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NEW SYNTHESIS OF SUBSTITUTED 3-ARYL-1-NAPHTHALDEHYDES[a]

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Abstract—A general, unequivocal procedure for the preparation of specifically substituted 3-aryl-1-naphthaldehydes was developed. Benzylmagnesium bromides with 5-aryl-2, 2-dimethyl-4-pentene-3-ones (**12**) gave exclusively 1,4-addition products, 5,6-diaryl-2,2-dimethyl-3-hexanones (**13**). The hexanones on oxidation with peracetic acid gave 3,4-diarylbutanoic acids (**14**), which were cyclized to tetralones (**15**). The tetralones on treatment with MeMgI followed by dehydration and dehydrogenation gave 3-aryl-1-methylnaphthalenes (**10**), which were converted into corresponding aldehydes (**11**). When benzylmagnesium bromides were added to 4-aryl-3-butene-2-ones (**1**), mixtures of 1,2 and 1,4-addition products were formed. Further treatment of these mixtures also yielded the desired methylnaphthalenes along with various identified side products.

1. INTRODUCTION

Unequivocal syntheses of multi-substituted naphthalenes have received little attention. Reported syntheses of 3-arylnaphthalenes[1,2] are cumbersome and unproductive. When we required specifically substituted 3-aryl-1-naphthaldehydes (**11**) for the preparation of some potential antimalarials, we developed a reaction sequence which is convenient and productive. In the course of the study several interesting points relative to the synthetic schemes were discovered and clarified.

The synthesis of the key intermediates, the 3-aryl-1-methylnaphthalenes (**10**), was planned initially to follow the 1,4-addition of benzylmagnesium halides to 4-aryl-3-butene-2-ones[3] (**1**) and the further steps outlined in Scheme I. It was found that 1,2 and 1,4-additions occurred to approximately equal extent, and the products were difficult or, in most cases, impossible to separate. Further treatments of the reaction mixtures gave the several compounds illustrated in Scheme I, the formations of which are described later.

The difficulties encountered in both the conjugate addition step and the cyclization step of Scheme I were eliminated by using 5 - aryl - 2,2 - dimethyl - 4 - pentene - 3 - ones (**12**) as the conjugated system. This gave only 1,4-addition products (**13**) which were facilely converted to butanoic acids (**14**) using the Baeyer–Villiger reaction[4] (Scheme II). Upon cyclization the acids (**14**) gave the tetralones (**15**) exclusively. Conversion of the tetralones to the 1-methyl-3-arylnaphthalenes (**10**) proceeded as expected. The 3-aryl-1-naphthaldehydes (**11**) were obtained by several routes: selenium dioxide oxidation of methylnaphthalenes (**10**), the Sommelet reaction *via* monobromomethylnaphthalenes (**16**), and hydrolysis of dibromomethylnaphthalenes (**17**) with silver nitrate. The last was the superior method.

In contrast to the behavior of the substituted butanoic acids (**14**) on treatment with polyphosphoric acid, the methyl ketones (**3**) yielded mixtures consisting of the corresponding naphthalenes (**10**), tetralins (**9**), and methanodibenzo-cycloheptanes (**8**). Formation of the cycloheptanes (**8**) can be explained by assuming that an intermediate carbonium ion, formed after ring closure of the ketones (**3**) cyclized intramolecularly by attack on the angular phenyl group.

The mixture of 1,2 and 1,4-addition products which were not separated gave three products which could be separated from one another after cyclodehydration and dehydrogenation: the 3-aryl-1-methylnaphthalenes (**10**), the cycloheptanes (**8**), and the 1-aryl-3-methylnaphthalenes (**4**), the latter probably arising from cyclization of the 1,2-addition products (**2**). The isomeric arylmethylnaphthalenes were distinguishable by their NMR spectra.[b]

NMR spectra of the intermediate tetralones (**15**) confirmed the assignment of structure in those cases where cyclization of the open chain systems could occur at either *o* or *p*-positions (relative to Y).[c] No isomer other than that arising from cyclization *para* to Y was found.

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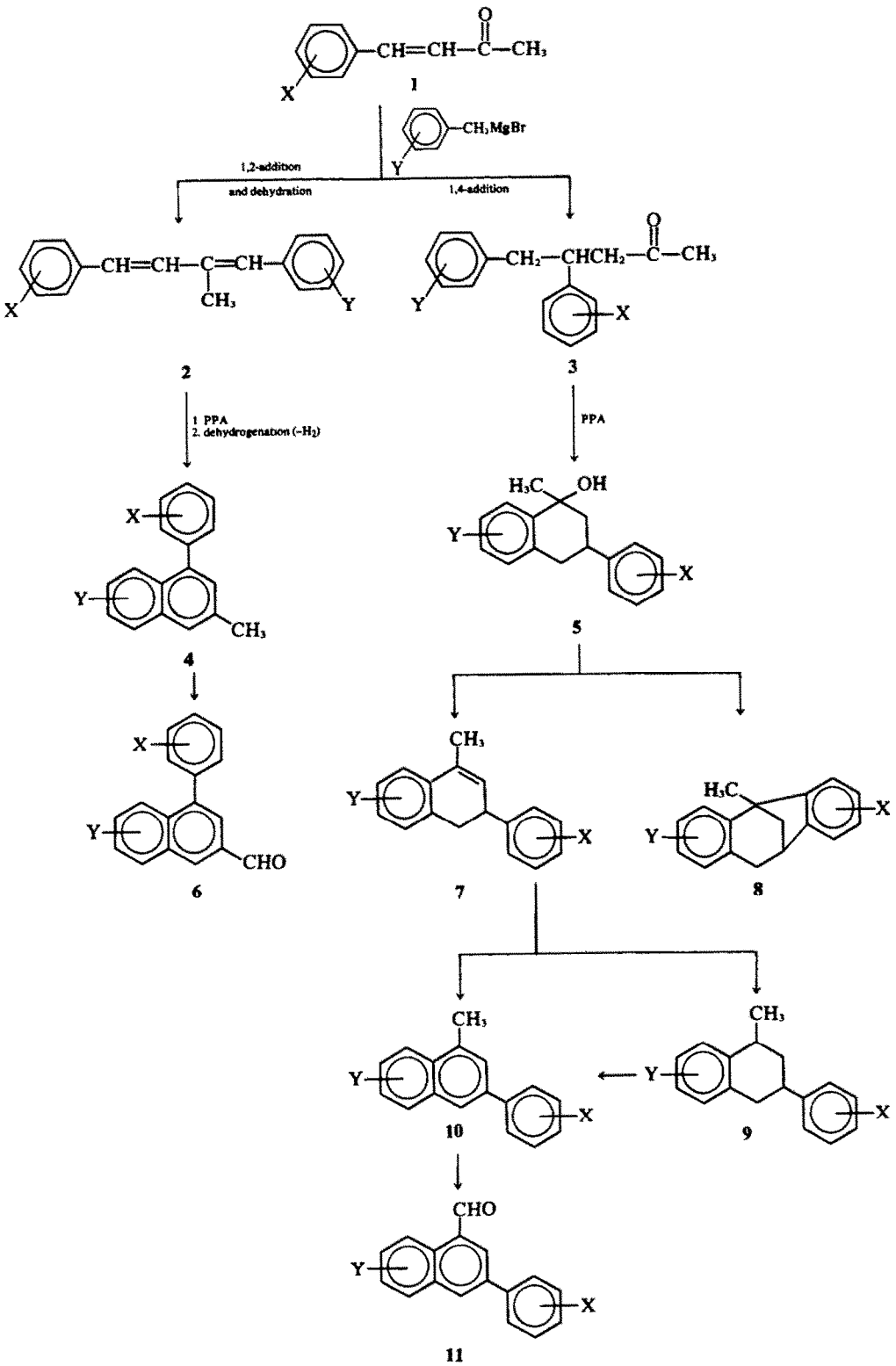
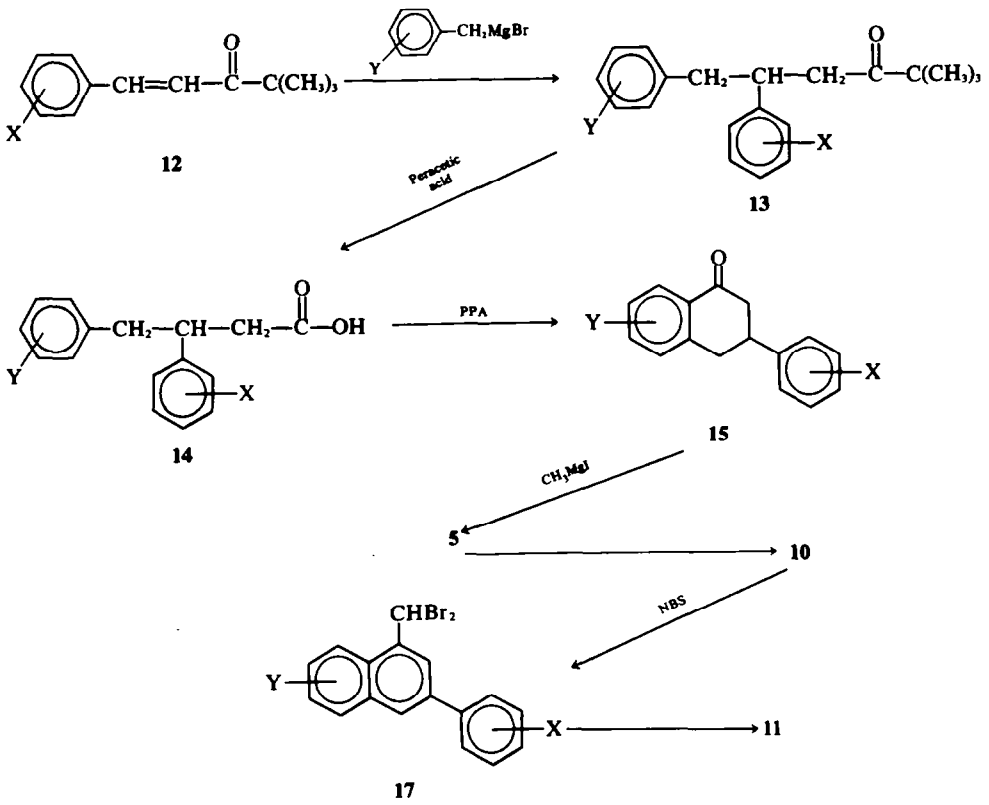
[b] 3-(4-Chlorophenyl)-1-methylnaphthalene (**10a**) prepared from pure **3a** gave a signal in NMR ($CDCl_3$) for the methyl protons at $\delta = 2{\cdot}70$ (s, 3H) as did **10b**, $\delta = 2{\cdot}71$ (s, 3H); **10c**, $\delta = 2{\cdot}65$ (s, 3H); **10e**, $\delta = 2{\cdot}65$ (s, 3H) and **10f**, $\delta = 2{\cdot}65$ (s, 3H) all prepared by Scheme II and **10d**, $\delta = 2{\cdot}69$ (s, 3H) prepared by Scheme I. 6-Chloro-1-(4-chlorophenyl)-3-methylnaphthalene (**4b**) gave a signal for methyl protons at $\delta = 2{\cdot}50$ (s, 3H).

[c] Chloromethoxy tetralone (**15e**). The structure of this tetralone was confirmed by NMR, which showed a singlet for one proton at $\delta = 7{\cdot}54$ ppm. Had cyclization taken place *o* to chlorine, the spectrum would not have a signal at this chemical shift.

6-Chlorotetralone (**15b**). The structure of this tetralone was also confirmed by NMR, which showed a doublet (J = 8 c/s) at $\delta = 8{\cdot}05$ ppm integrating for one proton, due to the two adjacent protons in the structure. The *ortho* cyclized structure can have no signal at this chemical shift.


1
CH3MgBr
1,2-addition
and dehydration
1,4-addition
2
3
1. PPA
2. dehydrogenation (-H2)
PPA
4
5
6
7
8
9
10
11

SCHEME I.



SCHEME II.

EXPERIMENTAL

M.ps were determined with a Thomas–Hoover capillary m.p. apparatus and are uncorrected. B.ps are also uncorrected. NMR spectra were obtained on a Varian A60 spectrometer. The mass spectra were obtained on a Hitachi RMU-6H spectrometer. Microanalyses were performed by Microanalysis, Inc., Wilmington, Delaware.

(A) 5 - *Aryl* - 2,2 - *dimethyl* - 4 - *pentene* - 3 - *ones* (12). The substituted benzaldehyde (1 mol) and 3,3-dimethyl-2-butanone (1 mol) were dissolved in EtOH (500 ml) and H_2O (100 ml). To this soln NaOH (3 g) in H_2O (30 ml) was added. The mixt was stirred at room temp for 1 hr and then solid NaOH (1 g) was added. A ppt began to form at this time. The mixt was stirred for a total of 4 hr and H_2O (400 ml) was added. The ppt was separated and washed with dil HCl and water.

(B) 5,6 - *Diaryl* - 2,2 - *dimethyl* - 3 - *hexanones* (13). A Grignard reagent was prepared from a benzyl halide (1·1 mol) and filtered (See Method I). To this soln 12 was added at room temp. The mixt was refluxed for 2 hr and then left overnight. It was decomposed with sat'd NH_4Cl soln. The Et_2O soln was decanted and dried. Et_2O was removed and the product was crystallized or distilled.

(C) 3,4-*Diaryl butanoic acids* (14). Peracetic acid was prepared[8] by stirring a mixt of AcOH (100 ml), H_2SO_4 (1·2 ml) and H_2O_2 (90%, 100 g) for 3 hr at 23°. It was diluted with AcOH (100 ml) and cooled to 10°. H_2SO_4 (80 ml) was added and during the addition the temp was maintained below 15°. To this soln 13 (0·2 mol) was added. The temp of the mixt was maintained from 65° to 70° until an exothermic reaction ceased, and then it was left overnight at room temp. The mixt was made alkaline with NaOH. This soln was washed with Et_2O to remove unreacted material, and then acidified. The product was extd with Et_2O. The Et_2O was removed.

CAUTION. A serious explosion occurred in our laboratory when a 2 mol reaction to prepare 3-(4-chlorophenyl)butanoic acid was carried out by this procedure.

(D) 3-*Aryl*-1-*tetralones* (15). A mixt of 14 and polyphosphoric acid was heated with stirring and under reduced pressure (water aspirator) for 3 hr. The mixt was cooled and poured into water. The ppt was filtered and washed with $NaHCO_3$.

(E) 3 - *Aryl* - 1 - *methyl* - 3,4 - *dihydronaphthalenes* (7). MeMgI was prepared from Mg (0·15 mol) and MeI (0·16 mol) in Et_2O, and to this soln 15 (0·1 mol) in Et_2O or THF was added. The mixt was refluxed for 2 hr. It was decomposed with sat'd NH_4Cl soln. The Et_2O soln was decanted and concd. The residue was heated at 90° for 3 hr under high vac. (Approx. 0·05 torr).

(F) *Methylnaphthalenes* (10). Chloranil (0·1 mol) and 7 (0·1 mol) were dissolved in min amount of toluene and the mixt was refluxed for 2 hr. The mixt was cooled to 0°, and ppt was filtered. Evaporation of toluene from the filtrate gave 10.

(G) *Bromomethylnaphthalenes.* A mixt of 10 (0·1 mol) NBS[4] (0·1 mol for monobromo and 0·2 mol for dibromo) and CCl_4 (30 ml) was refluxed under irradiation of 300 watt unfrosted lamp with shaking. After 30 min benzoyl peroxide (100 mg) was added. Refluxing, irradiating and shaking was continued until all solid floated on the top of liquid. The mixt was cooled slightly and

[4]NBS was refluxed in CCl_4, filtered hot, was washed with hot CCl_4 and dried just before use. If this was not done, free bromine was noticed refluxing in the mixt and the clean products were not obtained.

Table 1. Substituted naphthalenes

No.	X	Y	Method[a]	Yield %	mp°C	Solvent Crystn	Molecular Formula	%	Analyses C	H	Cl
10a	4-Cl	H	J	60[b]	60–2	MeOH	$C_{17}H_{13}Cl$	Calcd	80·79	5·18	14·03
								Found	80·53	5·12	14·14
16a	4-Cl	H	G	90	120–2	hexane	$C_{17}H_{12}BrCl$	Calcd	61·57	3·65	
								Found	61·78	3·77	
11a	4-Cl	H	K	56	122–3	aq acetone	$C_{17}H_{11}ClO$	Calcd	76·55	4·16	13·29
								Found	76·42	4·25	12·58
10b	4-Cl	6-Cl	J	—	75	MeOH	$C_{17}H_{12}Cl_2$	Calcd	71·10	4·21	24·69
			F	78				Found	71·47	4·16	24·30
16b	4-Cl	6-Cl	G	98	136–8	Et_2O	$C_{17}H_{11}BrCl_2$	Calcd	55·78	3·03	
								Found	54·95	3·07	
17b	4-Cl	6-Cl	G	98	145–7	Et_2O	$C_{17}H_{10}Br_2Cl_2$	Calcd	45·89	2·27	
								Found	46·13	2·31	
11b	4-Cl	6-Cl	K	50	123–6	aq acetone	$C_{17}H_{10}Cl_2O$	Calcd	67·79	3·34	23·54
			H	94				Found	67·57	3·66	23·41
10c	3,4-Cl_2	6-Cl	F	70[c]	117–8	acetone	$C_{17}H_{11}Cl_3$	Calcd	63·48	3·45	
								Found	63·53	3·57	
16c	3,4-Cl_2	6-Cl	G	90	173–4	acetone	$C_{17}H_{10}BrCl_3$	Calcd	50·98	2·52	
								Found	50·94	2·48	
11c	3,4-Cl_2	6-Cl	[d]	50	188–90	acetone	$C_{17}H_9Cl_3O$	Calcd	60·84	2·70	31·69
			H	70				Found	60·62	2·73	31·55
10d	4-Cl	7-MeO	J	—	125–7	MeOH	$C_{18}H_{15}ClO$	Calcd	76·46	5·35	12·54
								Found	76·27	5·52	12·64
11d	4-Cl	7-MeO	K	36	163–5	acetone	$C_{18}H_{13}ClO_2$	Calcd	72·86	4·41	11·95
								Found	72·93	4·41	11·75
10e	4-Cl	6-Cl-7-MeO	J	—	167–8	acetone	$C_{18}H_{14}Cl_2O$	Calcd	68·16	4·45	22·35
			F	87				Found	67·98	4·40	22·30
17e	4-Cl	6-Cl-7-MeO	G	91	180–81	acetone	$C_{18}H_{12}Br_2Cl_2O$	Calcd	45·51	2·55	
								Found	45·49	2·46	
16e	4-Cl	6-Cl-7-MeO	G	70	200–02	acetone	$C_{18}H_{13}BrCl_2O$	Calcd	54·58	3·31	
								Found	54·85	3·16	
11e	4-Cl	6-Cl-7-MeO	K	—	205–6	THF	$C_{18}H_{12}Cl_2O_2$	Calcd	65·28	3·62	21·41
			H	83				Found	65·37	3·80	21·18
10f	3,4-Cl_2	6-Cl-7-MeO	F	86	138–40	MeOH	$C_{18}H_{13}Cl_3O$	Calcd	61·48	3·73	30·24
								Found	61·47	3·87	30·37
17f	3,4-Cl_2	6-Cl-7-MeO	G	98	198–201	THF-acetone	$C_{18}H_{11}Br_2Cl_3O$	Calcd	42·44	2·18	
								Found	42·61	2·23	
11f	3,4-Cl_2	6-Cl-7-MeO	H	98	210–13	acetone	$C_{18}H_{11}Cl_3O_2$	Calcd	59·13	3·03	29·09
								Found	59·12	3·19	28·89
10g	3,5-$(CF_3)_2$	6-Cl	F	—	79–80	MeOH	$C_{19}H_{11}ClF_6$	Calcd	58·71	2·85	9·12
								Found	58·61	2·67	8·98
17g	3,5-$(CF_3)_2$	6-Cl	G	98	153–55	MeOH	$C_{19}H_9Br_2ClF_6$	Calcd	41·76	1·66	
								Found	42·23	1·70	

[a]Capital letter refers to experimental procedure: [b]from pentanone **3a**: [c]from tetralone **15c**: [d]Ref 5.

filtered. CCl_4 was removed from the filtrate and the compound was crystallized.

(H) *Naphthaldehydes* **(11)**, *from dibromomethylnaphthalenes* **(17)**. **17** (0·1 mol) was dissolved in EtOH and refluxed. To this refluxing soln $AgNO_3$ (0·3 mol) in H_2O was added and the mixt was refluxed for 1 hr. It was filtered and the solid was extracted with hot THF, which was added to the filtrate, and the solvents were removed.

(I) 5 - *Phenyl* - 4 - (4 - *chlorophenyl*) - 3 - *pentanone* **(3a)**. Mg (1 mol; powder 0·5 mol and turnings 0·5 mol) and Et_2O (2000 ml) were placed in a 3-neck flask equipped with a reflux condenser with drying tube, dropping funnel and a mechanical stirrer. The stirrer was run at high speed, Et_2O was refluxed and the benzyl chloride (0·4 mol) in Et_2O was added slowly (3 hr). This Grignard reagent was cooled and filtered into another 3-neck flask equipped with a thermometer (−100–50°), a dropping funnel with drying tube and mechanical stirrer. The Grignard reagent was cooled to −65°, and a mixt of 4-chlorobenzalacetate (0·22 mol) and cupric acetate monohydrate (0·02 mol) in THF was added. During the addition the temp of the mixt was maintained below −60°. After addition cooling bath was removed and the mixt was stirred overnight. It was decomposed with sat'd NH_4Cl soln. The ethereal soln was decanted and washed with sodium thiosulfate soln and dried. Et_2O was removed and the residue was distilled (170–80°/0·05 mm). The distillate was subjected to alternate crystallization from MeOH and hexane. From methanolic soln **3a** (1,4-addition product) was obtained and from hexane soln **2a** (1,2-addition product) was recovered.[e]

(J) 3 - (4 - *Chlorophenyl*) - 1 - *methylnaphthalene* **(10a)**. A mixt

[e]When substituted benzyl chlorides (3-Cl, 4-MeO, 3-Cl-4-MeO) were used the 1,4 (**3**) and 1,2-addition (**2**) products could not be separated and in the next reaction i.e. in cyclization were used as mixtures.

Table 2. Open chain intermediates

No.	X	Y	Method[a]	Yield %	mp/bp°C	Solvent Crystn.	Molecular Formula	%	Analyses C	H	Cl
3a	4-Cl	H	I	30	96–7	hexane	$C_{17}H_{17}ClO$	Calcd	74·86	6·28	13·00
								Found	75·10	6·32	13·15
13b	4-Cl	3-Cl	B	85	59–61	MeOH	$C_{20}H_{22}Cl_2O$	Calcd	68·77	6·35	20·30
								Found	68·85	6·40	20·59
14b	4-Cl	3-Cl	C	78	88–90	Et_2O-pet ether	$C_{16}H_{14}Cl_2O_2$	Calcd	62·15	4·56	22·93
								Found	62·38	4·41	23·17
13c	3,4-Cl_2	3-Cl	B	92	94–6	MeOH	$C_{20}H_{21}Cl_3O$	Calcd	62·60	5·52	27·72
								Found	62·30	5·61	27·48
13e	4-Cl	3-Cl-4-MeO[b]	B	87	179–82/ 0·04 mm	—	$C_{21}H_{24}Cl_2O_2$	Calcd	66·49	6·38	18·69
								Found	66·67	6·28	18·66
14e	4-Cl	3-Cl-4-MeO	C	39	149–51	MeOH	$C_{17}H_{16}Cl_2O_3$	Calcd	60·19	4·75	20·90
								Found	60·07	4·66	20·91
13f	3,4-Cl_2	3-Cl-4-MeO	B	85	88–90	MeOH	$C_{21}H_{23}Cl_3O_2$	Calcd	60·96	5·60	25·71
								Found	60·73	5·46	25·74
14f	3,4-Cl_2	3-Cl-4-MeO	C	54	127–9	MeOH	$C_{17}H_{15}Cl_3O_3$	Calcd	54·65	4·05	28·46
								Found	54·77	4·09	28·74
13g	3,5-$(CF_3)_2$	3-Cl	B	85	129–31/ 0·10 mm (mp 67–9)	—	$C_{22}H_{21}ClF_6O$	Calcd	58·61	4·69	
								Found	58·82	4·59	
14g	3,5-$(CF_3)_2$	3-Cl	C	84	119–22	MeOH aq MeOH	$C_{18}H_{13}ClF_6O_2$	Calcd	52·64	3·19	
								Found	53·23	3·05	

[a] Capital letter refers to experimental procedure; [b] Prepared from 3-chloro-4-methoxybenzyl chloride.[h]

Table 3. 1-Tetralones[a]

No.	X	Y	Yield %	mp°C	Solvent Crystn	Molecular Formula	%	Analyses C	H	Cl
15b	4-Cl	6-Cl	82	78–80	EtOH	$C_{16}H_{12}Cl_2O$	Calcd	66·00	4·15	24·35
							Found	65·88	4·06	24·57
15c	3,4-Cl_2	6-Cl	90	138–9	THF-Et_2O	$C_{16}H_{11}Cl_3O$	Calcd	59·02	3·40	32·66
							Found	58·94	3·57	31·88
15e	4-Cl	6-Cl-7-MeO	98	153–6	EtOH	$C_{17}H_{14}Cl_2O_2$	Calcd	63·57	4·39	22·08
							Found	63·36	4·34	22·34
15f	3,4-Cl_2	6-Cl-7-MeO	98	167–9	acetone	$C_{17}H_{13}Cl_3O_2$	Calcd	57·41	3·68	29·91
							Found	57·21	3·69	29·97
15g	3,5-$(CF_3)_2$	6-Cl	75	141–3	MeOH	$C_{18}H_{11}ClF_6O$	Calcd	55·05	2·82	
							Found	55·29	2·81	

[a] Method **D**, see Experimental.

of **3a** (0·1 mol) and PPA (200 gm) was heated slowly to 150°. The reaction was followed by the disappearance of the CO band in IR from the mixt. After the reaction was complete, it was cooled and poured into cold water. It was extracted with Et_2O and the extract was washed with $NaHCO_3$, dried and Et_2O was removed.[f] The residue was mixed with S or Se (0·2 mol) and was placed in a flask, which was attached to an aspirator through a H_2SO_4 trap. The mixt was heated to 250°. The reaction was followed by GLC. After the reaction was complete, the mixt was cooled and extracted with Et_2O. The ethereal soln was treated with Raney nickel and Et_2O was removed. The residue was distilled at 170–80°/0·05 mm.[g] The distillate was heated (90°, flask was completely immersed in oil) with rapid stirring under high vac (0·05 mm) until the pot residue[h] showed single peak in GLC.

Comp. **10**, **b**, **d**, and **e** were also prepared by this method.

(K) 3 - (4 - *Chlorophenyl*) - 1 - *naphthaldehyde* **(11)**. **10a** (0·1 mol) was dissolved in hot triglyme and the soln was heated to reflux. To this refluxing soln a freshly prepared SeO_2 (0·15 mol) in min amount of H_2O was added dropwise. The mixt was refluxed until oxidation was complete (GLC). Then it was cooled and poured into H_2O. The ppt was separated and washed with water.

Compds. **11**, **b**, **d**, and **e** were also prep. by this method.

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[f] When **3d** was used the residue deposited some crystals, which were characterized as 3-(4-chlorophenyl)-7-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene (**9d**), by NMR, mass and elemental analysis.

[g] When **3** was contaminated with **2**, (specially in the case of **3b**) the fraction before it contained mainly the 1-aryl-1-methylnaphthalene (**4b**) arising from **2b**.

[h] Some compound sublimed out which was characterized as cycloheptane **8a**.

Table 4. Miscellaneous compounds

No.	Substitutions	Method[a]	Yield%	mp°C	Solvent Crystn	Molecular Formula	%	Analyses C	H	Cl
2a	X = 4-Cl; Y = H	I	—	121–2	Et_2O	$C_{17}H_{15}Cl$	Calcd	80·15	5·93	13·92
							Found	80·07	5·93	13·75
4b	X = 4-Cl; Y = 6-Cl	J	—	127–8	Et_2O MeOH	$C_{17}H_{12}Cl_2$	Calcd	71·10	4·21	24·69
							Found	71·02	4·20	24·64
6b	X = 4-Cl; Y = 6-Cl	K	25	107–8	Et_2O	$C_{17}H_{10}Cl_2O$	Calcd	67·79	3·34	23·54
							Found	67·63	3·64	23·55
7e	X = 4-Cl; Y = 6-Cl-7-MeO	E	91	99–100	Et_2O	$C_{18}H_{16}Cl_2O$	Calcd	67·72	5·05	22·21
							Found	67·52	4·93	22·17
7f	X = 3,4-Cl_2; Y = 6-Cl-7-MeO	E	97	108–10	Et_2O	$C_{18}H_{15}Cl_3O$	Calcd	61·13	4·28	30·07
							Found	61·40	4·52	30·20
8a	X = 7-Cl; Y = H	J	—	135–8	hexane	$C_{17}H_{15}Cl$	Calcd	80·15	5·93	13·92
							Found	80·24	5·92	13·91
8b	X = 7-Cl; Y = 2-Cl	J	—	124–6	Et_2O	$C_{17}H_{14}Cl_2$	Calcd	70·60	4·88	24·52
							Found	70·35	4·78	24·40
9d	X = 4-Cl; Y = 7-MeO	J	—	105–7	Et_2O	$C_{18}H_{19}ClO$	Calcd	75·65	6·70	12·40
							Found	75·42	6·52	12·27
12c	X = 3,4-Cl_2	A	68	89–91	MeOH	$C_{13}H_{14}Cl_2O$	Calcd	60·72	5·49	27·57
							Found	60·55	5·34	27·57
12g	X = 3,5-$(CF_3)_2$	A	64	86–9	aq MeOH	$C_{15}H_{14}F_6O$	Calcd	55·56	4·35	
							Found	55·34	4·19	
	3,5-$(CF_3)_2$-benzaldehyde	[b]	60	bp 37°/ 1·3 mm	—	$C_9H_4F_6O$	Calcd	44·65	1·67	
							Found	44·91	1·86	

[a]Capital letter refers to experimental procedure; [b]according to Ref 7.

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