 watt) and a Philips MLU sun lamp (300 watt). Purification of crude reaction mixtures by flash column chromatography are referred to the use of the method reported by Clark Still *et al.* [10].

Methoxyphenyl 3-Methylbut-2-enoates **3-5**. General Procedure.

Following a general procedure of esterification described by Hassner and Alexanian [9], a solution of the starting phenol (40 mmoles), 3-methyl-2-enoic acid (40 mmoles), *N,N*-dicyclohexylcarbodiimide (40 mmoles) and 4-dimethylaminopyridine (4 mmoles) in methylene chloride (50 ml) was allowed to react for 6 hours at room temperature. The *N,N*-dicyclohexylurea was filtered off and the residue obtained after solvent removal was purified by flash column chromatography (silica gel, hexane: ethyl acetate/4:1) affording the corresponding ester as pure compound.

2-Methoxyphenyl 3-Methylbut-2-enoate (**3**).

This compound had mp 40-41° (94% yield); ir (carbon tetrachloride): 3020, 2960, 2840, 1745, 1260, 1200, 1125, 1065 and 865 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.95 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 3.75 (s, 3H, CH₃O), 5.87 (m, 1H, CH=) and 6.70-7.20 (4H, ArH); ms: 206 (M⁺, 8.5), 83 (M⁺ -123, 100); uv (ethanol): λ max (log ε), 218 (4.4) and 270 (3.5) nm.

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 69.86; H, 6.97.

3-Methoxyphenyl 3-Methylbut-2-enoate (**4**).

This compound was isolated as an oil (92% yield); ir (carbon tetrachloride): 3020, 2980, 2830, 1740, 1650, 1600, 1490, 1215, 1125 and 845 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.95 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 3.68 (s, 3H, CH₃O), 5.75 (m, 1H, CH=) and 6.30-7.40 (4H, ArH); ms: 206 (M⁺, 11), 83 (M⁺ -123, 100); uv (ethanol): λ max (log ε), 220 (4.3) and 2.72 (3.4) nm.

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 70.09; H, 6.97.

4-Methoxyphenyl 3-Methylbut-2-enoate (**5**).

This compound had mp 59-60° (95% yield); ir (carbon tetrachloride): 3020, 2980, 2835, 1740, 1650, 1500, 1200, 1125 and 865 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.95 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 3.22 (s, 3H, CH₃O), 5.83 (m, 1H, CH=) and 6.80-7.00 (4H, ArH); ms: 206 (M⁺, 11), 83

(M⁺ -123, 100); uv (ethanol): λ max (log ε), 223 (4.3) and 278 (3.5) nm.

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 70.12; H, 6.92.

Reactions of 2-Methoxyphenyl 3-Methylbut-2-enoate (**3**).

a) Reaction of Ester **3** in Methanesulfonic Acid.

A solution of the ester **3** (0.818 g, 3.9 mmoles) in methanesulfonic acid (15 ml) was heated at 70° for 1.5 hours. When the reaction was completed (*gc* monitoring), the crude reaction mixture was poured into ice-water (100 g) and extracted with diethyl ether (3 × 50 ml). The combined organic fractions were washed with 1*N* sodium hydroxide solution (3 × 50 ml), brine and dried over magnesium sulfate. The residue obtained after solvent removal (0.175 g) was purified by tlc (silica gel, hexane:ethyl acetate/3:1) to yield two major components which were identified as the dihydrocoumarin **6** (R_f 0.55, 0.048 g, 6%) and the methanesulfonate ester **7** (R_f 0.40, 0.052 g, 6%).

3,4-Dihydro-8-methoxy-4,4-dimethyl-2*H*-1-benzopyran-2-one (**6**).

This compound had mp 90-91°; ir (carbon tetrachloride): 2980, 1775, 1590, 1480, 1270, 1210 1170, 1110, 1060 and 910 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.35 (s, 6H, CH₃), 2.62 (s, 2H, CH₂), 3.88 (s, 3H, CH₃O) and 6.70-7.30 (3H, ArH); ms: 206 (M⁺, 65), 164 (M⁺ -32, 100).

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 70.05; H, 6.88.

2-Methoxyphenyl Methanesulfonate (**7**) [11].

This compound was characterized by hydrolysis to 2-methoxyphenol (**8**) (1*N* sodium hydroxide:tetrahydrofuran/1:1, 18 hours at 50°) and by *gc* and tlc comparisons with an authentic sample prepared according to the literature; ir (carbon tetrachloride): 3050, 2930, 2820, 1600, 1500, 1370, 1155, 1100 and 870 cm⁻¹; ¹H nmr (deuteriochloroform): δ 3.20 (s, 3H, CH₃SO₃), 3.88 (s, 3H, CH₃O) and 6.80-7.40 (4H, ArH); ms: 202 (M⁺, 33), 123 (M⁺ -79, 100).

The combined alkaline fractions were acidified with hydrochloric acid and extracted with diethyl ether (3 × 50 ml). The combined ethereal fractions were washed with water, brine and dried over magnesium sulfate. The residue obtained after solvent removal (0.630 g) was purified by column chromatography (silica gel, hexane:ethyl acetate/2:1) affording as major components 0.554 g (68% overall yield) of a mixture of hydroxyindanones **9:10** (70:30 isomeric ratio). In the ¹H nmr of this mixture, the following signals could be assigned to indanone **10** by subtraction of the absorptions of indanone **9**, prepared independently (see below).

6-Hydroxy-5-methoxy-3,3-dimethylindanone (**10**).

This compound had: ¹H nmr (deuteriochloroform): δ 1.39 (s, 6H, CH₃), 2.54 (s, 2H, CH₂), 4.01 (s, 3H, CH₃O), 5.80 (br, 1H, OH), 6.85 (s, 1H, ArH) and 7.19 (s, 1H, ArH).

Methylation of the Isomeric Mixture of Hydroxyindanones **9** and **10**. 5,6-Dimethoxy-3,3-dimethylindanone (**11**).

A mixture of **9** and **10** (70:30 isomeric ratio, 0.020 g, 0.09 mmole), excess of methyl iodide (1 ml) and anhydrous potassium carbonate (0.030 g, 0.22 mmole) in *N,N*-dimethylformamide (3 ml) was vigorously stirred for 6 hours at 50°. When the reaction was completed, the crude reaction mixture was cooled, poured into 6*N* hydrochloric acid (25 ml) and extracted with benzene (3 × 25 ml). The combined organic fractions were washed with 1*N* sodium hydroxide solution, brine and dried over magnesium sulfate. The residue obtained after solvent removal (0.017 g) crystallized on standing and it was identified as the indanone **11** (90% yield). Compound **11** had mp 68.5-69°; ir (carbon tetrachloride): 3000, 2980, 2830, 1590, 1510, 1265, 1225, 1150, 1035 and 910 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.41 (s, 6H, CH₃), 2.56 (s, 2H, CH₂), 3.90 (s, 3H, CH₃O), 3.99 (s, 3H, CH₃O), 6.86 (s, 1H, ArH) and 7.12 (s, 1H, ArH).

Anal. Calcd. for C₁₃H₁₆O₃: C, 70.89; H, 7.32. Found: C, 70.77; H, 7.33.

Finally, the column chromatographic separation of the acid fraction also afforded the *p*-acylphenolic derivative **12** (see description below) in 3% yield.

b) Reaction of Ester **3** in Polyphosphoric Acid.

A solution of **3** (0.500 g, 2.43 mmoles) in polyphosphoric acid (40 g) was heated for 30 minutes at 100° under vigorous stirring. After the reaction was completed (gc monitoring), the crude reaction mixture was treated in the usual way to afford 0.255 g (51 %) of the indanone **9**, mp, 126-127° (lit 128-129°) [12].

c) Reaction of Ester **3** with Aluminum Chloride.

Anhydrous aluminum chloride (1.75 g, 13.1 mmoles) was added to a solution of ester **3** (0.849 g, 4.1 mmoles) in nitromethane (20 ml) and the mixture was vigorously stirred at 70°. When the reaction was completed (3 hours, gc monitoring), the crude reaction mixture was poured into ice-hydrochloric acid and extracted with diethyl ether (3 × 50 ml). The combined organic fractions were washed with brine and dried over magnesium sulfate. The residue obtained after solvent removal (0.825 g) was purified by flash column chromatography (silica gel, hexane:ethyl acetate/2.5:1) affording a fraction of 0.407 g of a crystalline compound which was recrystallized from hexane and was identified as the *p*-acylphenolic derivative **12** (48 % yield). Additionally, 2-methoxyphenol (**8**, 0.178 g) was also isolated.

2-Methoxy-4(3-methylbut-2-enoyl)phenol (**12**) had mp 98-98.5°; ir (carbon tetrachloride): 3520, 2840, 1660, 1600, 1505, 1260, 1150 and 860 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.00 (s, 3H, CH₃), 2.17 (s, 3H, CH₃), 3.95 (s, 3H, CH₃O), 6.04 (s, 1H, OH), 6.70 (br s, 1H, CH=), 6.93 (d, 1H, J = 8.7 Hz, ArH) and 7.40-7.60 (2H, ArH); uv (ethanol): λ max (log ε), 238 (4.0), 286 (3.8) and 318 (3.9) nm.

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 70.01; H, 6.84.

Cyclization of Compound **12**.

A solution of **12** (0.106 g, 0.51 mmole) in methanesulfonic acid (10 ml) was heated 4 hours at 70°. Then the crude reaction mixture was poured into ice-water and extracted with diethyl ether (2 × 25 ml). The combined organic fractions were washed with brine and dried over magnesium sulfate. The residue obtained after solvent removal afforded 0.098 g (92 % yield) of a crystalline solid which was identified as the indanone **9**.

d) Photochemical Reaction of Ester **3**.

A 250 ml quartz flask containing a solution of the ester **3** (1.68 g, 8.15 mmoles) in methanol (100 ml) was irradiated with 254 nm uv light in a Rayonet reactor. When the reaction was completed (69 hours, gc monitoring), the residue obtained after solvent evaporation was purified by flash column chromatography (silica gel, hexane:ethyl acetate/3:1), to yield three major fractions corresponding to 2-methoxyphenol (**8**, 0.510 g equivalent to 51 % of starting material), the *p*-acylphenolic derivative **12** (0.353 g, 21 %) and the *o*-acylphenol **13** (0.366 g, 22 %).

6-Methoxy-2(3-methylbut-2-enoyl)phenol (**13**) had mp 110.5-111°; ir (carbon tetrachloride): 3450, 2940, 2840, 1640, 1590, 1450, 1360, 1250, 1235, 1030, 840 and 735 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.04 (s, 3H, CH₃), 2.22 (s, 3H, CH₃), 3.90 (s, 3H, CH₃O), 6.60-7.50 (3H, ArH) and 13.11 (s, 1H, OH); uv (ethanol): λ max (log ε), 2.24 (4.1), 282 (4.2) and 354 (3.5) nm.

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 69.95; H, 6.82.

Cyclization of Compound **13**.

A solution of **13** (0.060 g, 0.29 mmole) in methanesulfonic acid (10 ml) was stirred for 10 minutes at room temperature. Then the crude reaction mixture was poured into ice-water and extracted with diethyl ether (2 × 25 ml). The combined organic fractions were washed with 1*N* sodium hydroxide solution, brine and dried over magnesium sulfate. The residue obtained after solvent removal afforded 0.058 g (97 % yield) of a crystalline solid which was identified as the 4-chromanone **14**.

2,3-Dihydro-8-methoxy-2,2-dimethyl-4*H*-1-benzopyran-4-one (**14**) had mp 126-127° (lit 127°) [13]; ir (carbon tetrachloride): 2990, 2830, 1690, 1610, 1570, 1485, 1300, 1260, 1180, 1050 and 935 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.52 (s, 6H, CH₃), 2.73 (s, 2H, CH₂), 3.89 (s, 3H, CH₃O), 6.80-7.15 (2H, ArH) and 7.48 (dd, 1H, J = 2.2 Hz, J = 7.4 Hz, *H*-5); ms; 206 (M⁺, 50), 122 (M⁺ - 84, 100); uv (ethanol): λ max (log ε), 218 (4.2), 264 (3.9) and 338 (3.5).

Reactions of 3-Methoxyphenyl 3-Methylbut-2-enoate (**4**).

a) Reaction of Ester **4** in Methanesulfonic Acid.

Following the same procedure indicated for the ester **3**, a solution of the ester **4** (0.779 g, 3.78 mmoles) in methanesulfonic acid (15 ml) was heated for 1.5 hours at 70°. The treatment of the crude reaction mixture separating neutral and acid fractions allowed to isolate from the former 0.616 g (79 % yield) of the 4-chromanone **15** and from the latter 0.124 g (13 % yield) of the *p*-acylphenolic compound **16**.

2,3-Dihydro-7-methoxy-2,2-dimethyl-4*H*-1-benzopyran-4-one (**15**) had mp 80-80.5° (lit 81-82°) [6].

3-Methoxy-4(3-methylbut-2-enoyl)phenol (**16**) was isolated as an oil; ir (carbon tetrachloride): 3300, 2980, 2830, 1650, 1610, 1470, 1260, 1165, 1035, 960 and 850 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.88 (s, 3H, CH₃), 2.15 (s, 3H, CH₃), 3.65 (s, 3H, CH₃O), 6.35 (m, 1H, CH=), 6.40-6.70 (2H, ArH), 7.55 (d, 1H, J = 9.5 Hz, ArH) and 8.40 (br, 1H, OH).

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 70.01; H, 6.78.

b) Reaction of Ester **4** in Polyphosphoric Acid.

This reaction afforded analogous results as previously described [6].

c) Reaction of Ester **4** with Aluminum Chloride.

Following the same procedure indicated for ester **3**, a solution of ester **4** (0.705 g, 3.40 mmoles) in nitromethane (30 ml) was treated with anhydrous aluminum chloride (1.85 g, 13.6 mmoles). The usual working-up of the crude reaction mixture gave a residue (0.555 g) which was purified by flash column chromatography (silica gel, hexane:ethyl acetate/3:1), affording 0.260 g (37 % yield) of the 4-chromanone **15**, 0.069 g (10 % yield) of the compound **16** and 0.296 g of a pale yellow oil which was identified as the *o*-acylphenol **17** (42 % yield).

5-Methoxy-2(3-methylbut-2-enoyl)phenol (**17**).

This compound had: ir (carbon tetrachloride): 3020, 1690, 1645, 1450, 1380, 1250, 1135, 1020 and 860 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.07 (s, 3H, CH₃), 2.25 (s, 3H, CH₃), 3.90 (s, 3H, CH₃O), 6.30-6.80 (3H, CH=, ArH), 7.85 (d, 1H, J = 10.8 Hz, ArH) and 13.4 (s, 1H, OH).

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 69.55; H, 6.98.

d) Photochemical Reaction of Ester **4**.

Following the same procedure indicated for ester **3**, a solution of ester **4** (0.751 g, 3.64 mmoles) in methanol (90 ml) was irradiated at 254 nm for 24 hours. After usual work-up, further purification of the crude reaction mixture afforded 0.186 g (25 % yield) of compound **17**, 0.053 g (6 %) of the *p*-acylphenolic derivative **16** and 0.052 g (6 % yield) of a compound which was characterized as the 4-chromanone **18**.

2,3-Dihydro-5-methoxy-2,2-dimethyl-4*H*-1-benzopyran-4-one (**18**) had mp 118-119° (lit 123.5-124°) [14]; ir (KBr): 3020, 2945, 2820, 1685, 1595, 1570, 1465, 1245, 1085 and 880 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.43 (s, 6H, CH₃), 2.68 (s, 2H, CH₂), 3.90 (s, 3H, CH₃O), 6.46 (d, 1H, J = 8.3 Hz, ArH), 6.52 (d, 1H, J = 8.3 Hz, ArH) and 7.35 (dd, J = 8.3 Hz, ArH).

Reactions of 4-Methoxyphenyl 3-Methylbut-2-enoate (**5**).

a) Reaction of Ester **5** in Methanesulfonic Acid.

Following the same procedure indicated for the ester **3**, a solution of the ester **5** (0.920 g, 4.47 mmoles) in methanesulfonic acid (20 ml) was heated for 1.5 hours at 70°. The treatment of the crude reaction mixture separating neutral and acid fractions allowed to isolate from the former 0.474 g (52 % yield) of a yellow oil which was characterized as the dihydrocoumarin **19** and 0.119 g (13 % yield) of a compound which crystallized on standing and was identified as the 4-chromanone **20**.

3,4-Dihydro-6-methoxy-4,4-dimethyl-2*H*-1-benzopyran-2-one (**19**).

This compound was isolated as an oil; ir (carbon tetrachloride): 2985, 2840, 1780, 1500, 1420, 1270, 1200, 1170, 1050 and 890 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.32 (s, 6H, CH₃), 2.50 (s, 2H, CH₂), 3.78 (s, 3H, CH₃O) and 6.60-6.95 (3H, ArH).

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 69.65; H, 7.02.

2,3-Dihydro-6-methoxy-2,2-dimethyl-4H-1-benzopyran-4-one (**20**).

This compound had mp 71-72° (lit 74-75°) [15]; ir (carbon tetrachloride): 2990, 2830, 1675, 1615, 1485, 1430, 1275, 1230, 1040 and 865 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.49 (s, 6H, CH₃), 2.69 (s, 2H, CH₂), 3.79 (s, 3H, CH₃O) and 6.70-7.40 (3H, ArH).

In addition, from the acid fraction it was isolated a compound (0.190 g, 9%), which was characterized as the hydroxyindanone **21**.

7-Hydroxy-4-methoxy-3,3-dimethylindanone (**21**).

This compound had mp 104-106°; ir (carbon tetrachloride): 3350, 2975, 2830, 1675, 1615, 1490, 1450, 1290, 1200, 1045 and 865 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.48 (s, 6H, CH₃), 2.50 (s, 2H, CH₂), 3.81 (s, 3H, CH₃O), 6.60 (d, 1H, J = 8.4 Hz, ArH), 6.95 (d, 1H, J = 8.4 Hz, ArH) and 8.65 (s, 1H, OH).

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 69.88; H, 7.02.

b) Reaction of Ester **5** in Polyphosphoric Acid.

Following the same procedure indicated for the ester **3**, a solution of the ester **5** (0.540 g, 2.62 mmoles) was heated in polyphosphoric acid for 30 minutes at 100°. The treatment and further chromatographic purification of the crude reaction mixture afforded dihydrocoumarin **19** (0.054 g, 10%), 4-chromanone **20** (0.065 g, 12%) and a compound which was identified as the pyran-2-one **22** (0.097 g, 18% yield from the starting 3-methylbut-2-enoyl moiety) by comparison with an authentic sample independently prepared (see below).

Preparation of 4-Methyl-6(2-methylpropenyl)-2H-pyran-2-one (**22**).

To a solution of 3-methylbut-2-enoic acid (2.50 g, 25 mmoles) in methanesulfonic acid (15 ml) at 80°, it was added phosphorus pentoxide (2.50 g, 17.6 mmoles) and the mixture was vigorously stirred for 30 minutes. Then the crude reaction mixture was cooled, poured into ice-water and extracted with diethyl ether (3 × 50 ml). The combined organic fractions were washed with brine and dried over magnesium sulfate. The residue obtained after solvent removal afforded 1.70 g (83% yield) of the pyrone **22** as a crystalline solid.

This compound had mp 45-46° (lit 47°) [7]; ir (carbon tetrachloride): 2990, 2920, 1745, 1655, 1540, 1405, 1380, 1165, 970 and 845 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.90 (s, 3H, CH₃), 2.09 (s, 3H, CH₃), 2.15 (s, 3H, CH₃) and 5.75 (3H, CH=); ms: 164 (M⁺, 100), 149 (M⁺, -15, 52); uv (ethanol): λ max (log ε), 230 (4.2) and 329 (4.1) nm.

c) Reaction of Ester **5** with Aluminum Chloride.

Following the same procedure indicated for the ester **3**, a solution of the ester **5** (0.950 g, 4.61 mmoles) in nitromethane (30 ml) was treated with anhydrous aluminum chloride (2.45 g, 18.4 mmoles) for 3 hours at 70°. The working up of the crude reaction mixture gave a residue (0.893 g) which was purified by the usual chromatographic methods; gc/ms analysis allowed the detection of 4-methoxyphenol and hydroquinone by comparison with authentic standards. Additionally, four compounds were isolated: dihydrocoumarin **19** (0.168 g, 19%), hydroxyindanone **21** (0.045 g, 5%), *o*-acylphenolic derivative **23** (0.074 g, 6%) (see description below under photochemically assay) and hydroxycoumarin **24** (0.199 g, 25%).

3,4-Dihydro-6-hydroxy-4,4-dimethyl-2H-1-benzopyran-2-one (**24**).

This compound had: ir (chloroform): 3580, 3330, 3000, 2950, 1750, 1590, 1440, 1275, 1165, 1035, 900 and 825 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.30 (s, 6H, CH₃), 2.59 (s, 2H, CH₂), 5.80 (br, 1H, OH) and 6.50-6.90 (3H, ArH). The compound was characterized by methylation, accordingly, 0.65 g (0.32 mmole) was treated with excess of methyl iodide (2 ml), anhydrous potassium carbonate (0.100 g, 0.72 mmole) in *N,N*-dimethylformamide (10 ml) for 3 hours at 50°. The residue obtained after the usual work-up of the crude reaction mixture was identical to dihydrocoumarin **19** by gc and tlc analysis.

d) Photochemical Reaction of Ester **5**.

Following the same procedure indicated for ester **3**, a solution of ester **5** (1.00 g, 4.85 mmoles) in methanol (100 ml) was irradiated at 254 nm for 15 hours. The treatment and further purification of the crude reaction mixture afforded 0.363 g of 4-methoxyphenol (**25**) and 0.366 g of a yellow solid which was characterized as *o*-acylphenolic derivative **23** (37% yield).

4-Methoxy-2(3-methylbut-2-enoyl)phenol (**23**).

This compound had mp 48-49°; ir (carbon tetrachloride): 3530, 2970, 2830, 1640, 1580, 1480, 1280, 1210, 1160, 1040 and 840 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.10 (s, 3H, CH₃), 2.25 (s, 3H, CH₃), 3.77 (s, 3H, CH₃O), 6.70 (m, 1H, CH=), 6.80-7.20 (3H, ArH) and 9.15 (br, 1H, OH).

Anal. Calcd. for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 70.22; H, 6.89. Additionally, gc analysis of the crude reaction mixture showed the presence of compounds **19** and **20** as minor components (< 1%). Finally, an experiment carried out following the procedure described by Primo, *et al.* [5], but working in a Rayonet reactor, afforded 4-chromanone **20** in 55% yield.

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