## 13. $\gamma$ , $\gamma$ -Disubstituted Itaconic Acids. Part 1. The *Stobbe* condensation of 1-Arylnaphthyl Ketones with Diethyl Succinate

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## Summary

Arylnaphthyl ketones condense with diethyl succinate yielding the stereoisomeric half-esters 2a-2d which were subjected to a series of reactions leading to 1-phenylphenanthrene and 1,1'-binaphthyl derivatives. (E)-3-Ethoxycarbonyl-4-(4-methoxynaphth-1-yl)-4-arylbut-3-enoic acids (2b-d) were converted finally into the corresponding naphtho[1,2-c]fluorenones (9). The structure of the products was established by IR. and UV. spectroscopy. The effect of substituents on the relative proportions of (E)- and (Z)-half-esters 2 was determined by chromatography and UV. spectroscopy.

Awad et al. [1] claimed that the condensation of 1-benzoylnaphthalene (1a) with diethyl succinate in the presence of potassium t-bitoxide in t-butyl alcohol produced (E) half-ester 2a as the sole product. This result was attributed either to steric or/and polar factors. We have now found that the (Z)-2a isomer is also produced.

In order to study the rôle of the above mentioned factors in determining the ratio of the isomeric half-esters produced in this *Stobbe* condensation, aryl naphthyl ketones containing substituents of different polar nature either in the naphthyl or in both the naphthyl and the phenyl groups, 1-benzoyl-4-methoxynaphthalene (1b), 1-(p-methoxybenzoyl)-4-methoxynaphthalene (1c) and 1-(p-chlorobenzoyl)-4-methoxynaphthalene (1d), besides 1-benzoylnaphthalene (1a) were condensed with diethyl succinate.

The new ketones **1c** and **1d** were prepared by *Friedel-Crafts* condensation of *p*-methoxybenzoyl and *p*-chlorobenzoyl chloride with 1-methoxynaphthalene [2].

1-Benzoylnaphthalene (1a) and diethyl succinate. After condensation of 1benzoylnaphthalene (1a) with diethyl succinate [1], the crude half-ester mixture 2a (53%) was directly cyclized with sodium acetate in acetic anhydride. After crystallization the neutral product gave 1-acetoxy-3-ethoxycarbonyl-4-phenylphenanthrene (3a) (84%). Chromatography of the residue gave 4-acetoxy-2-ethoxycarbonyl-1,1'-binaphthyl (4a) (13%). The same relative amounts of 3a and 4a were estimated by the application of Dewar & Urch spectrophotometric method [3].



The structures of 3a and 4a were inferred from the appearance of strong bands at 775 and 720 cm<sup>-1</sup> (3a) and one band at 775 cm<sup>-1</sup> (4a), characteristic of out of plane bending frequencies of a monosubstituted phenyl group in 3a and the 4 adjacent hydrogen atoms of a 1,1'-binaphthyl derivative in 4a, respectively. The phenanthrene and 1,1'-binaphthyl structures were further substantiated by the UV. spectra of these compounds which resemble very closely those of 4-phenylphenanthrene [4] and 4-methoxy-1,1'-binaphthyl [1] and 1,1'-binaphthyl [5] respectively.

1-Benzoyl-4-methoxynaphthalene (1b) and diethyl succinate. The mixture of (E)- and (Z)-half-esters 2b obtained in the same way as 2a cyclized yielding 1-acetoxy-3-ethoxycarbonyl-9-methoxy-4-phenylphenanthrene (3b) (85%) and 4-acetoxy-2-ethoxycarbonyl-4'-methoxy-1,1'-binaphthyl (4b) (13%). The structures of 3b and 4b were inferred from the IR. (760 and 700 cm<sup>-1</sup> for 3b, 770 cm<sup>-1</sup> for 4b) and UV. spectra. The relative proportions of 3b and 4b estimated spectro-photometrically [3] were in good agreement with the amounts isolated.

The acetoxy-ethoxycarbonylphenanthrene derivative 3b was hydrolyzed and the resulting phenolic acid 5b was methylated to give 1,9-dimethoxy-3-methoxycarbonyl-4-phenylphenanthrene (6b). This was hydrolyzed to give the corresponding methoxy acid 7b, which was decarboxylated with copper in quinoline to 1,9dimethoxy-4-phenylphenanthrene (8b). Cyclization of the phenanthrene carboxylic acid 7b with phosphorus pentoxide in benzene gave 5,7-dimethoxy-9*H*-naphtho-



[1,2-c]fluoren-9-one (9b). The same fluorenone 9b was obtained by the following series of reactions. The crude half-ester 2b was hydrolyzed to give a crude dibasic acid from which (E)-3-carboxy-4-(4-methoxynaphth-1-yl)-4-phenylbut-3-enoic acid (11b) was isolated (85%). It was converted into its anhydride 12b by heating with acetyl chloride. The anhydride was isomerized by anhydrous aluminium chloride in nitrobenzene to [3-(4-methoxynaphth-1-yl)-1-oxo-inden-2-yl]acetic acid (13b), the dinitrophenylhydrazone of which cyclized spontaneously to a pyridazin-one derivative (cf. Gindy et al. [6]). The acid 13b was cyclized with sodium acetate in acetic anhydride to 7-acetoxy-5-methoxy-(H)-naphtho[1,2-c]fluoren-9-one (14b), which was converted to the above 5,7-dimethoxy-9(H)-naphtho[1,2-c]-fluoren-9-one (9b) by hydrolysis followed by methylation.

1-(p-Methoxybenzoyl)-4-methoxynaphthalene (1c) and diethyl succinate. The mixture half-esters 2c of (E)- and (Z)- obtained was directly cyclized and 1-acetoxy-3-ethoxycarbonyl-4-(p-methoxyphenyl)-9-methoxyphenanthrene (3c) was isolated (60%). By the same series of reactions this gave the corresponding compounds 5c, 6c, 7c, 8c and 9c. The structures assigned to these compounds are supported by IR. and UV. spectroscopy.

The residue after crystallization of 3c, yielded on chromatography, an oil which gave by hydrolysis 4-hydroxy-4'-6-dimethoxy- (1, 1'-binaphthyl-2-carboxylic acid (10c). This structure was inferred from the appearance of a broad band at 3460-2800 cm<sup>-1</sup> ( $\nu_{\rm CH}$ -bonded), a strong band at 1700 cm<sup>-1</sup> ( $\nu_{\rm C=O}$  aromatic acid) and a strong band at 775 cm<sup>-1</sup> (4 adjacent aromatic hydrogen atoms) [8].

Hydrolysis of the crude half-ester 2c gave a mixture of dibasic acids from which (E)-3-carboxy-4-(4-methoxynaphth-1-yl)-4-(p-methoxyphenyl)but-3-enoic acid (11c) was isolated. This acid was subjected to the same series of reactions as 11b to give 5,7,11-trimethoxy-9*H*-naphtho[1,2-c]fluoren-9-one (9c).

4-(p-Chlorophenyl)-1-methoxynaphthalene (1d) and diethyl succinate. The oily mixture 2d of (E)- and (Z)-half-esters was directly cyclized, giving 1-acetoxy-4-(p-chlorophenyl)-3-ethoxycarbonyl-9-methoxyphenanthrene (3d) (77%) and 4acetoxy-6-chloro-2-ethoxycarbonyl-4'-methoxy-1,1'-binaphthyl (4d) (19%). The relative proportions of 3d and 4d determined spectrophotometrically [3] were in agreement with the amounts isolated. The phenanthrene derivative 3d was subjected to the same series of reactions as 3b to give finally 4-(p-chlorophenyl)-1,9-dimethoxy-3-methoxycarbonylphenanthrene (6d). The structure of the latter compound was established by dechlorination by Pd on charcoal and hydrolysis [9] to 1,9-dimethoxy-4-phenylphenanthrene-3-carboxylic acid (7b). On hydrolysis 6d gave the acid 7d, which was decarboxylated to 4-(p-chlorophenyl)-1,9-dimethoxyphenanthrene (8d), and also cyclized to 11-chloro-5,7-dimethoxy-9Hnaphtho[c]fluoren-9-one (9d).

Hydrolysis of the crude mixture 2d of half-esters gave a mixture of dibasic acids from which (*E*)-3-carboxy-4-(*p*-chlorophenyl)-4-(4-methoxynaphth-1-yl)but-3-enoic acid (11d) was obtained (82%). This was subjected to the same series of reactions as 11b to give finally the same naphthofluorenone 9d.

The UV. spectra of the phenanthrene derivatives 3, 5, 6, 7, 8 showed the  ${}^{1}B_{b}$ ,  ${}^{1}L_{a}$  and  ${}^{1}L_{b}$  bands characteristic of the phenanthrene nucleus. Band  ${}^{1}L_{a}$ , attributed to the transverse polarization perpendicular to the symmetry axis, appeared as

discrete bands or as inflexions; the  ${}^{1}L_{b}$  band, however, appeared in most cases as an inflexion, being partially submerged by the  ${}^{1}L_{a}$  band. The binaphthyls 4 and 10 are characterized by the highly intense  ${}^{1}B_{b}$  band. The naphthofluorenones 9 and 14 are characterized by the relatively weak  $n - \pi^{*}$  transition band appearing above 400 nm.

Interpretation of results. The relative proportions of the two half-esters obtained in the *Stobbe* condensation of 1-benzoylnaphthalene, 1-benzoyl-4-methoxy-, 4-methoxy-1-*p*-methoxybenzoyl-, and 1-*p*-chlorobenzoyl-4-methoxynaphthalene were determined as their cyclization products, phenanthrene or 1,1'-binaphthyl derivatives, and are reported in *Table 1*.

Ketone	Isolation of the compounds	Spectroscopy of the crude mixture
1a, R = R' = H	6.3/1	6.2/1
<b>1b</b> , $\mathbf{R'} = \mathbf{H}$ , $\mathbf{R} = \mathbf{OCH}_3$	6.5/1	6.4/1
1c, $R = R' = OCH_3$	predominant/trace	-
$1d, R = OCH_3, R' = Cl$	4.0/1	4.0/1

Table 1. Ratio of (E)/(Z)-half-esters determined on the cyclization products

Taking 1-benzoylnaphthalene (1a) as reference ketone, introduction of a 4-methoxy group in the naphthalene nucleus appears to increase slightly the repulsive non-bonded interaction between the naphthyl and the ethoxycarbonyl group during the formation of the condensate anion (A) or (B), leading to a decrease the proportion of (B) relative to (A). Although the total yield of half-esters is increased by the introduction of a chlorine atom in the *para* position of the phenyl group owing to the increase in the electrophilic character of the carbonyl group, the relative proportion of the (*E*)-half-ester 1d is lower than the expected, if we take into consideration either one or both of the steric and polar factors. This discrepancy may be due to the indicated relative proportions of the half-esters being based on the proportions of the latter products may not reflect the true proportion of the corresponding half-ester, since a chlorine atom in the *para* position of the phenyl group as well as a methoxyl group in position 4 in the naphthyl group may inhibit the cyclization of the half-ester to different extents.



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## **Experimental Part**

IR. spectra were measured on a *Beckman* IR 20. UV. spectra were measured on a 3 Ratio Recording DK-2A Spectrophotometer, *Beckman*. Microanalyses were carried out in the Microanalytical Unit, Cairo University; m.p. are not corrected.

4-(p-Methoxybenzoyl)-1-methoxynaphthalene (1c) and 4-(p-chlorobenzoyl)-1-methoxynaphthalene (1d). An ice-cooled stirred mixture of p-methoxybenzoyl chloride (0.175 mole), or p-chlorobenzoyl chloride (0.175 mol) and 1-methoxynaphthalene (0.152 mol) in nitrobenzene (200 ml) was treated portionwise with powdered anhydrous AlCl<sub>3</sub> (1.5 mol). The temperature was allowed to rise to ca. 25° and the mixture stirred for 18 h, then worked up as usual (cf. [2]).

4-(p-Methoxybenzoyl)-1-methoxynaphthalene (1c): colourless crystals, m.p. 115-116° (from benzene).  $C_{19}H_{16}O_3$  (292.32) Calc. C 78.08 H 5.47% Found C 78.00 H 5.79%

Dinitrophenylhydrazone, red crystals, m.p. 280-281° (from glacial acetic acid).

C25H20N4O6 (472.44) Calc. N 11.86% Found N 11.50%

4-(p-Chlorobenzoyl)-1-methoxynaphthalene (1d): colourless crystals m.p. 127-128° (from benzene).

C18H13ClO2 (296.78) Calc. C 72.84 H 4.38 Cl 11.97% Found C 72.66 H 4.32 Cl 12.01%

Dinitrophenylhydrazone, deep red crystals, m.p. 298-299° (from glacial acetic acid).

C24H17CIN4O5 (476.90) Calc. Cl 7.45 N 11.75% Found Cl 7.37 N 11.69%

Heated with Pd/C 5% in tetralin for 3.5 h, [9] the ketone 1d gave 4-benzoyl-1-methoxynaphthalene [2]. Condensation of 4-benzoyl- (1b), 4-methoxybenzoyl- (1c), and 4-chlorobenzoyl-1-methoxynaphthalene (1d) with diethyl succinate. A solution of t-BuOK (from K (0.056 mol) and 25 ml t-BuOH) was added to the ketone (0.027 mol) and diethyl succinate (0.075 mol) and refluxed for 45 min. Then the same amounts of diethyl succinate and t-BuOK in t-BuOH were added, and the mixture refluxed 45 min more and worked up as usual [7].

The oily products proved to be mixtures of the stereoisomeric half-esters 2b (70%), 2c (30%) and 2d (90%).

Cyclization of the crude half-esters 2a-2d. The half-ester mixtures (0.015 mol) were refluxed with acetic anhydride (20 ml) and fused sodium acetate (0.015 mol) for 5 h and worked up as usual [7]. The neutral products were crystallized from benzene to give the corresponding 1-acetoxy-4-arylphenan-threne derivatives (3a-3d) (cf. Table 2).

The residue obtained after the separation of the acetoxy-arylphenanthrenes 3 was dissolved in benzene and the solution chromatographed through an aluminium oxide column (50 cm long, 1.2 cm diameter). Elution by benzene/acetone 1:1 and evaporation of the solvent gave in the series **a**, **b** and **d** a solid which was crystallized to give ethyl 4-acetoxy-1-1, 1'-binaphthyl-2-carboxylates 4**a**, 4**b** and 4**d** (see *Table 2*). The derivative 4**c** was obtained after chromatography as a viscous oil which gave by hydrolysis with 15% alcoholic KOH 4-hydroxy-6-methoxy-1-(4-methoxynaphth-1-yl)naphthalene-2-carboxylic acid (10c).

Determination of the isomeric acetoxyesters by UV. [3] in the crude oily cyclisation product of the crude half-esters. Values for  $E_{obs}/E_1$  were plotted vs. the values for  $E_2/E_1$ , where  $E_{obs}$  is the observed optical density of the mixture,  $E_1$  and  $E_2$  are the optical densities of the acetoxyesters 3 and 4 respectively, at the same wavelength. A straight line was obtained from which the ratio of 3 to 4 was calculated. The results are reported in *Table 1*.

1,9-Dimethoxy-4-phenyl-, 1,9-dimethoxy-4-(p-methoxyphenyl)- and 1,9-dimethoxy-4-(p-chlorophenyl) phenanthrene-3-carboxylic acids (7b, 7c, and 7d). The acetoxy esters 3b, 3c and 3d were saponified by boiling with 15% alcoholic KOH (2.5 h) to give the corresponding 1-hydroxy-4-phenylphenanthrene-3-

Com-	m.p. °C	Formula	Analysis %			UV.		IR. cm <sup>-1</sup>		
pound	Solvent <sup>a</sup> ) of cryst.	(M)	Calc. Found	С	Н	Cl	max	83	(KBr) C=O	ArH
<b>3a</b> <sup>b</sup> )	130-131 (B/P)	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub> (384.41)		78.11 78.00	5.24 5.30	-	208 223 257 ~ 300 340	28,960 28,450 30,990 10,160 1,270	1775 1740	775 720
3b	136-137 (B/P)	C <sub>26</sub> H <sub>22</sub> O <sub>5</sub> (414.44)		75.34 75.09	5.35 5.50	_	228 260 311 ~ 337	37,920 45,540 15,570 4,140	1760 1720	760 700
3c	170–171 (B/P)	C <sub>27</sub> H <sub>24</sub> O <sub>6</sub> (444.46)		72.96 73.24	5.44 5.70	-	$230 \\ 255 \\ \sim 279 \\ \sim 301 \\ \sim 312 \\ \sim 336$	35,080 36,850 20,870 15,100 13,320 3,550	1765 1720	775
3d	120-121 (B)	C <sub>26</sub> H <sub>21</sub> ClO <sub>5</sub> (448.90)		69.56 69.33	4.72 4.42	7.90 7.70	$228 \\ 261 \\ \sim 278 \\ 308 \\ \sim 336$	32,200 30,700 15,250 11,890 3,590	1770 1730	775
4a	125-126 (B/P)	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub> (384.41)		78.11 78.40	5.24 4.70	-	222 ~235 283 293	79,250 40,640 12,700 10,600	1780 1720	775
4b	105-106 (M)	C <sub>26</sub> H <sub>22</sub> O <sub>5</sub> (414.44)		75.34 75.60	5.35 5.71	-	212 ~ 290 303 ~ 314 336 ~ 346	103,500 16,560 19,040 16,560 8,280 4,970	1775 1720	770
4d	123-124 (B/P)	C <sub>26</sub> H <sub>21</sub> ClO <sub>5</sub> (448.9)		69.56 69.88	4.72 4.68	7.90 8.00	211 ~ 289 300 ~ 322	118,400 16,150 19,730 13,450	1770 1740	770
10c	250-251 (A)	C <sub>23</sub> H <sub>18</sub> O <sub>5</sub> (374.37)		73.79 74.20	4.85 5.11	_	211 288 298 318	72,990 17,320 17,760 14,210	1700	775

Table 2. A cetoxy-ethoxycarbonyl derivatives of phenylphenanthrene and binaphthyl

<sup>a</sup>) B/P = benzene/petroleum ether, B = benzene, M = methanol, A = acetic acid.

<sup>b</sup>) Awad et al. [1] reported  $\lambda_{max}$  225 nm, loge 4.55 and  $\lambda_{max}$  257 nm, loge 4.61.

Com-	m.p. °C	Formula	Analysis %				UV.		IR. $cm^{-1}$	
pound	Solvent <sup>a</sup> ) of cryst.	(M)	Calc. Found	с	н	Cl	max	8	(KBr) C=O	он
5b	238-239 dil (A)	C <sub>22</sub> H <sub>16</sub> O <sub>4</sub> (344.35)		76.73 76.50	4.68 4.95	-	225.5 256 ~ 307 349	33,370 29,410 9,800 2,750	1690	3360- 2340
5c	201-202 dil (A)	C <sub>23</sub> H <sub>18</sub> O <sub>5</sub> (374.37)		73.79 73.60	4.85 5.11	-	226 251 ~ 282 ~ 316 348	40,770 37,400 22,000 10,850 3,370	1690	3440- 3200
5d	235-236 (B)	C <sub>22</sub> H <sub>15</sub> ClO <sub>4</sub> (378.84)		69.74 69.60	3.99 4.33	9.37 8.80	227 258 306 347	37,280 30,280 10,600 3,030	1675	3520- 2520
6b	175-176 (B/P)	C <sub>24</sub> H <sub>20</sub> O <sub>4</sub> (372.40)		77.40 77.02	5.41 5.42	-	224 261 315 339	41,960 38,840 15,620 5,950	1720	
бс	138-139 (M)	C <sub>25</sub> H <sub>22</sub> O <sub>5</sub> (402.43)		74.61 74.80	5.51 5.70	-	230 254 ~ 317 ~ 342	38,990 33,570 14,670 4,980	1725	
6d	164-165 (B)	C <sub>24</sub> H <sub>19</sub> ClO <sub>4</sub> (406.86)		70.84 71.02	4.71 4.70	8.72 8.80	225 260 305 314 336	45,530 38,210 16,750 17,070 8,940	1730	
7b	264-265 (B/P)	C <sub>23</sub> H <sub>18</sub> O <sub>4</sub> (358.37)		77.08 76.79	5.06 5.29	-	224.5 257 308.5 342	45,820 37,520 14,030 4,300	1690	3300- 2560
7c	226-227 (B/P)	C <sub>24</sub> H <sub>20</sub> O <sub>5</sub> (388.40)		74.21 74.61	5.19 5.41	-	226 250 ~ 316 345	39,580 36,470 11,250 3,100	1690	3320- 2460
7d	280-281 (B/P)	C <sub>23</sub> H <sub>17</sub> ClO <sub>4</sub> (392.84)		70.32 69.86	4.36 4.09	9.03 8.60	226 260 ~ 306 317 345	45,530 36,110 14,920 13,350 5,500	1690	3180- 2450

Table 3. 3-Carboxy-4-phenylphenanthrene derivatives

<sup>a</sup>) A = acetic acid, B = benzene, B/P = benzene/petroleum ether, M = methanol.

Com-	m.p. °C cryst. in methanol	Formula (M)	Analysis	Analysis %				UV.		
pound			Calc. Found	С	Н	Cl	max	ε	ArH cm <sup>-1</sup> (KBr)	
8b	124-125	C <sub>22</sub> H <sub>18</sub> O <sub>2</sub>		84.05	5.77	_	224	50,500	750-705	
		(314.36)		84.08	5.78	_	253	34,000		
							~ 304	12,500		
							~ 342	2,830		
8c	159-160	$C_{23}H_{20}O_{3}$		80.20	5.85	-	227	44,700	770	
		(344.39)		80.23	5.81	-	241	36,500		
							$\sim 275$	21,300		
							$\sim 285$	20,600		
							~ 347	5,500		
8d	165-166	C <sub>22</sub> H <sub>17</sub> ClO <sub>2</sub>		75.74	4.91	10,18	225	53,000	840-770	
		(348.86)		75.74	4.67	9.60	258	33,100		
							~ 282	23,000		
							~ 311	10,800		
							345	3,140		

Table 4. 4-Arylphenanthrenes (8)

Table 5. Cis(Ph/COOH) 3-carboxy-4-(4-methoxynaphth-1-yl)-4-arylbut-3-enoic acids 11 and anhydrides 12

Com-	m.p. °C	Formula	Analysis	%	IR. $cm^{-1}$			
pound	Solvent <sup>a</sup> ) of cryst.	(M)	Calc. Found	С	Н	Cl	γc=0	<b>7</b> он
11b	190-191	C <sub>22</sub> H <sub>18</sub> O <sub>5</sub>		72.92	5.01		1700	3340-2440
	dil (A)	(362.36)		72.88	5.33	-		
11c	156-157	$C_{23}H_{20}O_{6}$		70.40	5.14	_	1710	3340-2560
	(B/A)	(392.39)		70.00	5.32	-	1680	
11d	155-156	C <sub>22</sub> H <sub>17</sub> ClO <sub>5</sub>		66.58	4,32	8.94	1720	3340-2240
	dil (A)	(396.83)		66.40	4.60	8,60	1680	
12b	184-185	C <sub>22</sub> H <sub>16</sub> O <sub>4</sub>		76.73	4.68	_	1840-	
	(B/P)	(344.35)		76.95	4.80	-	1770	
12c	146-147	$C_{23}H_{18}O_5$		73.79	4,85	-		
	(B/P)	(374.37)		74.01	5,20	-		
12d	173-174	C <sub>22</sub> H <sub>15</sub> ClO <sub>4</sub>		69.74	3,99	9.37		
		(378.84)		69 59	4 00	8 80		

carboxylic acids **5b**, **5c** and **5d** (*ca.* 92%). These were methylated with excess dimethyl sulfate in the presence of anhydrous  $K_2CO_3$  and acetone [7] to give the corresponding methoxy esters **6b**, **6c** and **6d** (*cf. Table 3*), which in turn were saponified with 15% alcoholic KOH to give the corresponding methoxy acids **7b**, **7c** and **7d** respectively (*cf. Table 3*).

1,9-Dimethoxy-4-phenyl-, 1,9-dimethoxy-4-(p-methoxyphenyl)- and 1,9-dimethoxy-4-(p-chlorophenyl)phenanthrene (8b, 8c and 8d). The methoxy acids (0.00167 mol) 7b, 7c and 7d were decarboxyl-

Com-	m.p. °C	Formula	Analysis	%	IR. $cm^{-1}$				
pound	Solvent <sup>a</sup> ) of cryst.	(M)	Calc. Found	С	Н	Cl	$\frac{\overline{(KBr)}}{C=O}$	ОН	ArH
13b <sup>b</sup> )	215-216	C <sub>22</sub> H <sub>16</sub> O <sub>4</sub>		76.73	4.68	_	1710	3260-	
	(B/P)	(344.35)		77.20	4.89	-		2500	
13c <sup>c</sup> )	221-222	C <sub>23</sub> H <sub>18</sub> O <sub>5</sub>		73.79	4.85	-	1740-	3460	830
	(A)	(374.37)		73.30	4.50	-	1720	2720	
13d <sup>d</sup> )	221-222	C <sub>22</sub> H <sub>15</sub> ClO <sub>4</sub>		69.74	3.99	9.37	1720	3460	830
,	(A)	(378.84)		70.00	4.01	9.20		2740	775

Table 6. 1-Oxo-inden-2-ylacetic acids 13

<sup>a</sup>) A = acetic acid, B/P = benzene/petroleum ether. <sup>b</sup>) Dinitrophenylhydrazone cyclized spontaneously to a pyridazinone derivative, m.p. 207-208° [6] (glacial acetic acid),  $C_{28}H_{18}N_4O_6$ , Calc. N 11.06, Found 10.83%. <sup>c</sup>) Dinitrophenylhydrazone cyclized to a pyridazinone derivative, m.p. 209-210° [6] (glacial acetic acid),  $C_{29}H_{20}N_4O_7$ , Calc. N 10.11%, Found 10.33%. <sup>d</sup>) Dinitrophenylhydrazone cyclised to a pyridazinone derivative, m.p. 264-265° [6] (glacial acetic acid),  $C_{28}H_{17}ClN_4O_6$ , Calc. N 10.36, Cl 6.50%, Found N 10.25, Cl 6.5%.

ated by refluxing (2 h) with copper bronze (0.0079 mol) in quinoline (6 ml) and worked up as usual [7] (cf. Table 4).

(E)-3-carboxy-4-(4-methoxynaphth-1-yl)-4-phenyl-, (E)-3-carboxy-4-(4-methoxynaphth-1-yl)-4-(p-methoxyphenyl)- and (E)-3-carboxy-4-(4-methoxynaphth-1-yl)-4-(p-chlorophenyl)-but-3-enoic acids (11b, 11c and 11d): The crude half-esters 2b, 2c and 2d were hydrolyzed with 15% alcoholic KOH (3 h). The (E)-acids were separated by crystallization (cf. Table 5).

The anhydrides 12b, 12c and 12d were prepared by refluxing the dibasic acids 11b, 11c and 11d, with acetyl chloride for 2 h, yield 97% (cf. Table 5).

3-(4-Methoxy) naphth-1-yl)-, 6-methoxy-3-(4-methoxynaphth-1-yl)- and 6-chloro-3-(4-methoxynaphth-1-yl)-1-oxo-inden-2-ylacetic acid (13b, 13c and 13d). The ice-cooled stirred solutions of the above anhydrides (0.049 mol) in nitrobenzene (20 ml) were treated portionwise with anhydrous AlCl<sub>3</sub> (0.105 mol) during 1 h and then stirred for a further 3 h. The temperature was then allowed to rise gradually to 20-25°, and each mixture was left for 3 days with occasional stirring before working up as usual [7] to obtain the inden-2-ylacetic acid (cf. Table 6).

7-Acetoxy-5-methoxy-, 7-acetoxy-5,11-dimethoxy- and 7-acetoxy-11-chloro-5-methoxy-9H-naphtho-[1,2-c]fluoren-9-ones (14b, 14c and 14d). The inden-2-ylacetic acids 13b, 13c and 13d (0.032 mol) were refluxed with sodium acetate (0.0973 mol) and acetic anhydride (10 ml) for 6 h then worked up as usual to obtain the acetoxy-fluorenones 14b, 14c and 14d (cf. Table 7).

5,7-Dimethoxy-, 5,7,11-trimethoxy- and 11-chloro-5,7-dimethoxy-9H-naphtho[1,2-c]fluoren-9-ones 9b, 9c and 9d. (i) A solution of each of the phenanthrene carboxylic acids 7b-7d (0.028 mol) was refluxed with phosphorus pentoxide (0.021 mol) in thiophene-free benzene (15 ml) for 2 h and worked up as usual to give the corresponding methoxy-fluorenone derivatives 9b-9d, (cf. Table 7).

(ii) The acetoxy-fluorenes (14b-14d) (0.015 mol) were refluxed with  $1 \ge 0.015$  NaOH (10 ml) for 2 h. The crude phenolic compounds (0.012 mol) were directly methylated with dimethyl sulfate (0.048 mol) and K<sub>2</sub>CO<sub>3</sub> (0.051 mol) in anhydrous acetone (10 ml) (10 h reflux). Crystallization of the product gave the same methoxy-fluorenones (cf. Table 7).

Dehalogenation of 4-(p-chlorophenyl)-1,9-dimethoxy-3-methoxycarbonylphenanthrene (6d) to (7b). (i) The ester 6d (1.0 g) was heated with 5% Pd/C (0.4 g) at 200° (nitrobenzene bath) for 3 h with frequent stirring. Dehalogenation and hydrolysis occurred simultaneously to give 1,9-dimethoxy-4-phenylphenanthrene-3-carboxylic acid 7b (0.8 g) (91%) m.p. 264-265° undepressed when mixed with an authentic sample [cf. 9].

(ii) When the reaction was carried out in boiling tetralin (5 ml) (2 h) dechlorination occurred without hydrolysis. Therefore, the product (ester) was hydrolyzed with boiling 10% NaOH (2 h) to give the same acid 7b [cf. 9].

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$\begin{array}{cccc} 260 & 20,74\\ 281 & 19,36\\ 298 & 17,22\\ \sim 320 & 19,02\\ 327 & 22,44 \end{array}$	) 1725
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$\begin{array}{cccc} 298 & 17,2: \\ \sim 320 & 19,0^{\circ} \\ 327 & 22,4^{\circ} \end{array}$	3
~ 320 19,04	0
377 77 4	0
327 22,44	0
344 29,58	0
387.5 3,94	3
466 2.3	C
<b>14c</b> 205-206 $C_{25}H_{18}O_5$ 75.37 4.55 - 216 48,10	0 1760
(A) (398.39) 75.35 4.43 - 243 53.65	0 1720
265 20.94	0
297 17.1	0
331 23.6	0
353 29.60	D
387.5 5.14	0
490 1.4	0
14d above $C_{24}H_{15}ClO_4$ 71.55 3.75 8.81 220 56.15	0
300 (A) (402.83) 71.01 3.90 8.93 237 47.94	0
363 21.7	0
280 19.4	0
$\sim 290$ 18.3	0
270 10,5. 330 23 9	0
347 314	0
$390  \Delta \Delta'$	0 0
460 2 <u>4</u>	1

Table 7. Naphthofluorenones 9 and 14

<sup>a</sup>) A = acetic acid, B = benzene.

<sup>b</sup>) Dinitrophenylhydrazone from benzene, m.p. 280-281°, C<sub>29</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub>, Calc. N 10.7, Found 10.6%.

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