# CHROMENES AND CHROMANONES. PART IV. [1]

# THE BIRCH REDUCTION OF 2,2-DIMETHYL-4-CHROMANONE AND ITS 7-SUBSTITUTED ANALOGUES

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Abstract - 2,2-Dimethyl-4-chromanone (**1a**), 2,2,7-trimethyl-4-chromanone (**1b**) and 7-methoxy-2,2-dimethyl-4-chromanone (**1c**) have been reduced by sodium or lithium in liquid ammonia with the presence or without of proton donor. The bicyclic or phenolic products were obtained. Products with reduced benzene ring only were also observed. The possible mechanisms of reductions are considered.

## INTRODUCTION

Continuing our studies on the Birch reduction of compounds with chromane system[2-3] we have taken 3- and 4-chromanones as substrates. We expected to obtain some bicyclic oxa-compounds which could be considered as nonaromatic analogues of precocenes. 4-Chromanone is interesting as a substrate in the studies on the Birch reduction mechanism because it possess one activating (carbonyl group) and one deactivating group (alkoxy group) for this reduction. Literature studies did not afford any information concerning the Birch reduction of these compounds. We found only some data[4,5] about reduction of $\alpha$-tetralone which can be considered as structurally related system only. In both cited works the reductions of $\alpha$-tetralone were carried out without additional source of protons.

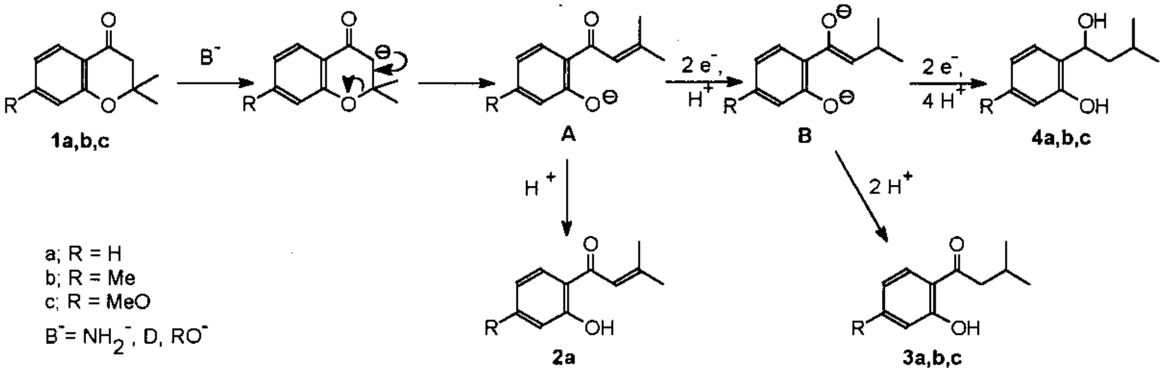
In this paper we present the results of the Birch reduction of 2,2-dimethyl-4-chromanone (**1a**) and its 7-methyl (**1b**) and 7-methoxy (**1c**) substituted analogues. 2,2-Dimethyl-4-chromanone (**1a**) was obtained from 2-hydroxyacetophenone according to procedure described by Kabbe[6] in 61% yield. 2,2,7-Trimethyl-4-chromanone (**1b**) and 7-methoxy-2,2-dimethyl-4-chromanone (**1c**) were synthesized[7,8] from *m*-cresol and resorcinol, respectively, in 40% and 50% yields.

## RESULTS AND DISCUSSION

Reductions of chromanones (**1a-c**) were carried out in two temperatures (-33 °C and -78 °C) and in the presence of alcohol (methyl or ethyl alcohol) as an additional source of protons or without alcohol. Sodium or lithium were used as a source of electrons. The results of experiments carried out are presented in Table.

The mixture of products was obtained in the each experiment. Composition of these mixtures strongly depended on the reaction conditions. The presence or absence of alcohol in the reaction medium had the most visible influence on the kind of products which were formed.

When the reaction was carried out without alcohol as an additional source of protons (Entries 1-6 and 16) the phenolic products dominated (50-70%) in product mixtures. Phenolic compounds (**2a**, **3a-c**, and **4a-c**) are formed as a result of the generation of keto-anion (**A**) from chromanone in the process of proton detachment by base, followed by C-O bond cleavage (Scheme 1).



Scheme 1

The proton abstraction can be caused by the amide anion ($NH_2^-$) as well as by dianion (**D**) formed by two electrons addition to chromanone in the early steps of its reduction process (Scheme 2). In the case of the reduction in the presence of small amount of alcohol the alkoxy-anion ($RO^-$) can also work as a base in this process. The isolation, in the separate experiment, of ketone (**2a**) as a product of action of sodium amide on chromanone (**1a**) in liquid ammonia at -78°C confirmed the suggestion that keto-anion (**A**) is formed under the basic medium of the Birch reduction. Keto-anion (**A**) is reduced through the dianion (**B**) to the keto and hydroxy-

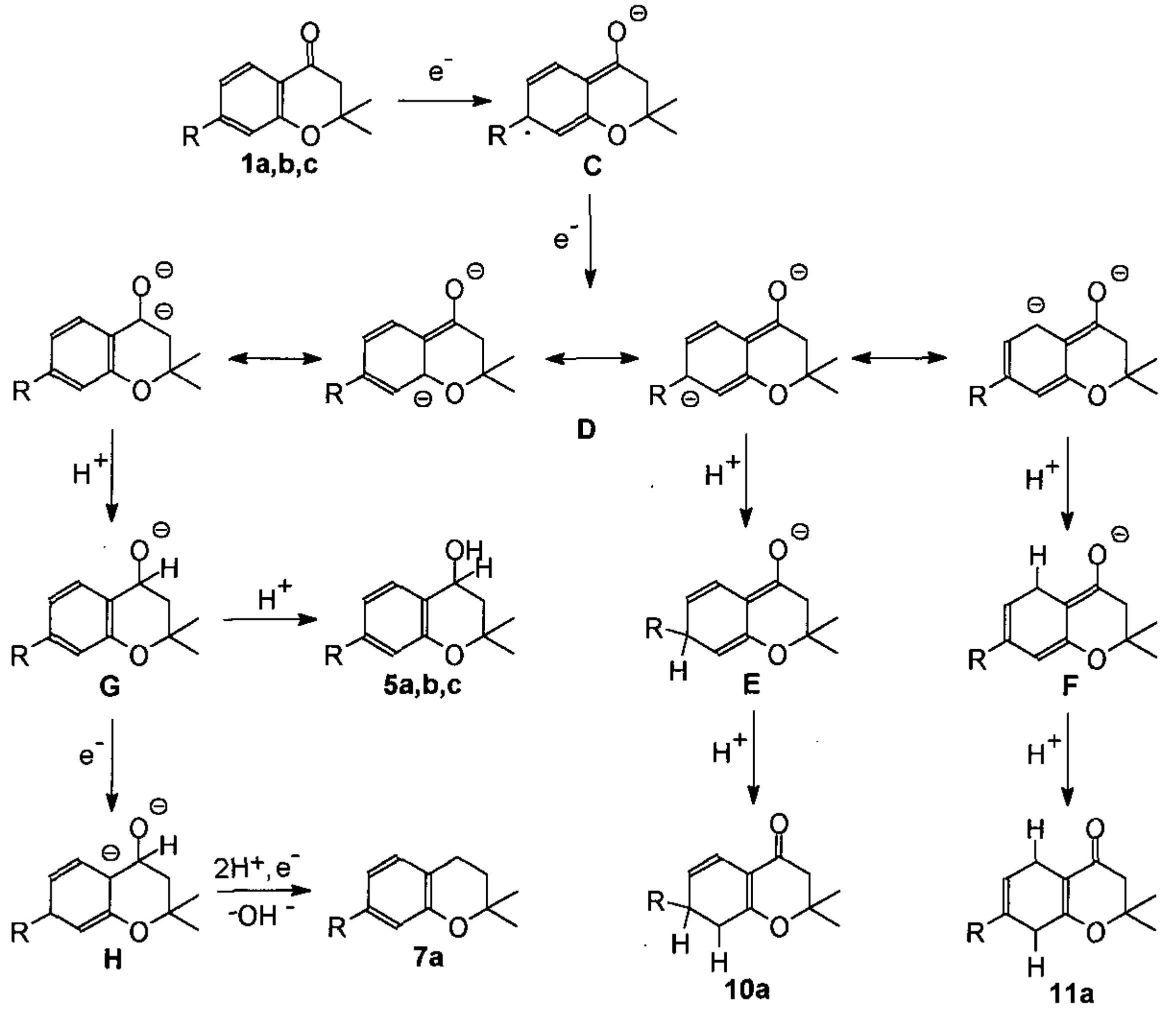
Table. Compositions (in % according to GC) of the product mixtures

| Entry | Metal | Alcohol | Temp | Time | R | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **8** | **9** | **10** | **10** | **11** | **12** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | (eq) | (eq) | (°C) | (min) |  | **a-c** | **a-c** | **a-c** | **a-c** | **a-c** | **a-c** | **a-c** | **a** | **b-c** | **a** | **a** | **b-c** | **a-c** | **a-c** |
| 1. | Na (2,1) | - | -33 | 5 | H | 3 | 15 | 44 | 17 | 11 | - | - | - | - | - | 7 | - | 3 | - |
| 2. | Na (2.1) | - | -78 | 15 | H | 23 | 1 | 46 | 10 | 13 | - | - | - | - | - | 6 | - | 1 | - |
| 3. | Li (2.1) | - | -78 | 15 | H | 17 | - | 48 | 4 | 14 | - | 3 | - | - | - | 13 | - | 1 | - |
| 4. | Li (4.1) | - | -33 | 60 | H | - | - | 45 | 27 | 4 | - | 14 | - | - | - | 9 | - | 1 | - |
| 5. | Li (4.1) | - | -78 | 60 | H | - | - | 54 | 9 | 3 | - | 24 | - | - | - | 10 | - | - | - |
| 6. | Li (10) | - | -78 | 60 | H | - | - | 28 | 39 | 11 | - | 10 | - | - | - | 12 | - | - | - |
| 7. | Li (2.1) | MeOH (70) | -78 | 5 | H | 34 | - | - | - | 16 | - | 14 | 1 | - | - | 35 | - | - | - |
| 8. | Li (10) | MeOH (10) | -78 | 60 | H | - | - | 1 | 2 | 1 | - | - | 24 | - | 6 | 66 | - | - | - |
| 9. | Li (10) | MeOH (70) | -33 | 25 | H | 3 | - | - | 2 | - | - | 5 | 48 | - | 10 | 32 | - | - | - |
| 10. | Li (10) | MeOH (70) | -78 | 10 | H | 1 | - | - | - | - | - | - | 45 | - | 10 | 44 | - | - | - |
| 11. | Na (10) | MeOH (70) | -78 | 25 | H | - | - | - | - | - | - | - | 63 | - | 13 | 24 | - | - | - |
| 12. | Na (10) | EtOH (70) | -78 | 30 | H | - | - | - | 5 | - | - | 8 | 67 | - | 5 | 15 | - | - | - |
| 13. | Na (10) | MeOH (70) | -78 | 15 | Me | - | - | - | - | 3 | 45 | - | - | 39 | - | - | 8 | - | 5 |
| 14. | Li (10) | MeOH (10) | -78 | 35 | Me | - | - | 10 | 9 | 2 | 9 | - | - | 30 | - | - | 27 | - | 13 |
| 15. | Li (10) | MeOH (70) | -78 | 10 | Me | - | - | - | 1 | 3 | 32 | - | - | 36 | - | - | 24 | - | 4 |
| 16. | Li (10) | - | -78 | 60 | MeO | - | - | 42 | 29 | 26 | - | - | - | - | - | 3 | - | - | - |
| 17. | Li (10) | MeOH (10) | -78 | 60 | MeO | - | - | 14 | 12 | 3 | 41 | - | 8 | 2 | 3 | 17 | - | - | - |
| 18. | Li (10) | MeOH (70) | -78 | 10 | MeO | - | - | - | - | 2 | 72 | - | 10 | 1 | 4 | 11 | - | - | - |
| 19. | Na (10) | MeOH (70) | -78 | 25 | MeO | - | - | - | - | 6 | 65 | - | 14 | 2 | 6 | 7 | - | - | - |

a, R=H; b, R=Me; c, R=MeO

phenols (**3a-c** and **4a-c**) respectively.

Among bicyclic products, formed in experiments without alcohol, we observed compounds with carbonyl group reduced: chromanols (**5a,c**), chromanes (**7a**) and products of the benzene ring reduction: ketones (**10a** and **11a**). No products with reduced both benzene ring and carbonyl group were identified. We did not observe the formation of any dimeric products as Marcinów and Rabideau[4] did. Plausible explanation of the formation of these products is given in the Scheme 2.

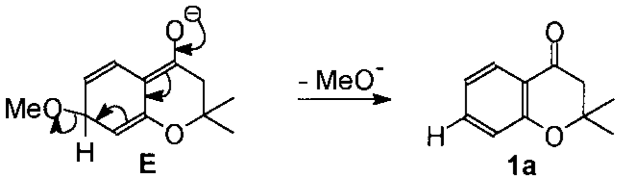


a, R = H; b, R = Me; c, R = MeO

Scheme 2

The radical anion (**C**), formed by the acceptation of one electron by chromanone, is a base not strong enough to abstract the proton from ammonia or substrate. Thus, it accepts the second electron to give dianion (**D**). The protonation of this dianion at C-7 or at C-5 leads to enolate anions (**E** or **F**) which after further protonation, during the qenching with aqueous $NH_4Cl$, are transformed into ketones (**10a** or **11a**) respectively.

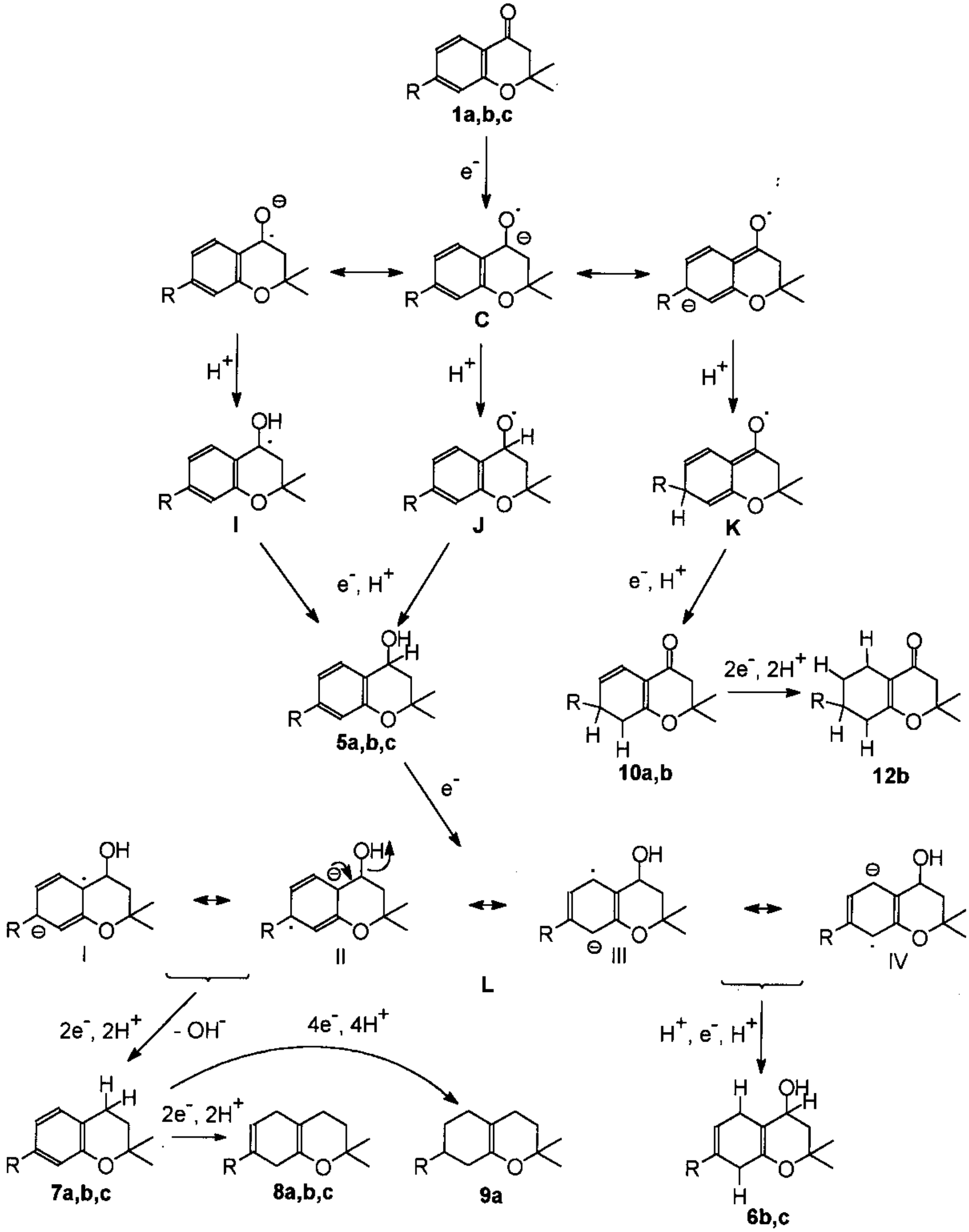
The presence of compounds (**8a**, **9a** and **10a**) in the product mixture of the reduction 7-methoxy-4-chromanone (**1c**) can be explained by demethoxylation of anion (**E**) to chromanone (**1a**) and its further reduction.



The protonation of dianion (**D**) at C-4 gives anion (**G**) which after acceptation, during the quenching, of the next proton undergoes into 4-chromanols (**5a-c**). Chromane (**7a**) can be formed from anion (**G**) through radical dianion (**H**) followed similar to Hall's mechanism of hydroxy group abstraction step.[5] Products (**5a-c** and **7a**), even if they are formed before the quenching, are resistant to further reduction in the condition without additional proton source.

The application of an alcohol as a source of protons has changed radically the ratio of phenolic and bicyclic products. Phenols were observed only in the experiments when the concentration of methyl or ethyl alcohol was relatively low (10 eq., Entries 8,14 and 17). In the experiments with 70 eq. of alcohol (Entries 10-13, 15, 18 and 19) bicyclic compounds were isolated as the only products of the chromanones reductions.

Interesting results afforded comparative analysis of the compositions of the product mixtures obtained from the reductions of chromanones (**1a**, **1b** and **1c**) carried out in the same conditions (Entries 10, 15 and 18). This analysis indicated that methoxy group promotes the reduction of benzene ring and the partially reduction of carbonyl group to hydroxy group. The quite large contribution of **7b** in the product mixture of the reduction of the 7-methyl analogue (**1b**) indicates that the methyl group at C-7 restricted the reduction of benzene ring and did not hinder the complete reduction of the carbonyl group. The explanation of the results obtained in the experiments with participation of alcohol as a source of protons is presented in Scheme 3. Alcohol delivers proton to radial anion (**C**) and this way transforms it to radicals (**I**, **J**) or to radical (**K**). Two first are then reduced to chromanols (**5a-c**) whereas last one to ketones


1a,b,c
e⁻
C
H⁺
I
J
K
e⁻, H⁺
e⁻, H⁺
5a,b,c
10a,b
2e⁻, 2H⁺
12b
e⁻
I
II
L
III
IV
2e⁻, 2H⁺
- OH⁻
4e⁻, 4H⁺
H⁺, e⁻, H⁺
7a,b,c
2e⁻, 2H⁺
8a,b,c
9a
6b,c
R
OH
O
H

Scheme 3

(**10a,b**) and to **12b**.

Further reduction of chromanols (**5a**-**c**) depends on the character of the group at C-7. When at C-7 is hydrogen, 4-chromanol (**5a**) is reduced to the chromane (**7a**) and next to ethers (**8a** or **9a**).[3] When methyl or methoxy group is present at C-7 position, chromanols (**5b** and **5c**) are reduced mostly to alcohols with partially reduced benzene ring (**6b** and **6c**) respectively. Such results can be explained by the stability of the radical anion (**L**) formed by electron acceptation by chromanols (**5a**-**c**).

The arrangement of double bonds in the structures I and II promotes the leaving of hydroxy group from the radical anion (**L**) and leads to chromane (**7a**). This pathway of the reduction of chromanols (**5a**-**c**) has occurred for radical anion (**L**) with hydrogen and, in less extent, with methyl group at C-7. In the case of radical anion (**L**) with electron-donating methoxy group at C-7, the structures I and II are not very probable. So, the reduction pathway of **5b** and **5c** leads, through structures III and IV of **L**, to alcohols (**6b** and **6c**).

## EXPERIMENTAL SECTION

$^1$H NMR spectra were recorded for solutions ($CCl_4$-$C_6D_6$, 7:1 or $CDCl_3$) with TMS as an internal standard, on a 80 MHz Tesla BS 587A spectrometer. IR spectra were determined with a SPECORD M80 infrared spectrophotometer. GC analyses were performed on a Hewlett Packard 5890 instrument using Ultra 1 (25 m × 0.32 mm) column. The compositions of product mixtures presented in Table were determinated by GC analyses. All reductions were carried out under an inert atmosphere of dry, oxygen free, nitrogen.

### Procedure for Metal-Ammonia Reduction

The metal was added in pieces for 5 min. to a solution of 2,2-dimethyl-4-chromanones (**1a-c**, 2 mmol in ammonia (50 ml)), containing THF (10 ml) and anhydrous proton donor (0-70 eq., see Table) at -78 °C. After 1 h or when blue color had disappeared, the reaction was quenched by adding aqueous saturated ammonium chloride solution. The ammonia was evaporated from the reaction mixture and saturated aqueous sodium chloride (10 ml) was added. Products were extracted with ethyl ether (3x10 ml). The combined ethereal solutions were washed with saturated aqueous sodium chloride (3x10 ml), and dried over anhydrous magnesium sulfate. Pure products were separated by column chromatography on 230-400 mesh silica gel 60 (Merck) with organic solvents which were mixtures of hexane and ethyl ether, ethyl acetate, THF or acetone. The yields were not optimized.

**2-(3-Methyl-1-oxa-2-butenyl)phenol** (**2a**): 11% yield (Entry 1); oil; $n_D^{20}$=1.5830; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.96, 2.17 (2s, 6H, C($CH_3$)$_2$), 6.40-7.70 (m, 5H, C=**CH**, $C_6$**H**$_4$), 12.65 (s, 1H, **OH**); IR(cm$^{-1}$): 3080(s,b), 1648(s), 1596(s), 764(s). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found C, 75.51; H, 7.08.

**2-(3-Methyl-1-oxabutyl)phenol** (**3a**): 13% (Entry 1); oil; $n_D^{20}$=1.5295; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 0.97 (d, J= 6 Hz, 6H, CH(C**H**$_3$)$_2$), 1.90-2.40 (m, 1H, C**H**($CH_3$)$_2$), 2.40-2.80 (m, 2H, C**H**$_2$), 6.50-7.70 (m, 4H, $C_6$**H**$_4$), 12.31 (s, 1H, O**H**); IR (cm$^{-1}$): 3080(s,b), 1648(s), 1592(m), 1384(m), 1372(m), 760(s). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H,7.92. Found C, 74.09; H, 7.82.

**2-(3-methyl-1-hydroxybutyl)phenol** (**4a**): 6% yield (Entry 1); oil; $n_D^{20}$=1.5185; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 0.75-1.00 (m, 6H, C($CH_3$)$_2$), 1.00-2.00 (m, 3H, C**H**$_2$C**H**), 2.55 (s, 1H, O**H**), 4.50-4.90 (m, 1H, C**H**OH), 6.50-7.20 (m, 4H, $C_6$**H**$_4$), 7.76 (s, 1H, O**H**); IR (cm$^{-1}$): 3356(s,b), 1596(m), 1384(m), 1372(m), 760(s). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found C, 73.18; H, 8.88.

**3,4-Dihydro-2,2-dimethyl-2*H*-1-benzopyran-4-ol** (**5a**): 10% yield (Entry 2); oil; $n_D^{20}$=1.5345; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.14, 1.28 (2s, 6H, C($CH_3$)$_2$), 1.52 (dd, J=13.5 Hz and 8.5 Hz, 1H, CH(OH)C**H**H), 1.83 (dd, J=13.5 Hz and 6.0 Hz, 1H, CH(OH)CH**H**), 2.98 (s, 1H, O**H**), 4.53 (dd, J=8.5 Hz and 6.0 Hz, 1H, C**H**(OH)CHH), 6.5-7.3 (m, 4H, $C_6$**H**$_4$); IR (cm$^{-1}$): 3384(s,b), 3052(w), 3028(w), 1620(m), 1592(m), 1128(s). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.53; H, 7.80.

**3,4-Dihydro-2,2-dimethyl-2*H*-1-benzopyran** (**7a**): 6% yield (Entry 5); oil; $n_D^{20}$=1.5240 (lit.,[9] 1.524).

**3,4,5,8-Tetrahydro-2,2-dimethyl-2*H*-1-benzopyran** (**8a**): 13% yield (Entry 10); oil; $n_D^{20}$=1.4930 (lit.,[2] 1.4950).

**3,4,5,6,7,8-Hexahydro-2,2-dimethyl-2*H*-1-benzopyran** (**9a**): 1% yield (Entry 10); oil; $n_D^{20}$=1.4800; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.28 (s, 6H, C($CH_3$)$_2$) 1.40-2.00 (m, 12 H, C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$, C**H**$_2$C**H**$_2$); IR (cm$^{-1}$): 1700(m), 1224(m), 1164(s). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found C, 79.87; H, 10.89.

**3,4,7,8-Tetrahydro-2,2-dimethyl-2*H*-1-benzopyran-4-one** (**10a**): 31% yield (Entry 10); oil; $n_D^{20}$=1.530; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.32 (s, 6H, C($CH_3$)$_2$), 2.10-2.40 (m, 6H, C**H**$_2$C**H**$_2$, COC**H**$_2$), 5.20-5.60, 6.20-6.50 (2m, 2H, C**H**=C**H**); IR (cm$^{-1}$): 3064(w), 1672(s), 1640(m), 1592(m), 1272(m). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found C, 74,27; H,8.13.

**3,4,5,8-Tetrahydro-2,2-dimethyl-2*H*-1-benzopyran-4-one (11a)**: 1% yield (Entry 1); solid; mp 33.5-37.5 °C; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.43 (s, 6H, $C(CH_3)_2$), 2.30-2.50 (m, 2H, $COCH_2$), 2.50-3.00 (m, 4H, $CH_2CH{=}CHCH_2$), 5.30-6.00 (m, 2H, CH=CH); IR (cm$^{-1}$): 3052(w), 1676(s), 1628(s). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found C, 74.42; H, 7.96.

**5-Methyl-2-(3-methyl-1-oxabutyl)phenol (3b)**: 4% yield (Entry 14); oil; $n_D^{20}$=1.5295; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 0.96 (d, J=6.5 Hz, 6H, $CH(CH_3)_2$), 2.25 (s, 3H, $C_6H_3CH_3$), 1.95-2.55 (m, 1H, $CH(CH_3)_2$), 2.66 (d, J=6.5 Hz, 2H, $CH_2$), 6.50-7.70 (m, 3H, $C_6H_3$), 12.37 (s, 1H, OH); IR (cm$^{-1}$): 3080(m,b), 1648(s), 1604(w), 1580(w), 1384(m), 1372(m), 800(s). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.79; H, 8.61.

**5-Methyl-2-(3-methyl-1-hydroxybutyl)phenol (4b)**: 5% yield (Entry 14); solid; mp 86-88 °C; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 0.75-1.00 (m, 6H, $CH(CH_3)_2$), 1.00-2.00 (m, 3H, $CH_2CH(CH_3)_2$), 2.02 (s, 1H, CHOH), 2.23 (s, 3H, $C_6H_3CH_3$), 4.50-4.90 (m, 1H, CHOH), 6.40-6.80 (m, 3H, $C_6H_3$), 7.12 (s,1H, $C_6H_3OH$); IR (cm$^{-1}$, nujol): 3400(s, b), 1624(m), 1604(w), 1384(m), 1372(m). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.40; H, 9.54.

**3,4-Dihydro-2,2,7-trimethyl-2*H*-1-benzopyran-4-ol (5b)**: 95% yield (it was obtained by $LiAlH_4$/$Et_2O$ reduction of **1b**); oil; $n_D^{20}$=1.5170; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.22, 1.35 (2s, 6H, $C(CH_3)_2$), 1.65 (dd, J=13.5 Hz and J=8.5 Hz, 1H, CH(OH)CHH), 1.87 (s, 1H, OH), 1.94 (dd, J=13.5 and J=6.0 Hz, 1H, CH(OH)CHH), 2.24 (s, 3H, $C_6H_3CH_3$), 4.58 (dd, J=8.5 Hz and J=6.0 Hz, 1H, CH(OH)CHH), 6.50-7.10 (m, 3H, $C_6H_3$); IR (cm$^{-1}$): 3368(s,b), 3050(w), 1632(m), 1584(m), 1128(s). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.24; H, 8.63.

**3,4,5,8-Tetrahydro-2,2,7-trimethyl-2*H*-1-benzopyran-4-ol (6b)**: 27% yield (Entry 15); oil; $n_D^{20}$=1.4970; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.18, 1.26 (2s, 6H, $C(CH_3)_2$), 1.65 (s, 3H, $C{=}C{-}CH_3$), 1.50-2.80 (m, 7H, $CHCH_2$, $CH_2CH{=}C(CH_3)CH_2$, OH), 3.75-4.10 (m, 1H, $CHCH_2$), 5.20-5.60 (m, 1H, $CH{=}C(CH_3)$); IR (cm$^{-1}$): 3400(s, b), 3080(w), 1716(s), 1700(m), 1160(s). Anal. Calcd for $C_{12}H_{18}O_2$: C,74.19; H,9.34. Found: C,74.04; H,9.50.

**3,4,5,8-Tetrahydro-2,2,7-trimethyl-2*H*-1-benzopyran (8b)**: 22% yield (Entry 15); oil; $n_D^{20}$= 1.4920; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.18 (s, 6H, $C(CH_3)_2$), 1.65 (s, 3H, $C{=}C{-}CH_3$), 1.35-2.10 (m, 4H, $CH_2CH_2$), 2.30-2.80 (m, 4H, $CH_2CH{=}C(CH_3)CH_2$), 5.20-5.65 (m, 1H, $CH{=}C{-}CH_3$); IR (cm$^{-1}$): 3050(w), 1720(s), 1688(m), 1244(m), 1164(s). Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H,10.19. Found: C, 81.54; H, 10.03.

**3,4,7,8-Tetrahydro-2,2,7-trimethyl-2*H*-1-benzopyran-4-one (10b)**: 15% yield (Entry 15);

solid; mp 41-42 °C; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.02 (d, J=6.5 Hz, 3H, CHC**H**$_3$), 1.31, 1.33 (2s, 6H, C(C**H**$_3$)$_2$), 1.90-2.75 (m, 5H, C**H**(CH$_3$)C**H**$_2$, COC**H**$_2$), 5.15-5.50, 6.30-6.60 (2m, 2H, C**H**=C**H**); IR (cm$^{-1}$, nujol): 1664(s), 1640(m), 1588(s). Anal. Calcd for $C_{12}H_{16}O_2$: C,74.97; H,8.39. Found: C,75.30; H,8.57.

**3,4,5,6,7,8-Heksahydro-2,2,7-trimethyl-2*H*-1-benzopyran-4-one** (**12b**): 3% yield (Entry 15); solid; mp 29-32 °C; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 0.97 (d, J=6 Hz, 3H, CHC**H**$_3$), 1.00-2.60 (m, 9H, C**H**$_2$C**H**(CH$_3$)C**H**$_2$, COC**H**$_2$), 1.28, 1.32 (2s, 6H, C(C**H**$_3$)$_2$); IR (cm$^{-1}$, nujol): 1676(s), 1628(s). Anal. Calcd for $C_{12}H_{18}O_2$: C,74.19; H,9.34. Found: C,73.91; H,9.21.

**5-Methoxy-2-(3-methyl-1-oxabutyl)phenol** (**3c**): 31% yield (Entry 16); oil; $n_D^{20}$= 1.5475; $^1$H NMR ($CDCl_3$) δ: 0.95 (d, J=6 Hz, CH(C**H**$_3$)$_2$), 2.00-2.55 (m, 1H, C**H**(CH$_3$)$_2$), 2.75 (d, J=7 Hz, 2H, C**H**$_2$), 3.80 (s, 3H, OC**H**$_3$), 6.30-7.80 (m, 3H, C$_6$**H**$_3$), 13.00 (s, 1H, OH); IR (cm$^{-1}$): 3080 (m, b), 1640(s,b), 840(s), 800(s). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C,68.93; H, 7.70.

**5-Methoxy-2-(3-methyl-1-hydroxybutyl)phenol** (**4c**): 20% yield (Entry 16); solid; mp 71-72 °C; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 0.65-1.00 (m, 6H, CH(C**H**$_3$)$_2$), 1.00-2.00 (m, 3H, C**H**$_2$C**H**), 2.60-3.35 (m, 1H, O**H**), 3.35 (s, 3H, OC**H**$_3$), 4.35-4.80 (m, 1H, C**H**OH), 6.00-6.80 (m, 3H, C$_6$**H**$_3$), 7.96 (s, 1H, OH); IR (cm$^{-1}$, nujol): 3460(s), 3200(s,b), 1628(s), 1608(s), 1532(s), 1384(m), 1372(m). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.10; H, 8.62.

**3,4-Dihydro-7-methoxy-2,2-dimethyl-2*H*-1-benzopyran-4-ol** (**5c**); 23% yield (Entry 16); oil; $n_D^{20}$=1.5330; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.18, 1.30 (2s, 6H, C(C**H**$_3$)$_2$), 1.30-2.15 (m, 3H, CH(O**H**)C**HH**), 3.59 (s, 3H, OC**H**$_3$), 4.53 (m, 1H, C**H**(OH)CHH), 6.00-7.30 (m, 3H, C$_6$**H**$_3$); IR (cm$^{-1}$): 3400(s,b), 1628(s), 1592(m), 1164(s). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 68.91; H, 7.67.

**3,4,5,8-Tetrahydro-7-methoxy-2,2-dimethyl-2*H*-1-benzopyran-4-ol** (**6c**): 41% yield (Entry 19); oil; $n_D^{20}$= 1.5110; $^1$H NMR ($CCl_4$:$C_6D_6$) δ: 1.14, 1.22 (2s, 6H, C(C**H**$_3$)$_2$), 1.40-2.10 (m, 2H, CH(OH)C**H**$_2$), 2.35-2.75 (m, 4H, C**H**$_2$CH=C(OCH$_3$)C**H**$_2$), 3.41 (s, 3H, OC**H**$_3$), 3.70-4.15 (m, 1H, C**H**(OH)CH$_2$), 4.25-4.70 (m, 1H, C**H**=C(OCH$_3$)); IR (cm$^{-1}$): 3380(s,b), 3060(w), 1712(s), 1692(m), 1252(s), 1212(s), 1164(s), 1148(s). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.27; H, 8.59.

**3,4,5,8-Tetrahydro-7-methoxy-2,2-dimethyl-2*H*-1-benzopyran** (**8c**): 1% yield (Entry 19); oil; $n_D^{20}$=1.4915 (lit.,[3] 1.4905)

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## REFERENCES

1. Part III. M. Anioł, B. Gabryś, and C. Wawrzeńczyk, „Insects. Chemical, Physiological and Environmental Aspects", Editor: Danuta Konopińska, University of Wrocław Press, 1995, 271-275.
2. M. Anioł, P. Łusiak, and C. Wawrzeńczyk, Heterocycles, 1994, **38**, 991.
3. M. Anioł and C. Wawrzeńczyk, Heterocycles, 1994, **38**, 2655.
4. Z. Marcinów and P. W. Rabideau, J. Org. Chem., 1988, **53**, 2117.
5. S. S. Hall, S. D. Lipsky, F. J. Mc Enroe, and A. P. Bortels, J. Org. Chem., 1971, **36**, 2588.
6. H. J. Kabbe, Synthesis, 1978, 886.
7. P. Sebok, J. Jeko, T. Timar, and J. C. Jaszberenyj, Tetrahedron Lett., 1992, **33**, 2791.
8. T. Timar and J. C. Jaszberenyj, J. Heterocycl. Chem., 1988, **25**, 871.
9. A. R. Bader and W. C. Bean, J. Am. Chem. Soc., 1958, **80**, 3073.

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