

**Reaction of 3-Carbethoxy-5,6-benzocoumarin With  
Anthranilic Acid And Synthesis & Some Reactions  
of 3(3',1'-Benzoxazin-4'-one)-5,6-benzocoumarin**

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**Summary:** Treatment of 3-carbethoxy-5,6-benzocoumarin (Ia) with anthranilic acid gives 4-anthraniloyl-3-carbethoxy-3,4-dihydro-5,6-benzocoumarin (IIa) and 3-carbethoxy-3,4-dihydro-5,6-benzocoumarin (IIIa) was synthesised also. Alkaline hydrolysis of (IIb) gave (IIIb). On the otherhand the action of anthranilic acid on (Ia) at 170°C gave (IIIc), (IIa) and (Id). Cyclization of (Id) by acetic anhydride occurred and (IV) was obtained. Acidic or basic hydrolysis of (IV) gave the same product (Ic). While ammonolysis of (IV) gave (Ie). The behaviour of both  $\delta$ -lactone and oxazinone rings in (IV) towards different amines, hydrazines were studied and aromatic hydrocarbons under Friedel-Crafts conditions.

In continuation of the previous studies [1-3] the present communication reports on the reaction of 3-carbethoxy-5,6-benzocoumarin (Ia), with anthranilic acid in boiling benzene for 1 hour gives 4-anthraniloyl-3-carbethoxy-3,4-dihydro-5,6-benzocoumarin (IIa), while if the time reaction increased to 3 hours. 3-carbethoxy 3,4-dihydro-5,6-benzocoumarin (IIIa) was obtained. The formation of (III) can be readily interpreted as the addition of anthranilic acid to  $C_3-C_4$  double bond to give (IIa) as intermediate product, followed by decomposition of (IIa) and resulting in addition of hydrogen to give (IIIa). The  $C_3-C_4$  double bond is conjugated not only with carbonyl group in the carbethoxy group but also with the carbonyl group of  $\delta$ -lactone i.e. the two carbonyl groups operate in the same direction. This prompted to report the hitherto unknown hydrogenation reaction of this activated  $C_3-C_4$  double bond.

The structure of (IIIa) was proved from the spectral data (cf. Tables 1,2) and independent synthesis via: (a) action of anhydrous aluminium chloride on a solution of (Ia) in toluene under Friedel-Crafts conditions, and (b) fusion of (Ia) with ammonium acetate at 170° resulted in the hydrogenation reaction at  $C_3-C_4$  double bond to give (IIIa) together with a product identified to be benzocoumarin-3 carbamide (Ib) by means of m.p. and mixed m.p. determination and comparison of IR spectra.

Treatment of (IIa) with acetic anhydride gave 4-(N-acetyl-anthraniloyl)-3,4-dihydro-3-carbethoxy-5,6-benzocoumarin (IIb). Alkaline hydrolysis of (IIb) gives 3,4-dihydro-5,6-benzocoumarin 3-carboxylic acid (IIIb) also by action of sodium hydroxide on (IIIa) gives a compound which was identified to be (IIIb) by m.p. and mixed m.p. and comparison of IR spectra.

Table-1: Physical data of synthesized compounds.

Compd.	M.p.°C colour	Solv. of cryst. Yield %	M.F. M.W.	Analysis Calcd / Found			IR data in cm <sup>-1</sup>
				C%	H%	N%	
(Ib)	280-81 (pale-yellow)	A (42)	C <sub>14</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub> (239)	70.29 69.98	3.77 3.81	5.86 5.98	νC=C at 1610, νC=O of amide at 1660, νC=O of δ-lactone at 1720-1740 and νNH at 3180-3340 (broad)
(Ic)	232-33 (colourless)	B (61)	C <sub>14</sub> H <sub>8</sub> O <sub>4</sub> (240)	70.00 70.20	3.40 3.36	-- --	νC=C at 1605, νC=O of acid at 1705, νC=O of δ-lactone at 1735 and νOH at 3440-3480 (broad)
(Id)	>300 (pale-yellow)	A (43)	C <sub>21</sub> H <sub>13</sub> N <sub>5</sub> O <sub>5</sub> (359)	70.19 69.45	3.62 3.39	3.89 3.72	νC=C at 1610, νC=O of amide at 1670, νC=O of acid 1710, νC=O of δ-lactone at 1735, νNH at 3180 and νOH at 3460
(Ie)	182-83 (colourless)	E (66)	C <sub>21</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> (358)	70.39 70.94	3.91 3.79	7.82 8.01	νC=C at 1600, νC=O of amide at 1680 νC=O of δ-lactone at 1740, and νNH at 3250-3380 cm <sup>-1</sup>
(If)	>300 (pale-yellow)	A (63)	C <sub>27</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> (434)	74.65 74.18	4.15 4.26	6.45 6.70	νC=C at 1610, νC=O of amide 1640-1660, νC=O of δ-lactone at 1710-1730 and νNH at 3280-3380 (broad)
(Ig)	>300 (yellow)	E+B (68)	C <sub>28</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub> (464)	72.41 73.04	4.31 4.55	6.03 6.34	νC=C at 1605-1615, νC=O of amide 1660, νC=O of δ-lactone at 1715-1740 and νNH at 3240-3395 (broad)
(Ih)	292-93 (yellow)		C <sub>28</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> (448)	75.00 75.23	4.46 4.35	6.25 6.47	
(Ii)	278-79 (pale-yellow)		C <sub>28</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> (448)	75.00 74.74	4.46 4.61	6.25 6.10	
(Ij)	218-19 (pale-yellow)	E (49)	C <sub>25</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> (414)	72.46 73.08	5.31 5.12	6.76 6.62	
(Ik)	286-87 (pale-yellow)	A (55)	C <sub>27</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> (449)	72.16 72.59	4.23 4.51	9.35 9.72	νC=C at 1610, νC=O of amide at 1640-1670, νC=O of δ-lactone at

Table-1 (cont'd.)

Compd.	M.p.°C colour	Solv. of cryst. Yield %	M.F. M.W.	Analysis Calcd / Found			IR data in cm <sup>-1</sup>
				C%	H%	N%	
							1720-1735 and νNH at 3240-3390
(IIa)	131-32 (colourless)	B+L.P (67)	C <sub>23</sub> H <sub>19</sub> NO <sub>6</sub> (405)	68.15 68.67	4.69 4.58	3.46 3.58	νC=O of acid at 1695, νC=O of ester, νC=O of δ-lactone at 1720, 1740, νNH at 3360 and νOH at 3460
(IIb)	171-172 (colourless)	B (65)	C <sub>25</sub> H <sub>21</sub> NO <sub>7</sub> (447)	67.11 67.83	4.70 4.38	3.13 3.25	νC=O of amide at 1640, νC=O of acid at 1660, νC=O of ester at 1720 and νOH (3440-3480)
(IIIa)	96-97 (colourless)	B+L.P (57)	C <sub>16</sub> H <sub>14</sub> O <sub>4</sub> (270)	71.11 71.70	5.18 5.09	--	νC=O of ester at 1745, νC=O of δ-lactone at 1760 and νCH aliph. at 2940, 3070
(IIIb)	143-44 (pale-yellow)	B (61)	C <sub>14</sub> H <sub>10</sub> O <sub>4</sub> (242)	69.42 69.80	4.13 4.04	--	νC=O of acid at 1690, νC=O of δ-lactone at 1740, νCH at 2940, 3080 and νOH at 3450
(IIIc)	238-39 (yellow)	E (64)	C <sub>20</sub> H <sub>15</sub> NO <sub>3</sub> (317)	75.71 75.40	4.73 4.81	4.42 4.29	νC=O of amide at 1680, νC=O of δ-lactone 1720-1740, νNH at 2940-3180 (broad)
(IIId)	128-29 (colourless)	L.P (68)	C <sub>27</sub> H <sub>19</sub> NO <sub>4</sub> (421)	76.96 76.63	4.51 4.70	3.33 3.45	νC=O of amide 1630, νC=O aryl at 1690, νC=O of δ-lactone at 1745, νCH <sub>2</sub> at 2890 and νNH at 3280-3380 (broad)
(IIIe)	278-79 (colourless)	E+B (66)	C <sub>28</sub> H <sub>21</sub> NO <sub>4</sub> (435)	77.24 77.65	4.83 4.71	3.22 3.12	νC=O of amide 1635, νC=O aryl at 1690, νC=O of δ-lactone at 1730-1740, νCH <sub>2</sub> at 2885 and νNH at 3260-3370 (broad)
(IIIf)	305-06 (colourless)	B (59)	C <sub>27</sub> H <sub>18</sub> NO <sub>4</sub> Cl (455.5)	71.13 71.52	3.95 3.81	3.07 3.19	
(IIIg)	167-68 (colourless)	B (63)	C <sub>29</sub> H <sub>23</sub> NO <sub>4</sub> (449)	77.51 77.78	5.12 5.28	3.12 3.15	νC=O of amide 1645, νC=O aryl at 1710, νC=O of δ-lactone at 1735, νCH <sub>2</sub> at 2890 and νNH 3190-3380 (broad)

Table-1 (cont'd.)

Compd.	M.p.°C colour	Solv. of cryst. Yield %	M.F. M.W.	Analysis Calcd / Found			IR data in cm <sup>-1</sup>
				C%	H%	N%	
(IIIh)	184-85 (colourless)	L.P (64)	C <sub>30</sub> H <sub>25</sub> NO <sub>4</sub> (463)	77.75 77.48	5.40 5.52	3.02 3.14	
(IV)	256-57 (colourless)	B+X (43)	C <sub>21</sub> H <sub>11</sub> NO <sub>4</sub> (341)	73.90 73.61	3.22 3.31	4.11 4.39	νC=C, νC=N at 1610, 1640 and νC=O of δ-lactone at 1730-1760 νC=C at 1640, νC=O of amide
(Va)	178-79 (colourless)	B+E (64)	C <sub>23</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> (403)	68.49 69.11	5.21 5.32	10.42 10.91	at 1640-1660, νNH at 3180-3340 and νOH at 3460-3480
(Vb)	208-09 (colourless)	B (61)	C <sub>25</sub> H <sub>25</sub> N <sub>3</sub> O <sub>4</sub> (431)	69.60 69.89	5.80 5.92	9.74 10.08	νC=C at 1590, νC=O of amide at 1645, νNH at 3190-3280 and νOH at 3450-3490
(Vc)	> 300 (orange)	P (58)	C <sub>21</sub> H <sub>19</sub> N <sub>5</sub> O <sub>4</sub> (405)	62.22 62.78	4.69 4.75	17.28 17.27	νC=C at 1600, νC=O of amide at 1640, νNH at 3080-3280 and νOH at 3440-3465 (broad)
(Vd)	> 300 (colourless)	A (74)	C <sub>25</sub> H <sub>23</sub> N <sub>5</sub> O <sub>6</sub> (489)	61.35 60.98	4.70 4.82	14.31 14.78	νC=C at 1595, νC=O of amide at 1630-1640, νC=O of acetyl at 1705, νNH at 3240 and νOH at 3440-3480 (broad)
(VI)	> 300 (colourless)	E+A (64)	C <sub>10</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub> (251)	57.89 58.07	5.22 4.96	-- --	νC=O of amide at 1640, νC=O of hydrazide, 1670 νCH <sub>2</sub> aliphatic at 2935 and νNH at 3080-3310 (broad)
(VII)	293-94 (brown)	E+A (66)	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> (340)	77.65 77.22	4.70 4.76	8.24 8.12	νC=N at 1630-1645, νOH at 3440-3490 (broad)
(VIIIa)	146-47 (colourless)	B (42)	C <sub>24</sub> H <sub>21</sub> NO <sub>3</sub> (371)	77.63 77.98	5.66 5.80	3.77 3.91	νC=N at 1635, νCH at 2840 and νC=O of δ-lactone at 1740
(VIIIb)	118-19 (colourless)	B+E (46)	C <sub>27</sub> H <sub>27</sub> NO <sub>3</sub> (413)	78.45 79.06	6.54 6.48	3.39 3.50	
(VIIIc)	163-64 (colourless)	B (42)	C <sub>29</sub> H <sub>27</sub> NO <sub>3</sub> (437)	79.63 79.98	6.18 6.10	3.20 3.31	νC=N at 1640, νCH at 2910 and νC=O of δ-lactone at 1735-1745
(VIIId)	300 (pale-yellow)	M (41)	C <sub>42</sub> H <sub>33</sub> NO <sub>6</sub> (647)	77.90 77.58	5.10 5.18	2.16 2.24	

Table-1 (cont'd.)

Compd.	M.p.°C colour	Solv. of cryst. Yield %	M.F. M.W.	Analysis			IR data in $\text{cm}^{-1}$
				Calcd / Found	C%	H%	N%
(VIIIe)	> 300 (pale-yellow)	M (56)	$\text{C}_{42}\text{H}_{33}\text{NO}_6$ (647)	77.90 77.41	5.10 5.21	2.16 2.10	$\nu\text{C}=\text{N}$ at 1625, $\nu\text{CH}$ at 2885 and $\nu\text{C}=\text{O}$ of $\delta$ -lactone at 1720-1730
(VIIIf)	236-37 (colourless)	B (48)	$\text{C}_{42}\text{H}_{33}\text{NO}_3$ (599)	84.14 83.92	5.51 5.62	2.34 2.46	
(VIIIg)	192-93 (Pale-yellow)	B (54)	$\text{C}_{42}\text{H}_{33}\text{NO}_3$ (599)	84.14 84.42	5.51 5.42	2.34 2.52	
(VIIIh)	173-74 (colourless)	L.P. (47)	$\text{C}_{42}\text{H}_{33}\text{NO}_3$ (599)	84.14 84.28	5.51 5.40	2.34 2.66	$\nu\text{C}=\text{N}$ at 1630-1640, $\nu\text{CH}$ at 2890 and $\nu\text{C}=\text{O}$ of $\delta$ -lactone at 1720-1735

A = Acetic acid, B = Benzene, E = Ethanol, X = xylene, L.P. = Light petrol (b.p. 80-100°C),  
M = Methanol, P = Pyridine

Table-2: PMR Data of some prepared compounds

Compd.	Structure	PMR data in , values
(Ib)		a) <u>s</u> , 1H, 6.71 b) <u>br</u> , 2H, 6.94 c) <u>m</u> , 6H, 7.41-8.35
(Ie)		a) <u>s</u> , 1H, 6.59 b), <u>br</u> , 2H, 6.73 c) <u>br</u> , 1H, 7.14 d) <u>m</u> , 10H, 7.28-8.44
(Ih)		a) <u>s</u> , 3H, 2.84 b) <u>s</u> , 1H, 6.48 c) <u>two br</u> , 2H, 7.28, 7.36 d) <u>m</u> , 14H, 7.42-8.38

Table-2: (cont'd..)

Compd.	Structure	PMR data in , values
(IIa)		a) <u>t</u> , <u>3H</u> , 1.38 b) <u>m</u> , <u>1H</u> , 2.34 c) <u>d</u> , <u>1H</u> , 3.41 d) <u>q</u> , <u>2H</u> , 4.18 e) <u>br</u> , <u>1H</u> , 4.68 f) <u>m</u> , <u>10</u> , 7.41-8.35 g) not shown
(IIIe)		a) <u>d</u> , <u>2H</u> , 1.68 b) <u>s</u> , <u>3H</u> , 2.82 c) <u>d</u> , <u>1H</u> , 4.19 d) <u>br</u> , <u>1H</u> , 7.28 e) <u>m</u> , <u>14H</u> , 7.34-8.39
(IV)		a) <u>s</u> , <u>1H</u> , 6.79 b) <u>m</u> , <u>10H</u> , 7.32-8.43
(Va)		a) two <u>t</u> , <u>6H</u> , 2.94-3.05 b) two <u>br</u> , <u>2H</u> , 5.13-5.37 c) <u>s</u> , <u>1H</u> , 5.64 d) <u>br</u> , <u>1H</u> , 7.38 e) <u>m</u> , <u>10H</u> , 7.42-8.29 f) <u>br</u> , <u>1H</u> , 8.79-8.81
(Vc)		a) two <u>t</u> , <u>4H</u> , 5.64 b) two <u>br</u> , <u>2H</u> , 6.85 c) <u>s</u> , <u>1H</u> , 5.72 d) <u>br</u> , <u>1H</u> , 7.29 e) <u>m</u> , <u>10H</u> , 7.38-8.44 f) <u>br</u> , <u>1H</u> , 8.74-8.76

Table-2 (Cont'd..)

Compd.	Structure	PMR data in , values
(VII)		a) <u>m</u> , <u>12H</u> , 7.40-8.14 b) two <u>s</u> , <u>2H</u> , 8.17-8.21 c) two <u>br</u> , <u>2H</u> , 8.67, 8.72
(VIIIa)		a) <u>m</u> , <u>1H</u> , 2.32 b) <u>s</u> , <u>6H</u> , 2.74 c) <u>d</u> , <u>3H</u> , 2.86 d) <u>d</u> , <u>1H</u> , 3.40 e) <u>m</u> , <u>10H</u> , 7.41-8.28

The authors in this study also describe the reaction of (Ia) with anthranilic acid at  $170^\circ$  to give 3-(N-phenyl)carbamido-3,4-dihydro-5,6-benzocoumarin (IIIc) as a main product with small yield of (IIIa) and a third product which was identified by independent synthesis via the condensation of the 5,6-benzocoumarin-3-carbonyl chloride with anthranilic acid to give 3-anthraniloxy 5,6-benzocoumarin (Id). The reaction of (Id) with acetic anhydride gives 3-(3',1'-benzoxazin-4-one)-5,6-benzocoumarin (IV).

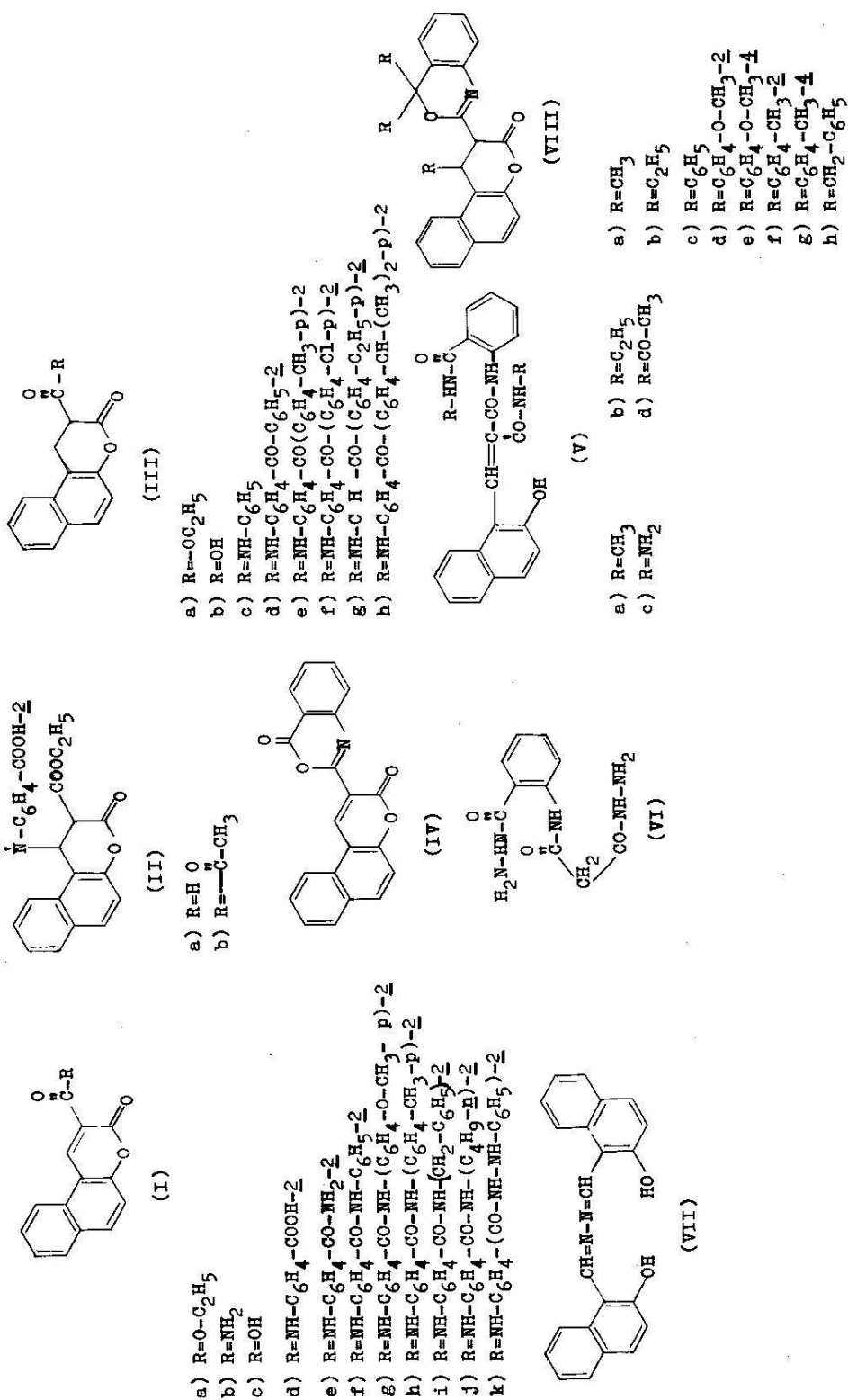
Compound (IV) can be also obtained by treatment of anthranilic acid in pyridine with the 5,6-benzocoumarin-3-carbonyl chloride.

Compound (IV) undergoes ring opening of the benzoxazine ring by hydrolysis [4,5]. The benzoxazine ring in (IV) was opened when treated with acetic / hydrochloric acids mixture to give compound identified to be 5,6-benzocoumarin-3-carboxylic acid (Ic) by means of m.p. and mixed

m.p. and comparison of IR data. On the other hand alkaline hydrolysis of (IV) is accompanied by a colour change from yellow to yellowish green fluorescence, thus both the  $\delta$ -lactone and oxazinone rings are readily hydrolysed by alkali to the salt of the dibasic acid which is further hydrolysed to give salt of the benzocoumarinic acid, which usually cannot be isolated as the acid which readily undergoes ring closure on acidification to give 5,6-benzocoumarin 3-carboxylic acid (Ic).

This investigation deals with the reaction of (IV) with ammonia furnished from ammonium acetate or urea to give 3-(2'-carbamidoanilino carbonyl)-5,6-benzocoumarin (Ie). (VI) is insoluble in alkali and not give colour reaction with alcoholic ferric chloride.

Treatment of (IV) with the more strong basic amines methyl and/or ethylamine with fission of both  $\delta$ -lactone and the oxazinone rings by two moles of the amine to give  $\alpha$ -(N-aryl





carbamido)-anilincarbonyl-(2'-N-aryl carbamido)-2-hydroxy-5,6-benzocinnamic acid (Va) and (b).

On treatment of ethanolic solution of (IV) with amines namely aniline, p-anisidine, p-toluidine, benzylamine and n-butylamine give 3-(2'-aryl or alkyl imino-carbonyl)-anilincarbonyl-5,6-benzocoumarins (If-j) respectively. The formation of (If-j) can be readily interpreted from the fact that the amines react rapidly with fission of benzoxazinone ring and not with  $\delta$ -lactone due to the weak basicity of the amines used. The absence of

haviour of (IV) towards aromatic hydrocarbons under Friedel-Crafts conditions. Thus (IV) reacts with aromatic hydrocarbons namely benzene, toluene, chlorobenzene, ethyl benzene and cumene to give 3-(2'-aryl carbonyl anilincarbonyl)-3,4-dihydro-5,6-

benzocoumarins (IIId-h) respectively. (IIId) resists dehydration on boiling with acetic anhydride.

In the present communication the reaction of (IV) with Grignard reagents was studied. Thus (IV) reacts with Grignard reagents namely, methylmagnesium iodide, ethyl-

magnesium iodide, phenylmagnesium bromide, *o*- and *p*-anisylmagnesium bromide, *o*- and *p*-tolylmagnesium bromide and benzylmagnesium chloride to give (VIIIa-h), respectively.

The products (If-j) are insoluble in alkali and do not give colour reaction with alcoholic ferric chloride. On hydrolysis of (If) with acetic acid and hydrochloric acid mixture gives 5,6-benzocoumarin-3-carboxylic acid (Ic). On treatment of ethanolic solution of (IV) with hydrazine hydrate at room temperature, the heterocyclic rings of both coumarin and oxazinone was opened to give the corresponding dihydrazide derivative (Ve). Compound (Ve) is soluble in alkali and gives colour reaction with alcoholic ferric chloride, and on treatment with acetic anhydride gives the diacetyl derivative (Vd) while treatment of the ethanolic solution of (IV) with phenylhydrazine gives (Ik).

On the otherhand treatment of (IV) with hydrazine hydrate in boiling ethanol gives (VI) and (VII).

As a point of interest, the present work investigated the be-

The compound (VIII) resists dehydration on boiling with acetic anhydride. Moreover, they exhibit no colour reaction with alcoholic ferric chloride.

All structures were established from correct analytical and physical spectral data (cf. Tables 1 & 2).

### Experimental

The infrared absorption spectra were determined with a Unicam SP.500 using KBr pellet technique. The NMR spectra were determined with a Varian A-60 (60 Mc) instrument,  $CDCl_3$  was used as a solvent and TMS as internal standard. Melting points were not corrected.

*Reaction of 3-carbethoxy-5,6-benzocoumarin (Ia) with anthranilic acid in boiling benzene: Formation of 4-anthraniloyl-3-carbethoxy-3,4-dihydro-5,6-benzocoumarin (IIa):*

To a solution of (Ia) (0.01 mole) in 50 ml benzene was added anthranilic acid (0.015 mole). The mixture

refluxed for 1 hour. The reaction mixture was evaporated, then stirred into cold water (200 ml) and the solid that separated was filtered off, then crystallized from a suitable solvent to give (IIa).

*Formation of 3-carbethoxy-3,4-dihydro-5,6-benzocoumarin (IIIa):*

*Method A.*

A mixture of (Ia) (0.01 mole), anthranilic acid (0.015 mole) and 50 ml benzene was refluxed for 3 hours. The reaction mixture was cooled and washed several times with 25% sodium carbonate, then water. The organic layer was concentrated, cooled and the solid product that separated was filtered off and then crystallized from a proper solvent to give IIIa. On acidification of the aqueous layer, the anthranilic acid was separated.

*Method B.*

To a cooled stirred mixture of 9.5 g. of anhydrous aluminium chloride and 30 ml of dry m-xylene or toluene at 10° was added a solution of (Ia) (2g.) in 50 ml of the above dry hydrocarbons. The temperature of the reaction mixture was maintained at 10 - 20° during addition. Stirring was continued for an additional 3 hours at room temperature and then the reaction mixture was refluxed with stirring for another 3 hours then the complex was decomposed with 250 ml of dilute hydrochloric acid (1:15). The benzene was evaporated and the solid product was filtered off and crystallized from a proper solvent to give (IIIa).

*Method C.*

A mixture of (Ia) and ammonium acetate (2 g.) was heated at 170° for 15 hours. The reaction mixture was cooled and washed with dilute hydro-

chloric acid (2 %). The solid product was filtered off and crystallized from a suitable solvent to give (IIIa) and the residue was crystallized from acetic acid to give 5,6-benzocoumarin-3-carbamide (Ib).

*Reaction of (IIa) with acetic anhydride: Formation of 4-(N-acetyl anthraniloyl)-3-carbethoxy-3,4-dihydro-5,6-benzocoumarin (IIb):*

A mixture of (IIa) (2 g.) and acetic anhydride (25 ml) was refluxed for ½ hr., cooled and then poured into crushed ice. The solid that obtained was filtered off and recrystallized from benzene to give (IIb).

*Alkaline hydrolysis of IIb: Formation of 3,4-dihydro-5,6-benzocoumarin-3-carboxylic acid (IIIb):*

A mixture (IIb) (1 g.) and ethanolic potassium hydroxide (20 ml; 5%) was heated on steam bath for 1 hr., cooled, then poured into water acidified with hydrochloric acid. The solid that separated was filtered off then recrystallized from benzene to give (IIIb).

*Reaction of (Ia) with anthranilic acid by fusion: Formation of (IIIa), 3-(N-phenyl carbamido)-3,4-dihydro-5,6-benzocoumarin (IIIc) and 3-anthraniloyl-5,6-benzocoumarin (Id):*

A mixture of (Ia) (0.01 mole) and anthranilic acid (0.015 mole) was heated at 170-175°C for 2 hours. The reaction mixture was cooled, the residue was stirred with saturated solution of sodium carbonate and extracted with benzene. The organic layer was evaporated and the residue on fractional crystallization gave (IIIa) and (IIIc) respectively. The aqueous layer was acidified with hydrochloric acid and the product was crystallized from acetic acid to give (Id). (cf. Table 1).

*Authentic sample of (IIIc):*

A mixture of (Ia) (0.02 mole) and aniline (0.03 mole) in ethanol (50 ml) was refluxed for 5 hours. After cooling the mixture was poured into 250 ml of dilute hydrochloric acid (1 : 15). The solid product was crystallized from a suitable solvent and identified by m.p. and mixed m.p. determination (237-238°C) and by comparison of IR data to be (IIIc).

*Authentic sample of (Id):*

Compound 5,6-benzocoumarin-3-carboxylic acid (Ic) (0.01 mole) was treated with thionyl chloride (25 ml), the reaction was worked up as usual to give the corresponding acid chloride. Dry benzene (200 ml) and anthranilic acid (0.02 mole) were added to the acid chloride. The mixture was heated on water bath for 3 hours, cooled and filtered from the anthranilic acid hydrochloride. The residue obtained after evaporation of benzene was crystallized from suitable solvent to give (Id). Identified by m.p. and mixed m.p. determination (> 300°C) and by comparison of IR data.

*Action of acetic anhydride on (Id):*  
*Formation of 3-(3',1'-benzoxazin-4'-one)-5,6-benzocoumarin (IV):*

A mixture of (Id) (2 g) and acetic anhydride (25 ml) was refluxed for 2 hours, cooled and stirred into cold water (200 ml). The residue was filtered off, washed several times with cold water and recrystallized from a proper solvent to give (IV).

*Preparation of authentic sample of (IV):*

To a solution of anthranilic acid (0.02 mole) in 20 ml pyridine was added 5,6-benzocoumarin-3-carbonyl chloride (0.01 mole). The reaction mixture was shaken for 15 min. and

then set aside at room temperature for further 1 hour, with occasional shaking. The reaction mixture was stirred into cold diluted hydrochloric acid and the precipitate was filtered off. The residue was washed free of pyridine with cold water and crystallized from a proper solvent to give (IV) identified by m.p. and mixed m.p. determination (254-255°C) and by comparison of IR data.

*Hydrolysis of (IV): Formation of 5,6-benzocoumarin-3-carboxylic acid (Ic):*

*A) Acid hydrolysis:*

A suspension of 1 g (IV) in 30 ml hydrochloric acid/acetic acid mixture (1:1) was heated under reflux for 5 hours, cooled then the solid that separated was filtered off, washed with water and crystallized from a suitable solvent to give (Ic).

*B) Alkaline hydrolysis:*

A mixture of 1 g (IV) and 20 ml of ethanolic potassium hydroxide (5 %) was heated under reflux for 3 hours, cooled, and poured into water (100 ml), acidified with hydrochloric acid. The solid separated out was crystallized from a suitable solvent to give (Ic).

*Ammonolysis of (IV): Formation of 3N-2-carbamido-anilino-carbonyl)-5,6-benzocoumarin (Ie):*

A mixture of (IV) (0.01 mole) ammonium acetate or urea (3 g) and ethanol (30 ml) was refluxed for 3 hours, cooled and stirred with 100 ml (1:15) dilute hydrochloric acid. The product that separated was filtered off and crystallized from ethanol to give (Ie).

*Aminolysis of (IV):*

- A) *Formation of o-(N-alkylcarbonyl)-anilinocarbonyl-(2'-N-arylcarbonyl)-2-hydroxy-5,6-benzocinnamic acid (Va and b):*

A solution of (IV) (0.01 mole) in 20 ml ethanol was refluxed for 3 hours, concentrated and cooled. The product separated was crystallized from a proper solvent to give (Va and b), respectively.

- B) *Formation of 3-(2'-aryl or alkyl carbonyl)-anilino-carbonyl-5,6-benzocoumarin (If-j):*

A solution of (IV) (0.01 mole) and primary amines namely aniline, p-anisidine, p-toluidine, benzylamine and n-butyl-amine (0.02 mole) in ethanol (25 ml) was heated under reflux for 3 hours. After concentration and cooling the product separated out was filtered off and crystallized from a suitable solvent to give (If-j), respectively.

*Hydrazinolysis:*

*Action of hydrazine hydrate and/or phenylhydrazine on (IV):*

- A) *At room temperature: Formation of (Vc) and (Ik):*

A mixture of (IV) (0.01 mole) and hydrazine hydrate and/or phenylhydrazine (0.025 mole) in ethanol (30 ml) was kept over-night at room temperature. The solid that separated was filtered off and recrystallized from a proper solvent to give the dihydrazide derivative (Vc) and/or (Ik) respectively.

*Conversion of (Vc) to (Vd):*

A suspension of (Vc) (1 g) in 15 ml acetic anhydride was refluxed for 2 hours after concentration and

cooling, poured into crushed ice, and the solid that separated was filtered off then recrystallized from a proper solvent to give (Vd).

- B) *In boiling ethanol: Formation of (VI) and (VII):*

To a solution of (IV) (2 g) in boiling ethanol (20 ml), hydrazine hydrate (1 ml) was added and the mixture was refluxed for 3 hours. Yellow crystals separated first, followed by a colourless solid after cooling the solution. The precipitate was filtered off and treated with hot ethyl acetate (70 ml), in which yellow crystals dissolved. The insoluble colourless product was washed with warmed ether (40 ml) to yield (VI), while the ethyl acetate extract concentrated, and cooled to give (VII).

*Friedel-Crafts reaction with (IV): Formation of 3(2'-aryl carbonyl)-3,4-dihydro-5,6-benzocoumarins (IIId-h):*

To a cooled stirred mixture of 9.5 g of anhydrous aluminium chloride and 50 ml from each of dry hydrocarbons namely benzene, toluene, chlorobenzene, ethylbenzene and cumene was added a suspension of (IV) in 50 ml of the corresponding hydrocarbons. The temperature of the reaction was maintained at 20° during addition. Stirring was continued for an additional 4 hours at room temperature and another 4 hours with heating on steam bath. The reaction product was decomposed with 250 ml of dilute hydrochloric acid. The organic layer was evaporated and the product that separated was filtered off and then crystallized from suitable solvent to give (IIId-h), respectively.

*Reaction of (IV) with Grignard reagents: Formation of (VIIIa-h):*

A solution of the Grignard reagent namely methyl magnesium



iodide, ethyl magnesium iodide, phenyl magnesium bromide, o-anisylmagnesium bromide, p-anisyl magnesium bromide, o-tolyl magnesium bromide, p-tolylmagnesium bromide and benzylmagnesium chloride (0.035 mole) in dry ether was treated with a solution of (IV) (0.01 mole) in dry benzene (50 ml). The ether was evaporated and the mixture was refluxed for 3 hours. The mixture was worked up as usual. The product that separated was filtered off and crystallized from the proper solvent to give (VIIIa-h), respectively.

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