Imidazolyl Derivatives of the Chroman Ring 3 [1]

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The synthesis of 2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-ones **4** is described starting from 2-acetoxybenzoyl chlorides and 1,2-dimethylimidazole. Chromones **4** undergo alkaline ring opening to the corresponding 1-(2-hydroxyphenyl)-2-(1-methyl-1*H*-imidazol-2-yl)ethenols **5** which give ring closure to 2-substituted 3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-ones or 2,3-dihydro-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-ones. The corresponding chromanols and chromenes can be easily obtained from chromones **4**.

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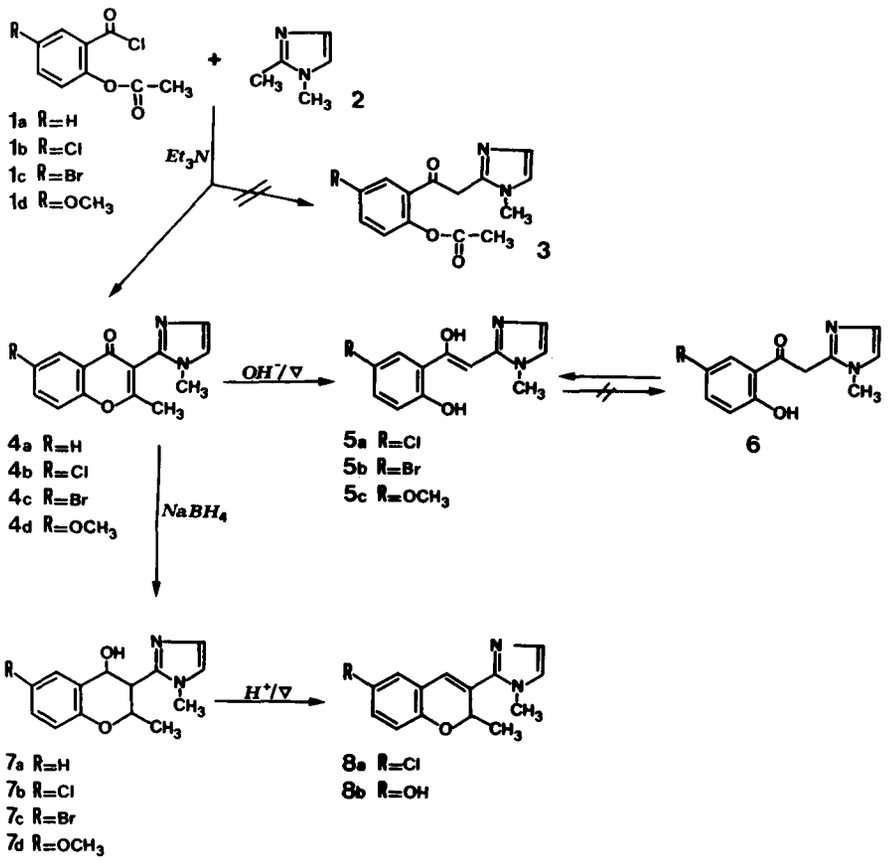
In search for new compounds of pharmacological interest containing the chroman and the imidazole ring in the same molecule we described in previous papers the synthesis of 2,3-dihydro-3-(1*H*-imidazol-1-yl)-4*H*-1-benzopyran-4-ones [2], 3-(1*H*-imidazol-1-yl)-4*H*-1-benzopyran-4-ones [1] and some derived compounds such as the corresponding chromanols and chromenes. Encouraged by the interesting pharmacological activities shown by some of those compounds [3] we took into consideration the synthesis of imidazol-2-yl analogues beginning with 2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-ones **4**.

By reacting 2-acetoxybenzoyl chlorides **1** with 1,2-dimethylimidazole under the conditions reported by Goodefroi for benzoylation of 1,2-disubstituted imidazoles [4], we attempted the preparation of 1-(2-acetoxyphenyl)-2-(1-methyl-1*H*-imidazol-2-yl)ethanones **3**. From the latter we hoped to obtain the chromones **4** directly through a Baker-Venkataraman rearrangement [5] or indirectly through

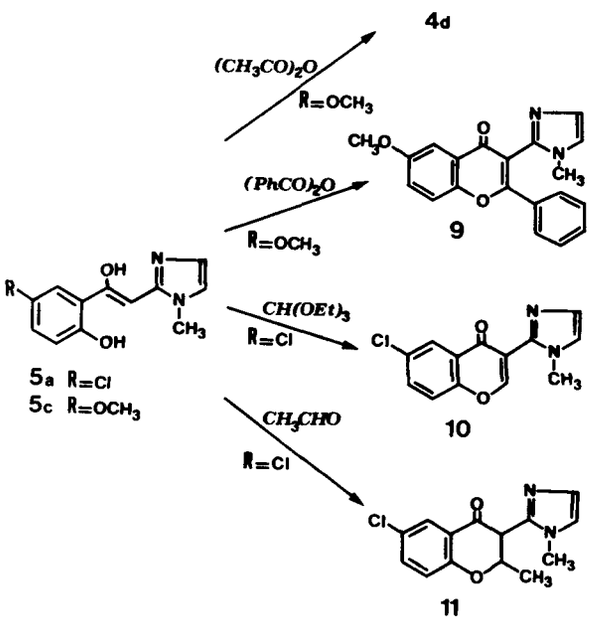
SCHEME 1

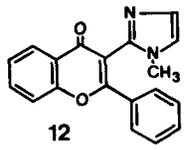


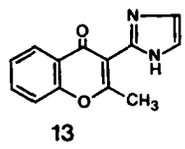
hydrolysis to 1-(2-hydroxyphenyl)-2-(1-methyl-1*H*-imidazol-2-yl)ethanones **6** and subsequent Kostanecki-Robinson type chroman ring closure [6]. As the reaction conditions of the benzoylation were not dissimilar from those of the Baker-Venkataraman rearrangement, the reaction of acetylsalicyl chlorides **1** with 1,2-dimethylimidazole proceeded one-pot to chromones **4** as shown in Scheme 1. Two equivalents of chloride **1** were reacted with **2** at room temperature in acetonitrile in the presence of two equivalents of triethylamine to give chromones **4** in a yield ranging from 50 to 60% of pure isolated product. When only one equivalent of chloride **1** was used, the yield was reduced to a half as if the initial intermediacy of enol benzoates had occurred, similarly to that reported in the cited literature describing the benzoylation of 1,2-disubstituted imidazoles [4b]. However none of such enol benzoates appeared to be present in the reaction mixture. Compounds **4** underwent the alkaline ring opening known to occur to chromones [7] giving, by short heating in aqueous sodium hydroxide, 1-(2-hydroxyphenyl)-2-(1-methyl-1*H*-imidazol-2-yl)-ethenols **5**, which do not exist, at least in normal conditions in the keto form **6**, as results from nmr data reported in the Experimental.

Compounds **5** are strict analogues of phenacylimidazoles described by Goodefroi [4b] as keto-enol mixtures; in our case the enol form is probably even more stabilized by the phenolic hydroxy group. Chromones **4** were reduced with sodium borohydride to the corresponding chromanols **7** in good yields. These are in the *trans-trans* configuration as results from nmr spectral data reported in the Experimental. Chromanols **7** could be easily dehydrated to the corresponding chromenes **8** by heating with concentrated sulphuric acid in acetic acid (**7b**) or concentrated hydrobromic acid (**7d**) in which case concomitant demethylation took place. Compounds **5** underwent chroman ring closure to corresponding chromones and chromanones in good yields as reported in Scheme 2. Compound **5c** was reacted with an excess of acetic anhydride at 100° giving back chromone **4d** or with an excess of benzoic anhydride by fusion at 120° giving flavone **9**. Compound **5a** was refluxed in an excess of triethylorthoformate to give chromone **10**. Finally compound **5a** reacted with acetaldehyde in acetic acid at 90°C giving chromanone **11** in pure *trans* form as results from nmr spectral data reported in the Experimental.

SCHEME 2




12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The synthesis of 2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-ones **4** from acetylsalicyl chlorides and 1,2-dimethylimidazole represents a new type of chromone ring synthesis. A two step synthesis of the chromone ring starting from acetylsalicyl chloride was reported in the literature [8] through a different reaction, involving the acetylation of methoxycarbonylmethylenetriphenylphosphorane and the high temperature decomposition of the intermediate triphenylphosphorane keto-ylide. To check whether our synthesis could be extended to flavones we reacted 1,2-dimethylimidazole with 2-benzoyloxybenzoyl chloride. Flavone **12** was isolated, in yield lower than for 2-methylchromones, after column chromatographic purification of an impure reaction mixture. Finally this reaction was attempted with 2-methylimidazole. In this case three equivalents of 2-acetoxybenzoyl chloride were used. Chromone **13** was isolated, in low yield, after acidic hydrolysis of an impure reaction mixture probably containing its *N*-imidazolyl acetylsalicylate. Work on this reaction is still in progress, especially aimed at extending the synthesis to other heterocyclic-substituted chromones.

EXPERIMENTAL

Melting points were determined on a Büchi melting point apparatus and are uncorrected. The ^{1}H nmr spectra were obtained on a Bruker HFX 90 MHz spectrometer in the solvents indicated. Chemical shifts are reported in ppm from TMS as internal standard and are given in δ units. Column chromatographic separations were performed on 0.05-0.20 nm silica gel (Carlo Erba).

6-Chloro-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-one (**4b**).

To a stirred solution of 2.8 g (29.1 mmoles) of 1,2-dimethylimidazole and 6.0 g (59.2 mmoles) of triethylamine in 20 ml of acetonitrile, 13.8 g (59.2 mmoles) of 2-acetoxy-5-chlorobenzoyl chloride (**1b**) in 20 ml of ace-

tonitrile were added portionwise at 10-15°. After stirring at room temperature for 3 hours the mixture was poured into water and extracted with methylene chloride. The solvent was evaporated and the resulting brown oil was extracted several times with a solution of 10% hydrochloric acid. The acidic aqueous layers were combined, neutralized with sodium bicarbonate and extracted with methylene chloride. The organic layer, dried over sodium sulfate and treated with charcoal was evaporated to dryness giving 4.2 g (56%) of **4b**, mp 178-180°. ^{1}H nmr (deuteriochloroform): 2.43 (3H, s, CCH_3), 3.60 (3H, s, NCH_3), 7.08 (1H, d, NC*H*CHN), 7.23 (1H, d, NCHC*H*N), 7.48 (1H, d, H-8), 7.68 (1H, dd, H-7), 8.20 (1H, d, H-5).

Anal. Calcd. for $C_{14}H_{11}ClN_2O_2$: C, 61.21; H, 4.03; N, 10.19; Cl, 12.90. Found: C, 61.03; H, 4.02; N, 10.16; Cl, 12.94.

By the above procedure, starting from the corresponding 2-acetoxybenzoyl chlorides, the following chromones **4** were prepared:

2-Methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-one (**4a**).

This compound was obtained from 2-acetoxybenzoyl chloride (**1a**), in 58% yield, mp 90-92°; ^{1}H nmr (deuteriochloroform): 2.29 (3H, s, CCH_3), 3.44 (3H, s, NCH_3), 6.90 (1H, broad s, NC*H*CHN), 7.00 (1H, broad s, NCHC*H*N), 7.11-7.65 (3H, m, H-6, H-7, H-8), 8.04 (1H, dd, H-5).

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.82; H, 5.02; N, 11.69.

6-Methoxy-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-one (**4d**).

This compound was obtained from 2-acetoxy-5-methoxybenzoyl chloride (**1d**), in 54% yield, mp 160-162°; ^{1}H nmr (deuteriochloroform): 2.29 (3H, s, CCH_3), 3.44 (3H, s, NCH_3), 3.75 (3H, s, OCH_3), 6.91 (1H, broad s, NC*H*CHN), 6.98 (1H, broad s, NCHC*H*N), 7.11 (1H, dd, H-7), 7.28 (1H, d, H-8), 7.40 (1H, d, H-5).

Anal. Calcd. for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.80; H, 5.23; N, 10.33.

6-Bromo-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-one Hydrochloride (**4c**).

This compound was obtained from 2-acetoxy-5-bromobenzoyl chloride (**1c**) in 52% yield, mp 303-305° dec; after salification with concentrated hydrochloric acid of the crude free base recovered after evaporation to dryness of the final organic extract.

Anal. Calcd. for $C_{14}H_{12}BrClN_2O_2$: C, 47.28; H, 3.40; N, 7.88; Br, 22.47; Cl^-, 9.97. Found: C, 47.37; H, 3.39; N, 7.90; Br, 22.52; Cl^-, 9.95.

The known 2-acetoxybenzoyl chlorides were prepared by reaction of the corresponding acid with phorphorus trichloride in refluxing benzene.

1-(5-Chloro-2-hydroxyphenyl)-2-(1-methyl-1*H*-imidazol-2-yl)ethenol (**5a**).

A mixture of 9.0 g (32.7 mmoles) of **4b** and 250 ml of 2*N* aqueous sodium hydroxide was stirred for 30 minutes at 95°. The mixture was filtered and the resulting clear solution was cooled and neutralized with hydrochloric acid. A solid precipitated was filtered, washed with water, dried and crystallized from isopropyl alcohol to give 5.9 g (71%) of **5a**, mp 190-192°; ^{1}H nmr (DMSO-d_6): 3.63 (3H, s, NCH_3), 5.88 (1H, s, C*H*COH), 6.76 (1H, d, phenyl H-3), 7.04 (1H, d, NC*H*CHN), 7.18 (1H, d, NCHC*H*N), 7.23 (1H, dd, phenyl H-4), 7.88 (1H, d, phenyl H-6), 12.48 (1H, broad s, enolic OH), 16.00 (1H, broad s, phenolic OH).

Anal. Calcd. for $C_{12}H_{11}ClN_2O_2$: C, 57.49; H, 4.42; N, 11.17; Cl, 14.14. Found: C, 57.61; H, 4.43; N, 11.20; Cl, 14.17.

1-(2-Hydroxy-5-methoxyphenyl)-2-(1-methyl-1*H*-imidazol-2-yl)ethenol (**5c**).

This compound was prepared by the above procedure, starting from **4d**, in 73% yield, mp 161-163°; ^{1}H nmr (DMSO-d_6): 3.58 (3H, s, NCH_3), 3.73 (3H, s, OCH_3), 5.76 (1H, s, C*H*COH), 6.50-7.30 (5H, m, benzene H and imidazole H), 13.00 (1H, broad s, enolic OH).

Anal. Calcd. for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.37. Found: C, 63.55; H, 5.74; N, 11.40.

1-(5-Bromo-2-hydroxyphenyl)-2-(1-methyl-1*H*-imidazol-2-yl)ethenol (**5b**).

This compound was prepared by the above procedure, starting from **4c**, in 60%, mp 198-200°; ^{1}H nmr (DMSO-d_6): 3.60 (3H, s, NCH_3), 5.70 (1H, s, C*H*COH), 6.67 (1H, d, phenyl H-3), 6.98 (1H, d, NC*H*CHN), 7.09 (1H, d, NCHC*H*N), 7.28 (1H, dd, phenyl 4-H), 7.90 (1H, d, phenyl H-6), 12.00 (1H, broad s, enolic OH).

Anal. Calcd. for $C_{12}H_{11}BrN_2O_2$: C, 48.83; H, 3.76; N, 9.49; Br, 27.07. Found: C, 48.91; H, 3.77; N, 9.51; Br, 27.12.

2,3-*trans*-3,4-*trans*-3,4-Dihydro-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-2*H*-1-benzopyran-4-ol (**7a**).

To a solution of 5.6 g (23.3 mmoles) of **4a** in 250 ml of methanol, 4.4 g (116.2 mmoles) of sodium borohydride was added portionwise at 10-15°. After stirring at room temperature for 3 hours the reaction mixture was poured into water. The *p*H of the mixture was adjusted to 7 by addition of 8% hydrochloric acid, then the methanol was evaporated under reduced pressure. After cooling the resulting solid was filtered, washed with water and dried to yield 3.2 g (56%) of **7a**, mp 209-211°; ^{1}H nmr (DMSO-d_6): 1.08 (3H, d, $CHCH_3$), 3.00 (1H, t, $J_{2,3} = J_{3,4} = 10$ Hz, OCHC*H*), 3.60 (3H, s, NCH_3), 4.31 (1H, dq, C*H*CH_3), 4.81 (1H, dd, C*H*OH), 5.49 (1H, d, OH), 6.9-7.6 (6H, m, benzene H and imidazole H).

Anal. Calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 69.01; H, 6.59; N, 11.50.

2,3-*trans*-3,4-*trans*-3,4-Dihydro-6-methoxy-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-2*H*-1-benzopyran-4-ol (**7d**).

This compound was prepared by the above procedure, starting from **4d**, in 58% yield, mp 162-164°; ^{1}H nmr (deuteriochloroform): 1.09 (3H, d, $CHCH_3$), 2.98 (1H, t, $J_{2,3} = J_{3,4} = 10$ Hz, OCHC*H*), 3.59 and 3.62 (3H each, two s, NCH_3 and OCH_3), 4.34 (1H, dq, C*H*CH_3), 4.96 (1H, d, C*H*OH), 6.62 (1H, broad s, NC*H*CHN), 6.67 (1H, broad s, NCHC*H*N), 6.76 (2H, d, H-7 and H-8), 7.00 (1H, broad s, H-5).

Anal. Calcd. for $C_{15}H_{16}N_2O_3$: C, 65.67; H, 6.61; N, 10.21. Found: C, 65.80; H, 6.60; N, 10.19.

2,3-*trans*-3,4-*trans*-6-Chloro-3,4-dihydro-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-2*H*-1-benzopyran-4-ol (**7b**).

This compound was prepared by the above procedure, starting from **4b**, in 85% yield, mp 203-205°; ^{1}H nmr (DMSO-d_6 and trifluoroacetic acid): 1.23 (3H, d, $CHCH_3$), 3.67 (1H, d, $J_{2,3} = J_{3,4} = 10$ Hz, OCHC*H*), 3.95 (3H, s, NCH_3), 5.11 (1H, d, C*H*OH), 6.80-7.80 (5H, m, benzene H and imidazole H).

Anal. Calcd. for $C_{14}H_{15}ClN_2O_2$: C, 60.32; H, 5.42; N, 10.04; Cl, 12.71. Found: C, 60.16; H, 5.41; N,10.01; Cl, 12.68.

2,3-*trans*-3,4-*trans*-6-Bromo-3,4-dihydro-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-2*H*-1-benzopyran-4-ol (**7c**).

This compound was prepared by the above procedure, starting from **4c**, in 70% yield, mp 238-240°; ^{1}H nmr (deuteriochloroform and DMSO-d_6): 0.98 (3H, d, $CHCH_3$), 2.97 (1H, t, $J_{2,3} = J_{3,4} = 10$ Hz, OCHC*H*), 3.66 (3H, s, NCH_3), 4.45 (1H, dq, C*H*CH_3), 4.94 (1H, dd, C*H*OH), 5.61 (1H, d, OH), 6.69 (1H, d, H-8), 6.90 (1H, broad s, NC*H*CHN), 6.93 (1H, broad s, NCHC*H*N), 7.21 (1H, dd, H-7), 7.60 (1H, d, H-5).

Anal. Calcd. for $C_{14}H_{15}BrN_2O_2$: C, 52.03; H, 4.68; N, 8.67; Br, 24.72. Found: C, 51.89; H, 4.68; N, 8.68; Br, 24.67.

2-(6-Chloro-2-methyl-2*H*-1-benzopyran-3-yl)-1-methyl-1*H*-imidazole (**8a**).

A solution of 1.3 g (4.6 mmoles) of **7b** in 45 ml of glacial acetic acid and 15 ml of concentrated sulfuric acid was heated at 80° for 2 hours. After cooling, the reaction mixture was poured into crushed ice, neutralized with ammonium hydroxide and extracted with methylene chloride. The organic layer was dried over sodium sulfate and evaporated to dryness. The resulting residue was taken up with ethyl ether, filtered and evaporated to dryness yielding 0.7 g (58%) of **8a**; ^{1}H nmr (deuteriochloroform): 1.42 (3H, d, $CHCH_3$), 3.79 (3H, s, NCH_3), 5.61 (1H, q, OCH), 6.51 (1H, s, OCHCC*H*), 6.65-7.15 (5H, m, benzene H and imidazole H).

Anal. Calcd. for $C_{14}H_{15}ClN_2O$: C, 64.49; H, 5.02; N, 10.74; Cl, 13.59. Found: C, 64.65; H, 5.01; N, 10.77; Cl, 13.63.

2-Methyl-3-(1-methyl-1*H*-imidazol-2-yl)-2*H*-1-benzopyran-6-ol Hydrobromide (**8b**).

A mixture of 4 g (14.5 mmoles) of **7d** and 150 ml of concentrated hydrobromic acid was heated at reflux for 4 hours. After cooling, the reaction mixture was poured into crushed ice. The solid was filtered, washed with water and dried to give 3.2 g (67%) of **8b**, mp 268-270°; ^{1}H nmr (DMSO-d_6): 1.36 (3H, d, CHC*H*$_3$), 4.00 (3H, s, NCH$_3$), 5.42 (1H, q, C*H*CH$_3$), 6.83 (3H, m, benzene H), 7.41 (1H, broad s, OCHCC*H*), 7.72 (1H, d, NC*H*CHN), 7.80 (1H, broad s, NCHC*H*N).

Anal. Calcd. for $C_{14}H_{15}BrN_2O_2$: C, 52.03; H, 4.69; N, 8.66; Br$^-$, 24.72. Found: C, 51.87; H, 4.70; N, 8.68; Br$^-$, 22.66.

6-Methoxy-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-one (**4d**).

A mixture of 0.7 g (2.8 mmoles) of **5c** and 50 ml of acetic anhydride was heated at 100° for 3 hours. After cooling, the reaction mixture was poured into crushed ice and 8% hydrochloric acid (10 ml) was added. The acidic aqueous solution was washed with methylene chloride, neutralized with 2*N* sodium hydroxide and extracted with methylene chloride. The organic layer was dried over sodium sulfate and evaporated to dryness giving 0.6 g (78%) of **4d**, mp 160-162°.

6-Methoxy-3-(1-methyl-1*H*-imidazol-2-yl)-2-phenyl-4*H*-1-benzopyran-4-one (**9**).

A mixture of 1 g (4.0 mmoles) of **5c** and 9.2 g (40.0 mmoles) of benzoic anhydride was heated at 120° for 3 hours. After cooling the reaction mixture was poured into crushed ice and extracted with methylene chloride. The organic layer was repeatedly extracted with a solution of 8% hydrochloric acid. The acidic aqueous solution, separated from the organic layer, was neutralized with sodium bicarbonate, extracted with methylene chloride and the solvent was evaporated to dryness yielding 0.68 g (50%) of **9**; ^{1}H nmr (deuteriochloroform): 3.65 (3H, s, NCH$_3$), 3.92 (3H, s, OCH$_3$), 7.10-7.70 (10H, m, benzene H and imidazole H).

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.77; H, 4.85; N, 8.43. Found: C, 72.46; H, 4.86; N, 8.45.

6-Chloro-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-one (**10**).

A mixture of 1.0 (4.0 mmoles) of **5a** and 40 ml of triethyl orthoformate was refluxed for 3 hours. The reaction mixture was cooled at 0° and the resulting solid was filtered and washed with ethyl ether to yield 0.6 g (57%), of **10**, mp 235-237°; ^{1}H nmr (deuteriochloroform): 3.66 (3H, s, NCH$_3$), 7.02 (1H, broad s, NC*H*CHN), 7.08 (1H, broad s, NCHC*H*N), 7.48 (1H, d, H-8), 7.65 (1H, dd, H-7), 8.22 (1H, d, H-5), 8.29 (1H, s, OCH).

Anal. Calcd. for $C_{13}H_9ClN_2O_2$: C, 59.90; H, 3.48; N, 10.74; Cl, 13.60. Found: C, 60.02; H, 3.48; N, 10.71; Cl, 13.57.

trans-6-Chloro-2,3-dihydro-2-methyl-3-(1-methyl-1*H*-imidazol-2-yl)-4*H*-1-benzopyran-4-one (**11**).

In a flask equipped with an efficient reflux condenser, a mixture of 4.7 g (18.7 mmoles) of **5a**, 50 ml of acetaldehyde and 500 ml of acetic acid was heated at 90° for 7 hours. The solvent was evaporated under reduced pressure and the residue, taken up with methylene chloride, was washed with water. The organic layer was dried and evaporated to give a solid residue which was chromatographed on a silica gel column, eluting with chloroform-methanol (14:1). The eluate, evaporated to dryness, then washed with ethyl ether, yielded, 3.2 g (61%) of **11**, mp 141-143°; ^{1}H nmr (deuteriochloroform): 1.46 (3H, d, CHC*H*$_3$), 3.61 (3H, s, NCH$_3$), 3.93 (1H, d, J = 12 Hz, OCHC*H*), 5.13 (1H, dq, OC*H*CH), 6.89 (1H, broad s, NC*H*CHN), 6.98 (1H, broad s, NCHC*H*N), 6.96 (1H, d, H-8), 7.42 (1H, dd, H-7), 7.79 (1H, d, H-5).

Anal. Calcd. for $C_{14}H_{13}ClN_2O_2$: C, 60.76; H, 4.73; N, 10.12; Cl, 12.81. Found: C, 60.90; H, 4.72; N, 10.15; Cl, 12.78.

3-(1-Methyl-1*H*-imidazol-2-yl)-2-phenyl-4*H*-1-benzopyran-4-one (**12**).

To a stirred solution of 1.2 (12.4 mmoles) of 1,2-dimethylimidazole and 2.5 g (24.8 mmoles) of triethylamine in 20 ml of acetonitrile, 6.46 g (24.8 mmoles) of 2-benzoyloxybenzoyl chloride in 20 ml of acetonitrile were added portionwise at 10-15°. After stirring at room temperature for 4 hours the mixture was poured into water and extracted with methylene chloride. The organic phase was extracted several times with a solution of 10% hydrochloric acid. The acidic aqueous layer were combined, neutralized with sodium bicarbonate and extracted with methylene chloride. The organic layer was dried over sodium sulfate and evaporated to give a residue which was chromatographed on a silica gel column, eluting with chloroform-methanol (18:1). The eluate evaporated to dryness yielded 1.1 g (29%) of **12**; ^{1}H nmr (deuteriochloroform): 3.48 (3H, s, NCH$_3$), 6.97 (1H, d, NC*H*CHN), 7.10 (1H, d, NCHC*H*N), 7.20-7.80 (8H, m, H-6, H-7, H-8 and phenyl H), 8.28 (1H, dd, H-5).

Anal. Calcd. for $C_{19}H_{14}N_2O_2$: C, 75.47; H, 4.66; N, 9.26. Found: C, 75.27; H, 4.66; N, 9.29.

The known 2-benzoyloxybenzoyl chloride was prepared by reaction of the corresponding acid with an excess of refluxing thionyl chloride.

3-(1H-Imidazol-2-yl)-2-methyl-4*H*-1-benzopyran-4-one (**13**).

To a solution of 2.7 g (32.8 mmoles) of 2-methylimidazole and 10.0 g (98.8 mmoles) of triethylamine in 50 ml of acetonitrile, 19.6 g (98.8 mmoles) of **1a** in 35 ml of acetonitrile were added portionwise at 10-15° under stirring. After keeping at room temperature for 3 hours the mixture was poured into water, then extracted with methylene chloride and the solvent was evaporated to dryness. The resulting dark oil was dissolved in a mixture of 10 ml of glacial acetic acid and 10 ml of 36% hydrochloric acid. The mixture was heated at 90° for 3 minutes, then was concentrated under reduced pressure and the residue, taken up with 100 ml of water, was washed with methylene chloride. The aqueous solution was alkalinized with sodium bicarbonate and extracted with methylene chloride. The organic layer was dried over sodium sulfate and evaporated to give a residue which was chromatographed on a silica gel column, eluting with chloroform-methanol (45:1). The eluate, evaporated to dryness, yielded 1.5 g (20%) of **13**, mp 138-140°; ^{1}H nmr (DMSO-d_6): 2.80 (3H, s, CH$_3$), 7.15 (2H, broad s, imidazole H), 7.40-8.00 (3H, m, H-6, H-7, H-8), 8.14 (1H, dd, H-5), 10.30 (1H, broad s, NH).

Anal. Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.45; N, 12.38. Found: C, 68.84; H, 4.44; N, 12.41.

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