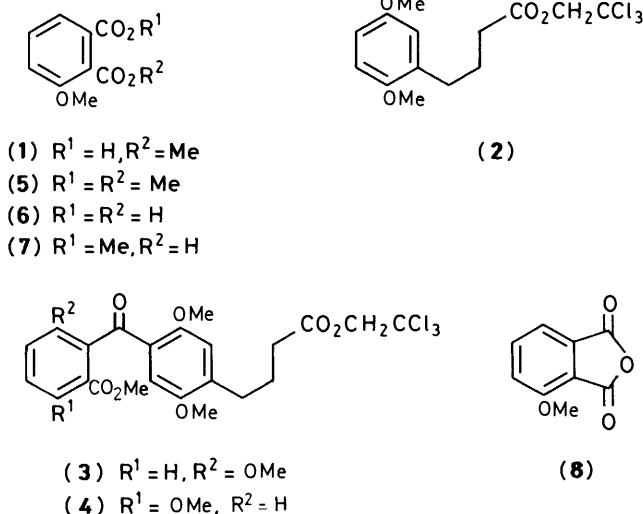


Facile Interconversion of the Isomeric Acid Chlorides Derived from Half Methyl Esters of 3-Methoxyphthalic Acid

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The isomeric acid chlorides obtained by treating the half methyl esters of 3-methoxyphthalic acid with thionyl chloride interconvert so readily that it is not practical to isolate one acid chloride free of the other. At equilibrium the main isomer is the acid chloride derived from the 1-methyl ester. When either half ester is treated with thionyl chloride at 20 °C for 2 h and the crude acid chloride so formed treated with 1,4-dimethoxybenzene in the presence of stannic chloride the only benzophenone derivative obtained is that derived from the more stable acid chloride.

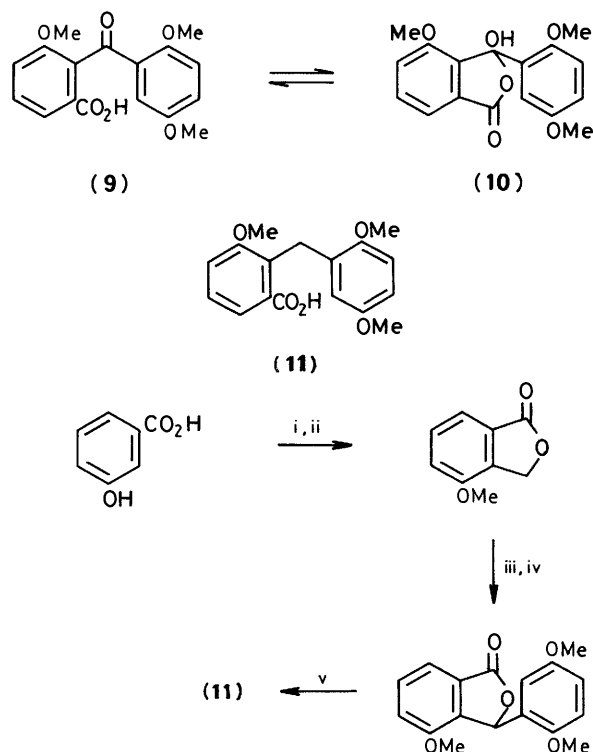
The Friedel-Crafts reaction of a phthalic acid derivative (usually an anhydride) with an aromatic compound followed by cyclisation of the product (usually a keto acid) is an important synthetic route to anthraquinones.¹ In connection with the regiospecific synthesis of anthracyclinones we treated 2-methyl 3-methoxyphthalate (1) with thionyl chloride and then allowed the product to react with compound (2) in the presence of stannic chloride. This gave keto ester (3) (53% yield), not the expected keto ester (4). That the product had the ester group *meta* to the methoxy group was demonstrated by cleaving a portion with potassium *t*-butoxide-water reagent² to give 3-methoxybenzoic acid as the major product but no 2-methoxybenzoic acid. The formation of the keto ester (3) clearly involves a rearrangement in which *the ester group is retained*. This prompted us to investigate this reaction sequence further and we now report the results. Rearrangements involving the acid chlorides of half esters of 3- and 4-nitrophthalic acids are known,³⁻⁵ but examples involving the corresponding derivatives of 3-methoxyphthalic acid appear not to have been reported. Friedel-Crafts reactions using derivatives of 3-methoxy- or 3-acetoxy-phthalic acid half esters have been carried out before,^{6,7} but not under circumstances where similar rearrangements would be detected.



Dimethyl 3-methoxyphthalate (5) was synthesized from 2,5-dihydroanisole and dimethyl acetylenedicarboxylate,⁸ and was converted into the corresponding diacid (6), half methyl esters (1) and (7),⁹ and anhydride (8) by standard methods. It is interesting to note that in the i.r. spectra of compounds (1), (5), (6), and (7) the 2-carbonyl group appears at a somewhat higher

frequency (13–20 cm^{-1}) than expected for a simple conjugated carbonyl group, indicating that the 2-carbonyl group in these compounds is twisted out of the plane of the aromatic ring.

The half ester (1) was treated with thionyl chloride at 20 °C for 2 h and the crude product so obtained treated with 1,4-dimethoxybenzene in the presence of stannic chloride. The keto ester produced was hydrolysed with alkali. This afforded solely the rearranged keto acid (9) [22% yield based on (1)], which was isolated in the hydroxyphthalide (10) form. A similar reaction sequence carried out starting with the half ester (7) also gave the hydroxyphthalide [25% yield based on (7)] as the only isolable product. The modest yields obtained in these reactions result mainly because the acid chlorides substantially decompose to the anhydride (8) under the reaction conditions (see below) and the anhydride (8) is not an active acylating agent in the presence of stannic chloride. The anhydride (8) does, however, react with 1,4-dimethoxybenzene in the presence of aluminium chloride to give, directly, the same hydroxyphthalide (10) (30% yield).



Scheme. Reagents and conditions: i, HCHO, H^+ ; ii, NaOH, Me_2SO_4 ; iii, *N*-bromosuccinimide; iv, 1,4-dimethoxybenzene, $SnCl_4$; v, Zn, NaOH

The structure of the keto acid (**9**) was demonstrated first by cleavage using the potassium *t*-butoxide–water reagent,² which gave 3-methoxybenzoic acid but no 2-methoxybenzoic acid, and second by reduction (Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$) to the acid (**11**) which was shown to be identical with an authentic sample. The latter was synthesized as shown in the Scheme.

To determine whether the acid chlorides rearranged prior to the Friedel-Crafts reactions the half esters (**1**) and (**7**) were separately treated with freshly distilled thionyl chloride at 20 °C and samples were removed after 2 and 18 h and analysed first by i.r. spectroscopy then, after quenching with water, by i.r. and ^1H n.m.r. spectroscopy, and by t.l.c. The results, summarised in the Table, indicate: (i) that in both reactions all of the starting acid had reacted within 2 h and the main product was the corresponding acid chloride though in each case a small amount of the isomeric acid chloride was also present, (ii) that after 18 h both reactions contained both acid chlorides and that in both cases the main one present was acid chloride (**13**), and (iii) that the amount of anhydride present increased with time. It is clear from these results that the acid chlorides (**12**) and (**13**) interconvert readily at 20 °C, that at equilibrium the main one present was acid chloride (**13**), and that they both slowly decompose to the anhydride. As a consequence it is impractical to isolate the pure acid chlorides. Attempts to prepare the acid chlorides using oxalyl chloride were unsuccessful. In the phthalic acid series the interconversion described above is the most facile to date.



Goncalves and Brown have shown that the acid chlorides prepared by treating 1-ethyl- (**14**) and 2-ethyl- (**15**) 3-nitrophthalates with thionyl chloride do not rearrange during their preparation (1 h at *ca.* 79 °C), but that the 2-ethyl ester (**15**) yields the rearranged acid chloride (**16**) on treatment for 2 h with stannic chloride in benzene.⁵ Under similar conditions 1-ethyl ester (**14**) gives the same acid chloride (**16**). According to Chase and Hey, however, the acid chlorides derived from 1-methyl (**17**) and 2-methyl ethers (**18**) do interconvert during their preparation with thionyl chloride, with the acid chloride derived from (**17**) being the more stable isomer.⁴ When acid chlorides prepared from 1-methyl (**17**) or 1-ethyl (**14**) 3-nitrophthalate or the 1-methyl 4-nitrophthalate are used in Friedel-Crafts reactions rearranged products are obtained,^{3,4} in some cases as the only products.^{4,5}

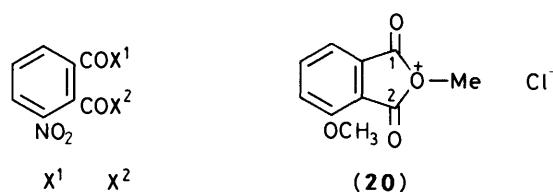
No explanation has yet been offered as to why the acid chlorides from the 1-esters (**14**) and (**17**) of 3-nitrophthalic acid should respectively be more stable than the isomeric acid chlorides derived from the 2-esters (**15**) and (**18**). However, the fact that the acid chloride (**13**) from 1-methyl 3-methoxyphthalate (**7**) is also more stable than its isomer strongly suggests that the effect is steric in origin. Since *iso*- and *tere*-phthalic acid derivatives do not undergo analogous rearrangements,^{3,4} those occurring with the 3-methoxy-, 3-nitro-, and 4-nitro-phthalic acid derivatives are almost certainly intramolecular and we suggest that species of the type (**20**) may be intermediates. Attack by the chloride at the 1-carbonyl group will give the acid chloride (**12**), attack at the 2-carbonyl group will give the acid chloride (**13**), whilst attack at the methyl will give, irreversibly, the anhydride (**8**).

During the Friedel-Crafts reactions the interconversion of the acid chlorides (**12**) and (**13**), like the conversion of the acid chloride (**19**) into (**16**),⁵ is probably catalysed by the Lewis acid.

Table. Composition of reaction mixtures obtained by treating the half esters (**1**) and (**7**) with thionyl chloride at 20 °C

Half ester used	Reaction time (h)	Composition of product ^a		
		Acid chloride (12) (%)	Acid chloride (13) (%)	Anhydride (8) (%)
(1)	2	76	19	5
(7)	2	7	91	2
(1)	18	5	39	56
(7)	18	14	56	30

^a Determined by quenching the reaction mixtures with water and analysing the mixture of products by 100 MHz ^1H n.m.r. spectroscopy using the methoxy signals (half ester methoxycarbonyl group and methoxy group present in the anhydride). The figures quoted are probably accurate to $\pm 5\%$. The i.r. spectra of the crude acid chloride products, and the i.r. spectra and thin layer chromatograms of the quenched products were qualitatively in agreement with the n.m.r. data.



	x^1	x^2
(14)	Et	OH
(15)	OH	Et
(16)	Et	Cl
(17)	Me	OH
(18)	OH	Me
(19)	Cl	Et

The fact that Friedel-Crafts reactions involving acid chlorides (**13**) and (**16**) tend to give products from these chlorides alone suggests that they are more reactive than their isomers. Again, since both the 3-nitro and 3-methoxy compounds show the same tendency, this is probably for steric reasons though in the case of the 3-methoxy compound the acylium ion will also be stabilised by the *ortho*-methoxy group.

Experimental

M.p.s were determined using a Hewitt hot-stage microscope and are uncorrected. Organic solutions were dried with magnesium sulphate. The i.r. spectra of solid samples were recorded as KBr discs and liquid samples as thin films using a Nicolet MX1 FT-IR spectrometer. ^1H N.m.r. spectra were recorded at 100 MHz for solutions in deuteriochloroform containing tetramethylsilane as internal reference with a JEOL FX100 FT instrument. Microanalyses were carried out using a Carlo-Erba elemental analyser. Thin layer chromatography (t.l.c.) was performed using Merck silica gel 60 F_{254} aluminium foils (0.2 mm bed thickness). Development was carried out using a mixture of ethyl acetate–light petroleum (b.p. 60–80 °C)–acetic acid in the ratio 40:55:5. Spots were detected by shortwave u.v. light and/or a mixture of concentrated sulphuric acid–ethanol (3:2) at 110 °C.

Dimethyl 3-Methoxyphthalate (**5**).—The following procedure is an improvement on that reported previously.⁸ A mixture of dimethyl acetylenedicarboxylate (142 g, 1 mol), 1-methoxycyclohexa-1,4-diene (110 g, 1 mol), and dichloromaleic anhydride (1.0 g, 6 mmol) was placed in a dropping funnel

above a 3-necked flask flushed with nitrogen. A portion (20 g) of the mixture was run into the flask gently heated to 100 °C. A vigorous evolution of ethylene occurred above 60 °C. The remainder of the mixture was then added dropwise to maintain a steady evolution of gas. When all the mixture had been added the reaction vessel was heated at 130 °C for 30 min. The mixture was cooled and crystallised from methanol (250 ml). This gave the desired product as pale yellow crystals (157.5 g, 70%), m.p. 77–78 °C (lit.,¹⁰ 77–77.5 °C); ν_{\max} . 1 739 and 1 726 cm^{-1} ; δ 3.85 (3 H, s, 1-CO₂CH₃), 3.89 (3 H, s, 2-CO₂CH₃), 3.95 (3 H, s, OCH₃), and 7.08–7.58 (3 H, m, ArH); t.l.c., one spot R_F 0.49.

2-Methyl 3-Methoxyphthalate (1).—A mixture of the dimethyl ester (5) (22.4 g, 0.1 mol), potassium hydrogen carbonate (10.0 g, 0.1 mol), methanol (300 ml), and water (100 ml) was heated under reflux for 24 h. Isolation of the acidic products by standard procedures gave acid (1) (20.8 g, 99%), m.p. 138–141 °C (lit.,⁹ 141–143 °C); ν_{\max} . 1 742 and 1 694 cm^{-1} ; δ 3.88 (3 H, s, CO₂CH₃) and 3.95 (3 H, s, OCH₃) and 7.0–7.6 (3 H, m, ArH); t.l.c., one spot R_F 0.29.

3-Methoxyphthalic Acid (6).—Treatment of the diester (5) (50 g) with potassium hydroxide (7%) in water–ethanol (1:1) gave the diacid (6) (43.1 g, 99%), m.p. 170.5–174 °C; (lit.,¹⁰ 173–174 °C); ν_{\max} . 1 707 and 1 687 cm^{-1} ; t.l.c., one spot R_F 0.03.

3-Methoxyphthalic Anhydride (8).—The diacid (6) (20 g) was heated at 200 °C until evolution of water vapour ceased. Sublimation of the residue gave the anhydride (8) (17.3 g, 95%) as white needles, m.p. 164–165 °C (lit.,¹⁰ 163–164 °C); ν_{\max} . 1 847 and 1 788 cm^{-1} ; δ 4.08 (3 H, s, OCH₃) and 7.0–7.6 (3 H, m, aromatic); t.l.c., one spot R_F 0.32.

1-Methyl 3-Methoxyphthalate (7).—A mixture of 3-methoxyphthalic acid (15.0 g), methanol (400 ml), and Amberlyst 15 beads (3.0 g) was heated under reflux for 48 h. The cooled liquor was then decanted off from the catalyst and evaporated to dryness. Isolation of the acidic products by standard procedures gave the acid (7) (10.5 g, 65%) as white needles, m.p. 149–153 °C (lit.,⁹ 151.5–153.5 °C); ν_{\max} . 1 722 and 1 707 cm^{-1} ; δ 3.92 (3 H, s, CO₂CH₃) and 3.95 (3 H, s, OCH₃) and 7.0–7.6 (3 H, m, ArH); t.l.c., one main spot R_F 0.18.

2,2,2-Trichloroethyl 4-[2,5-Dimethoxyphenyl]butyrate (2).—Friedel-Crafts reaction of succinic anhydride with 1,4-dimethoxybenzene catalysed by aluminium trichloride,¹¹ followed by Wolf Kishner reduction of the product¹¹ gave 4-(2,5-dimethoxyphenyl)butyric acid (49% overall), m.p. 64–66 °C (lit.,¹¹ 68–69 °C). The acid was converted into the acid chloride using oxalyl chloride. Reaction of the acid chloride with 2,2,2-trichloroethanol and triethylamine in tetrahydrofuran (THF) gave the title compound (2) (87% yield), b.p. 195–197 °C at 10 mmHg; ν_{\max} . 1 755 cm^{-1} ; δ 1.83–2.70 (6 H, m, CH₂CH₂CH₂), 3.6–3.7 (6 H, d, 2 OCH₃), 4.63 (2 H, s, OCH₂CCl₃), and 6.6–6.7 (3 H, m, aromatic-H) (Found: C, 47.0; H, 4.5; Cl, 29.6. C₁₄H₁₇Cl₃O₄ requires C, 47.2; H, 4.8; Cl, 29.9%).

Friedel-Crafts Acylation of Ester (2) starting with the Acid (1).—The half ester (1) (9.5 g, 45 mmol) was stirred under dry nitrogen with thionyl chloride (45 ml, freshly distilled) at 20 °C. After 2 h most of the remaining thionyl chloride was distilled off under reduced pressure (15 mmHg). Carbon tetrachloride (50 ml) was added to the residue and most of this was similarly distilled off. This left a solution of the crude acid chloride free of thionyl chloride (no i.r. band at 1 233 cm^{-1}). The crude acid chloride solution was added to a stirred solution of trichloroethyl ester (2) (9.5 g 27 mmol) in dichloromethane (50 ml) maintained at 0 °C after which stannic chloride (4.5 ml) was

added. The mixture was stirred for 12 h during which time the temperature rose to 20 °C. It was then cooled in ice and diluted with cold hydrochloric acid (1M; 50 ml). Ether extraction (3 × 50 ml) and recovery gave the crude product which, by i.r. spectroscopic analysis, contained a substantial amount of anhydride. The mixture was, therefore, treated with methanol (50 ml) and heated under reflux for 4 h. Excess of methanol was evaporated and the residue dissolved in ether (150 ml). The ethereal solution was washed with saturated aqueous sodium carbonate (20 ml) and water (20 ml). Evaporation of the ether from the dried solution gave an oily residue (13.0 g), a portion (2.00 g) of which was purified by t.l.c. This gave the keto ester (3) as a clear oil (1.20 g, corresponding to 53%); ν_{\max} . 1 755, 1 730, and 1 660 cm^{-1} ; δ 1.8–2.8 (2 H, m, -CH₂CCl₃), 6.56 (1 H, s, aromatic-H), and 6.8–7.5 (4 H, m, aromatic-H) (Found: C, 52.3; H, 4.6. C₂₄H₂₆O₈Cl₃ requires C, 52.5; H, 4.7%).

Using the published procedures² a portion (10 mg) of the product was cleaved with the potassium t-butoxide–water reagent and the products analysed. The cleavage gave a mixture of acids (equivalent to a cleavage yield of 56%), which included 3-methoxybenzoic acid (54% of theoretical maximum yield) and 3-methoxyphthalic acid (2%) but no 2-methoxybenzoic acid.

Friedel-Crafts Acylation of 1,4-Dimethoxybenzene starting with the Acid (1).—Using the procedure described in the preceding experiment, the acid (1) (2.50 g) was treated with thionyl chloride and the product so obtained allowed to react with stannic chloride (1.5 ml) and 1,4-dimethoxybenzene (1.65 g) in dichloromethane (20 ml). The crude keto ester was isolated and then hydrolysed with aqueous potassium hydroxide (10%; 50 ml) and ethanol (50 ml) at reflux temperature. After 18 h the reaction mixture was concentrated to 10 ml under reduced pressure, diluted with water (100 ml), and the neutral products extracted with ether (2 × 50 ml). The aqueous solution was acidified to pH 1 with concentrated hydrochloric acid and extracted with dichloromethane (3 × 50 ml). Note that the solubility properties of 3-methoxyphthalic acid are such that most of it remained in the aqueous layer. The combined extracts were washed with water (50 ml), dried, and evaporated to dryness. Recrystallisation of the residue from toluene gave off-white crystals (820 mg) of the hydroxyphthalide (10) form of the keto acid (9) (22% yield), m.p. 184–186 °C; ν_{\max} . 1 743, 1 753, and 3 400 cm^{-1} ; δ 3.72 (3 H, s, OCH₃), 3.83 (6 H, s, OCH₃), and 6.80–7.75 (7 H, m, OH and ArH) (Found: C, 64.8; H, 5.0. C₁₇H₁₆O₆ requires C, 64.6; H, 5.1%).

Using the published procedures² a portion (10 mg) of the product was cleaved with the potassium t-butoxide–water reagent and the products analysed. Cleavage gave a mixture of acids (equivalent to a cleavage yield of 60%) which included 3-methoxybenzoic acid (70% of theoretical maximum yield) and 3-methoxyphthalic acid (30%) but no 2-methoxybenzoic acid.

Friedel-Crafts Acylation of 1,4-Dimethoxybenzene Starting with the Acid (7).—The procedure was identical with that used in the preceding experiment except that acid (7) replaced acid (1). The product (955 mg, 25% yield), m.p. 184–186 °C, was shown by mixed m.p., i.r. and ¹H n.m.r. spectroscopy to be the same as that obtained in the preceding experiment.

Friedel-Crafts Acylation of 1,4-Dimethoxybenzene starting with the Anhydride (8).—A mixture of 3-methoxyphthalic anhydride (8) (2.14 g), 1,4-dimethoxybenzene (1.65 g), and nitrobenzene (10 ml) was vigorously stirred under nitrogen and cooled to 0 °C. Aluminium trichloride (2.6 g) was cautiously added in portions and when the addition was complete the mixture was stirred at 20 °C under nitrogen for 18 h. The reaction was quenched with hydrochloric acid (1M; 10 ml) and transferred to a separating funnel with ether (100 ml). The

organic layer was washed with hydrochloric acid (1M; 2 × 50 ml) then extracted with aqueous sodium hydroxide (1M; 3 × 50 ml). The combined alkaline layers were acidified with concentrated hydrochloric acid then extracted with dichloromethane (3 × 50 ml). The combined extracts were washed with water (50 ml), dried, and evaporated to dryness. The residue (1.13 g), m.p. 188–193 °C, was identified by mixed m.p. and comparison of both i.r. and ¹H n.m.r. spectra which showed the same hydroxyphthalide product (**10**) (30% yield) as was obtained in the two preceding experiments.

A similar experiment carried out using stannic chloride in place of aluminium trichloride only afforded starting materials or their hydrolysis products.

Reduction of the Hydroxyphthalide (10).—The hydroxyphthalide (**10**) (500 mg) was dissolved in trifluoroacetic acid (5 ml). Triethylsilane (0.6 ml) was added and the mixture stirred under dry nitrogen for 18 h. The mixture was transferred to a separating funnel with ether (150 ml) and washed with water until neutral. The ether solution was extracted with aqueous sodium carbonate (1M; 3 × 50 ml) and the combined extracts were acidified to pH 1 with concentrated hydrochloric acid and extracted with dichloromethane (3 × 50 ml). These extracts were combined, washed with water, dried, and evaporated to dryness. The residue (343 mg), m.p. 190–193 °C, was shown by mixed m.p. and by i.r. and ¹H n.m.r. spectroscopy to be identical with an authentic sample of acid (**11**) synthesized as described below.

Synthesis of 2-[2,5-Dimethoxybenzyl]-3-methoxybenzoic Acid (11).—Using the literature procedure¹² 3-hydroxybenzoic acid was converted into 4-hydroxyphthalide (33% yield), m.p. 255–262 °C (lit.,¹² 254 °C), and the product methylated to give 4-methoxyphthalide (71% yield), m.p. 128–129 °C (lit.,¹² 127 °C).

A mixture of 4-methoxyphthalide (10.0 g), *N*-bromosuccinimide (10.9 g), and carbon tetrachloride (300 ml) was heated under reflux for 4 h whilst being irradiated by a 500 W tungsten lamp. The reaction mixture was then cooled to 20 °C and filtered. Evaporation of the filtrate to dryness gave 3-bromo-4-methoxyphthalide (14.0 g) as an off-white solid that fumed heavily in the open air; ν_{\max} 1 784 cm⁻¹; δ 3.06 (3 H, s, OCH₃), 7.20 (1 H, s, CHBr), and 7.00–7.70 (3 H, m, ArH).

A mixture of the above bromophthalide (10.0 g), 1,4-dimethoxybenzene (17.1 g), and dry dichloromethane (200 ml) was stirred at 20 °C under dry nitrogen for 30 min. Stannic chloride (5.0 ml) was then added and the mixture was stirred for a further 4 h. The reaction mixture was quenched with cold water (400 ml), transferred to a separating funnel, washed with hydrochloric acid (1M; 2 × 150 ml) and saturated aqueous sodium hydrogen carbonate (3 × 100 ml), dried, and evaporated to dryness to leave the crude phthalide. This was treated with zinc dust (75 g), copper sulphate pentahydrate (0.6 g), and aqueous sodium hydroxide (10%; 500 ml). The mixture was heated under reflux for 24 h, cooled, and filtered and the residues were washed with water (15 ml). The combined filtrate and washings were washed with ether (3 × 150 ml) and then acidified to pH 1; the resulting precipitate was extracted with dichloromethane (3 × 100 ml). The combined extracts were

washed with water (200 ml), dried, and evaporated to dryness to afford the *title compound* (**11**) (8.9 g, 66% yield based on the bromophthalide), m.p. 191–193 °C; ν_{\max} 1 690 and 2 200–3 400 cm⁻¹; δ 4.35 (2 H, s, benzylic CH₂), 3.65 (3 H, s, OCH₃), 3.73 (3 H, s, OCH₃), 3.77 (3 H, s, OCH₃), and 6.40–7.65 (6 H, m, ArH) (Found: C, 67.6; H, 6.1. C₁₇H₁₈O₅ requires C, 67.5; H, 6.0%).

Experiments Summarised in the Table.—The following is typical of the experiments summarised in the Table.

The acid (**1**) (1.00 g) was stirred under nitrogen with freshly distilled thionyl chloride (5 ml) at 20 °C. After 2 h carbon tetrachloride (20 ml) was added and the mixture reduced in volume to ca. 5 ml using a rotary evaporator operating at 10 mmHg and a water-bath at 20 °C. The addition and evaporation of solvent was repeated twice. This gave a solution of the crude acid chloride.

The i.r. spectrum of a sample of the solution was measured. The band at 1 233 cm⁻¹ present in the spectrum of thionyl chloride and the carbonyl bands due to carboxyl-carbonyls of the starting half esters were absent. There were bands at 1 742 and 1 765 cm⁻¹ attributable to the acid chloride formally derived from acid (**1**), bands at 1 726 and 1 803 cm⁻¹ attributable to the acid chloride formally derived from acid (**7**), and bands at 1 788 and 1 847 cm⁻¹ due to the anhydride (**8**).

The remainder of the solution of the crude acid chloride was quenched by stirring with water overnight and the mixture was extracted with dichloromethane (3 × 25 ml). The combined extracts were dried and evaporated to dryness and the residue was analysed by i.r. and ¹H n.m.r. spectroscopy and the t.l.c. using the data reported above for the pure compounds.

Acknowledgements

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