209. *Phenylpropiolic Acids. Part VI.* The Cyclisation of Dissimilarly Substituted Phenylpropiolic Anhydrides to the Corresponding 1-Phenylnaphthalenes.*

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Dissimilarly substituted phenylpropiolic anhydrides have been prepared but not isolated. They cyclise directly to a mixture of isomeric 1-phenylnaphthalene-2 : 3-dicarboxylic anhydrides. Their derived dibasic acids give 1-phenylnaphthalenes on decarboxylation.

The present investigation is an extension of a previous study by Baddar and El-Assal [1] who suggested the formation of dissimilarly substituted phenylpropiolic anhydrides by the interaction between equimolecular amounts of arylpropioloyl chloride with arylpropiolic acids in benzene. These anhydrides cyclise readily under the conditions of the reaction to the corresponding 1-phenylnaphthalenes, and since the two aryl radicals of the arylpropiolic anhydrides are dissimilar, the product was a mixture of two isomeric 1-phenylnaphthalene derivatives. The aim was to study the effect of different substituents on the mode of cyclisation of these anhydrides.

When *p*-chlorophenylpropiolic acid was self-condensed it gave 7-chloro-1-*p*-chlorophenylnaphthalene-2 : 3-dicarboxylic anhydride (Ia) identical with a specimen prepared by the Stobbe condensation.[2] This anhydride with aluminium chloride in nitrobenzene gave 3′ : 7-dichloro-3 : 4-benzofluorenone-1-carboxylic acid (IIa); an isomeric anhydride (Ib) failed to do so.[3] Since 5-methoxy-1-*o*-methoxyphenyl- [4] (Ic) and 5-methyl-1-*o*-tolylnaphthalene-2 : 3-dicarboxylic anhydride [3] (Id) are readily converted into their corresponding benzofluorenones (II), it appears that the failure of the chloro-compound (Ib) to do so is due to the interaction between the bulky chlorine atom and the 8-hydrogen atom, which prevents the required coplanarity.

When *o*-chlorophenylpropioloyl chloride was refluxed with *o*-methoxyphenylpropiolic acid in benzene, a mixture of anhydrides was obtained from which 1-*o*-chlorophenyl-5-methoxy- (Ie) and 5-chloro-1-*o*-methoxy-phenylnaphthalene-2 : 3-dicarboxylic anhydrides (If) were isolated. The structure of the latter was established by decarboxylating its derived dibasic acid to 5-chloro-1-*o*-methoxyphenylnaphthalene (IVf), identical with a specimen prepared by heating 5-chloro-1 : 2 : 3 : 4-tetrahydro-1-*o*-methoxyphenyl-1-naphthol (Vf) with selenium. This tertiary alcohol was prepared from 5-chloro-1-tetralone in the usual way, this in turn being prepared by reduction of *o*-chlorocinnamic acid with lithium aluminium hydride to 3-*o*-chlorophenylpropan-1-ol which was converted into the bromide and then by a Grignard reaction into γ-*o*-chlorophenylbutyric acid which was cyclised. The same two isomeric anhydrides (Ie and f) were obtained by cyclisation of dissimilarly substituted dibenzylidenesuccinic anhydrides.[2]

When *o*-chlorophenylpropioloyl chloride was refluxed with *o*-tolylpropiolic acid in benzene, it gave the anhydrides (Ig and h) which were isolated and identified, together with (Id).[3]

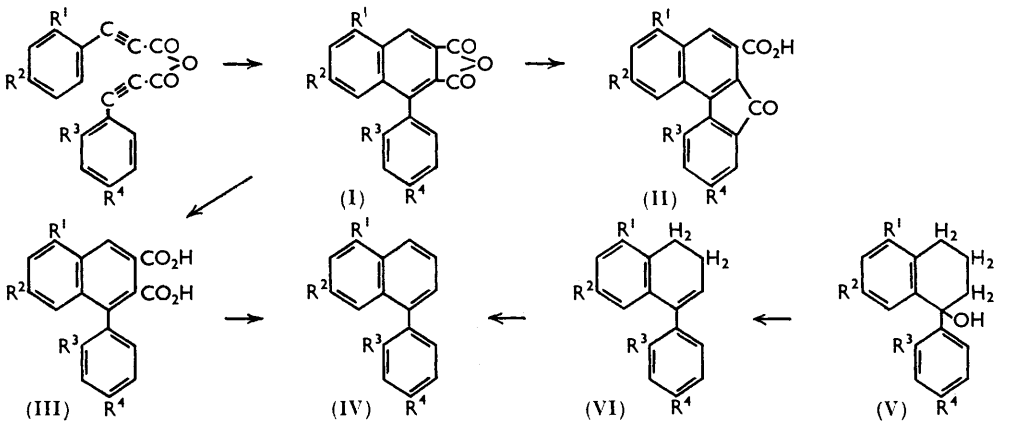
Interaction of *o*-chlorophenylpropioloyl chloride (or acid) and *p*-chlorophenylpropiolic acid (or chloride) gave a mixture of anhydrides from which 7-chloro-1-*p*-chlorophenylnaphthalene-2 : 3-dicarboxylic anhydride (Ia) was isolated as the main product. The product also contained a small quantity of 7-chloro-1-*o*-chlorophenylnaphthalene-2 : 3-dicarboxylic anhydride (Ii).

* Part V, *J.*, 1955, 465.

[1] Baddar and El-Assal, *J.*, 1951, 1844.
[2] Baddar, El-Assal, Doss, and Shehab, *J.*, 1959, 1016.
[3] Baddar, El-Assal, and Doss, *J.*, 1955, 461.
[4] Baddar, *J.*, 1947, 224.

Refluxing *o*-chlorophenylpropioloyl chloride with severally phenyl-, *p*-methoxyphenyl-, *p*-tolyl-, and *p*-chlorophenyl-propiolic acid gave 1-phenyl-, 7-methoxy-1-*p*-methoxyphenyl-,[5] 7-methyl-1-*p*-tolyl-,[3] and 7-chloro-1-*p*-chlorophenyl-naphthalene-2 : 3-dicarboxylic anhydride, respectively, as the only anhydrides isolated. However, *p*-chlorophenylpropioloyl chloride with phenylpropiolic acid as usual gave a mixture of anhydrides from which the two anhydrides (Ij and k) were isolated.

Condensation of *p*-methoxyphenylpropioloyl chloride with phenylpropiolic acid in the usual manner gave a mixture of anhydrides from which were isolated the two compounds (Il and m), obtained also by cyclisation of the dissimilarly substituted dibenzylidenesuccinic anhydride prepared by a two-step Stobbe condensation.[2]



	R^1	R^2	R^3	R^4
a	H	Cl	H	Cl
b	Cl	H	Cl	H
c	OMe	H	OMe	H
d	Me	H	Me	H
e	OMe	H	Cl	H
f	Cl	H	OMe	H
g	Cl	H	Me	H

	R^1	R^2	R^3	R^4
h	Me	H	Cl	H
i	H	Cl	Cl	H
j	H	Cl	H	H
k	H	H	H	Cl
l	H	OMe	H	H
m	H	H	H	OMe

The structure of the anhydrides (Ig, j, and m) was established by decarboxylating the derived dibasic acid to the corresponding 1-phenylnaphthalene derivatives, which were identical with authentic specimens prepared by the Grignard reaction as usual.[1] However, the structure of the anhydrides (Ie, h, and i) rested on their failure to give a 3 : 4-benzofluorenone derivative, which indicates the presence of the chlorine atom in the 2′-position.

The preferential formation of a 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride resulting from the self-condensation of the unsubstituted or the *p*-substituted phenylpropiolic acid, when one of the reactants is *o*-chlorophenylpropiolic acid or its acid chloride, may be due either to the steric effect of the bulky *o*-chlorine atom or to the relative stability of the acid chloride.

However, most of the above results can be interpreted by the mechanism put forward by Baddar and El-Assal.[1]

Experimental

p-*Chlorocinnamic Acid.*—This was prepared in the usual manner [3] from *p*-chlorobenzaldehyde (25 g.), malonic acid (22·2 g.), ethanol (50 ml.), and pyridine (3·1 ml.). The product (26 g.), crystallised from ethanol, had m. p. 249—250° (cf. Skraup and Beng,[6a] and Gabriel and Herzberg,[6b] give m. p. 240—242°).

[5] Baddar and El-Assal, *J.*, 1948, 1267.
[6] (*a*) Skraup and Beng, *Ber.*, 1927, **60**, 946; (*b*) Gabriel and Herzberg, *Ber.*, 1883, **16**, 203.

αβ-*Dibromo*-β-p-*chlorophenylpropionic Acid*.—The above cinnamic acid (10 g.) in acetic acid (15 ml. was treated with bromine (3 ml.) in acetic acid (15 ml.) on a boiling-water bath for 1 hr. Dilution with water precipitated αβ-dibromo-β-*p*-chlorophenylpropionic acid (~ 18 g.), m. p. 194—195° (from benzene) (Found: Halogen, 57·3. Calc. for $C_9H_7O_2ClBr_2$: Halogen, 57·1%). Reich *et al.*[7] give m. p. 187°.

p-*Chlorophenylpropiolic Acid*.—The dibromo-acid (25 g.) in 25% methanolic potassium hydroxide (100 ml.) gave (cf. refs. 8 and 3) *p*-chlorophenylpropiolic acid (*ca.* 13 g.), m. p. 192—193° (from benzene) (Found: Cl, 19·4. Calc. for $C_9H_5O_2Cl$: Cl, 19·7%) (cf. Newman and Merrill [9]).

7-*Chloro*-1-p-*chlorophenylnaphthalene*-2 : 3-*dicarboxylic Anhydride* (Ia).—*p*-Chlorophenylpropiolic acid (5 g.) was refluxed with acetic anhydride (20 ml.) for 5 hr. The product (*ca.* 2·5 g.) was repeatedly crystallised from benzene, to give the *anhydride*, m. p. 266—267° (Found: C, 62·6; H, 2·4; Cl, 20·8. $C_{18}H_8O_3Cl_2$ requires C, 63·0; H, 2·3; Cl, 20·7%).

3′ : 7-*Dichloro*-3 : 4-*benzofluorenone*-1-*carboxylic Acid* (IIa).—The anhydride (3 g.) was heated with anhydrous aluminium chloride (15 g.) and nitrobenzene (50 ml.) on a boiling-water bath for 4 hr. with stirring. Nitrobenzene was removed with steam, and the product extracted with ammonia. The insoluble ammonium salt was acidified; the liberated *acid* (2·9 g.) crystallised from benzene or nitrobenzene in deep-red needles, m. p. 317—318° (Found: C, 62·7; H, 2·3; Cl, 20·5. $C_{18}H_8O_3Cl_2$ requires C, 63·0; H, 2·3; Cl, 20·7%).

p-*Chlorophenylpropioloyl Chloride*.—This *chloride* was prepared from the acid (18 g.) and thionyl chloride (50 ml.) (2 hours' refluxing) and distilled at 100—105°/1 mm., then crystallised from light petroleum (b. p. 40—60°); it had m. p. 68—69° (Found: Cl, 35·7. $C_9H_4OCl_2$ requires Cl, 35·7%).

Action of p-*Chlorophenylpropioloyl Chloride on* o-*Chlorophenylpropiolic Acid*.—A mixture of acid (9 g.) and freshly prepared chloride (9·9 g.) in dry benzene (100 ml.) was refluxed for 36 hr. Removal of benzene left a solid (A) which was washed with ether, then repeatedly crystallised from benzene, to give the anhydride (Ia), m. p. and mixed 266—267°. The product separating from the benzene mother-liquor on storage was fractionally crystallised from the same solvent to give the *anhydride* (Ii), m. p. 196—197°, depressed on admixture with either anhydride (Ia or b) (Found: C, 62·6; H, 2·6; Cl, 20·6. $C_{18}H_8O_3Cl_2$ requires C, 63·0; H, 2·3; Cl, 20·7%). When the anhydride (Ii) (0·5 g.) had been heated for 4 hr. at 40° with aluminium chloride (2·5 g.) in nitrobenzene (10 ml.), it was recovered unchanged.

Action of o-*Chlorophenylpropioloyl Chloride on* o-*Methoxyphenylpropiolic Acid*.—Freshly prepared *o*-chlorophenylpropioloyl chloride (9·9 g.) and *o*-methoxyphenylpropiolic acid [4] (8·8 g.) in benzene (100 ml.) were refluxed for 30 hr. The product (*ca.* 7·5 g.) precipitated on cooling (m. p. 240—246°) gave, on repeated crystallisation from benzene, 1-o-*chlorophenyl*-5-*methoxynaphthalene*-2 : 3-*dicarboxylic anhydride* (Ie) in lemon-yellow crystals (*ca.* 1·5 g.), m. p. 251—252°, depressed on admixture with the anhydride (Ic or b) (Found: C, 67·2; H, 2·95; Cl, 10·5. $C_{19}H_{11}O_4Cl$ requires C, 67·35; H, 2·95; Cl, 10·5%).

The benzene mother-liquor was evaporated and the oily residue diluted with ether (100 ml.) and kept overnight. The precipitated product (*ca.* 5 g.), m. p. 220—224°, was fractionally crystallised from benzene. The first fraction was identified as the previous anhydride. The benzene mother-liquor afforded on slow evaporation crystals, which on repeated crystallisation from the same solvent gave 5-*chloro*-1-o-*methoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (If), m. p. 198—199° (*ca.* 0·6 g.), depressed on admixture with the above isomeric anhydride and with anhydride (Ib) (Found: C, 67·3; H, 3·1; Cl, 10·4%).

3-o-*Chlorophenylpropan*-1-*ol*.—*o*-Chlorocinnamic acid (91 g.) was added during 1 hr. to a stirred suspension of lithium aluminium hydride (40 g.) in ether (100 ml.) at 0°. Then the mixture was refluxed for an hour and worked up as usual. The product was distilled, to give 3-o-*chlorophenylpropan*-1-*ol*, b. p. 100—101°/2 mm. (*ca.* 82 g.), n_D^{25} 1·5390 (Found: C, 63·7; H, 6·7; Cl, 20·6. $C_9H_{11}OCl$ requires C, 63·3; H, 6·45; Cl, 20·8%).

1-*Bromo*-3-o-*chlorophenylpropane*.—3-*o*-Chlorophenylpropan-1-ol (75 g.) and 40% hydrobromic acid (200 ml.) were refluxed for 5 hr., then worked up as usual and distilled, to give 1-*bromo*-3-o-*chlorophenylpropane* (*ca.* 70 g.), b. p. 95—96°/2 mm. (Found: C, 46·4; H, 4·45; Halogen, 49·1. $C_9H_{10}ClBr$ requires C, 46·25; H, 4·3; Halogen, 49·4%).

[7] Reich, Araus, Potok, and Tempel, *Helv. Chim. Acta*, 1920, **3**, 793.
[8] Reimer, *J. Amer. Chem. Soc.*, 1942, **64**, 2510.
[9] Newman and Merrill, *ibid.*, 1955, **77**, 5549.

γ-o-Chlorophenylbutyric Acid.—The Grignard reagent [from 1-bromo-3-*o*-chlorophenylpropane (50·5 g.) and magnesium (5·3 g.) in ether (200 ml.)] was rapidly added to solid carbon dioxide, left for 4 hr., and worked up as usual. The *acid* produced crystallised from light petroleum (b. p. 60—80°), then having m. p. 94—95° (*ca.* 20 g.) (Found: C, 60·3; H, 5·6; Cl, 17·8. $C_{10}H_{11}O_2Cl$ requires C, 60·45; H, 5·5; Cl, 17·9%).

5-Chloro-1-tetralone.—*γ-o*-Chlorophenylbutyric acid (15 g.) was kept in anhydrous hydrogen fluoride (120 ml.) for 2 days, then worked up as usual. The *product*, crystallised from light petroleum (b. p. 40—60°), had m. p. 67·5—68·5° (*ca.* 7 g.) (Found: C, 66·4; H, 5·2; Cl, 19·4. $C_{10}H_9OCl$ requires C, 66·5; H, 5·0; Cl, 19·7%). Its 2 : 4-*dinitrophenylhydrazone* formed deep-red needles (from benzene), m. p. 259—260° (Found: C, 53·6; H, 3·8; N, 15·9. $C_{16}H_{13}O_4N_2Cl$ requires C, 53·3; H, 3·7; N, 15·5%).

5-Chloro-1 : 2 : 3 : 4-tetrahydro-1-o-methoxyphenyl-1-naphthol (Vf).—5-Chloro-1-tetralone (5 g.) in dry ether (50 ml.) was added during 30 min. to a stirred solution of *o*-methoxyphenylmagnesium bromide [from *o*-bromoanisole (7·2 g.) and magnesium (1·4 g.) in ether (50 ml.)]. The mixture was left overnight and worked up as described by Baddar and El-Assal.[5] The product was distilled and the fraction boiling at 170—175°/2 mm. (*ca.* 7 g.) was collected, then crystallised from methanol to give the *tetralol*, m. p. 134—135° (Found: C, 70·8; H, 6·0; Cl, 12·2. $C_{17}H_{17}O_2Cl$ requires C, 70·7; H, 6·0; Cl, 12·3%). The presence of the hydroxyl group was confirmed by the infrared spectrum.

5-Chloro-1-o-methoxyphenylnaphthalene (IVf).—(i) The above tertiary alcohol (1 g.) and selenium powder (0·7 g.) were heated at 300—310° for 2 hr. The product was purified by chromatography over alumina [light petroleum (b. p. <40°) was used as a developer]. On repeated crystallisation from methanol, *5-chloro-1-o-methoxyphenylnaphthalene*, m. p. 96—97°, was obtained (Found: C, 75·7; H, 4·7; Cl, 13·0. $C_{17}H_{13}OCl$ requires C, 76·0; H, 4·8; Cl, 13·2%). (ii) The acid (IIIf) (0·5 g.) [prepared from the anhydride] was heated in quinoline (4 ml.) with copper-bronze (0·2 g.) at 205—210° (nitrobenzene-bath) for 30 min. with stirring. More copper-bronze (0·2 g.) was added in portions during 2 hr., stirring and heating were continued for a further hour, and the whole was worked up as usual. The product was purified by distillation (b. p. 180—190°/2 mm.), followed by crystallisation from methanol, to give 5-chloro-1-*o*-methoxyphenylnaphthalene (IVf) (0·25 g.), m. p. 96—97°, undepressed on admixture with a specimen prepared by method (i) (Found: C, 76·0; H, 5·0; Cl, 13·1%).

Action of o-*Chlorophenylpropioloyl Chloride on* o-*Tolylpropiolic Acid.*—Freshly prepared *o*-chlorophenylpropioloyl chloride (9·9 g.) and *o*-tolylpropiolic acid (8 g.) in benzene (100 ml.) were refluxed for 32 hr. Removal of benzene left an oil which was treated with dry ether (100 ml.) and left overnight. The precipitated crystals were washed with ether (*ca.* 8 g.; m. p. 165—175°). Crystallisation of this product (5 g.) from benzene gave *5-chloro-1-o-tolylnaphthalene-2 : 3-dicarboxylic anhydride* (Ig) (*ca.* 1·5 g.), m. p. 182—182·5°, depressed on admixture with anhydride [3] (Ib) (Found: C, 71·1; H, 3·65; Cl, 10·4. $C_{19}H_{11}O_3Cl$ requires C, 70·7; H, 3·4; Cl, 11·0%). The benzene mother-liquor yielded on storage another fraction, which after repeated crystallisation from benzene gave 5-methyl-1-*o*-tolylnaphthalene-2 : 3-dicarboxylic anhydride [3] (Id) (*ca.* 0·7 g.), m. p. and mixed m. p. 162—163°. Attempts to isolate the anhydride (Ih) from the product were unsuccessful. However, its presence was inferred from the following evidence:

A finely powdered mixture of the product (2 g.) from the above experiment with aluminium chloride (10 g.) was added during 10 min. to stirred nitrobenzene (20 ml.) so that the temperature did not rise above 40—50°. The mixture was left for 3 days at room temperature with occasional stirring and warming to 50°, then worked up as usual.[3] Acidification of the clear ammoniacal extract precipitated a mixture of acids which was filtered off and dried (*ca.* 2 g.). It was extracted with ether, and the colourless ethereal solution was filtered from the insoluble red product. Distillation of ether left a residue (*ca.* 0·17 g.) which was dissolved in chloroform and run through 9 : 1 silica–calcite, with 1 : 1 ether–light petroleum (b. p. 50—60°) as developer. The product (*ca.* 0·15 g.) was heated with acetyl chloride (1 ml.), then crystallised from benzene, to give *1-o-chlorophenyl-5-methylnaphthalene-2 : 3-dicarboxylic anhydride* (*ca.* 0·1 g.), m. p. 244—246° depressed on admixture with the anhydride (Ig, d, or b) (Found: C, 71·0; H, 3·7; Cl, 10·6. $C_{19}H_{11}O_3Cl$ requires C, 70·7; H, 3·4; Cl, 11·0%). The red-brown ether-insoluble residue was fractionally crystallised from benzene. The first fraction, m. p. 218—220°, gave on crystallisation from the same solvent *1′-chloro-5-methyl-3 : 4-benzofluorenone-1-carboxylic acid* (IIg) (*ca.* 0·6 g.), depressed on admixture with the acid (IId) (Found: C, 71·3; H, 3·6; Cl, 10·2.

$C_{19}H_{11}O_3Cl$ requires C, 70·7; H, 3·4; Cl, 11·0%). The second fraction, m. p. 230—234°, on repeated crystallisation from benzene gave this acid (IId) (*ca.* 0·6 g.), m. p. 236—238°, undepressed on admixture with an authentic specimen.[3]

8-*Chloro*-1 : 2-*dihydro*-4-o-*tolylnaphthalene* (VIf).—5-Chloro-1-tetralone (5 g.) in dry ether (50 ml.) was added dropwise to ethereal *o*-tolylmagnesium bromide [from *o*-bromotoluene (7 g.) and magnesium (1·4 g.)] in ether (50 ml.) during 30 min. with occasional stirring, left overnight, then worked up as usual.[1,5] The *product* was fractionated (b. p. 160—165/2 mm.; 6·5 g.), triturated with ether, then crystallised from methanol; it had m. p. 92—93° (Found: C, 79·9; H, 6·0; Cl, 13·7. $C_{17}H_{15}Cl$ requires C, 80·15; H, 6·0; Cl, 13·9%).

1-*Chloro*-5-o-*tolylnaphthalene* (IVg).—(i) The dihydro-compound (VIf) (1 g.) and selenium powder (0·7 g.) were heated at 300—310° for 3 hr. The product (0·7 g.) was chromatographed over alumina, then distilled (b. p. 170—180°/3 mm.). Nitration [10] gave an inseparable mixture. (ii) The acid (IIIg) (0·5 g.) and copper-bronze (0·4 g.) in quinoline (4 ml.) were treated as described for the decarboxylation above. The product was chromatographed, then distilled in a vacuum (b. p. 160—180°/2 mm.). The infrared spectra of this compound and that obtained by the previous method were identical. The identity of both products was also established by dehalogenation to the same 1-*o*-tolylnaphthalene (see next experiment).

1-o-*Tolylnaphthalene*.—(i) 1 : 2-Dihydro-4-*o*-tolylnaphthalene (0·5 g.) and 10% palladised charcoal (0·05 g.) were heated at 200—210° for 1 hr. The product, crystallised from methanol, gave 1-o-*tolylnaphthalene*, m. p. 72—73° (*ca.* 0·4 g.) (Found: C, 93·5; H, 6·65. $C_{17}H_{14}$ requires C, 93·4; H, 6·6%). (ii) 1-Chloro-5-*o*-tolylnaphthalene (0·5 g.) (obtained by the above two methods), tetralin (0·7 ml.), and 10% palladised charcoal (0·05 g.) were heated at 200—210°, then worked up as described in method (i). Crystallisation from methanol gave 1-*o*-tolylnaphthalene, m. p. and mixed m. p. 72—73° (Found: C, 93·6; H, 6·7%).

Action of o-*Chlorophenylpropioloyl Chloride on Phenyl-*, p-*Methoxyphenyl-*, p-*Tolyl-, and* p-*Chlorophenyl-propiolic Acid*.—A mixture from freshly prepared *o*-chlorophenylpropioloyl chloride [1,3] (19·9 g.) and phenylpropiolic acid (14·6 g.) in dry benzene (200 ml.) was worked up as usual after 32 hours' refluxing. The semi-solid product was triturated with ether (100 ml.), then crystallised from benzene to give 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (I) in pale-yellow crystals (*ca.* 10 g.), m. p. and mixed m. p. 252—253°. The ethereal mother-liquor gave, overnight, another crop (*ca.* 2·7 g.) of the same product.

A mixture from the same acid chloride (19·9 g.) and *p*-methoxyphenylpropiolic acid (17·6 g.) in benzene (200 ml.) was similarly worked up. The solid product (7·5 g.) precipitated from ether crystallised from benzene, to give 7-methoxy-1-*p*-methoxyphenylnaphthalene-2 : 3-dicarboxylic anhydride, m. p. and mixed m. p. 216—217°.[5] Unchanged *p*-methoxyphenylpropiolic acid [5] (*ca.* 0·5 g.) was recovered from the ethereal mother-liquor.

A mixture from the same acid chloride (19·9 g.) and *p*-tolylpropiolic acid (16 g.) in benzene (200 ml.), when similarly worked up, gave a solid (*ca.* 4 g.) after trituration with ether. This on crystallisation from benzene gave 7-methyl-1-*p*-tolylnaphthalene-2 : 3-dicarboxylic anhydride [3] in pale-yellow crystals (*ca.* 3·5 g.), m. p. and mixed m. p. 267—268°.

Similarly, a mixture from the above acid chloride (19·9 g.) and *p*-chlorophenylpropiolic acid (18 g.) in benzene (200 ml.) gave *p*-chlorophenylpropiolic acid (*ca.* 6·5 g.) as the first crop. Evaporation of the benzene mother-liquor left a viscous oil which on trituration with ether and then crystallisation from benzene gave the anhydride (Ia) (*ca.* 1·5 g.), m. p. and mixed m. p. 266—267°. Another fraction of the same anhydride (*ca.* 6·5 g.) was obtained on storage.

Action of p-*Chlorophenylpropioloyl Chloride on Phenylpropiolic Acid*.—Freshly prepared *p*-chlorophenylpropioloyl chloride (3·2 g.), phenylpropiolic acid (2·3 g.), and dry benzene (80 ml.) were refluxed for 35 hr. The precipitated product was filtered off and thoroughly washed with ether (*ca.* 1·5 g.). Repeated crystallisation from benzene gave the *anhydride* (Ij), m. p. 251—252°, depressed on admixture with a specimen of anhydride (Ia) or 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride (Found: C, 70·0; H, 3·0; Cl, 11·3. $C_{18}H_9O_3Cl$ requires C, 70·0; H, 2·9; Cl, 11·6%).

The original benzene mother-liquor was concentrated and on storage yielded another fraction (colourless) which was filtered off and washed with ether. On repeated crystallisation from benzene this gave the *anhydride* (Ik) (*ca.* 0·4 g.), m. p. 210—212°, depressed on admixture with the preceding two anhydrides or (Ia) (Found: C, 69·8; H, 2·8; Cl, 11·4%).

[10] Baddar, El-Assal, and Gindy, *J.*, 1948, 1270.

7-*Chloro*-1-*tetralone*.—Freshly distilled γ-*p*-chlorophenylbutyric acid [11] (40 g.) was left in anhydrous hydrogen fluoride (200 ml.) overnight, then worked up as described for the 5-chloro-derivative. The product (*ca.* 30 g.) was distilled (b. p. 150—155°/5 mm.), then crystallised from light petroleum (b. p. 55—65°), to give 7-chloro-1-tetralone, m. p. 94—95° (*ca.* 26 g.) (von Braun [12] gave m. p. 94° and Schroeter,[13] m. p. 96—97°) (Found: C, 66·7; H, 5·2; Cl, 19·5. Calc. for $C_{10}H_9OCl$: C, 66·5; H, 5·0; Cl, 19·7%).

7-*Chloro*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenyl*-1-*naphthol* (Vj).—7-Chloro-1-tetralone (9 g.) in ether (40 ml.) was gradually added to phenylmagnesium bromide [from bromobenzene (12 g.) and magnesium (1·8 g.) in ether (80 ml.)], then worked up as usual. The product (*ca.* 14 g.) was fractionally distilled (b. p. 175—180°/2 mm.), then repeatedly crystallised from methanol to give the *tetralol*, m. p. 81—82° (*ca.* 10 g.) (Found: C, 74·2; H, 5·7; Cl, 13·4. $C_{16}H_5OCl$ requires C, 74·3; H, 5·8; Cl, 13·7%). The structure of this tertiary alcohol was confirmed by its infrared spectrum.

7-*Chloro*-1-*phenylnaphthalene* (IVj).—(i) The above tertiary alcohol (3 g.) and selenium powder (2·5 g.) were heated at 320—330° for 3 hr., then worked up as usual. 7-*Chloro*-1-*phenylnaphthalene* (*ca.* 1·5 g.) had m. p. 77—78° (from methanol) (Found: C, 80·2; H, 4·7; Cl, 14·6. $C_{16}H_{11}Cl$ requires C, 80·5; H, 4·6; Cl, 14·8%). (ii) 7-Chloro-1-phenylnaphthalene-2 : 3-dicarboxylic acid (0·3 g.) (obtained from the anhydride as usual) was decarboxylated with copper-bronze (0·2 g.) in quinoline (5 ml.) as usual. The product was distilled (b. p. 150—155°/3 mm.; 0·2 g.), then crystallised from methanol to give 7-chloro-1-phenylnaphthalene, m. p. and mixed m. p. 77—78° (Found: C, 79·85; H, 4·6; Cl, 14·2%).

p-*Methoxyphenylpropioloyl Chloride*.—A mixture of *p*-methoxyphenylpropiolic acid [5] (3·6 g.) and thionyl chloride (3·5 ml.) was left overnight at 25—30°, then distilled (b. p. 150—160°/2 mm.) to give the *chloride* as a lemon-yellow oil (Found: Cl, 18·6. $C_{10}H_7O_2Cl$ requires Cl, 18·25%).

Action of p-*Methoxyphenylpropioloyl Chloride on Phenylpropiolic Acid*.—Freshly prepared *p*-methoxyphenylpropioloyl chloride (5·4 g.) and phenylpropiolic acid (4·5 g.) in benzene (80 ml.) were refluxed for 30 hr. The crystalline product was filtered off, and washed with ether. On repeated crystallisation from benzene, 1-p-*methoxyphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (Im) was obtained in lemon-yellow crystals (*ca.* 1·4 g.), m. p. 261—262°, depressed on admixture with 7-methoxy-1-*p*-methoxyphenyl-[5] or 1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride (Found: C, 74·8; H, 4·2; OMe, 8·7. $C_{19}H_{12}O_4$ requires C, 75·0; H, 3·95; OMe, 10·2%). The benzene mother-liquors from the reaction mixture were concentrated, to give a second crop (*ca.* 1·55 g.), m. p. 205—210°. On crystallisation of this from benzene, the first fraction proved to be the above anhydride (Im). The second fraction, m. p. 220—250° (*ca.* 1·8 g.), gave, on repeated crystallisation from the same solvent, the *anhydride* (Il) in pale yellow crystals, m. p. 266—268°, depressed on admixture with its above isomer, with 7-methoxy-1-*p*-methoxyphenyl-,[5] and with 1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride (Found: C, 74·9; H, 3·9%).

1-p-*Methoxyphenylnaphthalene* (IVm).—1-*p*-Methoxyphenylnaphthalene-2 : 3-dicarboxylic acid (0·5 g.) (prepared from the anhydride) was decarboxylated with copper-bronze (0·4 g.) in quinoline (5 ml.) as usual. The product was distilled (b. p. 176—178°/1 mm.), then crystallised from dilute ethanol, to give 1-*p*-methoxyphenylnaphthalene (*ca.* 0·3 g.), m. p. 116—116·5°, undepressed on admixture with an authentic specimen [14] (Found: C, 87·0; H, 5·8; OMe, 12·8. Calc. for $C_8H_{14}O$: C, 87·2; H, 6·0; OMe, 13·0%).

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