487. *Phenylpropiolic Acids. Part VII.* The Self-condensation of 2-Methoxy-4- and -5-methylphenylpropiolic Acid.*

By F. G. BADDAR, E. H. GHALY, and M. F. EL-NEWEIHY.

2-Methoxy-4- and -5-methylphenylpropiolic acid are converted by acetic anhydride into 5-methoxy-7-methyl-1-(2-methoxy-4-methylphenyl)- and 5-methoxy-8-methyl-1-(2-methoxy-5-methylphenyl)-naphthalene-2,3-dicarboxylic anhydride, identical with the cyclisation products from di-(2-methoxy-4- and -5-methylbenzylidene)succinic anhydride, respectively. The first two anhydrides are converted by aluminium chloride into 5,6′-dimethoxy-4′,7- and -3′,8-dimethyl-3,4-benzofluorenone-1-carboxylic acid.

The ultraviolet spectra of the first two anhydrides as well as those of the di(arylmethylene)succinic acids are discussed.

2-METHOXY-4-METHYLPHENYLPROPIOLIC acid was prepared by condensing 2-methoxy-*p*-tolualdehyde with malonic acid in presence of pyridine[1] to give 2-methoxy-4-methylcinnamic acid, which was treated with bromine, then dehydrobrominated to the propiolic acid. When the latter was refluxed with acetic anhydride, it was converted into 5-methoxy-7-methyl-1-(2-methoxy-4-methylphenyl)naphthalene-2,3-dicarboxylic anhydride (IIa). Its structure was established as follows: (i) It is insoluble in sodium carbonate solution, and its cold alkaline solution does not discharge the colour of potassium permanganate; this proved that it is the anhydride of an *ortho*-dibasic acid, and is not a cyclobutadiene derivative.[2] (ii) It is identical with the anhydride obtained by cyclising the anhydride of di-(2-methoxy-4-methylbenzylidene)succinic acid (IIIa) in sunlight.[3] The acid (IIIa) was prepared by condensing 2-methoxy-*p*-tolualdehyde with diethyl succinate in presence of potassium t-butoxide. (iii) Its ultraviolet spectrum is identical with that of 5-methoxy-1-*o*-methoxyphenylnaphthalene-2,3-dicarboxylic anhydride.[4]

The anhydride (IIa) was treated with aluminium chloride in nitrobenzene to give 5,6′-dimethoxy-4′,7-dimethyl-3,4-benzofluorenone-1-carboxylic acid, identified as its methyl ester (IVa; R″ = Me). Decarboxylation of the acid with copper bronze in quinoline gave the fluorenone (V).

2-Methoxy-5-methylphenylpropiolic, prepared from 6-methoxy-*m*-tolualdehyde in a similar manner to the 4-methyl isomer, was refluxed with acetic anhydride to give the naphthalenedicarboxylic anhydride (IIb). Its structure was established by conversion, when heated with ammonium carbonate, into the imide (showing that it is an *ortho*-dibasic anhydride [2]), and by methods analogous to (i—iii) above.

Aluminium chloride in nitrobenzene converted the anhydride (IIb) into 5,6′-dimethoxy-3′,8-dimethyl-3,4-benzofluorenone-1-carboxylic acid (IVb; R″ = H).

The self-condensation of the above arylpropiolic acids takes place through intermediate formation of the anhydrides (Ia and b) (cf. Baddar *et al.*[3,5,6]).

The spectra of the 1-arylnaphthalene-2,3-dicarboxylic anhydrides (IIa and b) are

---

* Part VI, *J.*, 1959, 1027.

[1] Walling and Wolfstern, *J. Amer. Chem. Soc.*, 1947, **69**, 852.

[2] Cf. Baddar, *J.*, 1947, 224.

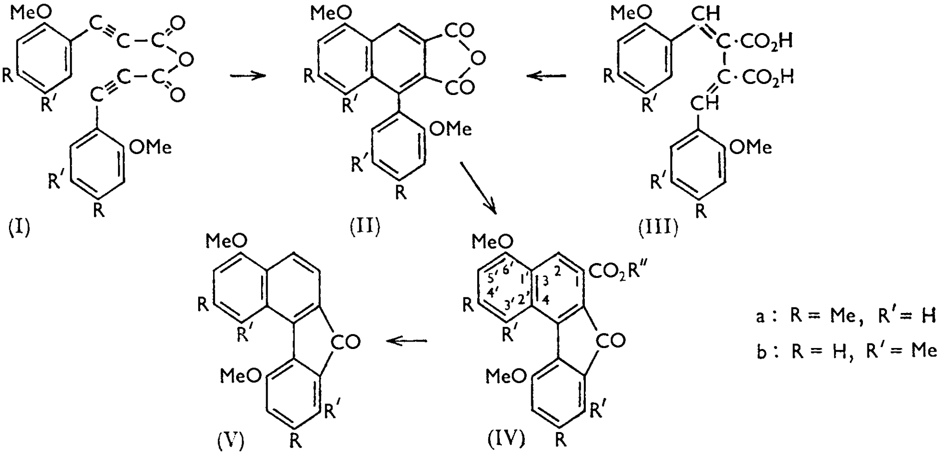
[3] Baddar, El-Assal, and Doss, *J.*, 1955, 451.

[4] Baddar and Sawiris, *J.*, 1956, 395.

[5] Baddar and El-Assal, *J.*, 1948, 1267.

[6] Baddar and El-Assal, *J.*, 1951, 1844.

similar to those of 5-methoxy-1-(phenyl- and *o*-methoxyphenyl)naphthalene-2,3-dicarboxylic anhydride.[4] They reveal on comparison with 1-phenylnaphthalene-2,3-dicarboxylic anhydride[4] a bathochromic shift, with a minimum at *ca.* 300 mμ, which is not observed in the parent anhydride. This difference in absorption is reflected in the colour: the new anhydrides are yellow, the parent anhydride is colourless.



The absorption spectra of these molecules are considered to be similar to those of the corresponding naphthalene derivatives.[7]

The hyperchromic effect observed in the absorption of anhydride (IIa) at 274 mμ, when compared with that of (IIb) may be attributed to a slight contribution of the 4'-methyl group in the electronic excitation in the vertical direction, and/or to a slight inhibition of resonance of the phenyl group as a whole with the naphthalene nucleus of (IIb) caused by the 8-methyl group.[4]

The diarylmethylenesuccinic acids (IIIa and b) could be considered as derivatives of 1,4-diphenylbuta-1,3-diene,[8] yet they differ widely from it in their absorption spectra, both in the position of the bands and in their intensity [cf. the spectra of (IIIa and b) (cf. Table) with that of 1,4-diphenylbuta-1,3-diene [8]]. This is probably due to partial inhibition of resonance in the butadiene system by the bulky 2,3-carboxylic groups. The intensity of absorption of acid (IIIa) is higher than that of (IIIb), since in the former compound the methyl group is conjugated with the butadiene system.

Compound	$\lambda_{max.}$ (mμ)	ε	$\lambda_{min.}$ (mμ)	ε
(IIa)	275—274	42,150	302—301	2788
	384—367 †	7966		
(IIb)	274	31,250	304	1580
	~379—376	7782		
	392—380 †	7814		
(IIIa)	283	21,110	311—310	16,240
	332	19,200		
(IIIb)	275—274	18,720	314	10,210
	337	12,270		

~ Inflexion. † Very close bands of poor persistence.

EXPERIMENTAL

Ultraviolet spectra were measured with a Beckman DU spectrophotometer for acetic acid solutions.

2-Methoxy-4- and -5-methylcinnamic Acid.—A mixture of 2-methoxy-*p*-tolualdehyde or

---

[7] Jones, *Chem. Rev.*, 1943, **32**, 1.

[8] Alberman, Haszeldine, and Kipping, *J.*, 1952, 3284.

6-methoxy-*m*-tolualdehyde (15 g., 1 mol.), malonic acid (15·6 g., 1·5 mol.), ethanol (20 ml.), and pyridine (2·5 ml.) was heated on a boiling-water bath for 7—8 hr., and worked up as usual.[1] 2-*Methoxy*-4-*methylcinnamic acid*, crystallised from ethanol, had m. p. 209° (85%) (Found: C, 68·4; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%). 2-*Methoxy*-5-*methylcinnamic acid*, crystallised from benzene–light petroleum (b. p. 80—100°), had m. p. 147° (47 g., 80%) (Found: C, 68·8; H, 6·4%), and its ethyl ester (prepared by use of hydrogen chloride and ethanol) had b. p. 148—150°/0·5 mm., n_D^{20} 1·5538.

αβ-*Dibromo*-β-(2-*methoxy*-4-*methylphenyl*)*propionic Acid*.—A boiling stirred suspension of 2-methoxy-4-methylcinnamic acid (10 g., 1 mol.) in carbon tetrachloride (70 ml.) was treated portionwise with a solution of bromine (8·4 g., 1 mol.) in carbon tetrachloride (20 ml.) during 45 min., then stirred for a further 15 min. The product (87%) crystallised from benzene–light petroleum (b. p. 60—80°) to give the *dibromo-acid*, m. p. 155° (Found: C, 37·0; H, 3·3; Br, 45·8. $C_{11}H_{12}Br_2O_3$ requires C, 37·5; H, 3·4; Br, 45·4%).

2-*Methoxy*-4-*methylphenylpropiolic Acid*.—The dibromo-acid (50 g., 1 mol.) was refluxed in 20% alcoholic potassium hydroxide (180 ml.) for 6 hr. and worked up as usual.[2] On crystallisation (5·5 g., 21%) from light petroleum (b. p. 60—80°) 2-*methoxy*-4-*methylphenylpropiolic acid* was obtained, with m. p. 155—156° (Found: C, 69·1; H, 5·7. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%). An inferior yield was obtained by using the " rapid " method.[9]

Di-(2-*methoxy*-4-*methylbenzylidene*)*succinic Acid* (IIIa).—A mixture of diethyl succinate (5·5 g., 1 mol.) and 2-methoxy-*p*-tolualdehyde (9·5 g., 2 mol.) in dry ether (30 ml.) was quickly added to a stirred suspension of powdered freshly prepared alcohol-free potassium t-butoxide (8 g., 2 mol.) in dry ether (50 ml.) at −15° to −18°. The mixture was kept below 0° for 4 days, then at 20—25° for several hours with occasional stirring. It was decomposed with water, the ether layer was distilled off, and the aqueous layer was refluxed for 2 hr. to hydrolyse any monoethyl ester present. The cold alkaline solution was extracted with ether to remove any neutral material, and the aqueous layer was acidified with hydrochloric acid. The aqueous acidic layer was decanted, the product was extracted 2—3 times with boiling water, and the insoluble acid was filtered off (4·4 g., 36%). It crystallised from acetic acid to give pale yellow *di*-(2-*methoxy*-4-*methylbenzylidene*)*succinic acid*, m. p. 252—253° (Found: C, 68·3; H, 6·1. $C_{22}H_{22}O_6$ requires C, 69·1; H, 5·8%).

5-*Methoxy*-7-*methyl*-1-(2-*methoxy*-4-*methylphenyl*)*naphthalene*-2,3-*dicarboxylic Anhydride* (IIa).—(i) A suspension of di-(2-methoxy-4-methylbenzylidene)succinic acid (0·5 g.) in acetyl chloride (3 ml.) was refluxed for 1 hr. Acetyl chloride was distilled off, and the crude anhydride (*ca.* 0·4 g.), not being easily crystallised, was used directly in the following step.

A solution of di-(2-methoxy-4-methylbenzylidene)succinic anhydride (0·5 g.) in benzene (5 ml.) was treated with a crystal of iodine and left in sunlight for 10 days (March). Distillation of the benzene left a residue which was heated in a vacuum at 100° for 2 hr. Repeated crystallisation from acetic acid gave 5-*methoxy*-7-*methyl*-1-(2-*methoxy*-4-*methylphenyl*)*naphthalene*-2,3-*dicarboxylic anhydride* in yellow needles, m. p. 238° (Found: C, 72·5; H, 5·2. $C_{22}H_{18}O_5$ requires C, 72·9; H, 5·0%). (ii) 2-Methoxy-4-methylphenylpropiolic acid (5 g.) was refluxed with acetic anhydride (15 ml.) for 3 hr. The product crystallised from acetic acid to give anhydride in yellow needles, m. p. 238° (65—70%), undepressed on admixture with the specimen prepared by method (i).

Methyl 5,6′-*Dimethoxy*-4′,7-*dimethyl*-3,4-*benzofluorenone*-1-*carboxylate* (IVa; R″ = Me).—Nitrobenzene (18 ml.) was cooled with stirring to −5° and treated portionwise with a finely powdered mixture of the anhydride (1·5 g.) and aluminium chloride (7·5 g.). The whole was kept at 0° for 2—3 hr. and then left at 20—30° for 3 days with occasional stirring. The product was dissolved in aqueous ammonia, and after filtration acidified. The precipitated acid (80%), being difficultly soluble in most organic solvents, was directly esterfied by diazomethane in dioxan–ether. The *methyl ester* crystallised from dioxan in scarlet plates, m. p. 198—199°. Analytical data indicated that the ester contained one molecule of dioxan (Found: C, 70·3; H, 5·7. $C_{23}H_{20}O_5,C_4H_8O_2$ requires C, 69·8; H, 6·1%). Dioxan of crystallisation could only be removed by heating the ester in a vacuum at 150° for *ca.* 24 hr. (Found: C, 72·55; H, 5·4. Calc. for $C_{23}H_{20}O_5$: C, 73·4; H, 5·4%).

5,6′-*Dimethoxy*-4′,7-*dimethyl*-3,4-*benzofluorenone* (V).—The acid (0·2 g.) was stirred in quinoline (7 ml.) at 200—210° for 2—3 hr., during which copper bronze (*ca.* 0·15 g.) was added

[9] Reimer, *J. Amer. Chem. Soc.*, 1942, **64**, 2510.

portionwise. The product crystallised from benzene to give *5,6'-dimethoxy-4',7-dimethyl-3,4-benzofluorenone* in red plates, m. p. 210—211° (Found: C, 79·4; H, 5·4. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%).

Ethyl α,β-Dibromo-β-(2-methoxy-5-methylphenyl)propionate.—The ice-cold stirred solution of ethyl 2-methoxy-5-methylcinnamate (29 g., 1 mol.) in carbon tetrachloride (60 ml.) was treated portionwise with bromine (25·5 g., 1·2 mol.) in carbon tetrachloride (20 ml.) and stirred for a further hr.,[10] then worked up as usual (yield 85%). On crystallisation from light petroleum (b. p. 60—80°) *ethyl αβ-dibromo-β-(2-methoxy-5-methylphenyl)propionate*, m. p. 127°, was obtained (Found: C, 41·2; H, 4·15; Br, 41·8. $C_{13}H_{16}Br_2O_3$ requires C, 41·1; H, 4·2; Br, 42·05%).

2-Methoxy-5-methylphenylpropiolic Acid.—The above dibromo-ester (10 g., 1 mol.) was treated with 20% alcoholic potassium hydroxide (35 ml.), left for 2 hr. at room temperature, then refluxed for 15 hr. and worked up as usual. The precipitated acid (3·4 g., 68%) crystallised from benzene–light petroleum (b. p. 60—80°) to give *2-methoxy-5-methylphenylpropiolic acid*, m. p. 139° (Found: C, 69·45; H, 5·3. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3%). The same yield was obtained when the procedure was carried out in two steps.[11]

Di-(2-methoxy-5-methylbenzylidene)succinic Acid (IIIb).—A mixture of diethyl succinate (7·5 g., 1 mol.) and 6-methoxy-*m*-tolualdehyde (13 g., 2 mol.) in dry ether (30 ml.) was quickly added to a stirred suspension of powdered freshly prepared alcohol-free sodium ethoxide (6·8 g., 2 mol.) in dry ether (50 ml.) at −15° to −18°. The reaction was completed as in the analogous experiment, and the precipitated acid (8·3 g., 50%) crystallised from ether–benzene or dilute acetic acid to give *di-(2-methoxy-5-methylbenzylidene)succinic acid* in pale yellow needles, m. p. 207—208° (Found: C, 69·8; H, 5·9. $C_{22}H_{22}O_6$ requires C, 69·1; H, 5·8%).

The *anhydride* was prepared by refluxing the acid (0·5 g.) with acetyl chloride (3 ml.) for 0·5 hr. Removal of the acetyl chloride left a residue, which was triturated with ether, then crystallised from benzene–light petroleum (b. p. 40—60°) in yellow needles, m. p. 230—231° (Found: C, 72·3; H, 5·65. $C_{22}H_{20}O_5$ requires C, 72·5; H, 5·5%).

5-Methoxy-8-methyl-1-(2-methoxy-5-methylphenyl)naphthalene-2,3-dicarboxylic Anhydride (IIb).—(i) A solution of di-(2-methoxy-5-methylbenzylidene)succinic anhydride (0·5 g.) in benzene (10 ml.) and a crystal of iodine were left in sunlight for 12 days (November), and worked up as in the analogous experiment. On crystallisation from acetic acid *5-methoxy-8-methyl-1-(2-methoxy-5-methylphenyl)naphthalene-2,3-dicarboxylic anhydride* was obtained in yellow fine rods, m. p. 243°, depressed to 200—208° on admixture with the original anhydride (Found: C, 72·9; H, 5·05. $C_{22}H_{18}O_5$ requires C, 72·9; H, 5·0%). (ii) 2-Methoxy-5-methylphenylpropiolic acid (5 g.) was refluxed with acetic anhydride (15 ml.) for 3 hr. and worked up as usual. The product (3 g., 64%) crystallised from acetic acid to give the above anhydride in fine yellow rods, m. p. and mixed m. p. 243—244°.

5-Methoxy-8-methyl-1-(2-methoxy-5-methylphenyl)naphthalene-2,3-dicarboximide.—The previous anhydride (1 g.) was thoroughly powdered with ammonium carbonate (1·7 g.), and the mixture heated by a direct flame with frequent shaking until it melted. The mixture was heated gently, being kept just molten, until no more ammonia was evolved. The product, insoluble in sodium carbonate, crystallised from ethanol to give the *imide* in pale yellowish-green crystals, m. p. 278° (0·2 g., 20%) (Found: C, 73·3; H, 5·5; N, 3·9. $C_{22}H_{19}O_4N$ requires C, 73·1; H, 5·3; N, 3·9%). Its infrared spectrum showed a sharp band at 3226 $cm.^{-1}$ (KBr wafer), characteristic of the NH of imides and secondary amides.[12]

5,6'-Dimethoxy-3',8-dimethyl-3,4-benzofluorenone-1-carboxylic Acid (IVb; R'' = H).—Nitrobenzene (18 ml.) was cooled with stirring to −5°, treated portionwise with a finely powdered mixture of the preceding anhydride (1·5 g.) and aluminium chloride (7·5 g.), and worked up as in the analogous experiment. The precipitated acid (1·2 g., 80%) crystallised from dioxan to give *5,6'-dimethoxy-3',8-dimethyl-3,4-benzofluorenone-1-carboxylic acid* in needles, m. p. 253—254° (Found: C, 72·4; H, 5·0. $C_{22}H_{18}O_5$ requires C, 72·9; H, 5·0%).

A'IN SHAMS UNIVERSITY, FACULTY OF SCIENCE,
CAIRO, U.A.R.

[*Received, November 24th,* 1960.]

---

[10] *Org. Synth.*, Coll. Vol., II, 1943, p. 270.

[11] Hariharan and Sudborough, *J. Indian Inst. Sci.*, 1925, **8**, *A*, 189; *Chem. Abs.*, 1925, **19**, 3263.

[12] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., 1956, p. 178.