3-Benzoyl-3,4-dihydro-2*H*,5*H*-1-benzopyrano[4,3-*b*]pyran-5-ones by Condensation of 4-Hydroxycoumarins with Enone Mannich Bases

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Dedicated to Professor Dr. Gottfried Heinisch, Institute of Pharmaceutical Chemistry, University of Innsbruck (Republic of Austria) on the occasion of his 60th birthday

Starting from 4-hydroxycoumarins **4** and 1-aryl-2-(dimethylaminomethyl)prop-2-en-1-ones **2** the title compounds **6** have been synthesized. The reaction is initiated by addition of the C-3 carbon atom of 4-hydroxycoumarin to the enone double bond of the Mannich base, subsequent deamination affords the intermediate 3-(2-benzoylallyl)-4-hydroxycoumarin **8**, followed by ring closure. Depending on the reaction time, varying proportions of the ketones **6** and **8** are formed and support the mechanism defined. The spectroscopic data of all products unambiguously distinguish between the coumarin and the chromone structures in favor of the former.

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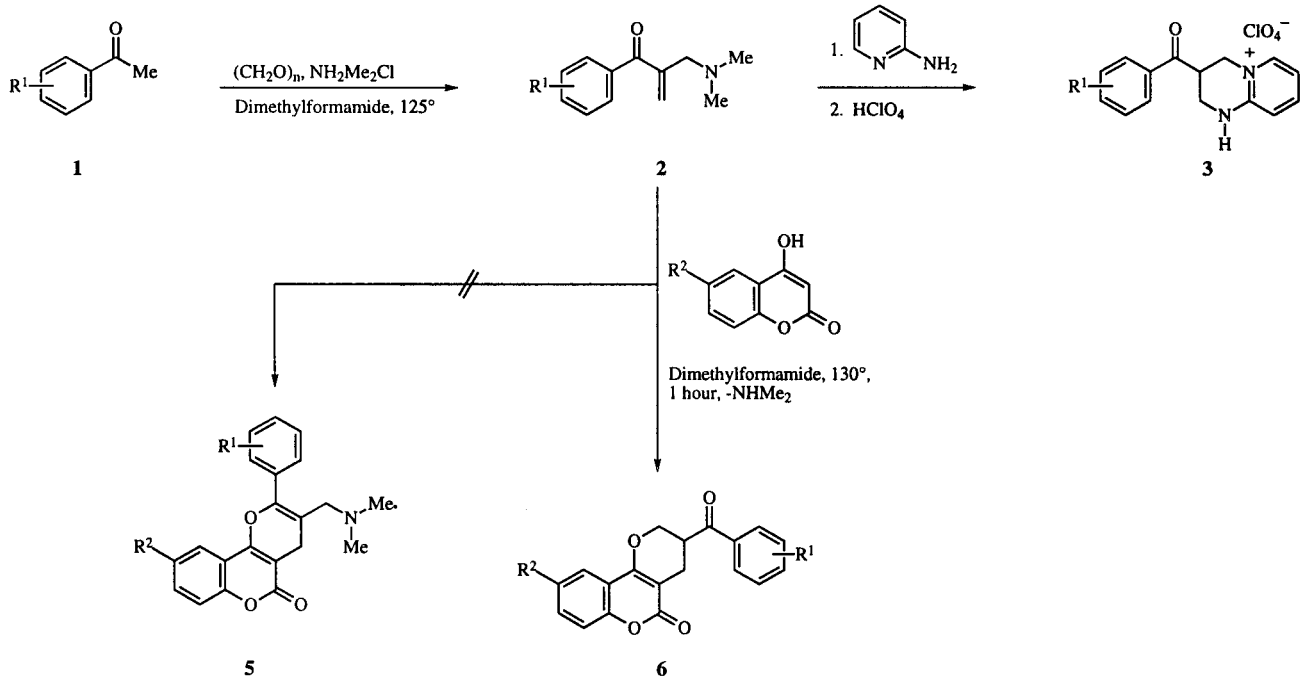
The enone Mannich bases **2** are easily accessible by heating of aryl methyl ketones **1**, paraformaldehyde, and dimethylamine hydrochloride in dimethylformamide. They are isolated and stored as hydrochloride salts [1]. According to their structure the conclusion may be drawn that altogether three electrophilic centers can be involved in an addition-elimination mechanism which enables these versatile reagents to be excellent precursors for ring closure reactions. We described recently a convenient preparation of novel 3-benzoyl-3,4-dihydro-2*H*-pyrido-[1,2-*a*]pyrimidines by condensation of the enone Mannich bases **2** with 2-aminopyridines demonstrating that despite the polyfunctional character of both reactants a unique mode of reaction had taken place [2]. In order to study the reactivity of other than *N*-nucleophiles we selected 4-hydroxycoumarines **4** as representative *O*,*C*-nucleophiles. They should be capable to cyclize with **2** yielding anellated pyrane derivatives such as **5** or **6** (see Scheme 1). The spectroscopic data of the condensation products unambiguously established the structure of the 3-benzoyl-3,4-dihydro-2*H*,5*H*-1-benzopyrano[4,3-*b*]pyran-5-ones **6** unsubstituted in position 2 and 4. According to a literature search the synthesis of such heterocycles has not been described up to now.

Certainly, pyranocoumarins with a different substitution pattern are well known in the literature. In connection with the biological potencies as anticoagulants *e.g.* warfarin the cyclization of 3-substituted 4-hydroxycoumarins had been performed [4-7]. The preparation of these and other pyranocoumarins [8-14] involves two, three or more steps starting from 4-hydroxycoumarin, *e.g.* Michael addition to an α,β-unsaturated carbonyl compound, reduction of the keto group followed by thermal or Lewis acid catalyzed cyclic dehydration of the corresponding alcohol [6]. Interestingly, the Michael condensation of 2-methylene-1,3-dicarbonyl compounds with 4-hydroxycoumarin gives rise to 2,2,3-trisubstituted 3,4-dihydro-2*H*-pyrano-[3,2-*c*][1]benzopyran-5-ones regioselectively but not stereoselectively after ring closure by acid treatment [13]. This two step reaction is rather similar to our condensations with enone Mannich bases described here, as both reagents are propenone derivatives with three electrophilic centers. Otherwise, there are several one step condensations for the synthesis of 3,4-dihydro-2*H*,5*H*-1-benzopyrano[4,3-*b*]pyran-2,5-diones from 4-hydroxycoumarin and α,β-unsaturated acyl chlorides as well as corresponding carbonyl compounds [15-18] or from phenol and 2-phenyl-1,1,3-tris(ethoxycarbonylpropane) [19,20].

As mentioned above, we found a procedure for preparing the 3-benzoyl-3,4-dihydro-2*H*,5*H*-1-benzopyrano-[4,3-*b*]pyran-5-ones **6** in up to 84% yield by heating the 4-hydroxycoumarin **4** with two equivalents of the enone Mannich base **1** in dimethylformamide as the solvent to 130-140° for 1.5 hours. Prolonged heating does not improve the yields, instead the products obtained after recrystallization are colored yellowish, probably due to thermal decomposition. The spectroscopic characterization of the isolated products revealed that - as anticipated - an addition-elimination mechanism had taken place (see Mechanism). In the first step, the carbon atom 3 adds to the double bond affording the saturated intermediate **7** [3]. Next, the third electrophilic center is generated by elimination of Me_2NH_2Cl to form the enone **8** followed by a second addition reaction to the ring closed heterocycle **6**. Whereas **7** could not be isolated, the intermediate enone **8**

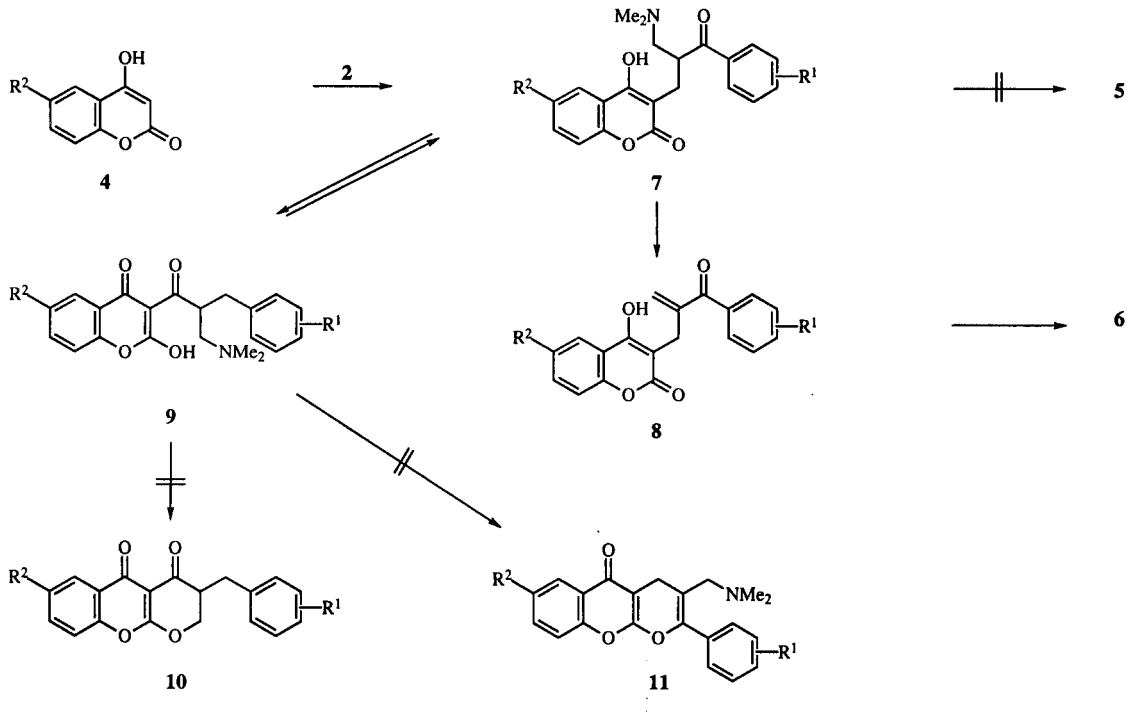
Scheme 1



1 2 3 5 6

1-4, 6	a	b	c	d	e	f	g	h	i	k	l	m
R^1	H	4-Me	4-Br	4-OMe	3,4-Cl_2	3,4-$(OMe)_2$	H	4-Br	H	4-Me	H	3,4-$(OMe)_2$
R^2	H	H	H	H	H	H	Me	Me	Cl	Cl	Br	Br

Mechanism



4 7 8 9 10 11

was detected by tlc and could be characterized when the heating was stopped already after 15 minutes as a mixture together with **6**. A more detailed analysis of the temperature and solvent dependence of the reaction sequence was performed employing high pressure liquid chromatography and will be published elsewhere [21]. Obviously, attack at the keto carbonyl group of the enone Mannich base **2** by 4-hydroxycoumarin with formation of the corresponding benzopyranopyran **5** does not occur. The existence of the tautomeric forms **4** and 2-hydroxychromone has been demonstrated by Arndt [22] who obtained a mixture of 4-methoxycoumarin and 2-methoxychromone on treatment of 4-hydroxycoumarin with diazomethane. The determination of coumarin or chromone structures for the reaction products is important to this work as well, since the structurally different isomers **5** and **6** from **7** as well as **10** and **11** from **9** are possible ring closure reactions. In fact, nmr spectroscopy can unambiguously distinguish between the dimethylamino compounds **5** and **11** on the one hand and the pyranocoumarins **6** and **10** on the other hand. This is not easily achieved for the coumarin or chromone structures of **6** and **10**, respectively. Of the methods which have been used for studying 4-hydroxycoumarin/2-hydroxychromone tautomerism, only infrared spectroscopy has the capability to distinguish tautomeric substances both in solution and in the crystalline state [23]. The ir spectra of the isolated products are not consistent with the conceivable follow-up products **10** and **11** giving evidence that ring closure at C-2 of the coumarin ring does not occur (see Mechanism).

Mechanism.

All the spectroscopic and analytical data obtained for the compounds **6a-6m** prove the structure given for the anellated coumarins **6**. The physical characteristics and spectroscopic data of **6a-m** are listed in Tables 1 to 3. The assignment of the ^{1}H- and ^{13}C nmr data was accomplished with the help of correlated spectroscopy, *i.e.* H,H-COSY with **6a**, as well as CH-COSY- and COLOC-experiments with **6h**. Assignment of the signals of the aroyl-substituent was aided by the use of incremented values [24]. A special feature in the ^{1}H nmr-spectra of **6** is the ABMNX-system of the saturated part of the ring system. The coupling constants given in Table 2 were obtained after resolution enhancement by multiplication of the free induction decay with the sine function and first order analysis of the complex splitting pattern of the multiplets between 2.7 and 4.7 ppm. Not unexpectedly, the methylene group at position 2 exhibits a geminal coupling of about 11 Hz due to the oxygen in α-position, the value of the methylene group in position 4 is about 17 Hz for this coupling. Furthermore only one of the protons in each

Table 1

Physical Data and IR of Benzopyrano[4,3-*b*]pyridins **6a-m**

Compound 6	Yield (%)	Mp (°C) (Recrystallization Solvent)	Molecular Formula (Molecular Weight)	Analysis Calcd./Found C	H	IR (cm^{-1}) Potassium Bromide
a	78	186	$C_{19}H_{14}O_4$	74.51	4.61	1685, 1678, 1626,
		ethanol	306.3	74.22	4.42	1574, 1494, 1380
b	73	184	$C_{20}H_{16}O_4$	75.00	5.03	1696, 1674, 1626,
		ethanol	320.3	74.70	5.11	1494, 1378, 1276
c	82	188	$C_{19}H_{13}BrO_4$	59.24	3.40	1688, 1684, 1624,
		ethanol	385.2	58.88	3.66	1584, 1494, 1378
d	63	160	$C_{20}H_{16}O_5$	71.45	4.80	1688, 1680, 1624,
		ethanol	336.3	71.18	4.92	1576, 1494, 1378
e	73	247 dec	$C_{19}H_{12}Cl_2O_4$	60.82	3.22	3030, 1690, 1678,
		toluene	375.2	60.57	3.16	1630, 1574, 1380
f	70	219 dec	$C_{21}H_{18}O_6$	68.84	4.95	2980, 2850, 1702,
		toluene	366.4	68.48	5.07	1660, 1630, 1588
g	80	195	$C_{20}H_{16}O_4$	75.00	5.03	3080, 1682, 1626,
		ethanol	320.3	74.66	5.22	1582, 1468, 1380
h	83	211	$C_{20}H_{15}BrO_4$	60.18	3.79	1680, 1628, 1504,
		toluene	399.2	59.78	3.90	1468, 1396, 1280
i	84	198	$C_{19}H_{13}ClO_4$	66.96	3.84	3080, 1694, 1688,
		toluene	340.8	66.73	3.95	1626, 1570, 1482
k	67	198	$C_{20}H_{15}ClO_4$	67.71	4.26	1696, 1674, 1624,
		toluene	354.8	67.55	4.17	1572, 1484, 1422
l	79	199	$C_{20}H_{16}BrO_4$	59.24	3.40	1694, 1688, 1624,
		toluene	385.2	59.01	3.36	1566, 1480, 1378
m	64	175	$C_{21}H_{17}BrO_6$	56.64	3.85	1694, 1660, 1620,
		toluene	445.3	56.33	3.90	1596, 1484, 1376

Table 2

^{1}H-NMR Shifts of Compounds **6a-m** in ppm (Deuteriochloroform, relative to Tetramethylsilane)

6a	7.99 (d, 7.5 Hz, 2H, H-2'), 7.77 (dd, 8.0/1.3 Hz, 1H, H-10), 7.63 (t, 7.5 Hz, H-4'), 7.51 (m, 3H, H-8, H-3'), 7.31 (d, 8.2 Hz, 1H, H-7), 7.28 (t, 7.6 Hz, 1H, H-9), 4.74 (ddd, 11.1/3.4/1.1 Hz, 1H, H-2a), 4.37 (dd, 11.1/8.0 Hz, 1H, H-2b), 3.95 (m, 1H, H-3), 3.02 (ddd, 16.9/5.7/1.1 Hz, 1H, H-4a), 2.73 (dd, 16.9/8.2 Hz, 1H, H-2b)
6b	7.89 (d, 8.2 Hz, 2H, H-2'), 7.76 (d, 7.7 Hz, 1H, H-10), 7.51 (t, 8.2 Hz, 1H, H-8), 7.30 (d, 8.2 Hz, 2H, H-3'), 7.27-7.24 (m, 2H, H-9, H-7), 4.72 (ddd, 11.2/3.4/2.1 Hz, 1H, H-2a), 4.35 (dd, 11.1/10.0 Hz, 1H, H-2b), 3.92 (m, 1H, H-3), 2.99 (ddd, 17.2/3.8/1.8 Hz, 1H, H-4a), 2.73 (dd, 17.2/10.3 Hz, 1H, H-2b), 2.43 (s, 3H, 4'-Me)
6c	7.86 (d, 8.6 Hz, 2H, H-2'), 7.75 (d, 7.4 Hz, 1H, H-10), 7.65 (d, 8.6 Hz, 2H, H-3'), 7.52 (t, 8.0 Hz, 1H, H-8), 7.27 (m, 2H, H-9, H-7), 4.71 (ddd, 11.1 Hz [a]), 1H, H-2a), 1H, H-2a), 4.36 (dd, 11.0/9.8 Hz, 1H, H-2b), 3.89 (br m, 1H, H-3), 2.99 (dd, 16.8/5.8 Hz, 1H, H-4a), 2.71 (dd, 17.2/10.2 Hz, 1H, H-2b)
6d	7.98 (d, 8.9 Hz, 2H, H-2'), 7.78 (dd, 7.8/1.4 Hz, 1H, H-10), 7.53 (td, 8.2/1.4 Hz, 1H, H-8), 7.32 (d, 8.1 Hz, 1H, H-7), 7.31 (t, 8.0 Hz, 1H, H-9), 6.98 (d, 8.9 Hz, 2H, H-3'), 4.72 (ddd, 11.4/3.4/2.2 Hz, 1H, H-2a), 4.36 (dd, 11.2/10.0 Hz, 1H, H-2b), 3.90 (s, 3H, 4'-OMe), 3.89 (br m, 1H, H-3), 3.01 (ddd, 17.2/5.4/1.8 Hz, 1H, H-4a), 2.73 (dd, 17.2/10.6 Hz, 1H, H-2b)
6e	8.04 (d, 1H, 1.8 Hz, H-2'), 7.80 (m, 2H, H-10, H-6'), 7.61 (d, 8.3 Hz, 1H, H-5'), 7.54 (t, 7.8 Hz, 1H, H-8), 7.32 (m, 2H, H-7, H-9), 4.71 (ddd, 12.0/3.0/1.0 Hz [a], 1H, H-2a), 4.37 (dd, 11.2/9.8 Hz, 1H, H-2b), 3.87 (br m, 1H, H-3), 3.03 (ddd, 17.4/5.0/1.0 Hz, 1H, H-4a), 2.74 (dd, 17.2/10.0 Hz, 1H, H-2b)
6f	7.89 (d, 1H, 7.8 Hz, H-10), 7.63 (d, 1H, 8.0 Hz, H-6'), 7.54 (d, 2.0 Hz, 1H, H-2'), 7.53 (t, 7.5 Hz, 1H, H-8), 7.32 (m, 2H, H-7, H-9), 6.93 (d, 8.4 Hz, 1H, H-5'), 4.72 (ddd, 11.2/3.5/2.0 Hz, 1H, H-2a), 4.37 (dd, 11.0/10.3 Hz, 1H, H-2b), 3.98/3.95 (2 x s, 6H, 3'-OMe/4'-OMe), 3.90 (br m, 1H, H-3), 3.03 (ddd, 17.0/6.0/2.0 Hz [a], 1H, H-4a), 2.74 (dd, 17.3/10.3 Hz, 1H, H-2b)
6g	8.00 (d, 7.2 Hz, 2H, H-2'), 7.62 (t, 7.0 Hz, 1H, H-4'), 7.55 (s [a], 1H, H-10), 7.51 (t, 7.2 Hz, 2H, H-3'), 7.32 (d, 8.5 Hz, 1H, H-8), 7.20 (d, 8.5 Hz, 1H, H-7), 4.72 (ddd, 10.4 Hz [a], 1H, H-2a), 4.36 (dd, 10.7/10.4 Hz, 1H, H-2b), 3.95 (m, 1H, H-3), 3.03 (ddd, 17.2 Hz [a], 1H, H-4a), 2.71 (dd, 17.2/10.0 Hz, 1H, H-2b), 2.41 (s, 3H, 9-Me)
6h	7.85 (d, 8.3 Hz, 2H, H-2'), 7.65 (d, 8.3 Hz, 2H, H-3'), 7.54 (s, 1H, H-10), 7.32 (d, 8.7 Hz, 1H, H-8), 7.18 (d, 8.7 Hz, 1H, H-7), 4.70 (ddd, 12.0 Hz [a], 1H, H-2a), 4.35 (dd, 11.0/10.4 Hz, 1H, H-2b), 3.89 (m, 1H, H-3), 2.98 (ddd, 17.6/4.0 Hz [a], 1H, H-4a), 2.69 (dd, 17.2/10.3 Hz, 1H, H-2b), 2.40 (s, 3H, 9-Me)
6i	7.99 (d, 8.2 Hz, 2H, H-2'), 7.73 (s, 1H, H-10), 7.63 (t, 7.0 Hz, 1H, H-4'), 7.52 (t, 7.4 Hz, 2H, H-3'), 7.45 (d, 8.2 Hz, 1H, H-8), 7.24 (d, 9.0 Hz [a], 1H, H-7), 4.73 (ddd, 11.7 Hz [a], 1H, H-2a), 4.38 (dd, 10.4/9.5 Hz, 1H, H-2b), 3.96 (m, 1H, H-3), 3.01 (ddd, 16.0 Hz [a], 1H, H-4a), 2.74 (dd, 17.4/9.8 Hz, 1H, H-2b)
6k	7.89 (d, 7.6 Hz, 2H, H-2'), 7.74 (s, 1H, H-10), 7.46 (d, 8.2 Hz, 1H, H-8), 7.31 (d, 7.6 Hz, 2H, H-3'), 7.25 (d, 9.1 Hz [a], 1H, H-7), 4.72 (ddd, 10.6 Hz [a], 1H, H-2a), 4.38 (dd, 10.6/10.1 Hz, 1H, H-2b), 3.94 (m, 1H, H-3), 3.01 (ddd, 17.2/4.5 Hz, 1H, H-4a), 2.73 (dd, 17.2/10.2Hz, 1H, H-2b), 2.44 (s, 3H, 9-Me)
6l	7.99 (d, 7.4 Hz, 2H, H-2'), 7.89 (s, 1H, H-10), 7.65-7.50 (m, 4H, H-8, H-3', H-4'), 7.20 (d, 8.5 Hz, 1H, H-7), 4.74 (ddd, 10.0 Hz [a], 1H, H-2a,), 4.38 (dd, 11.1/10.0 Hz, 1H, H-2b), 3.97 (m, 1H, H-3), 3.01 (ddd, 17.2/4.5 Hz, 1H, H-4a), 2.73 (dd, 17.2/10.2 Hz, 1H, H-2b), H-2b), 2.44 (s, 3H, 9-Me)
6m	7.89 (s, 1H, H-10), 7.63 (d, 9.0 Hz [a], 1H, H-6'), 7.59 (d, 8.5 Hz, 1H, H-8), 7.53 (s, 1H, H-2'), 7.19 (d, 8.7 Hz, 1H, H-7), 6.93 (d, 9.0 Hz [a], 1H, H-5'), 4.70 (ddd, 11.5 Hz [a], 1H, H-2a), 4.37 (dd, 10.6/10.2 Hz, 1H, H-2b), 3.97/3.94 (2 x s, 6H, 3'-OMe, 4'-OMe), 3.90 (m, 1H, H-3), 2.99 (ddd, 16.0 Hz [a], 1H, H-4a), 2.75 (dd, 17.2/10.4 Hz, 1H, H-2b)

[a] Approximate values given due to superposition of signals or low resolution.

methylene group shows a ^{4}J coupling which can be evaluated to be in the order of 1.8 Hz. Similarly, the shifts of the ^{13}C nmr data upon introduction of substituents into position 9 can be characterized by typical shifts which follow the same order as reported values [24].

In summary, treatment of 4-hydroxycoumarines **4** with enone Mannich bases **2** offers a very promising, synthetically simple to perform and straightforward route to 3-benzoyl-3,4-dihydro-2*H*,5*H*-1-benzopyrano[4,3-*b*]pyran-5-ones **6** and can be extended to include other enolic heterocycles. The resulting bi- or polycyclic pyrano anellated heterocycles are not only interesting targets themselves but are also valuable educts for reduction or condensation processes giving potential drug molecules.

EXPERIMENTAL

The ir spectra were recorded as potassium bromide pellets on a Perkin-Elmer FT-ir 16 PC spectrometer, ν in cm^{-1}, and the mass spectra on a HP 5989 MS engine A. The ^{1}H and ^{13}C nmr spectra were obtained on a Bruker ARX 300. Chemical shifts

Table 3

^{13}C-NMR Shifts of Compounds **6a-m** in Deuteriochloroform

	C-2	C-3	C-4	C-4a	C-5	C-6a	C-7	C-8	C-9	C-10	C-10a	C-10b	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C=O
6a	68.0	39.0	23.7	100.4	162.5	152.2	116.5	131.7	123.9	122.4	115.2	159.6	135.3	129.0	128.4	133.7			198.9
6b [a]	68.1	38.8	23.8	100.4	162.5	152.2	116.5	131.6	123.9	122.4	115.2	159.5	132.8	128.5	129.6	144.9			198.4
6c	67.8	38.9	23.7	100.2	162.5	152.2	116.5	131.7	123.9	122.4	115.1	159.6	134.0	129.9	132.3	129.2			197.9
6d [b]	68.3	38.6	24.0	100.6	162.6	152.3	116.6	131.7	123.9	122.4	115.3	159.7	128.3	130.8	114.2	164.2			197.3
6e	67.7	39.2	23.7	100.1	162.5	152.3	116.7	131.9	124.1	122.5	115.1	159.7	134.8	131.2	134.0	138.8	130.4	127.4	196.8
6f [c]	68.3	38.4	24.0	100.5	162.6	152.2	116.5	131.6	123.9	122.4	115.2	159.6	128.5	110.3	154.0	149.5	110.2	123.3	197.3
6g [d]	68.0	39.0	23.8	100.2	162.7	150.4	116.3	132.7	133.6	122.1	114.8	159.6	135.3	129.0	128.4	133.9			198.9
6h [d]	67.8	39.0	23.8	100.0	162.6	150.4	116.3	132.7	133.7	122.1	114.7	159.6	134.0	129.9	132.3	129.2			198.0
6i	68.2	38.8	23.6	101.3	161.9	150.5	118.0	131.6	129.5	122.1	116.3	158.5	135.2	129.0	128.4	134.0			198.6
6k [e]	68.3	38.6	23.7	101.4	162.0	150.5	118.0	131.6	129.5	122.1	116.3	158.5	132.7	128.5	129.7	145.1			198.2
6l	68.2	38.7	23.6	101.3	161.9	151.0	118.3	134.5	116.7	125.1	116.8	158.5	135.1	129.0	128.4	134.0			198.6
6m [f]	68.5	38.3	23.9	101.5	161.9	151.0	118.3	134.4	116.8	125.1	116.8	158.4	128.4	110.4	154.1	149.5	110.2	123.2	197.0

[a] 4'-Me 21.6 ppm; [b] 4'-OMe 55.6 ppm; [c] 3',4'-$(OMe)_2$ 56.0/56.1 ppm; [d] 9-Me 20.9 ppm; [e] 4'-Me 21.7 ppm; [f] 3',4'-$(OMe)_2$ 56.1/56.2 ppm, the signal of C-9 and C-10a are isochronous in deuteriochloroform, they can be distinguished in a 1/1 mixture of deuteriochloroform and dimethylsulfoxide-d_6 (116.4 and 116.5 ppm).

Table 4

Electron Impact Mass Spectra m/z (I, %B) of Compounds **6a-m** with 70 eV Ionization Energy

6a	306	(M^+, 4)	202	(14)	201	(100)	121	(13)	105	(91)	92	(12)	77	(95)	53	(14)	51	(32)	43	(6)
6b	320	(M^+, 11)	202	(14)	201	(100)	121	(7)	120	(6)	119	(44)	92	(7)	91	(32)	65	(13)	63	(4)
6c	386	(M^+ ^{81}Br, 3)	202	(14)	201	(100)	185	(16)	183	(16)	157	(9)	155	(9)	121	(8)	76	(8)	44	(19)
6d	336	(M^+, 8)	202	(14)	201	(100)	135	(64)	121	(6)	107	(12)	92	(15)	77	(23)	64	(8)	53	(5)
6e	374	(M^+ ^{35}Cl, 2)	202	(14)	201	(100)	175	(11)	173	(17)	147	(7)	145	(12)	129	(5)	121	(10)	92	(5)
6f	366	(M^+, 26)	202	(14)	201	(100)	166	(7)	165	(62)	137	(10)	121	(8)	92	(9)	79	(10)	77	(13)
6g	320	(M^+, 9)	216	(15)	215	(100)	135	(7)	128	(5)	105	(37)	78	(6)	77	(33)	53	(5)	51	(10)
6h	400	(M^+ ^{81}Br, 2)	235	(10)	216	(15)	215	(100)	185	(15)	183	(14)	135	(10)	105	(23)	77	(22)	43	(20)
6i	340	(M^+ ^{35}Cl, 3)	237	(33)	236	(14)	235	(100)	215	(4)	155	(6)	128	(7)	105	(78)	77	(62)	44	(8)
6k	354	(M^+ ^{35}Cl, 8)	237	(33)	235	(100)	119	(99)	9	(70)	84	(22)	65	(30)	59	(17)	51	(18)	49	(39)
6l	386	(M^+ ^{81}Br, 6)	281	(63)	279	(63)	235	(6)	201	(9)	128	(9)	105	(100)	77	(79)	53	(15)	51	(25)
6m	446	(M^+ ^{81}Br, 5)	165	(46)	86	(32)	84	(58)	69	(51)	55	(34)	51	(38)	49	(100)	53	(56)	41	(48)

were expressed in δ (ppm) downfield from tetramethylsilane as an internal reference or relative to the signal of deuteriochloroform (77.0 ppm). Microanalyses were carried out in the Microanalytical laboratory of the Institute of Anorganic Chemistry, University of Kiel. Merck Kieselgel 60 F_{254} on aluminium sheets was used for tlc monitoring.

3-Benzoyl-3,4-dihydro-2*H*,5*H*-1-benzopyrano[4,3-*b*]pyran-5-ones **6**. General Procedure.

To a solution of 2 mmoles of **2** in dimethylformamide (3 ml) was added 4-hydroxycoumarin **4** (1 mmole), and the mixture was heated in an oil bath at 130-140° for 1.5 hours. After cooling the mixture was diluted with 25 ml of water and stirred for 15 minutes in an ice-bath. The precipitate was filtered by suction, washed twice with 10 ml of water, dried, and recrystallized from the solvent given (see Table 1).

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