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1-8*H*-PYRANO[3,2-*g*]BENZOXAZOL-8-ONES FROM 7-METHOXYIMINO-4-METHYLCHROMENE-2,8-DIONE

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Abstract: *7-Methoxyimino-4-methylchromene-2,8-dione* ***3****, easily prepared from the quinone* ***1*** *reacts thermally with methylaromatics* ***5(a-g)****, benzyl derivatives* ***13(a-c)****, halo derivatives* ***14(a-c)*** *to give mainly oxazolocoumarins. Products* ***8(a-d)*** *are obtained from* ***5(a-d)****,* ***13(a-c)****. Compound* ***9*** *is obtained from* ***5(a-c)*** *and* ***13(a-c)****, compounds* ***15(a-c)*** *are obtained from* ***14(a-c)****, the aminophenol* ***10*** *and coumarin* ***16*** *are obtained from* ***5f*** *and* ***14c*** *respectively, while coumarin* ***12*** *is obtained from* ***5g****. The reaction of* ***3*** *with N-methylaniline and N,N-dimethylbenzylamine gives compound* ***10*** *and* ***8a*** *respectively.*

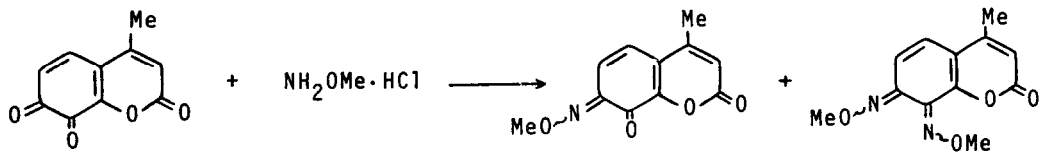
Sakachi and Ichikawa[1] reported in 1966 the synthesis of ethyl 2-methyl-8-oxo-8*H*-pyrano[3,2-*g*]benzoxazole-7-carboxylate by fusion of ethyl 7-acetamido-8-hydroxy-3-coumarincarboxylate with phosphorus pentoxide. Similar treatment of 7-acetamido-6-hydroxy- and of 5-acetamido-6-hydroxy-3-coumarincarboxylates led to the corresponding pyrano[2,3-*f*] and pyrano[3,2-*e*]benzoxazoles in about 50% yield. In a previous paper we reported[2] that 10-(methoxyimino)phenanthren-9-one reacts thermally with several methyl substituted aromatic systems to give 2-aryl (or heteroaryl)substituted phenanthro[9,10-*d*]oxazoles in 9-58% yield. The oxazole ring formation involves participation of the methyl substituent. Very recently we found[3] that several α-substituted methylaromatic compounds Ar-CH_2-Y (where Y = Br, OH, OCOR, COR, SH, NH_2) as well as N-methylamines, react with the same monoxime to give 2-aryl-, 2-amino- and/or unsubstituted phenanthro-[9,10-*d*]oxazoles, involving participation of their -CH_2-Y or N-CH_3 carbon atom into the oxazole ring formation. Most probably homolytic bond scissions and bond formations occur in these reaction sequences. Recently we also reported[4] that the easily prepared[5]

4-methylchromene-2,7,8-trione **1** reacts with benzoyl-, acetyl-, alkoxycarbonyl-, aryl- and vinylmethylenetriphenylphosphoranes to give coumarins 7,8-fused onto furan, pyran and dioxole rings.

The work detailed here involves synthesis of the title 7-methoxyimino-4-methylchromene-2,8-dione **3** and its reactions with the methyl substituted aromatic compounds **5(a-g)** with aryl acetates **13(b,c)** with halo derivatives **13a**, **14(a-c)** as well as with N-methyl-amines $C_6H_5NHCH_3$ and $C_6H_5CH_2N(CH_3)_2$ in order to prepare new oxazolocoumarins. The reactions studied and the products obtained are depicted in Schemes 1-4.

Results and Discussion

The starting compound **3** was synthesized directly from *o*-quinone **1** and methoxylamine hydrochloride **2** (Scheme 1). Although it is known[6,7] that treatment of coumarins with hydroxylamine results in the opening of the pyrone ring, in case compound **2** was added to a methanol solution of an equimolar amount of quinone **1**, a 33% yield of the oxime **3** was readily formed as an orange coloured precipitate separated by filtration. Dioxime **4** was also obtained in 10% yield by chromatographic separation of the filtrate. Due to the resonance effect of the adjacent pyrone ring the 7-CO oxygen atom of compound **1** is protonated by the acid present easier than the 8-CO one, leading to the formation of the 7-methoxyimino- and not to that of the 8-methoxyimino- isomer, which constitutes the alternative possibility. The structure of the sole monoxime obtained was confirmed by the X-ray analysis of compound **8a**, prepared from **3** and is discussed below. It is of interest to note that the reaction of **1** with phosphorus ylides, under neutral or basic conditions, led to Wittig olefination only of the 8-CO-group[4].

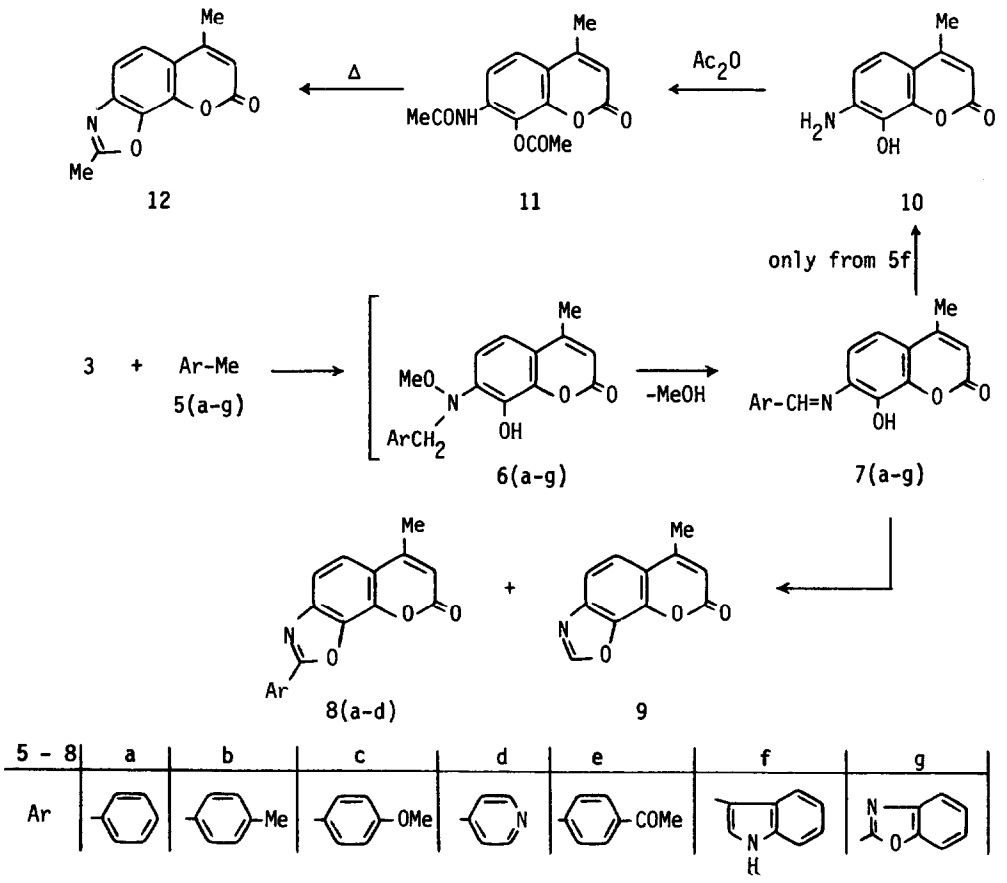


1 2 3 4

Scheme 1

Treatment of compound **3** for 6 days with boiling toluene **(5a)**, used also as a solvent, and separation of the reaction mixture by column chromatography, afforded compounds **8a** and **9** in 20% and 22% yield respectively (Scheme 2). The analytical and

spectral data of the oxazoles obtained agree well with the suggested structures. The structure of compound **8a** was unequivocally confirmed by X-ray analysis (Fig. 1) proving beyond any doubt, that the monoxime prepared in Scheme 1 and used in the reaction with **5a** is the 7-methoxyimino- isomer. The reaction mechanism depicted in Scheme 2 is similar to the one we previously suggested[2] for the reactions of 10-(methoxyimino)-phenanthren-9-one with analogous methyl-compounds, mentioned above.



Scheme 2

By treatment of **3** with boiling p-xylene **(5b)**, 4-methylanisole **(5c)** or 4-picoline **(5d)**, used also in excess as solvents, for 5 days, 2.5 h and 11 h respectively (the reaction mixture was examined by t.l.c. and refluxed up to the time all the oxime was

consumed), compounds **8b** (10%), **8c** (16%) and **8d** (26%) were obtained, along with compound **9** in the first (20%) and the second (19%) reactions. The reaction of **3** with 4-methylacetophenone (**5e**), heated at 195°C for 2.5 h afforded only compound **9** (27%).

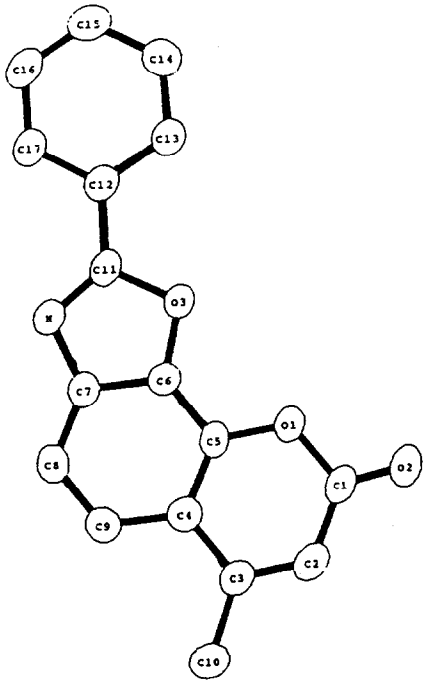


Fig. 1. Perspective view of compound **8a**

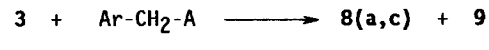
Of special interest are the reactions of **3** with melted 3-methylindole (**5f**) (heated at ~170°C for 2 h) and with 2-methylbenzoxazole (**5g**) (heated at ~170°C for 2 h) as they gave very complex reaction mixtures from which there were isolated 7-amino-8-hydroxy-4-methylcoumarin **10** (51%) and 2,6-dimethyl-8*H*-pyrano[3,2-*g*]benzoxazol-8-one **12** (12%) respectively (Scheme 2), instead of the expected 2-heteroaryl-derivatives **8f** and **8g**.

The formation of compound **10** can be explained by supposing further hydrolysis of the corresponding imine intermediate **7f**, instead of its cyclisation to oxazole derivatives. More evidence is necessary to explain the formation of compound **12**, also prepared in a control experiment by treatment of compound **10** with acetic anhydride and further heating of the intermediate bis-acetyl derivative **11** thus formed. This experiment supports further the correctness of the structure of compounds **10** and **12** sugge-

sted above, but does not explain the formation of **12** from **5g**. Although compound **5g** was hydrolysed to 2-acetaminophenol, detected in the reaction studied, its prolonged heating with compound **10** did not afford compound **12**, as it was indicated by t.l.c.. Probably compound **12** is formed directly from **3** and **5g**.

The isolation of compound **9** in the thermal reactions of **3** studied, prompted us to examine the possibility of a thermal dehydration of the latter to the former, probably by an initial thermal isomerisation[8] to the corresponding N-methyl nitrone. When compound **3** was heated at 140°C for 2 days it remained unchanged, as indicated by t.l.c. examination of the sample.

Treatment of compound **3** with boiling benzyl chloride (**13a**) for 14 h gave compounds **8a** (29%) and **9** (16%) (Scheme 3).



13(a-c)

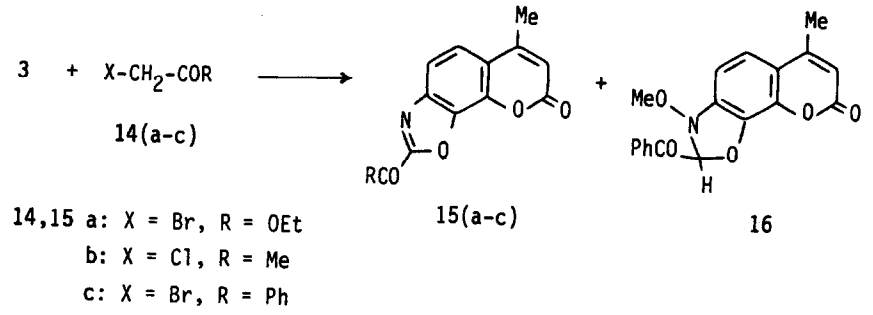
13a: Ar = Ph, A = Cl
b: Ar = Ph, A = CO_2Me
c: Ar = 4-MeO-C_6H_4, A = CO_2Me

Scheme 3

When a solution of **3** in methyl phenyl acetate (**13b**) was refluxed for 2 h products **8a** (15%) and **9** (28%) were again obtained. Similarly, when a melted mixture of **3** and an excess of methyl 4-methoxyphenyl acetate (**13c**) was heated at ~130°C for 14 h it afforded compounds **8c** (32%) and **9** (10%). Polar bond scissions and bond formations towards the final steps leading to products **8a**, **8c** via elimination of H-$COOCH_3$, seem to be impossible in two last reactions, in agreement with a previous observation[3] of ours concerning some similar reactions.

Furthermore we studied the reactions of **3** with some α-haloesters and ketones, depicted in Scheme 4. Treatment of **3** with boiling ethyl bromoacetate (**14a**) for 1 day afforded ethyl 6-methyl-8-oxo-8*H*-pyrano[3,2-*g*]benzoxazole-2-carboxylate (**15a**) in 48% yield. The reaction of **3** with chloroacetone (**14b**), heated at reflux for 2 h, gave the 2-acetyloxazole **15b** in 25% yield. When a solution of a mixture of **3** and excess of phenacylbromide (**14c**) in benzene was heated at reflux for 7 days 2-benzoyloxazole **15c** (23%) and the unexpected 2-benzoyl-3-methoxy-6-methyl-2,3-dihydro-8*H*-pyrano[3,2-*g*]benzoxazol-8-one (**16**) (18%) were obtained. On heating at ~150°C for 2 days, compound **16** gave compo-

und 15c, as it was indicated by the examination of the sample with ^{1}H-NMR spectroscopy.



14,15 a: X = Br, R = OEt
b: X = Cl, R = Me
c: X = Br, R = Ph

Scheme 4

Obviously, formation of an intermediate similar to **6** (Scheme 2), having the $C_6H_5COCHBr$- instead of the $ArCH_2$- N-substituent, followed by cyclisation with HBr elimination can account for the formation of compound **16**. Although the formation of an *o*-hydroxyimine intermediate of type **7** was previously proved[2] to proceed in similar reactions, giving further 2-substituted oxazoles of type **8** (Scheme 2) an intermediate of type **16** can also account for the formation of compound **15c** at least. The reactions described in Scheme 4 seem to lead to an interesting method for the preparation of 2-alkoxycarbonyl(or acyl, or aroyl)oxazoles and are under further consideration.

Finally, reaction of **3** with N-methylaniline and with N,N-dimethylbenzylamine did not afford the expected[3] 2-aminoderivatives of compound **9**. When a mixture of **3** with an excess of N-methylaniline was refluxed for 10 min all starting monoxime was consumed and further separation of the reaction mixture by column chromatography gave compound **10** in 58% yield. The reaction of **3** with boiling N,N-dimethylbenzylamine for 1.5 h lead to compound **8a** in 20% yield.

Experimental

M.p.s are uncorrected and were determined on a Kofler hot-stage apparatus. IR spectra were obtained with a Perkin-Elmer 297 spectrophotometer as Nujol mulls. ^{1}H-NMR spectra were recorded with deuteriochloroform as solvent on a Bruker AW 80 (80 MHz) spectrometer with tetramethylsilane as the internal standard. Mass spectra were determined on a VG-250 spectrometer with ionization energy maintained at 70 eV. Light petroleum refers to the fraction of 40-60°C.

Preparation of 7-Methoxyimino-4-methylchromene-2,8-dione (3) and 7,8-Bismethoxyimino-4-methylchromene-2-one (4). To a stirred solution of compound **1** (0.57 g, 3 mmol) in methanol (60 mL) methoxylamine hydrochloride (0.249 g, 3 mmol) was added. After 3-5 minutes an orange precipitate was formed and separated by filtration to give compound **3** (0.213 g, 33%), m.p. 195-197°C (dichloromethane); IR (Nujol) ν: 1742, 1730, 1655 and 1630 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.32 (3H, s), 4.33 (3H, s), 6.43 (1H, s), 6.70 (1H, d, J =

9.6 Hz), 7.01 (1H, d, J = 9.6 Hz); MS m/z: 219 (M^+, 100%), 191 (76), 163 (57) and 160 (70); Anal. calcd for $C_{11}H_9NO_4$ (219.19): C, 60.27; H, 4.14; N, 6.39%. Found C, 60.31; H, 4.28; N, 6.48%. The solvent of the filtrate was removed in a rotary evaporator and the residue chromatographed on silica gel with light petroleum -ethyl acetate (1:1) as the eluent to afford compound **4** (82 mg, 10%), m.p. 165-167°C (dichloromethane); IR (Nujol) v: 1735, 1720 and 1635 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.26 (3H, s), 4.13 (3H, s), 4.32 (3H, s), 6.22 (1H, s), 6.67 (1H, d, J = 8.4 Hz), 7.05 (1H, d, J = 8.4 Hz); MS m/z: 248 (M^+, 100%), 231 (17), 217 (16), 203 (12) and 186 (51); Anal. calcd for $C_{12}H_{12}N_2O_4$ (248.24): C, 58.06; H, 4.87; N, 11.29%; Found: C, 58.27; H, 4.79; N, 11.28%.

Reaction of Compound 3 with Toluene (5a). A solution of **3** (0.11 g, 0.5 mmol) in toluene (2 mL) was refluxed for 6 days. The solvent was evaporated under reduced pressure and the residue chromatographed on silica gel with light petroleum - ethyl acetate (from 1:1 up to 1:2) as the eluent to give two fractions. The first fraction gave **6-methyl-2-phenyl-8*H*-pyrano[3,2-*g*] benzoxazol-8-one (8a)** (28 mg, 20%), m.p. 216-218°C (light petroleum - ethyl acetate); IR (Nujol v: 1720 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.48 (3H, s), 6.27 (1H, s), 7.15-7.73 (5H, m), 8.17-8.38 (2H, m); MS m/z: 277 (M^+, 100%), 249 (80) and 233 (9); Anal. calcd for $C_{17}H_{11}NO_3$ (277.28): C, 73.64; H, 4.00; N, 5.05%; Found C, 73.88; H, 4.01; N, 4.98%. The next fraction gave **6-methyl-8*H*-pyrano[3,2-*g*]-benzoxazol-8-one (9)** (22 mg, 22%), m.p. 196-198°C (light petroleum - dichloromethane); IR (Nujol) v: 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.55 (3H, s), 6.33 (1H, s), 7.59 (1H, d, J = 8.5 Hz), 7.66 (1H, d, J = 8.5 Hz) and 8.26 (1H, s); MS m/z: 201 (M^+, 100%), 195 (31), 173 (94), 172 (56) and 167 (81); Anal. calcd for $C_{11}H_7NO_3$ (201.17): C, 65.67; H, 3.51; N, 6.96%; Found: C, 65.48; H, 3.39; N, 6.68%.

Reaction of Compound 3 with p-Xylene (5b). A solution of **3** (0.219 g, 1 mmol) in **5b** (4 mL) was refluxed for 5 days. Evaporation of the solvent under reduced pressure and column chromatography of the residue on silica gel, using light petroleum - ethyl acetate as eluent gave first **6-methyl-2(4-tolyl)-8*H*-pyrano[3,2-*g*]benzoxazol-8-one (8b)** (26 mg, 10%), m.p. 214-216°C (dichloromethane - light petroleum); IR (Nujol) v: 1728 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.41 (3H, s), 2.43 (3H, s), 6.25 (1H, s), 7.22 (2H, d, J = 8 Hz), 7.35-7.60 (2H, m), and 8.05 (2H, d, J = 8 Hz); MS m/z: 291 (M^+, 82%), 263 (100) and 235 (13); Anal. calcd for $C_{18}H_{13}NO_3$ (291.29): C, 74.21; H, 4.50; N, 4.81%; Found: C, 74.08; H, 4.38; N, 4.68%. The next fraction gave compound **9** (41 mg, 21%).

Reaction of Compound 3 with 4-Methylanisole (5c). A solution of compound **3** (0.219 g, 1 mmol) in **5c** (3 mL) was heated at reflux for 2.5 h. Separation of the reaction mixture with column chromatography on silica gel with light petroleum - ethyl acetate as the eluent gave **6-methyl-2(4-methoxyphenyl)-8*H*-pyrano[3,2-*g*]benzoxazol-8-one (8c)** (49 mg, 16%), m.p. 255-256°C (dichloromethane - light petroleum); IR (Nujol) v: 1723 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.51 (3H, s), 3.88 (3H, s), 6.29 (1H, s), 7.06 (2H, d, J = 8 Hz), 7.47-7.75 (2H, m), and 8.15 (2H, d, J = 8 Hz); MS m/z: 307 (M^+, 100%), 279 (45), 264 (15) and 236 (9); Anal. calcd for $C_{18}H_{13}NO_4$ (307.29): C, 70.35; H, 4.26; N, 4.40%; Found: C, 70.31; H, 4.40; N, 4.49%. The next fraction gave compound **9** (38 mg, 19%).

Reaction of Compound 3 with 4-Picoline (5d). A solution of **3** (0.219 g, 1 mmol) in **5d** (5 mL) was refluxed for 11 h. Water was added to the cooled reaction mixture, which was further extracted with dichloromethane (5x20 mL), the organic layer was washed with water (30 mL), dried (Na_2SO_4) and the solvent was removed in a rotary evaporator. Column chromatography of the residue on silica gel, using light petroleum - ethyl acetate (1:1) as eluent gave **6-methyl-2(4-pyridyl)-8*H*-pyrano[3,2-*g*]benzoxazol-8-one (8d)** (73 mg, 26%), m.p. 209-211°C (dichloromethane - light petroleum); IR (Nujol) v: 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.52 (3H, s), 6.30 (1H, s), 7.66 (2H, br s), 8.15 (2H, d, J = 7.5 Hz) and 8.82 (2H, d, J = 7.5 Hz); MS m/z: 278 (M^+, 67%), 251 (15), 250(100), 249 (15) and 222 (6); Anal. calcd for $C_{16}H_{10}N_2O_3$ (278.26): C, 69.06; H, 3.62; N, 10.07%; Found: C, 69.08; H, 3.91; N, 10.01%.

Reaction of 3 with 4-Methylacetophenone (5e). A solution of **3** (0.438 g, 2 mmol) in **5e** (5 mL) was refluxed for 2.5 h and the reaction mixture separated by column chroma-

tography on silica gel with light petroleum - ethyl acetate (1:1 up to 0:1) as eluent to give after elution of the rest of **5e**, compound **9** (0.106 g, 27%).

Reaction of 3 with 3-Methylindole (5f). A melted mixture of **3** (0.219 g, 1 mmol) and **5f** (0.262 g, 2 mmol) was heated at ~170°C for 2 h. Chromatography on silica gel with light petroleum -ethyl acetate (4:1 up to 1:1) as the eluent gave after elution of the starting compound **5f**, **7-amino-8-hydroxy-4-methylcoumarin (10)** (98 mg, 51%), m.p. 223-227°C (dec) (ethanol); IR (Nujol) ν: 3445, 3360, 1725 and 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$-DMSO-d_6) δ: 2.32 (3H, s), 4.75 (2H, br s), 5.91 (1H, s), 6.65 (1H, d, J = 8 Hz), 6.96 (1H, d, J = 8 Hz) and 8.90 (1H, br s); MS m/z: 191 (M^+, 100%), 163 (76), 135 (31) and 118 (12); Anal. calcd for $C_{10}H_9NO_3$ (191.18): C, 62.82; H, 4.75; N, 7.33%; Found: C, 62.93; H, 4.91; N, 7.48%.

Reaction of 3 with 2-Methylbenzoxazol (5g). A solution of **3** (0.328 g, 1.5 mmol) in **5g** (2 mL) was heated at 170°C for 2 h. Chromatography on silica gel with light petroleum - ethyl acetate (4:1 up to 1:1) as the eluent gave **2-acetylaminophenol** (0.106 g), m.p. 199-201°C (lit[9]. m.p. 201°C). The following fractions gave **2,6-dimethyl-8*H*-pyrano-[3,2-*g*]benzoxazol-8-one (12)** (38 mg, 12%). m.p. 188-191°C (dichloromethane - light petroleum); IR (Nujol) ν: 1725 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.50 (3H, s), 2.72 (3H, s), 6.26 (1H, s), and 7.52 (2H, s); MS m/z: 215 (M^+, 88), 186 (31) 187 (100), 159 (13) and 130 (6); Anal. calcd for $C_{12}H_9NO_3$ (215.20): C, 66.97; H, 4.22; N, 6.51%; Found: C, 66.78; H, 4.36; N, 6.61%.

8-Acetoxy-7-acetylamino-4-methylcoumarin (11). A mixture of compound **10** (38 mg, 0.2 mmol) in acetic anhydride (0.5 mL) was heated at 90°C for 30 min.The precipitate formed was separated by filtration to give compound **11** (42 mg, 77%), m.p. 222-225°C (dichloromethane); IR (Nujol) ν: 3330, 1750, 1740 and 1695 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.20 (3H, s), 2.41 (3H, s), 2.47 (3H, s), 6.19 (1H, s), 7.25-7.65 (2H, m) and 8.30 (1H, br s); MS m/z: 275 (M^+, 4%), 233 (44), 191 (100), 163 (16) and 43 (39); Anal. calcd for $C_{14}H_{13}NO_5$ (275.25): C, 61.09; H, 4.76; N, 5.09%; Found: C, 61.32; H, 4.98; N, 5.15%.

Transformation of Compound 11 to Compound 12. Compound **11** (20 mg, 0.07 mmol) was heated at 210-220°C for 2 h. Chromatography on silica gel with dichloromethane - ethyl acetate (4:1) as the eluent gave compound **12** (9 mg, 58%).

Reaction of 3 with Benzyl Chloride (13a). A solution of **3** (82 mg, 0.37 mmol) in **13a** (2 mL) was refluxed for 14 h. Chromatography on silica gel with light petroleum - ethyl acetate (3:2 up to 1:2) as the eluent gave compound **8a** (30 mg, 29%) and from the following fractions compound **9** (12 mg, 16%).

Reaction of 3 with Methyl Phenyl Acetate (13b). A solution of **3** (0.219 g, 1 mmol) in **13b** (5mL) was refluxed for 2 h. Chromatography on silica gel with light petroleum -ethyl acetate (3:2 up to 2:3) as the eluent gave firstly compound **8a** (42 mg, 15%) and from the following fractions compound **9** (56 mg, 28%).

Reaction of 3 with Methyl 4-Methoxyphenyl Acetate (13c). A solution of **3** (0.219 g, 1 mmol) in **13c** (2 mL) was heated at 130°C for 14 h. Chromatography on silica gel with light petroleum -ethyl acetate (3:2 up to 1:3) as the eluent gave, after elution of the starting ester, compound **8c** (98 mg, 32%) and from the next fractions compound **9** (20 mg, 10%).

Reaction of 3 with Ethyl Bromoacetate (14a). A solution of **3** (80 mg, 0.36 mmol) in **14a** (1 mL) was refluxed for 24 h. Chromatography on silica gel with light petroleum ethyl acetate 1:1) as the eluent gave **ethyl 6-methyl-8-oxo-8*H*-pyrano[3,2-*g*]benzoxazole-2-carboxylate (15a)** (48 mg, 48%), m.p. 198-200°C (ether); IR (Nujol) ν: 1735 and 1725 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.50 (3H, t, J = 6.4 Hz), 2.54 (3H, s), 4.57 (2H, q, J = 6.4 Hz), 6.40 (1H, s), 7.66 (1H, d, J = 8.8 Hz) and 7.81 (1H, d, J = 8.8 Hz); MS m/z: 273 (M^+, 100%), 247 (7), 245 (6), 228 (15), 219 (25), 217 (20), 201 (38) and 200 (21); Anal. calcd for $C_{14}H_{11}NO_5$ (273.24): C, 61.54; H, 4.06; N, 5.13%; Found: C, 61.28; H, 4.00; N,

4.98%.

Reaction of 3 with Chloracetone (14b). A solution of **3** (0.328 g, 1.5 mmol) in **14b** (3 mL) was heated at reflux for 2 h. Chromatography on silica gel with light petroleum - ethyl acetate (1:1) as the eluent, gave **2-acetyl-6-methyl-8-oxo-8*H*-pyrano[3,2-*g*]-benzoxazol-8-one (15b)** (90 mg, 25%), m.p. 215-217°C (ether); IR (Nujol) ν: 1726 and 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.54 (3H, s), 2.83 (3H, s), 6.38 (1H, s), 7.67 (1H, d, J = 9.5 Hz) and 7.78 (1H, d, J = 9.5 Hz); MS m/z: 243 (M^+, 100%), 215 (21) and 200 (55); Anal. calcd for $C_{13}H_9NO_4$ (243.21): C, 64.20; H, 3.73; N, 5.67%; Found: C, 64.52; H, 3.48; N, 5.92%.

Reaction of 3 with 2-Bromoacetophenone (14c). A solution of **3** (0.328 g, 1.5 mmol) in **14c** (3 mL) was heated under reflux for 7 days. Chromatography on silica gel with light petroleum -ethyl acetate (1:1) as the eluent gave two fractions. The first fraction afforded **2-benzoyl-6-methyl-8*H*-pyrano[3,2-*g*]benzoxazol-8-one (15c)** (0.105 g, 23 %), m.p. 204-206°C (dichloromethane); IR (Nujol) ν: 1735, 1700 and 1665 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.54 (3H, s), 6.39 (1H, s), 7.37-7.92 (5H, m), 8.42-8.66 (2, m); MS m/z: 305 (M^+, 100%), 277 (8) and 200 (8); Anal. calcd for $C_{18}H_{11}NO_4$ (305.28): C, 70.81; H, 3.63; N, 4.59; Found: C, 70.71; H, 3.54; N, 4.30%; The second fraction gave **2-benzoyl-3-methoxy-6-methyl-2,3-dihydro-8*H*-pyrano[3,2-*g*]benzoxazol-8-one (16)** (90 mg, 18%), m.p. 151-153°C (ether); IR (Nujol) ν: 1730 and 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 2.55 (3H, s), 3.87 (3H, s), 5.98 (1H, s), 6.35 (1H, s), 7.44-7.91 (5H, m), and 8.24-8.61 (2H, m); MS m/z: 305 (M - CH_3OH, 38%) and 200 (54). Anal. calcd for $C_{19}H_{15}NO_5$ (337.32): C, 67.65; H, 4.48; N, 4.15%; Found: C, 67.32; H, 4.20; N, 4.35%.

Reaction of 3 with N-Methylaniline. A solution of **3** (0.3 g, 1.36 mmol) in N-methylaniline (1 mL) was refluxed for 10 min. After cooling of the reaction mixture a precipitate was formed, separated by filtration and washed with dichloromethane (1 mL) to give compound **10** (100 mg). Chromatography of the filtrate on silica gel with dichloromethane - light petroleum - ethyl acetate (10:0:0 up to 10:1:3) as the eluent gave as the last fraction an additional amount of compound **10** (50 mg, total yield 58%).

Reaction of 3 with N,N-Dimethylbenzylamine. A solution of **3** (0.3 g, 1.36 mmol) in N,N-dimethylbenzylamine (2 mL) was refluxed for 1.5 h. Chromatography on silica gel with dichloromethane - light petroleum - ethyl acetate (10:1:1) as the eluent gave compound **8a** (75 mg, 20%).

X-Ray Crystallographic Analysis of Compound 8a. The compound $C_{17}H_{11}NO_3$, M = 277.28, crystallizes in space group $P2_1/c$, a=14.3156(8), b=7.0868(4), c=13.2112(7) Å, β=102.812(2)°, v=1306.93(7) $Å^3$, Z=4, D=1.40, D=1.409 s cm^{-3}, F(000)=576, μ=7.60 cm.

Diffraction measurments were made on a $P2_1$ Nicolet diffractometer upgraded by Crystal Logic using Ni-filtered Cu radiation. Unit cell dimentions were determined and refined by using the angular settings of 28 automatically centered reflections in the range 23<2θ<55. Intensity data were recorded using a θ-2θ scan to 2θ(max)=125° with scan speed 3.0°/min and scan range 1.9° plus $\alpha_1\alpha_2$ separation. Three standard reflecti-ons monitored every 97 reflections showed less than 3% variation and no decay. Lorentz polarization and ψ-scan absorption correction were applied using Crystal Logic software.

Symmetry equivalent data were averaged with R=0.0323 to give 2079 independent reflections from a total 2380 collected. The structure was solved and refined by full-matrix least-squares techniques with SHELX-76[10] using only 1863 reflections with Fo>2.0σ(Fo) and refining 234 parameters. All hydrogen atoms were located by difference maps and their positions were refined isotropically. All non-hydrogen atoms were refined anisotropically.

The final values for R, Rw and GOF, for observed data are 0.0386, 0.0505 and 2.01 respectively. The maximum and minimum residual peaks in the final difference map were 0.12 and -0.19 e/$Å^3$. The largest shift/esd in the final cycle was 0.025.

See paragraph at the end of this article concerning supplementary material available.

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