

# DECARBOXYLATION, DURING THEIR AROMATIZATION BY Pd/C, OF SOME 3,4-OCTAHYDRONAPHTHO-7,8-BENZOCOUMARINS

## SYNTHESIS OF 1,2'-BINAPHTHYLS AND 2,2'-BINAPHTHYLS

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(Received in UK 9 September 1976; Accepted for publication 4 October 1976)

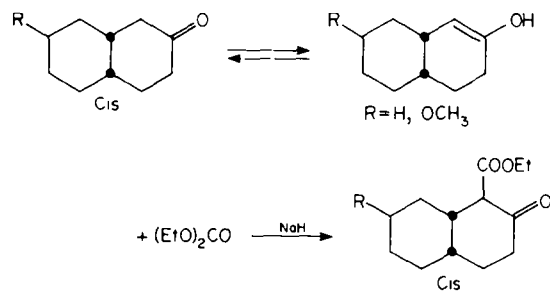
**Abstract**—Some 3',4'-cyclohexa-1',2'-dihydro- and 1',2'-cyclohexa-3',4'-dihydro-3,4,7,8-dibenzocoumarins **2** and **3** were prepared by catalytic condensation between a naphthol and a  $\alpha$ -carbethoxy-*cis*-decalone (–1 or –2). These compounds, when treated with Pd/C at 260°, undergo, beside aromatization, a complete decarboxylation of the lactone ring. A mechanism, involving H transfer through a  $\pi$ -allylic palladium complex is described.

Only few methods have been reported for the synthesis of binaphthyls,<sup>1-6</sup> and only one was quite general: reaction of a naphthalene-magnesium bromide with a tetralone, followed by an aromatization of the dihydro-compound obtained.

We have shown previously<sup>7</sup> that aromatization by means of Pd/C of some 1',2',3',4' - tetrahydro - 3,4,7,8 - dibenzocoumarins led to 2-arylnaphthalenes. In order to prepare binaphthyls, we have attempted to synthesise  $\alpha$ -pyrones **1**, **2** and **3**, and to submit them to treatment with Pd/C.

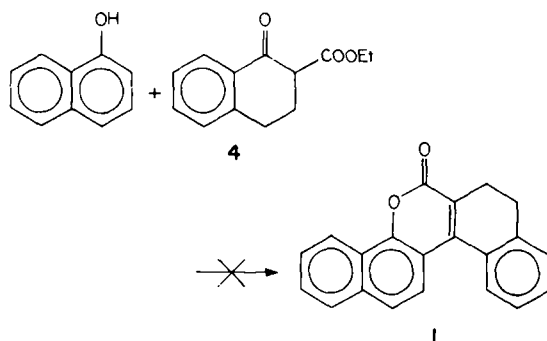
### 1. Synthesis of $\alpha$ -pyrones **1**, **2**, **3**

Synthesis of these compounds can be performed by catalytic condensation (Pechmann reaction) of a naphthol with a  $\beta$ -keto-ester: 2 - carbethoxy - 1 - tetralone **4**,<sup>8</sup> 2 - carbethoxy - 1 - decalone **5** and 1 - carbethoxy - 2 - decalone **6**, are easily prepared by carbethoxylation of the corresponding tetralone or decalone.<sup>9</sup> *cis*-1- and -2-decalones were synthesised.<sup>10</sup> In the case of *cis*-2-decalones, the carbethoxylation was an electrophilic attack on the double bond of the enolic form, and enolization of *cis*-2-decalones was achieved at position one,<sup>11</sup> the carbethoxyl group was added in position one.

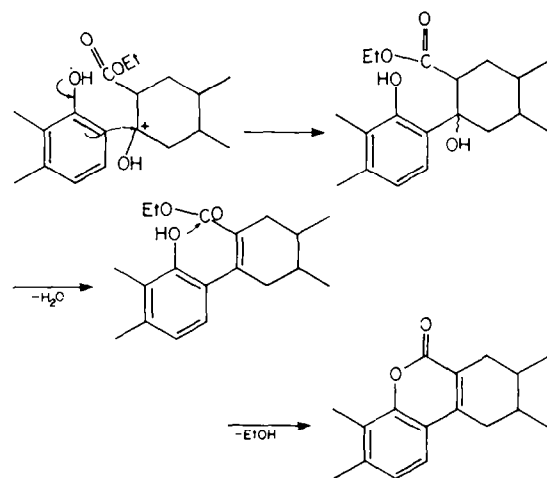


(1) *Attempted synthesis of 1',2' - dihydro - 3,4 - naphtho - 7,8 - benzocoumarins 1*. Catalytic reaction between **4** and naphthols did not furnish condensation products with the reagents: hydrochloric acid, poly-

phosphoric acid, phosphorous oxychloride or aluminium chloride. Previously, Buu-Hoi<sup>12</sup> attempted, without success the same condensation.



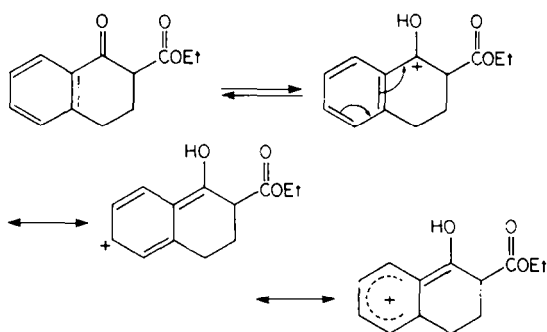
In order to explain the lack of reactivity of **4**, we supposed that, in the acid-catalyzed Pechmann reaction, the ketonic carbonyl of the  $\beta$ -ketoester **4** was protonated first, leading to cation **4a**, then this cation attacked the naphthol at the *ortho*-position in respect to the OH group. Dehydration and cyclization in coumarin occurred with elimination of ethanol (Scheme 1).



Scheme 1.

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In the case of **4**, the aromatic ring conjugated with the ketonic carbonyl decreased the positive charge of the latter by delocalization, the structure of the molecule allowing the coplanarity of the benzene ring with the cation, allowing interaction of the  $\pi$ -orbitals with the cation (Scheme 2).



Scheme 2.

This hypothesis was confirmed by the reactivity of the  $\alpha$  - carbethoxy - decalones.

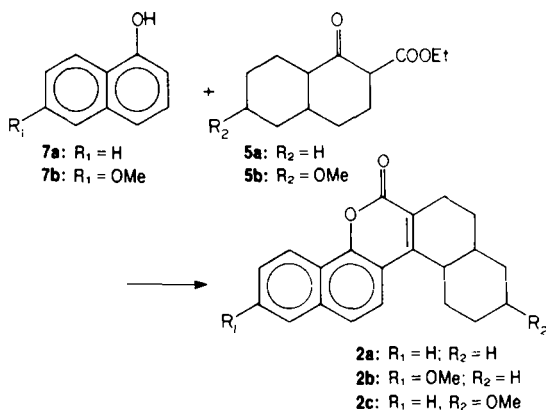
(2) *Synthesis of 3',4' - cyclohexa - 1',2' - dihydro - 3,4,7,8 - dibenzocoumarins 2*. Catalytic condensation between 2 - carbethoxy - 1 - decalone **5** and several naphthols was carried out, in one case with ethanol/hydrochloric acid,<sup>12</sup> but sometimes it required a stronger catalytic reagent such as phosphorus oxychloride.<sup>13</sup> In all cases we obtained compounds **2**, however, yields were reached not less than 40% (see Table 1; Scheme 3).

These low yields could be explained by the cycloalkyl group *ortho* to the ketonic carbonyl, which could decrease the carbonyl positive charge, or induce steric hindrance in the neighborhood of this carbonyl, since we used only 2 - carbethoxy - *cis* - 1 - decalones.

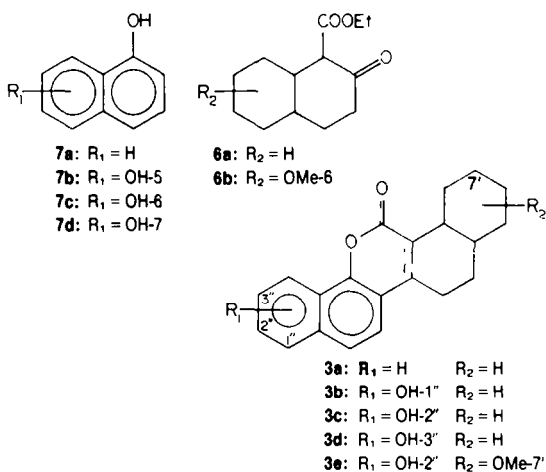
(3) *Synthesis of 1',2' - cyclohexa - 3',4' - dihydro - 3,4,7,8 - dibenzocoumarins 3*. The deactivating effect of a cycloalkyl ring *ortho* to the carbonyl in compounds **5** was confirmed by the great reactivity of the 1 - carbethoxy - 2 -

decalone **6**, in which this group is far from the ketonic carbonyl.

Actually compounds **6** did react with naphthols in 60-88% yields in ethanol saturated with hydrochloric acid giving compounds **3** (Table 2; Scheme 4).



Scheme 3.



Scheme 4.

Table 1. Products 2: Yields and physical data

Naphthol	$\beta$ -keto-ester	Catalyst	3',4'-Cyclohexa-1',2'-dihydro-3,4,7,8-dibenzocoumarins 2				Methyl derivative 2'		
			Yield (%)	m.p. (°C)	IR: $\nu_{C=O}$ (cm <sup>-1</sup> )	Molecular formula	m.p. (°C)	IR: $\nu_{C=O}$ (cm <sup>-1</sup> )	Molecular formula
<b>7a</b>	<b>5a</b>	POCl <sub>3</sub> /Bz	<b>2a</b> 38	207	1700	C <sub>21</sub> H <sub>20</sub> O <sub>2</sub>			
<b>7b</b>	<b>5a</b>	HCl/EtOH	<b>2b</b> 36	280	1680	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	218	1700	C <sub>22</sub> H <sub>22</sub> O <sub>3</sub>
<b>7a</b>	<b>5b</b>	POCl <sub>3</sub> /Bz	<b>2c</b> 36	222	1700	C <sub>22</sub> H <sub>22</sub> O <sub>3</sub>			

Table 2. Products 3: Yields and physical data

Naphthols	$\beta$ -keto-ester	1',2'-Cyclohexa-3',4'-dihydro-3,4,7,8-dibenzocoumarins 3				Methyl derivatives 3'			
		Yields (%)	m.p. (°C)	IR: $\nu_{C=O}$ (cm <sup>-1</sup> )	Molecular formula	h°	m.p. (°C)	IR: $\nu_{C=O}$ (cm <sup>-1</sup> )	Molecular formula
<b>7a</b>	<b>6a</b>	<b>3a</b> 88	221	1705	C <sub>21</sub> H <sub>20</sub> O <sub>2</sub>				
<b>7b</b>	<b>6a</b>	<b>3b</b> 72	284	1680	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	<b>3'b</b>	222	1705	C <sub>22</sub> H <sub>22</sub> O <sub>3</sub>
<b>7c</b>	<b>6a</b>	<b>3c</b> 87	286	1675	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	<b>3'c</b>	224	1695	C <sub>22</sub> H <sub>22</sub> O <sub>3</sub>
<b>7d</b>	<b>6a</b>	<b>3d</b> 75	265	1680	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	<b>3'd</b>	210	1705	C <sub>22</sub> H <sub>22</sub> O <sub>3</sub>
<b>7e</b>	<b>6b</b>	<b>3e</b> 60	295	1680	C <sub>22</sub> H <sub>22</sub> O <sub>4</sub>				

The mass spectra of all compounds **2** and **3** exhibit a molecular ion  $M^+$  corresponding to the proposed structure, and a fragmentation characteristic of  $\alpha$ -pyrones: an intense ion  $M^+ - 56$ , formed by loss of two  $C=O$ .<sup>14</sup>

## II Aromatization and decarboxylation of **2** and **3** by Pd/C: formation of 1,2'-binaphthyls **8** and 2,2'-binaphthyls **9**

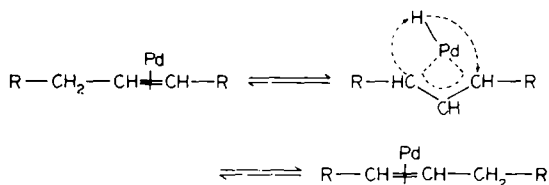
$\alpha$ -Pyrones **2b** and **3b** to **3d**, which have a free OH group, were methylated (giving **2'b** and **3'b** to **3'd**) prior to treatment by Pd/C. In hydroxy compounds with high m.p.s (m.p.  $>260^\circ$ ), there would be poor contact between the catalyst and the substrate, thereby resulting in low yields.

Compounds **2** (**2a** and **2'b**) and **3** (**3a**, **3'b**, **3'c**, **3'd**) when heated at  $260^\circ$  with catalytic amounts of Pd/C (10%), during 12 hr, underwent a total decarboxylation of the lactonic ring with aromatization of saturated rings, and led respectively to 1,2'-binaphthyls **8** and 2,2'-binaphthyls **9** (Table 3; Scheme 5).

This aromatization of  $\alpha$ -pyrones permitted easy access to binaphthyls in high yields. Furthermore, by this method only one isomer was obtained, the methods hitherto described gave a mixture of 2,2'- and 1,2'-binaphthyls.

**Mechanism.** It is well known that during isomerization of olefin catalysed by a transition metal (group VIII) such as palladium, the olefin and palladium form a  $\pi$ -allylic

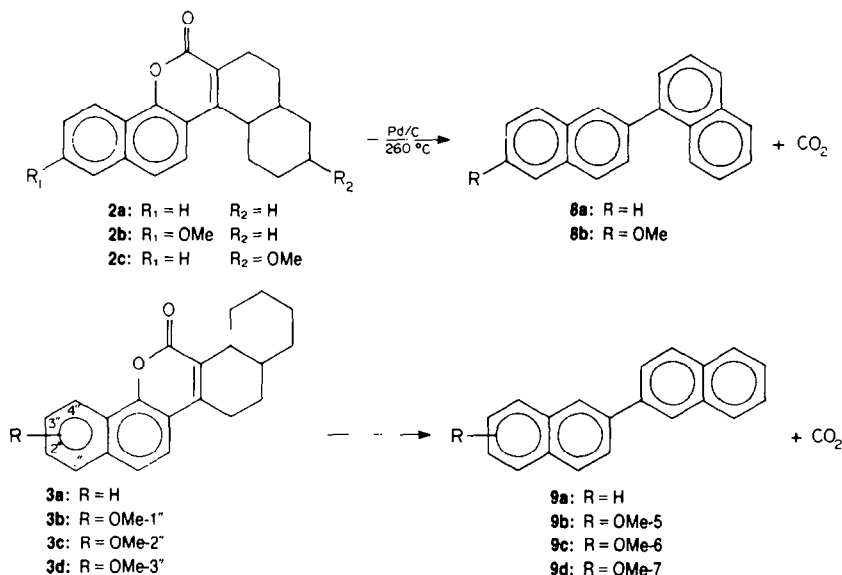
complex.<sup>15,16</sup> An intramolecular reaction takes place which does not need additional hydrogen.<sup>17</sup>



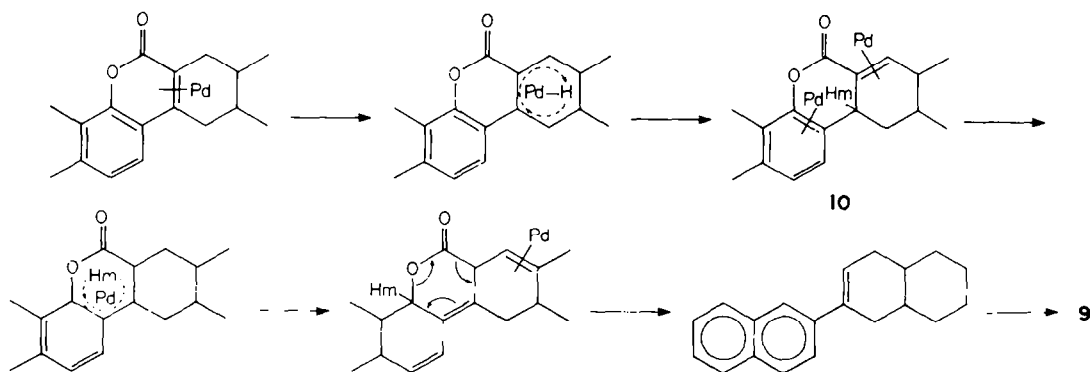
We suggest that during aromatization of  $\alpha$ -pyrones, coordination of the metal atom with the double bond of the lactone ring occurs, and then, a  $\pi$ -allylpalladium complex allowing migration of the hydrogen atom ( $H_m$ ) to the  $C_4$  atom **10**.

Another migration of  $H_m$  by a similar process to the  $C_6$  position leads to a new intermediate **11**, which is able to undergo decarboxylation by a classic mechanism. Then, further dehydrogenation leads to binaphthyls (Scheme 6).

In such a mechanism, we suppose that decarboxylation occurs before aromatization. This supposition has been supported by trapping the released  $CO_2$  by means of a barium hydroxide solution: we observed that  $CO_2$  was released during the first hour of heating, whereas for complete aromatization longer time is required.



Scheme 5.



Scheme 6.

Table 3. Products 8 and 9: Yields and physical data

Substrate	Products	Yield (%)	m.p. (°C)	Molecular formula	UV: $\lambda_{\max}$ (nm)
2a R <sub>1</sub> = H	8a R <sub>1</sub> = H	90	78 (1)	C <sub>20</sub> H <sub>14</sub>	214, 256, 305
2'b R <sub>1</sub> = OMe	8b R <sub>1</sub> = OMe	65	140	C <sub>21</sub> H <sub>16</sub> O	216, 254, 308
3a	9a R <sub>1</sub> = H	90	186 (1)	C <sub>20</sub> H <sub>14</sub>	214, 260, 300
3'b	9b R <sub>1</sub> = OMe-5	36	172	C <sub>21</sub> H <sub>16</sub> O	216, 255, 306
3'c	9c R <sub>1</sub> = OMe-6	80	201	C <sub>21</sub> H <sub>16</sub> O	215, 255, 306
3'd	9d R <sub>1</sub> = OMe-7	60	142	C <sub>21</sub> H <sub>16</sub> O	214, 257, 308

## EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 137E spectrophotometer as films or in KBr; NMR spectra on a Varian A60 spectrometer (TMS as internal standard), and mass spectra using a Thomson-Houston THN208 spectrograph. M.ps (Kofler microscope) are uncorrected.

All elemental analysis were performed by the Laboratoire de Chimie organique de la Faculté des Sciences Paris VI, and are in agreement with the proposed structure within 0.2% error.

2 - Carbethoxy - cis - 1 - decalones 5. They were prepared by carbethoxylation of *cis*-1-decalone.<sup>10</sup> 5a C<sub>13</sub>H<sub>20</sub>O<sub>3</sub> (90%), b.p. 125°/0.5 mmHg,  $n_D^{24}$ : 1.4910; IR:  $\nu_{C=O}$ : 1748 (ester), 1715 (ketone) cm<sup>-1</sup>;  $\nu_{C=C}$ : 1720 (enol form) cm<sup>-1</sup>. 5b C<sub>14</sub>H<sub>22</sub>O<sub>4</sub> (85%), b.p. 130°/0.5 mmHg, IR:  $\nu_{C=O}$ : 1740, 1712, 1655 cm<sup>-1</sup>;  $\nu_{C=C}$ : 1712 cm<sup>-1</sup>.

1 - Carbethoxy - 2 - decalones 6. Obtained as described above for 5. 6a C<sub>13</sub>H<sub>20</sub>O<sub>3</sub> (92%), b.p. 130°/0.5 mmHg;  $n_D^{23}$ : 1.4922; IR:  $\nu_{C=O}$ : 1740, 1715, 1660 cm<sup>-1</sup>,  $\nu_{C=C}$ : 1712 cm<sup>-1</sup>. 6b C<sub>14</sub>H<sub>22</sub>O<sub>4</sub> (82%), b.p. 145°/1 mmHg; IR:  $\nu_{C=O}$ : 1740, 1715, 1660 cm<sup>-1</sup>;  $\nu_{C=C}$ : 1620 cm<sup>-1</sup>.

3',4' - Cyclohexa - 1',2' - dihydro - 3,4,7,8 - dibenzocoumarins 2a, 2c

*General procedure.* 0.01 m of naphthol, 0.015 m of 5, 2 ml of freshly distilled POCl<sub>3</sub> in 15 ml of anhyd. benzene were refluxed during 2 hr and allowed to stand for 24 hr at room temp. The solvent was removed under low pressure, and the residual mixture was washed successively with AcONa soln and water. The products 2a and 2c were recrystallized from ether and ethanol respectively. 2b was obtained as described below for 3.

1',2' - Cyclohexa - 3',4' - dihydro - 3,4,7,8 - dibenzocoumarins 3a-3e

*General procedure.* In a cooled (-5°) soln of 0.01 m of naphthol, 0.012 m of 6 and 30 ml of EtOH, gaseous HCl was bubbled through until saturation. The soln was allowed to stand for 20 hr at room temp., then, heated on a water-bath for 1 hr. After cooling, HCl was bubbled through again and the soln left for 2 days. EtOH was then removed, the solid was washed with water and recrystallized from EtOH or EtOH-benzene.

*Methylated derivatives of 2(b,c) and 3(b,c,d,e)*

These compounds were obtained from 2 and 3 respectively by

methylation with dimethylsulphate and potassium carbonate in dry acetone.

1,2'-Binaphthyl 8a and 2,2'-binaphthyl 9a. 1 g of  $\alpha$ -pyrone (2a or 3a respectively) and 300 mg of Pd/C (15%) were quickly heated to 260°, during 14 hr. Then boiling benzene was added to the mixture. After filtration and partial evaporation of the benzene, pure binaphthyl crystallized.

1,2'-Binaphthyl 8b and 2,2'-binaphthyls 9b, 9c, 9d. Methylated  $\alpha$ -pyrones 2'b, 3'b, 3'c and 3'd were obtained by Pd/C as described above for 2a. Crystallization afforded the substituted binaphthyls. Purification of which was achieved by a preparative chromatography on a silicagel column (hexane-benzene).

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