13. γ,γ-Disubstituted Itaconic Acids. Part 1. The *Stobbe* condensation of 1-Arylnaphthyl Ketones with Diethyl Succinate

by **Victorine B. Baghos (Mrs.), Farid H. Nasr and Munir Gindy**

Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt

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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.

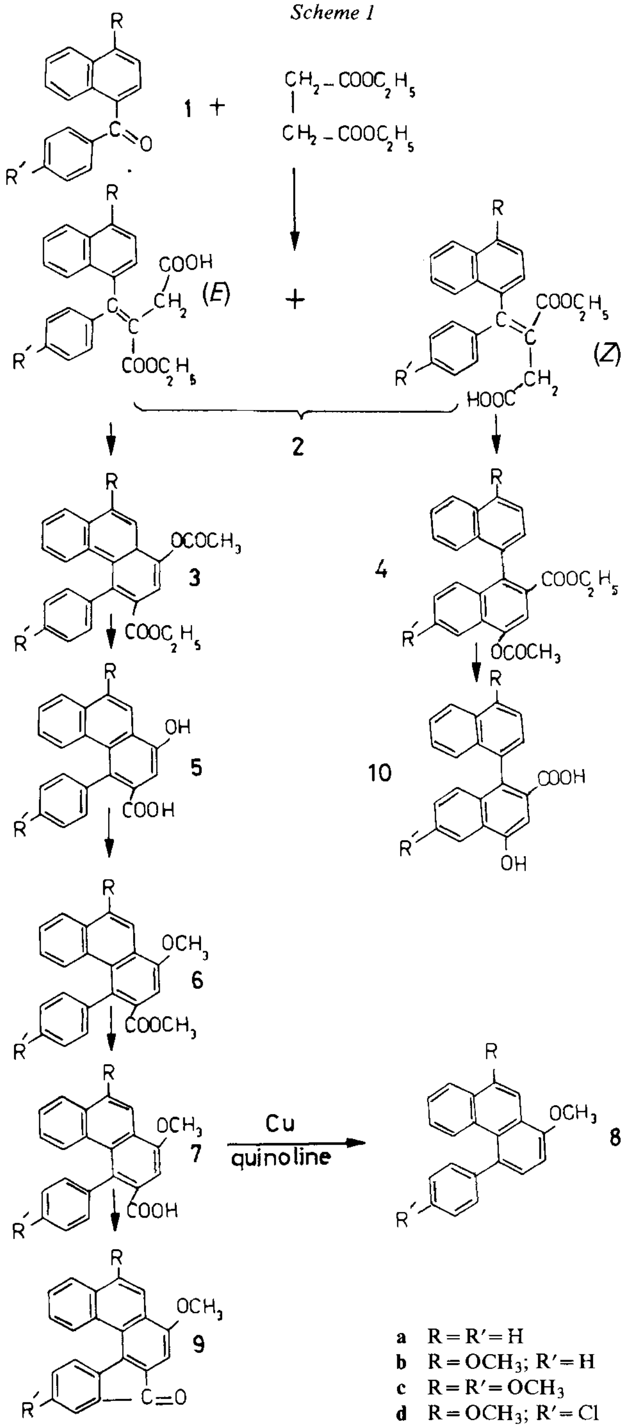
Awad et al. [1] claimed that the condensation of 1-benzoylnaphthalene (**1a**) with diethyl succinate in the presence of potassium *t*-bitoxide in *t*-butyl alcohol produced (*E*) half-ester **2a** as the sole product. This result was attributed either to steric or/and polar factors. We have now found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

Scheme 1



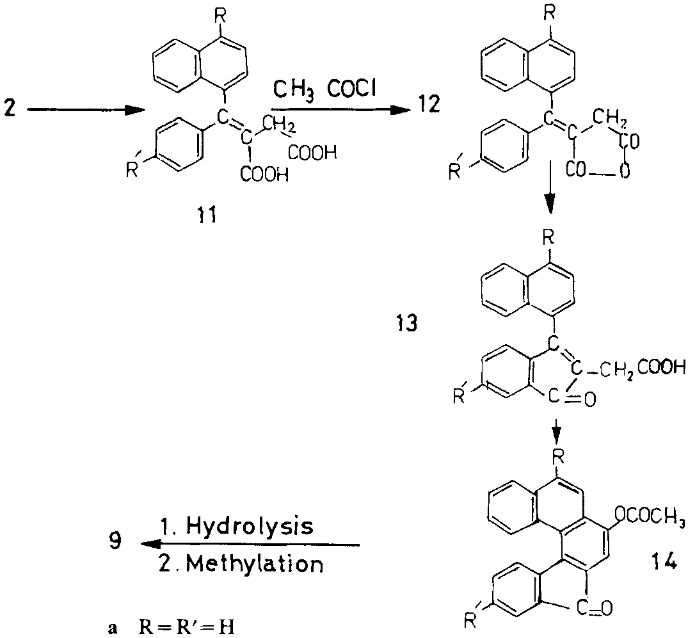
a R = R′ = H
b R = OCH_3; R′ = H
c R = R′ = OCH_3
d R = OCH_3; R′ = Cl

The structures of **3a** and **4a** were inferred from the appearance of strong bands at 775 and 720 cm^{-1} (**3a**) and one band at 775 cm^{-1} (**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^{-1} for **3b**, 770 cm^{-1} for **4b**) and UV. spectra. The relative proportions of **3b** and **4b** estimated spectrophotometrically [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 1,9-dimethoxy-4-phenylphenanthrene (**8b**). Cyclization of the phenanthrene carboxylic acid **7b** with phosphorus pentoxide in benzene gave 5,7-dimethoxy-9*H*-naphtho-

Scheme 2



a R = R' = H
b R = OCH_3; R' = H
c R = R' = OCH_3
d R = OCH_3; R' = Cl

[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 pyridazinone 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^{-1} (ν_{OH}-bonded), a strong band at 1700 cm^{-1} ($\nu_{C=O}$ aromatic acid) and a strong band at 775 cm^{-1} (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 4-acetoxy-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-9*H*-naphtho[*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**.

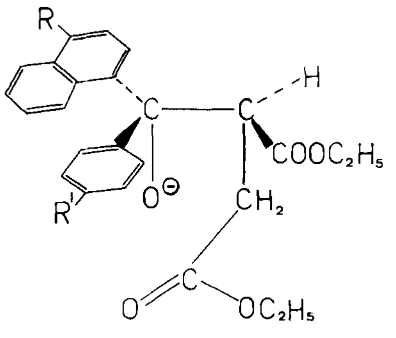
The UV. spectra of the phenanthrene derivatives **3**, **5**, **6**, **7**, **8** showed the ^1B_b, ^1L_a and ^1L_b bands characteristic of the phenanthrene nucleus. Band ^1L_a, attributed to the transverse polarization perpendicular to the symmetry axis, appeared as discrete bands or as inflexions; the ^1L_b band, however, appeared in most cases as an inflexion, being partially submerged by the ^1L_a band. The binaphthyls **4** and **10** are characterized by the highly intense ^1B_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.*

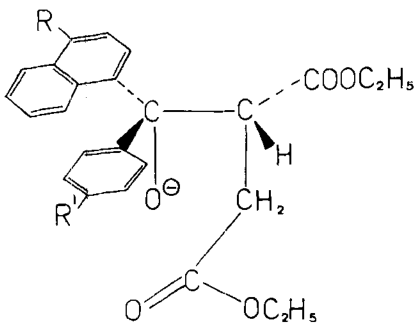
Table 1. *Ratio of* (E)/(Z)-*half-esters determined on the cyclization products*

Ketone	Isolation of the compounds	Spectroscopy of the crude mixture
1a, R = R' = H	6.3/1	6.2/1
1b, R' = H, R = 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

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 corresponding cyclization products. Accordingly, the relative amounts 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 halfester to different extents.



(A)



(B)

The authors wish to express their thanks to Prof. *F. G. Baddar*, Department of Chemistry, Kewait University, for valuable discussion.

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 $AlCl_3$ (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).

$C_{25}H_{20}N_4O_6$ (472.44) Calc. N 11.86% Found N 11.50%

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

$C_{18}H_{13}ClO_2$ (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).

$C_{24}H_{17}ClN_4O_5$ (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-arylphenanthrene 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 **4a**, **4b** and **4d** (see *Table 2*). The derivative **4c** 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-

Table 2. *Acetoxy-ethoxycarbonyl derivatives of phenylphenanthrene and binaphthyl*

Compound	m.p. °C Solvent[a]) of cryst.	Formula (M)	Analysis % Calc. Found	C	H	Cl	UV. max	ε	IR. cm^{-1} (KBr) C=O	ArH
3a[b])	130-131	$C_{25}H_{20}O_4$		78.11	5.24	-	208	28,960	1775	775
	(B/P)	(384.41)		78.00	5.30	-	223	28,450	1740	720
							257	30,990		
							~300	10,160		
							340	1,270		
3b	136-137	$C_{26}H_{22}O_5$		75.34	5.35	-	228	37,920	1760	760
	(B/P)	(414.44)		75.09	5.50	-	260	45,540	1720	700
							311	15,570		
							~337	4,140		
3c	170-171	$C_{27}H_{24}O_6$		72.96	5.44	-	230	35,080	1765	775
	(B/P)	(444.46)		73.24	5.70	-	255	36,850	1720	
							~279	20,870		
							~301	15,100		
							~312	13,320		
							~336	3,550		
3d	120-121	$C_{26}H_{21}ClO_5$		69.56	4.72	7.90	228	32,200	1770	775
	(B)	(448.90)		69.33	4.42	7.70	261	30,700	1730	
							~278	15,250		
							308	11,890		
							~336	3,590		
4a	125-126	$C_{25}H_{20}O_4$		78.11	5.24	-	222	79,250	1780	775
	(B/P)	(384.41)		78.40	4.70	-	~235	40,640	1720	
							283	12,700		
							293	10,600		
4b	105-106	$C_{26}H_{22}O_5$		75.34	5.35	-	212	103,500	1775	770
	(M)	(414.44)		75.60	5.71	-	~290	16,560	1720	
							303	19,040		
							~314	16,560		
							336	8,280		
							~346	4,970		
4d	123-124	$C_{26}H_{21}ClO_5$		69.56	4.72	7.90	211	118,400	1770	770
	(B/P)	(448.9)		69.88	4.68	8.00	~289	16,150	1740	
							300	19,730		
							~322	13,450		
10c	250-251	$C_{23}H_{18}O_5$		73.79	4.85	-	211	72,990	1700	775
	(A)	(374.37)		74.20	5.11		288	17,320		
							298	17,760		
							318	14,210		

[a]) B/P = benzene/petroleum ether, B = benzene, M = methanol, A = acetic acid.

[b]) *Awad et al.* [1] reported λ_{max} 225 nm, logε 4.55 and λ_{max} 257 nm, logε 4.61.

Table 3. *3-Carboxy-4-phenylphenanthrene derivatives*

Compound	m.p. °C Solvent[a]) of cryst.	Formula (M)	Analysis % Calc. Found	C	H	Cl	UV. max	UV. ε	IR. cm^{-1} (KBr) C=O	OH
5b	238-239	$C_{22}H_{16}O_4$		76.73	4.68	-	225.5	33,370	1690	3360-
	dil (A)	(344.35)		76.50	4.95	-	256	29,410		2340
							~307	9,800		
							349	2,750		
5c	201-202	$C_{23}H_{18}O_5$		73.79	4.85	-	226	40,770	1690	3440-
	dil (A)	(374.37)		73.60	5.11	-	251	37,400		3200
							~282	22,000		
							~316	10,850		
							348	3,370		
5d	235-236	$C_{22}H_{15}ClO_4$		69.74	3.99	9.37	227	37,280	1675	3520-
	(B)	(378.84)		69.60	4.33	8.80	258	30,280		2520
							306	10,600		
							347	3,030		
6b	175-176	$C_{24}H_{20}O_4$		77.40	5.41	-	224	41,960	1720	
	(B/P)	(372.40)		77.02	5.42	-	261	38,840		
							315	15,620		
							339	5,950		
6c	138-139	$C_{25}H_{22}O_5$		74.61	5.51	-	230	38,990	1725	
	(M)	(402.43)		74.80	5.70	-	254	33,570		
							~317	14,670		
							~342	4,980		
6d	164-165	$C_{24}H_{19}ClO_4$		70.84	4.71	8.72	225	45,530	1730	
	(B)	(406.86)		71.02	4.70	8.80	260	38,210		
							305	16,750		
							314	17,070		
							336	8,940		
7b	264-265	$C_{23}H_{18}O_4$		77.08	5.06	-	224.5	45,820	1690	3300-
	(B/P)	(358.37)		76.79	5.29	-	257	37,520		2560
							308.5	14,030		
							342	4,300		
7c	226-227	$C_{24}H_{20}O_5$		74.21	5.19	-	226	39,580	1690	3320-
	(B/P)	(388.40)		74.61	5.41	-	250	36,470		2460
							~316	11,250		
							345	3,100		
7d	280-281	$C_{23}H_{17}ClO_4$		70.32	4.36	9.03	226	45,530	1690	3180-
	(B/P)	(392.84)		69.86	4.09	8.60	260	36,110		2450
							~306	14,920		
							317	13,350		
							345	5,500		

[a]) A = acetic acid, B = benzene, B/P = benzene/petroleum ether, M = methanol.

Table 4. *4-Arylphenanthrenes* (**8**)

Compound	m.p. °C cryst. in methanol	Formula (M)	Analysis % Calc. Found	C	H	Cl	UV. max	ε	IR. ArH cm^{-1} (KBr)
8b	124-125	$C_{22}H_{18}O_2$		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	
							~275	21,300	
							~285	20,600	
							~347	5,500	
8d	165-166	$C_{22}H_{17}ClO_2$		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 5. Cis*(Ph/COOH) 3-carboxy-4-(4-methoxynaphth-1-yl)-4-arylbut-3-enoic acids* **11** *and anhydrides* **12**

Compound	m.p. °C Solvent[a]) of cryst.	Formula (M)	Analysis % Calc. Found	C	H	Cl	IR. cm^{-1} $\gamma_{C=O}$	γ_{OH}
11b	190-191	$C_{22}H_{18}O_5$		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	$C_{22}H_{17}ClO_5$		66.58	4.32	8.94	1720	3340-2240
	dil (A)	(396.83)		66.40	4.60	8.60	1680	
12b	184-185	$C_{22}H_{16}O_4$		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	$C_{22}H_{15}ClO_4$		69.74	3.99	9.37		
		(378.84)		69.59	4.00	8.80		

[a]) A = acetic acid, B/P = benzene/petroleum ether.

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-

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

Compound	m.p. °C Solvent[a]) of cryst.	Formula (M)	Analysis % Calc. Found				IR. cm^{-1} (KBr)		
				C	H	Cl	C=O	OH	ArH
13b[b])	215-216	$C_{22}H_{16}O_4$		76.73	4.68	-	1710	3260-	
	(B/P)	(344.35)		77.20	4.89	-		2500	
13c[c])	221-222	$C_{23}H_{18}O_5$		73.79	4.85	-	1740-	3460	830
	(A)	(374.37)		73.30	4.50	-	1720	2720	
13d[d])	221-222	$C_{22}H_{15}ClO_4$		69.74	3.99	9.37	1720	3460-	830
	(A)	(378.84)		70.00	4.01	9.20		2740	775

[a]) A = acetic acid, B/P = benzene/petroleum ether. [b]) 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%. [c]) 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%. [d]) 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 $AlCl_3$ (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 1N NaOH (10 ml) for 2 h. The crude phenolic compounds (0.012 mol) were directly methylated with dimethyl sulfate (0.048 mol) and K_2CO_3 (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].

Table 7. *Naphthofluorenones* **9** *and* **14**

Compound	m.p. °C Solvent[a]) of cryst.	Formula (m)	Analysis % Calc. Found C	H	Cl	UV. max nm	ε	IR. cm^{-1} (KBr) C=O
9b[b])	183-184	$C_{23}H_{16}O_3$	81.16	4.74	-			1700
	(A)	(340.36)	80.50	4.89	-			
9c	156-157	$C_{24}H_{18}O_4$	77.82	4.90	-			1700
	(B)	(370.38)	78.01	5.17	-			
9d	155-156	$C_{23}H_{15}ClO_3$	73.70	4.03	9.46			1710
	(B)	(374.82)	74.11	4.09	9.40			
14b	246-247	$C_{24}H_{16}O_4$	78.25	4.38	-	215	54,700	1775
	(A)	(368.37)	78.57	4.45	-	224	52,360	1725
						260	20,740	
						281	19,380	
						298	17,230	
						~ 320	19,040	
						327	22,440	
						344	29,580	
						387.5	3,940	
						466	2,350	
14c	205-206	$C_{25}H_{18}O_5$	75.37	4.55	-	216	48,100	1760
	(A)	(398.39)	75.35	4.43	-	243	53,650	1720
						265	20,940	
						297	17,170	
						331	23,680	
						353	29,600	
						387.5	5,140	
						490	1,480	
14d	above	$C_{24}H_{15}ClO_4$	71.55	3.75	8.81	220	56,180	
	300 (A)	(402.83)	71.01	3.90	8.93	237	47,940	
						363	21,720	
						280	19,470	
						~ 290	18,350	
						330	23,970	
						347	31,460	
						390	4,490	
						460	2,471	

[a]) A = acetic acid, B = benzene.

[b]) Dinitrophenylhydrazone from benzene, m.p. 280-281°, $C_{29}H_{20}N_4O_6$, Calc. N 10.7, Found 10.6%.

REFERENCES

[1] *W. I. Awad, F. G. Baddar & M. I. B. Selim,* J. chem. Soc. *1962,* 1854.

[2] *L. F. Fieser & C. K. Bradsher,* J. Amer. chem. Soc. *61,* 417 (1939).

[3] *M. J. S. Dewar & D. S. Urch,* J. chem. Soc. *1957,* 345.

[4] *A. D. Campbell,* J. chem. Soc. *1954,* 3659.

[5] *Sillam & Stern,* 'An Introduction to Electronic Absorption spectroscopy in Organic Chemistry', Edward Arnold Ltd., London 1955, p. 245.

[6] *M. Gindy, V. B. Baghos & A. M. Shaban,* J. chem. Soc. (C) *1970,* 1905.

[7] *F. G. Baddar, L. S. El-Assal & V. B. Baghos,* J. chem. Soc. *1958,* 986.

[8] *L. J. Bellamy,* 'The infrared spectra of Complex Molecules', John Wiley, N.Y., London 1958, 145.

[9] a) *F. G. Baddar, N. Latif & H. A. A. Regaila,* J. Indian chem. Soc. *52,* 1177 (1975); b) *W. Awad, F. G. Baddar, F. A. Fouli, S. M. A. Omran & M. I. B. Selim,* J. chem. Soc. (C) *1968,* 507.