ON THE REACTION OF SUBSTITUTED PHENOLS AND 3-METHYLBUT-2-ENOIC ACID. A COMPARATIVE STUDY[1]

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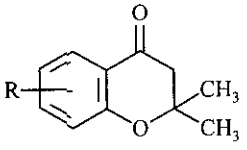
Abstract — A systematic and comparative study of the reaction of a series of substituted phenols and 3-methylbut-2-enoic acid in zinc chloride/phosphorus oxychloride and aluminum chloride/phosphorus oxychloride reveals that the formation of phenolic esters and 2,2-dimethyl-4-chromanones is strongly influenced by the substituents, their position on the aromatic ring of the starting phenols. Based on our study, a mixed Friedel-Crafts and Fries rearrangement mechanism is in operation in these reactions.

Substituted 2,2-dimethyl-4-chromanones (**1**) are valuable intermediates in the syntheses of potentially useful modern pesticides, such as precocenes[2] (**2**) and other bioactive compounds,[3] including benzopyran derivatives such as cromakalim (**3**) and related analogues which are recently discovered potassium channel openers.[4]



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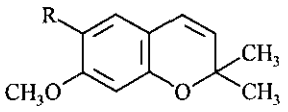
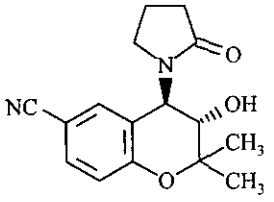


2 R = H or CH_3O



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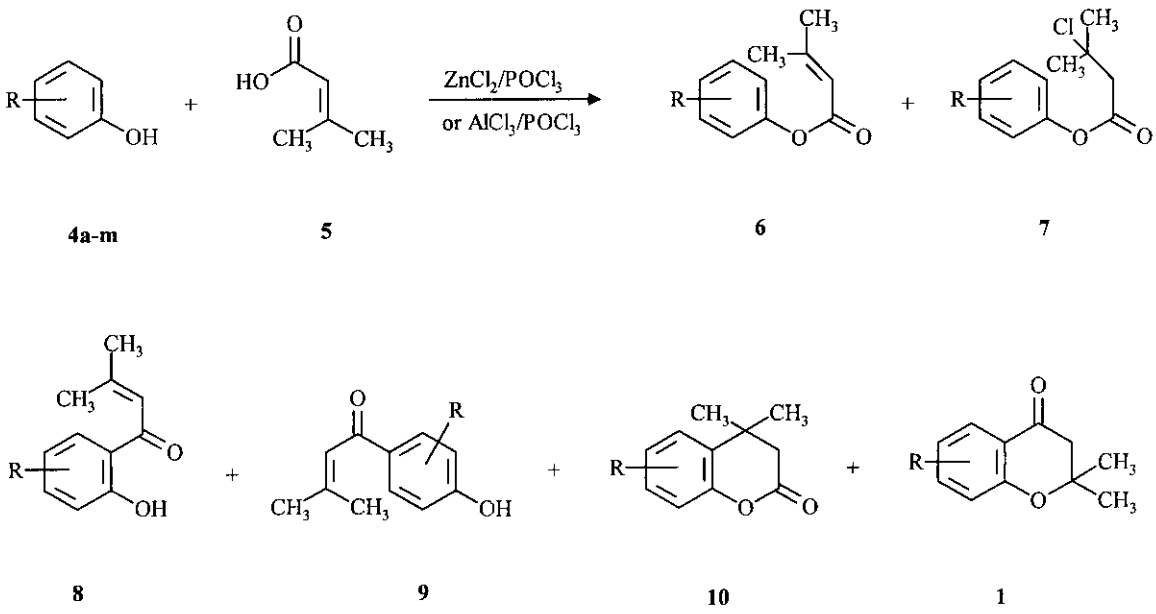
There are several methods available for the preparation of substituted 2,2-dimethyl-4-chromanones;[5] not all of them, however, are suitable for the syntheses of those 4-chromanones having any kind of substitution pattern on the aromatic ring.[6] In the course of our ongoing research program in the field of benzopyran derivatives,[7] we were interested in the syntheses of a systematic series of 2,2-dimethyl-4-chromanones bearing various substituents in different positions of the aromatic ring. Evaluating the existing, preparatively advantageous methods, we found that the most widely used procedure consists of the Friedel-Crafts reaction and/or Fries rearrangement between different substituted phenols and 3-methylbut-2-enoic acid (**5**) (or acid chloride) in the presence of an appropriate Lewis acid in a suitable solvent.[8] In spite of this fact, however, we realized that a truly systematic and comparative study of the products resulting from *C*- and/or *O*-acylation, Fries rearrangement and subsequent heterocyclization sequence has not been reported.[9] It is well known that a reagent comprised freshly fused zinc chloride and phosphorus oxychloride can be very efficient in the syntheses of substituted 7-hydroxy-2,2-dimethyl-4-chromanones.[10] There is also a report on the use of fused aluminum chloride/phosphorus oxychloride for the same purpose.[11] We have shown earlier that the use of unfused zinc chloride/phosphorus oxychloride is superior in the syntheses of substituted 7-hydroxy-2,2-dimethyl-4-chromanones.[12] An optimum amount of water (5% is normally present in unfused, commercial zinc chloride) resulted in a 10- to 100-fold decrease in reaction time compared to that for anhydrous, freshly fused zinc chloride/phosphorus oxychloride. These findings and literature data[6,8] prompted us to perform a systematic and comparative study of the reaction of substituted phenols and 3-methylbut-2-enoic acid using these two above mentioned reagent systems, and we now report some of our findings on these reactions.

In our synthetic study, phenol (**4a**) and various substituted phenols (**4b-m**) were reacted with 3-methylbut-2-enoic acid (**5**) in zinc chloride/phosphorus oxychloride and aluminum chloride/phosphorus oxychloride (Scheme 1). The progress of the reactions was monitored by gc and tlc. Using repeated column chromatography each component of the reaction mixture was separated and purified. The structure of the pure components was determined by ^{1}H-nmr and ms measurements. A series of quantitative gc and hplc studies (using these pure components as an external standard) of the crude reaction mixture was done. Based on these quantitative data, we calculated conversions of each reaction as well as yields of the corresponding components formed. Relevant data are given in Tables 2 and 3.



Scheme 1.

We have reported earlier[13] that the product composition could also be determined by ^{1}H-nmr spectroscopy. The product composition measured by ^{1}H-nmr was in good agreement with those data calculated from quantitative gc and hplc measurements (see Table 1).

Table 1. **Comparative data for the reaction of phenol (4a) with 5 in zinc chloride/phosphorus oxychloride**

Method [(a)]	**4a**	**5**	**6a**	**7a**	**9a**	**10a**	**1a**
gc	1.1 %	-	5.3 %	76.0 %	9.0 %	3.5 %	3.9 %
hplc	1.0 %	0.4 %	5.6 %	75.2 %	9.8 %	3.6 %	3.6 %
^{1}H-nmr	-	-	5 %	80 %	9 %	3 %	3 %

[(a)] For detailed parameters and conditions see Experimental.

Table 2. **Reactions of substituted phenols with 3-methylbut-2-enoic acid in zinc chloride/phosphorus oxychloride**

Phenol **4**	R	Reaction time (h)	Conversion (%)	Yield[a] (%)					
				6	**7**	**8**	**9**	**10**	**1**
a	H	52	87	5.3	76.0	-	9.0	3.5	3.9
b	2-OH	4	72[b]	53.0	20.8	-	-	-	-
c	3-OH	3	92	-	-	74.8	-	-	23.7[c]
d	4-OH	0.5	76[b]	61.0	7.8	-	-	-	-
e	2-Me	46	94	-	63.5	-	25.5	3.9	6.0
f	3-Me	46	93	-	36.6	-	9.0	3.8[c]	50.0[c]
g	4-Me	30	94	-	83.0	-	-	7.0	9.8
h	2-MeO	4	89	-	68.3	30.3	-	-	-
i	3-MeO	4	89	7.3	-	36.8	-	-	51.5[c]
j	4-MeO	36	90	5.8	93.2	-	-	-	-
k	2-Cl	71	91	4.5	94.7	-	-	-	-
l	3-Cl	71	93	3.0	96.4	-	-	-	-
m	4-Cl	48	93	-	99.6	-	-	-	-

[a] Based on the quantitative gc and hplc analysis.

[b] Unreacted 3-methylbut-2-enoic acid was measured up to 20%.

[c] 7-substituted derivative.

The data in Table 2 show that while the conversion was high in all cases, the outcome of the reaction was very dependent on the substitution (substituent and position) of the starting phenols. The reaction of phenol (**4a**) and 3-methylbut-2-enoic acid (**5**) afforded a multicomponent reaction mixture. The main product was the ester (**7a**) arising from addition of hydrochloric acid to the alkene portion of the α,β-unsaturated ester (**6a**). Hydrochloric

acid was formed *in situ* from the reaction between phosphorus oxychloride and water. Using shorter reaction time (2 h) we proved the **6a** → **7a** sequence, since in this particular case the main product was the α,β-unsaturated ester (**6a**). A mechanism for the formation of 1-(4-hydroxyphenyl)-3-methyl-2-buten-1-one (**9a**) could not be easily decided. This latter compound could be formed by para-acylation of the starting phenol (**4a**) or para-Fries rearrangement reaction of the corresponding ester (**6a**).

Table 3. **Reactions of substituted phenols with 3-methylbut-2-enoic acid in aluminum chloride/phosphorus oxychloride**

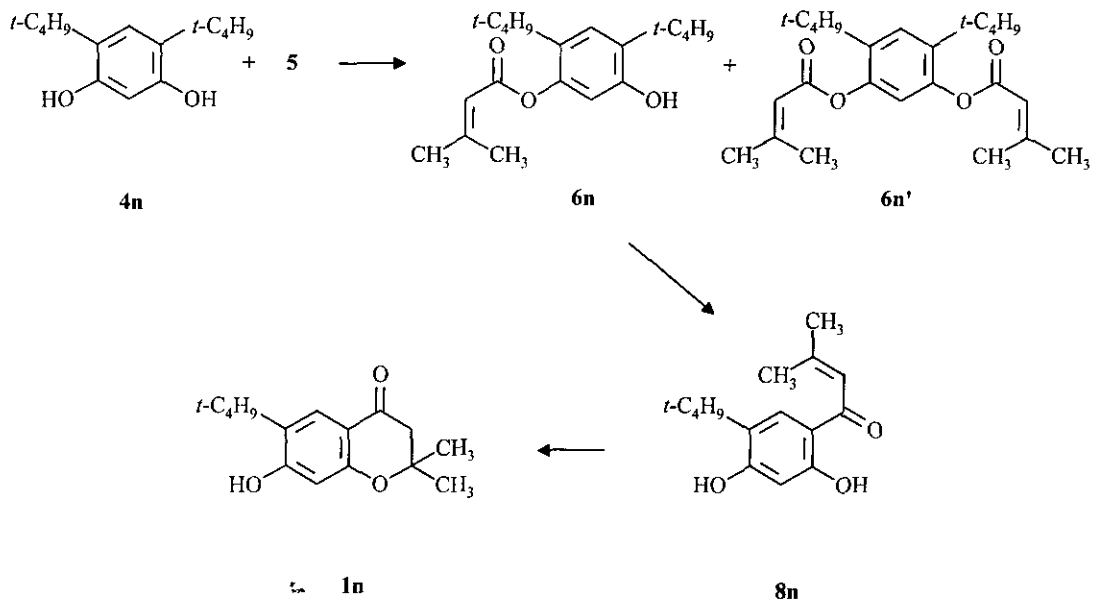
Phenol	R	Reaction time (h)	Conversion (%)	Yield[a] (%)		
4				**6**	**7**	**8**
a	H	0.1	92	99.5	-	-
b	2-OH	0.5	75	56.4[b]	1.0	-
c	3-OH	1.0	95	-	-	99.8
d	4-OH	0.25	90	99.6	-	-
e	2-Me	0.5	93	94.6	5.0	-
f	3-Me	1.0	90	82 4	5.0	12.0
g	4-Me	0.5	91	95.7	4.0	-
h	2-MeO	0.5	93	99.7	-	-
i	3-MeO	0 5	95	-	-	99.8
j	4-MeO	0.5	94	99.9	-	-
k	2-Cl	0.5	91	99.8	-	-
l	3-Cl	0.5	92	98.8	0.5	-
m	4-Cl	0.5	92	98.7	0.5	-

[a] Based on the quantitative gc and hplc analysis.

[b] + 42% *bis-O*-acrylate (**6b'**) was also measured.

The formation of 3,4-dihydro-4,4-dimethylcoumarin (**10a**) could be rationalized by the intramolecular Friedel-Crafts alkylation reaction of **7a** or acid catalyzed cyclization of **6a**. There are examples of the cyclization of vinyl phenyl ketones of type **8** in both acidic[14] and alkaline media.[15] This explains why we were not able to detect the ketone of type **8a**, since it cyclized to the corresponding 2,2-dimethyl-4-chromanone (**1a**) under acidic reaction conditions. The reaction of pyrocatechol (**4b**) and hydroquinone (**4d**) showed somewhat lower conversion. These two phenols were very sensitive to the acidic reaction media and a considerable amount of tarry material was formed. This is why we found a larger amount of unreacted 3-methylbut-2-enoic acid (**5**) in the final reaction mixture. Friedel-Crafts *O*-acylation reaction was the main pathway. Accordingly the main products were the corresponding α,β-unsaturated esters (**6b**) and (**6d**) together with those saturated esters (**7b**) and (**7d**) in these two reactions. When the starting phenol contained substituents at position 3 (**4c, f, i**) there was a possibility for the formation of two regioisomers in the course of cyclisation leading to **10** and **1**. However, the only regioisomer that we detected in each reaction was the corresponding 7-substituted dihydrocoumarin (**10**) or 7-substituted 4-chromanone (**1**). This observation could be explained by steric reasons. When the starting phenol contained an electron withdrawing substituent (**4k, l, m**) the reaction afforded mainly the corresponding saturated esters (**7k, l, m**). The aromatic ring was deactivated towards ring closure by a Friedel-Crafts type mechanism. Table 2 clearly shows that in the case of the 3-hydroxy and 3-methoxy starting compounds (**4c** and **4i**, respectively) the formation of the *C*-acylated products (**8c** and **8i**, respectively) is preferred. These compounds can be either isolated or cyclized in alkaline media to furnish the corresponding 4-chromanones (**1**) in high yielding reactions.[12,16]

The progress of the reaction of **4c** with **5** was monitored by gc. After 5 minutes reaction time we detected the 1-(2,4-dihydroxyphenyl)-3-methyl-2-buten-1-one (**8c**) and the unreacted 3-methylbut-2-enoic acid (**5**) but we failed to detect any trace of α,β-unsaturated ester (**6c**). This observation might serve as proof for a Friedel-Crafts *C*-acylation, however a fast Fries rearrangement reaction of the ester (**6c**) could be also responsible for the formation of the ketone (**8c**). The only example when we were able to prove the reaction mechanism was the reaction of 4,6-di-*tert*-butylresorcinol (**4n**) with **5** in zinc chloride/phosphorus oxychloride and aluminum chloride/phosphorus oxychloride (Scheme 2).



Scheme 2.

The progress of these reactions was followed by gc and tlc. After 30 minutes the reactions were stopped and the reaction mixtures were worked up. The main components were separated by column chromatography and their structures were determined by ^{1}H-nmr and ms measurements. These isolated and purified intermediates served as the basis of quantitative gc analysis in further runs Figures 1 and 2 clearly show the reaction sequence. Applying unfused zinc chloride/phosphorus oxychloride, the α,β-unsaturated ester (**6n**) formed first by *O*-acylation and subsequently afforded ketone (**8n**) *via* ortho- or para-Fries rearrangement reaction. The latter was transformed to the 6-*tert*-butyl-7-hydroxy-2,2-dimethyl-4-chromanone (**1n**) in the acid catalyzed ring closure reaction. When using aluminum chloride/phosphorus oxychloride the α,β-unsaturated ester (**6n**) formed faster and the corresponding diester (**6n'**) was also produced. Ortho- or para-Fries rearrangement of the ester (**6n**) also took place faster at the beginning of the reaction. However its conversion to ketone (**8n**) needed longer reaction time since the corresponding 4-chromanone (**1n**) was not produced. A gc/ms study of these reaction mixtures revealed that isobutylene was generated as a result of Fries rearrangement of **6n** (see Experimental).

Figure 1. **Gc monitoring of the reaction of 4n with 5 in zinc chloride/phosphorus oxychloride**

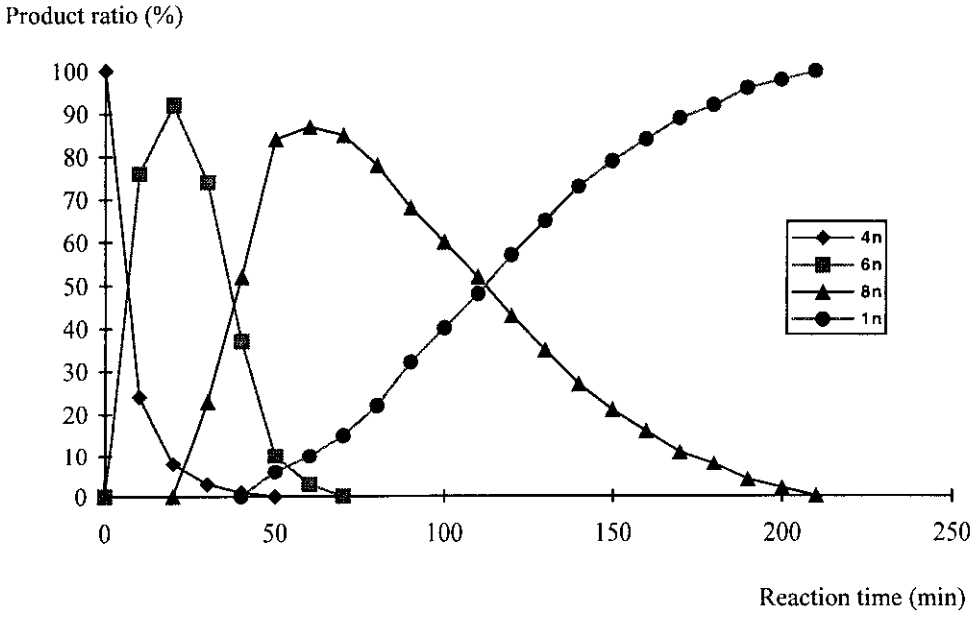
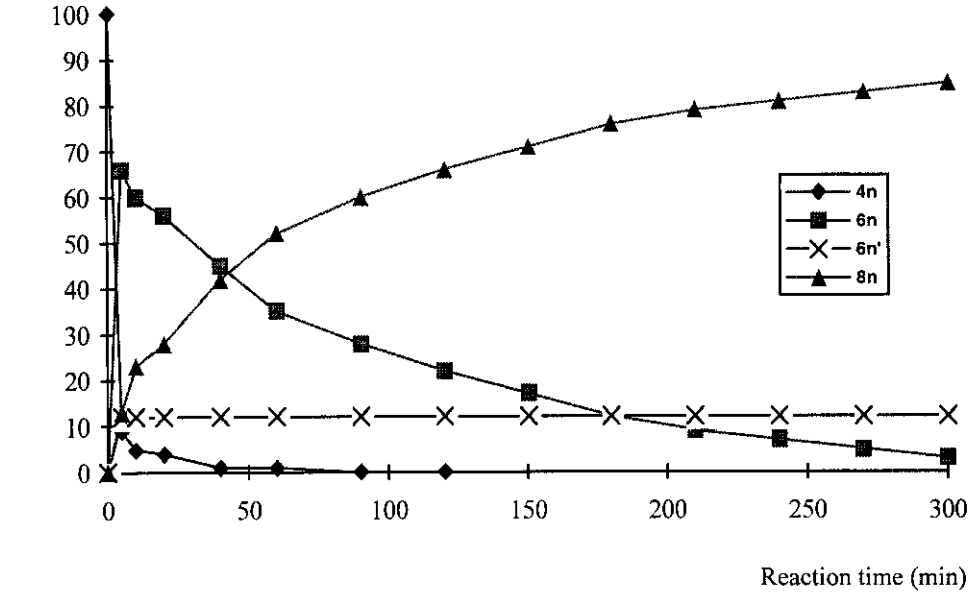


Figure 2. **Gc monitoring of the reaction of 4n with 5 in aluminum chloride/phosphorus oxychloride**



Based on the data summarized in Table 3 we could come to a similar conclusion concerning the mechanism of the reactions of phenols in aluminum chloride/phosphorus oxychloride. However, these data show several differences as well. Since the aluminum chloride is stronger Lewis acid than the zinc chloride, the corresponding reaction times were considerably decreased. The main product in each case (except **4c** and **4i**) was the corresponding α,β-unsaturated ester (**6**). Because of the short reaction times the addition of hydrochloric acid to the alkene portion of the unsaturated ester (**6**) was not favoured.

CONCLUSIONS

It has been found that both the zinc chloride/phosphorus oxychloride and aluminum chloride/phosphorus oxychloride systems are beneficial for the synthesis of substituted 2,2-dimethyl-4-chromanones in the case of resorcinol type starting phenols. This is in agreement with those of reported observations.[10-12, 16-18] With other phenols containing methyl substituents the reaction mixtures are rather complicated and the separation of substituted 2,2-dimethyl-4-chromanones formed is difficult. Also, the 2- or 4-substituted phenols with a hydroxy or methoxy substituents fail to cyclize to the corresponding 4-chromanones. When the starting phenol is not of resorcinol type, the synthetic method is superior for the preparation of the α,β-unsaturated esters of type **6** and the saturated ones of type **7** in aluminum chloride/phosphorus oxychloride and zinc chloride/phosphorus oxychloride, respectively. Consequently these systems provide simple and economic alternative method for the synthesis a wide range of esters (**6**) and (**7**) compared to those using the acid chloride procedure. The exact mechanism responsible for the formation of the corresponding products (except the reaction from 4,6-di-*tert*-butylresorcinol) has not yet been proven. We think that Friedel-Crafts *O*- and/or *C*-acylation, ortho- and/or para-Fries rearrangement, Friedel-Crafts alkylation and acid catalyzed ring closure mechanisms are working simultaneously in these reactions.

EXPERIMENTAL

Melting points were determined with a Koffler hot-stage apparatus and are uncorrected. Analytical thin-layer chromatography was performed on precoated aluminium-backed 0.2 mm silica gel plates. Column chromatography was carried out with Kieselgel 60 silica gel using 6:1 benzene-methanol or dichloromethane as the eluent. ^{1}H-Nmr spectra were determined for solutions in deuteriochloroform with TMS internal reference on a Varian Gemini-200 instrument. Gas chromatography (gc) measurements were performed on a Hewlett-

Packard 5890 instrument. gc conditions: column: DB-5, 15 m x 0.25 mm 0.25 μm, carrier gas: helium 35 cm/s, injector: splitless, 240 °C, detector: FID, 240 °C, oven: 60 °C (1 min), 20 °C/min, 240 °C (8 min). gc/ms conditions: column: SPB-5, 30 m x 0.25 mm 1.0 μm, carrier gas: helium 50 cm/s, injector: splitless, 240 °C, ms: EI, 70 eV, oven: 50 °C (1 min), 20 °C/min, 260 °C. hplc studies were carried out on a Waters 600 instrument equipped with a Waters 991 detector. hplc conditions: column: Nova-Pak C_{18}, 3.9 mm x 15 cm 4 μm, mobile phase: methanol-water 65:35, flow: 1.0 ml/min, detector: UV dioda array (190-400 nm). ms data were obtained on a VG TRIO-2 mass spectrometer in EI mode at 70 eV. Microanalyses were performed by Microlaboratory, L. Kossuth University, Debrecen, Hungary. Solvents were used either as purchased or dried and purified by standard methods.

General Procedure

To a stirred mixture of phosphorus oxychloride (20 ml, 218 mmol) and 3-methylbut-2-enoic acid (1.1 g, 11 mmol), zinc chloride (2.04 g, 15 mmol) or aluminum chloride (2.00 g, 15 mmol) and phenol (10 mmol) were added at room temperature. The reaction was monitored by gc and tlc. When the starting phenol disappeared (see Table 2 and Table 3) the mixture was poured onto crushed ice (200 g), extracted with ether (3x30 ml) and the ethereal solution was dried over sodium sulfate. The solvent was removed in vacuum. Using repeated column chromatography each component of the reaction mixture was separated and purified.

Typical procedure for the cyclization of 8c

Compound (**8c**) (1.92 g, 10 mmol) was dissolved in 2% aqueous sodium hydroxide solution (50 ml) and stirred at room temperature for 1 h. The solution was then cooled below 10 °C and acidified to pH 1 with concentrated hydrochloric acid. The solid was filtered, washed with water and dried. The crude product was crystallized from ethanol/water to afford of **1c** in 92% yield.

Blank experiment

Isobutylene was bubbled with stirring in phosphorus oxychloride (20 ml, 218 mmol) containing aluminum chloride (2.00 g, 15 mmol) for 30 min at room temperature. The mixture was poured onto crushed ice (200 g), extracted with ether (3x30 ml), dried over sodium sulfate and studied by gc/ms. The mass spectra of the components gave fragmentation patterns characteristic of the oligomers derived from isobutylene. Typical

peaks were as follows: *m/z* 43, 57, 71, 85. Comparison of these spectra with those of reference spectra in the spectrum library showed a perfect fit. A similar gc/ms investigation of the reaction mixtures of **4n** with **5** led to the same result.

Phenyl 3-methylbut-2-enoate (6a) mp 30-31 °C (lit.,[19] mp 30.5 °C) ^{1}H-Nmr: 1.97 (3H, d, J = 1.5 Hz, CH_3), 2.22 (3H, d, J = 1.5 Hz, CH_3), 5.93 (1H, m, C*H*), 7.05-7.45 (5H, m, Ar-*H*); ms (m/z): 176 (M^+, 3%), 94 (3), 83 (100), 65 (5), 55 (32).

2'-Hydroxyphenyl 3-methylbut-2-enoate (6b) oil. ^{1}H-Nmr: 1.95 (3H, d, J = 1.5 Hz, CH_3), 2.21 (3H, d, J = 1.5 Hz, CH_3), 5.92 (1H, m, C*H*), 6.80-7.45 (4H, m, Ar-*H*); ms (m/z): 192 (M^+, 2%), 110 (2), 83 (100), 55 (30); Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.80; H, 6.12.

Pyrocatechol *bis*-(3-methylbut-2-enoate) (6b') oil. ^{1}H-Nmr: 1.98 (6H, d, J = 1.5 Hz, CH_3), 2.20 (6H, d, J = 1.5 Hz, CH_3), 5.88 (2H, m, C*H*), 7.20 (4H, m, Ar-*H*); ms (m/z): 274 (M^+, 4%), 192 (12), 83 (100), 55 (43); Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.16; H, 6.50.

4'-Hydroxyphenyl 3-methylbut-2-enoate (6d) mp 111-113 °C (methanol). ^{1}H-Nmr: 1.98 (3H, d, J = 1.5 Hz, CH_3), 2.23 (3H, d, J = 1.5 Hz, CH_3), 4.06 (1H, br s, O*H*), 5.90 (1H, m, C*H*), 6.73 (2H, m, Ar-*H*), 6.91 (2H, m, Ar-*H*); ms (m/z): 192 (M^+, 3%), 110 (17), 83 (100), 55 (47); Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.95; H, 6.11.

2'-Methylphenyl 3-methylbut-2-enoate (6e) oil. ^{1}H-Nmr: 1.97 (3H, d, J = 1.5 Hz, CH_3), 2.18 (3H, s, CH_3), 2 22 (3H, d, J = 1.5 Hz, CH_3), 5.95 (1H, m, C*H*), 6.96-7 46 (4H, m, Ar-*H*); ms (m/z): 190 (M^+, 3%), 108 (6), 83 (100), 55 (34); Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.86; H, 7.18.

3'-Methylphenyl 3-methylbut-2-enoate (6f) oil. ^{1}H-Nmr: 1.96 (3H, d, J = 1.5 Hz, CH_3), 2.22 (3H, d, J = 1.5 Hz, CH_3), 2.34 (3H, s, CH_3), 5.90 (1H, m, C*H*), 6.85-7.30 (4H, m, Ar-*H*); ms (m/z): 190 (M^+, 3%), 108 (6), 83 (100), 55 (35); Anal. Calcd for $C_{12}H_{14}O_2$: C, 75 76; H, 7.41. Found: C, 75.90; H, 7.28.

4'-Methylphenyl 3-methylbut-2-enoate (6g) oil. ^{1}H-Nmr: 1.95 (3H, d, J = 1.5 Hz, CH_3), 2.21 (3H, d, J = 1.5 Hz, CH_3), 2.32 (3H, s, CH_3), 5.89 (1H, m, C*H*), 6.98 (2H, m, Ar-*H*), 7.16 (2H, m, Ar-*H*); ms (m/z): 190 (M^+, 3%), 108 (8), 83 (100), 55 (28); Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.80; H, 7.25.

2'-Methoxyphenyl 3-methylbut-2-enoate (6h) mp 40-41 °C (petroleum ether) (lit.,[9] mp 40-41 °C).

3'-Methoxyphenyl 3-methylbut-2-enoate (6i) oil (lit.,[9] bp oil).

4'-Methoxyphenyl 3-methylbut-2-enoate (6j) mp 61-62 °C (methanol) (lit.,[9] mp 59-60 °C).

2'-Chlorophenyl 3-methylbut-2-enoate (6k) oil. ^{1}H-Nmr: 2.00 (3H, d, J = 1.5 Hz, C*H*$_3$), 2.24 (3H, d, J = 1.5 Hz, C*H*$_3$), 5.99 (1H, m, C*H*), 7.10-7.48 (4H, m, Ar-*H*); ms (m/z): 210 (M^+, 1%), 128 (2), 83 (100), 55 (35); Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.71; H, 5.26. Found: C, 62.89; H, 5.11.

3'-Chlorophenyl 3-methylbut-2-enoate (6l) oil. ^{1}H-Nmr: 1.98 (3H, d, J = 1.5 Hz, C*H*$_3$), 2.22 (3H, d, J = 1.5 Hz, C*H*$_3$), 5.90 (1H, m, C*H*), 6.96-7.36 (4H, m, Ar-*H*); ms (m/z): 210 (M^+, 1%), 128 (2), 83 (100), 55 (37); Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.71; H, 5.26. Found: C, 62.93; H, 5.20.

4'-Chlorophenyl 3-methylbut-2-enoate (6m) oil. ^{1}H-Nmr: 1.98 (3H, d, J = 1.5 Hz, C*H*$_3$), 2.22 (3H, d, J = 1.5 Hz, C*H*$_3$), 5.89 (1H, m, C*H*), 7.04 (2H, m, Ar-*H*), 7.34 (2H, m, Ar-*H*); ms (m/z): 210 (M^+, 1%), 128 (2), 83 (100), 55 (38); Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.71; H, 5.26. Found: C, 62.77; H, 5.13.

2',4'-Di-*tert*-butyl-5'-hydroxyphenyl 3-methylbut-2-enoate (6n) oil (lit.,[18] bp oil).

2',4'-Di-*tert*-butylresorcinol *bis*-(3-methylbut-2-enoate) (6n') mp 127-129 °C (methanol). ^{1}H-Nmr: 1.33 (18H, s, *t*-Bu-Hs), 1.98 (6H, d, J = 1.5 Hz, C*H*$_3$), 2.22 (6H, d, J = 1.5 Hz, C*H*$_3$), 5.91 (2H, m, C*H*), 6.79 (1H, s, Ar-*H*), 7.36 (1H, s, Ar-*H*); ms (m/z): 386 (M^+, 5%), 304 (41), 222 (14), 83 (100); Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.58; H, 8.87. Found: C, 74.75; H, 8.64.

Phenyl 3-chloro-3-methylbutanoate (7a) oil. ^{1}H-Nmr: 1.78 (6H, s, C*H*$_3$), 3.01 (2H, s, C*H*$_2$), 7.04-7.42 (5H, m, Ar-*H*); ms (m/z): 212 (M^+, 1%), 176 (3), 119 (8), 94 (61), 83 (100), 55 (42); Anal. Calcd for $C_{11}H_{13}O_2Cl$: C, 62.12; H, 6.16. Found: C, 62.20; H, 6.11.

2'-Hydroxyphenyl 3-chloro-3-methylbutanoate (7b) oil. ^{1}H-Nmr: 1.80 (6H, s, C*H*$_3$), 3.05 (2H, s, C*H*$_2$), 6.81-7.15 (4H, m, Ar-*H*); ms (m/z): 228 (M^+, 2%), 192 (3), 119 (8), 110 (51), 83 (100), 55 (56); Anal. Calcd for $C_{11}H_{13}O_3Cl$: C, 57.77; H, 5.72. Found: C, 57.86; H, 5.63.

4'-Hydroxyphenyl 3-chloro-3-methylbutanoate (7d) oil. ^{1}H-Nmr: 1.81 (6H, s, C*H*$_3$), 3.04 (2H, s, C*H*$_2$), 6.76 (2H, m, Ar-*H*), 6.94 (2H, m, Ar-*H*); ms (m/z). 228 (M^+, 2%), 192 (4), 119 (5), 110 (55), 83 (100), 55 (44); Anal. Calcd for $C_{11}H_{13}O_3Cl$: C, 57.77; H, 5.72. Found: C, 57.82; H, 5.60.

2'-Methylphenyl 3-chloro-3-methylbutanoate (7e) oil. ^{1}H-Nmr: 1.81 (6H, s, C*H*$_3$), 2.20 (3H, s, C*H*$_3$), 3.08 (2H, s, C*H*$_2$), 7.10-7.25 (4H, m, Ar-*H*); ms (m/z): 226 (M^+, 1%), 190 (6), 119 (5), 108 (67), 83 (100), 55 (39); Anal. Calcd for $C_{12}H_{15}O_2Cl$: C, 63.57; H, 6.66. Found: C, 63.60; H, 6.60.

3'-Methylphenyl 3-chloro-3-methylbutanoate (7f) oil. ^{1}H-Nmr: 1.81 (6H, s, C*H*$_3$), 2.35 (3H, s, C*H*$_3$), 3.04 (2H, s, C*H*$_2$), 6.95-7.20 (4H, m, Ar-*H*); ms (m/z): 226 (M^+, 1%), 190 (8), 119 (3), 108 (78), 83 (100),

55 (40); Anal. Calcd for $C_{12}H_{15}O_2Cl$: C, 63.57; H, 6.66. Found: C, 63.65; H, 6.59.

4'-Methylphenyl 3-chloro-3-methylbutanoate (7g) oil. ^{1}H-Nmr: 1.81 (6H, s, CH_3), 2.34 (3H, s, CH_3), 3 05 (2H, s, CH_2), 6.98 (2H, m, Ar-*H*), 7.18 (2H, m, Ar-*H*); ms (m/z): 226 (M^+, 1%), 190 (8), 119 (6), 108 (67), 83 (100), 55 (44); Anal. Calcd for $C_{12}H_{15}O_2Cl$: C, 63.57; H, 6.66. Found: C, 63.62; H, 6.58.

2'-Methoxyphenyl 3-chloro-3-methylbutanoate (7h) oil. ^{1}H-Nmr: 1.81 (6H, s, CH_3), 3.10 (2H, s, CH_2), 3.80 (3H, s, CH_3O), 6.82-7.25 (4H, m, Ar-*H*); ms (m/z): 242 (M^+, 3%), 206 (5), 119 (5), 124 (100), 83 (60), 55 (45); Anal. Calcd for $C_{12}H_{15}O_3Cl$: C, 59.38; H, 6.23. Found: C, 59.42; H, 6.20.

4'-Methoxyphenyl 3-chloro-3-methylbutanoate (7j) oil. ^{1}H-Nmr: 1.80 (6H, s, CH_3), 3.03 (2H, s, CH_2), 3.79 (3H, s, CH_3O), 6.88 (2H, m, Ar-*H*), 7.03 (2H, m, Ar-*H*); ms (m/z): 242 (M^+, 3%), 206 (12), 119 (3), 124 (100), 83 (40), 55 (28); Anal. Calcd for $C_{12}H_{15}O_3Cl$: C, 59.38; H, 6.23. Found: C, 59.50; H, 6.19.

2'-Chlorophenyl 3-chloro-3-methylbutanoate (7k) oil. ^{1}H-Nmr: 1.84 (6H, s, CH_3), 3.14 (2H, s, CH_2), 7.10-7.48 (4H, m, Ar-*H*); ms (m/z): 246 (M^+, 1%), 210 (1), 119 (21), 128 (42), 83 (100), 55 (38); Anal. Calcd for $C_{11}H_{12}O_2Cl_2$: C, 53.45; H, 4.89. Found: C, 53.60; H, 4.80.

3'-Chlorophenyl 3-chloro-3-methylbutanoate (7l) oil. ^{1}H-Nmr: 1.81 (6H, s, CH_3), 3.04 (2H, s, CH_2), 6.98-7.38 (4H, m, Ar-*H*); ms (m/z): 246 (M^+, 1%), 210 (1), 119 (30), 128 (40), 83 (100), 55 (60); Anal. Calcd for $C_{11}H_{12}O_2Cl_2$: C, 53.45; H, 4.89 Found: C, 53.62; H, 4.81. .

4'-Chlorophenyl 3-chloro-3-methylbutanoate (7m) oil. ^{1}H-Nmr: 1.80 (6H, s, CH_3), 3.03 (2H, s, CH_2), 7.04 (2H, m, Ar-*H*), 7.34 (2H, m, Ar-*H*); ms (m/z): 246 (M^+, 1%), 210 (1), 119 (22), 128 (42), 83 (100), 55 (58); Anal. Calcd for $C_{11}H_{12}O_2Cl_2$: C, 53 45; H, 4.89. Found: C, 53.61; H, 4.80.

1-(2,4-Dihydroxyphenyl)-3-methyl-2-buten-1-one (8c) mp 76-78 °C (50% ethanol) [lit.,[16] mp 77-78 °C (50% ethanol)].

1-(2-Hydroxy-3-methoxyphenyl)-3-methyl-2-buten-1-one (8h) mp 110-111 °C (ethanol) (lit.,[9] mp 110.5-111 °C).

1-(2-Hydroxy-4-methoxyphenyl)-3-methyl-2-buten-1-one (8i) mp 55-56 °C (methanol) (lit.,[9] mp no data). ^{1}H-Nmr: 2.02 (3H, d, J = 1.5 Hz, CH_3), 2.20 (3H, d, J = 1 5 Hz, CH_3), 3.85 (3H, s, CH_3O), 6.22 (2H, m, Ar-*H*), 6.69 (1H, m, C*H*), 7.70 (1H, m, Ar-*H*), 13.36 (1H, s, O*H*); ms (m/z): 206 (M^+, 8%), 191 (100), 151 (23), 108 (8), 95 (6), 83 (8), 69 (7), 55 (13).

1-(3-*tert*-Butyl-4,6-dihydroxyphenyl)-3-methyl-2-buten-1-one (8n) oil (lit.,[18] bp oil).

1-(4-Hydroxyphenyl)-3-methyl-2-buten-1-one (9a) mp 100-101 °C (ethanol). ^{1}H-Nmr: 2.00 (3H, d, J = 1.5 Hz, C*H*$_3$), 2.18 (3H, d, J = 1.5 Hz, C*H*$_3$), 5.77 (1H, s, O*H*), 6.70 (1H, m, C*H*), 6.87 (2H, m, Ar-*H*), 7.88 (2H, m, Ar-*H*); ms (m/z): 176 (M^+, 35%), 175 (55), 161 (100); Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.02; H, 6.79. $C_{11}H_{12}O_2$: C, 74.97; H, 6.86.

1-(4-Hydroxy-3-methylphenyl)-3-methyl-2-buten-1-one (9e) mp 128-129 °C (methanol).^{1}H-Nmr: 2.00 (3H, d, J = 1.5 Hz, C*H*$_3$), 2.17 (3H, d, J = 1.5 Hz, C*H*$_3$), 2.28 (3H, s, C*H*$_3$), 5.63 (1H, s, O*H*), 6.70 (1H, m, C*H*), 6.81 (1H, d, J_1 = 8 Hz, Ar-*H*), 7.72 (1H, dd, J_1 = 8 Hz, J_2 = 2 Hz, Ar-*H*), 7.77 (1H, d, J_2 = 2 Hz, Ar-*H*); ms (m/z): 190 (M^+, 24%), 189 (26), 175 (100), 160 (16), 147 (18), 135 (48), 107 (13), 83 (27), 77 (38), 55 (30); Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.81; H, 7.39.

1-(4-Hydroxy-2-methylphenyl 3-methyl-2-buten-1-one (9f) mp 100-101 °C (ethanol). ^{1}H-Nmr : 1.97 (3H, d, J = 1.5 Hz, C*H*$_3$), 2.12 (3H, d, J = 1.5 Hz, C*H*$_3$), 2.46 (3H, s, C*H*$_3$), 6.00 (1H, s, O*H*), 6.45 (1H, m, C*H*), 6.68 (2H, m, Ar-*H*), 7.52 (1H, d, J = 9 Hz, Ar-*H*); ms (m/z): 190 (M^+, 12%), 189 (4), 175 (100), 160 (14), 147 (23), 135 (37), 107 (15), 83 (21), 77 (34), 55 (28); Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.88; H, 7.35. $C_{12}H_{14}O_2$: C, 75.76; H, 7.41.

3,4-Dihydro-4,4-dimethylcoumarin (10a) oil (lit.,[19] bp 107-109 °C$_{3mm}$). ^{1}H-Nmr: 1.36 (6H, s, C*H*$_3$), 2.64 (2H, s, C*H*$_2$), 7.02-7.36 (4H, m, Ar-*H*); ms (m/z): 176 (M^+, 48%), 161 (100), 134 (19), 133 (18), 119 (22), 115 (28), 105 (18), 91 (34), 65 (12), 51 (16).

3,4-Dihydro-4,4,8-trimethylcoumarin (10e) oil (lit.,[19] mp 29 °C). ^{1}H-Nmr: 1.36 (6H, s, C*H*$_3$), 2.32 (3H, s, C*H*$_3$), 2.62 (2H, s, C*H*$_2$), 6.98-7.20 (3H, m, Ar-*H*); ms (m/z): 190 (M^+, 55%), 175 (100), 148 (43), 133 (47), 115 (18), 105 (32), 91 (42), 77 (31), 65 (15), 51 (22).

3,4-Dihydro-4,4,7-trimethylcoumarin (10f) mp 59-60 °C (*n*-hexane) [lit.,[19] mp 59.5 °C (petroleum ether)]. ^{1}H-Nmr: 1.34 (6H, s, C*H*$_3$), 2.35 (3H, s, C*H*$_3$), 2.62 (2H, s, C*H*$_2$), 6.85-7.24 (3H, m, Ar-*H*); ms (m/z): 190 (M^+, 36%), 175 (100), 148 (12), 133 (16), 116 (11), 105 (13), 91 (23), 77 (17).

3,4-Dihydro-4,4,6-trimethylcoumarin (10g) mp 64-65 °C (*n*-hexane) [lit.,[19] mp 64.5 °C (petroleum ether)]. ^{1}H-Nmr: 1.34 (6H, s, C*H*$_3$), 2.34 (3H, s, C*H*$_3$), 2.61 (2H, s, C*H*$_2$), 6.94 (1H, d, J=8Hz, Ar-*H*), 7.01-7.12 (2H, m, Ar-*H*); ms (m/z): 190 (M^+, 65%), 175 (100), 148 (48), 133 (37), 115 (12), 105 (26), 91 (33).

2,2-Dimethyl-4-chromanone (1a) mp 89-90 °C (ethanol) (lit.,[20] mp 88-90 °C).^{1}H-Nmr: 1.48 (6H, s, C*H*$_3$), 2.64 (2H, s, C*H*$_2$), 6.96 (2H, m, Ar-*H*), 7.47 (1H, m, Ar-*H*), 7.86 (1H, dd, J_1 = 2.0 Hz, J_2 = 10 Hz, Ar-*H*); ms (m/z): 176 (M^+, 40%), 161 (100), 121 (72), 120 (69), 92 (82), 63 (36).

7-Hydroxy-2,2-dimethyl-4-chromanone (1c) mp 171-172 °C (50% ethanol) [lit.,[16] mp 171-172 °C (50% ethanol)].

2,2,8-Trimethyl-4-chromanone (1e) oil (lit.,[19] bp oil). ^{1}H-Nmr: 1.46 (6H, s, C*H*$_3$), 2.22 (3H, s, C*H*$_3$), 2.70 (2H, s, C*H*$_2$), 6.86 (1H, m, Ar-*H*), 7.31 (1H, m, Ar-*H*), 7.70 (1H, m, Ar-*H*); ms (m/z): 190 (M^+, 52%), 175 (100), 135 (68), 134 (64), 106 (83), 78 (18), 77 (25), 51 (17).

2,2,7-Trimethyl-4-chromanone (1f) mp 69-70 °C (ethanol) (lit.,[20] mp 68-70 °C).^{1}H-Nmr: 1.40 (6H, s, C*H*$_3$), 2.34 (3H, s, C*H*$_3$), 2.68 (2H, s, C*H*$_2$), 6.77 (2H, m, Ar-*H*), 7.74 (1H, d, J = 8 Hz, Ar-*H*); ms (m/z): 190 (M^+, 38%), 175 (100), 135 (72), 134 (64), 106 (34), 78 (42), 77 (41), 51 (27).

2,2,6-Trimethyl-4-chromanone (1g) oil (lit.,[21] bp oil). ^{1}H-Nmr: 1.44 (6H, s, C*H*$_3$), 2.29 (3H, s, C*H*$_3$), 2.70 (2H, s, C*H*$_2$), 6.83 (1H, d, J_1 = 8.5 Hz, Ar-*H*), 7.28 (1H, dd, J_1 = 8.5 Hz, J_2 = 2Hz, Ar-*H*), 7.65 (1H, d, J_2 = 2 Hz, Ar-*H*); ms (m/z): 190 (M^+, 38%), 175 (100), 135 (64), 134 (60), 106 (20), 105 (15), 78 (20), 77 (25), 52 (12), 51 (17).

2,2-Dimethyl-7-methoxy-4-chromanone (1i) mp 78-79 °C (ethanol) [lit.,[16] mp 77-79 °C (ethanol)].

6-*tert*-Butyl-7-hydroxy-2,2-dimethyl-4-chromanone (1n) mp 216-217 °C (50% ethanol) [lit.,[18] mp 216-217 °C (50% ethanol)].

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