

321. β -Aroylpropionic Acids. Part VII.* The Action of Grignard Reagents on Succinic Anhydride, Methylsuccinic Anhydride, and β -Aroyl- and β -Aroyl- α -methyl-propionic Acids and their Esters.

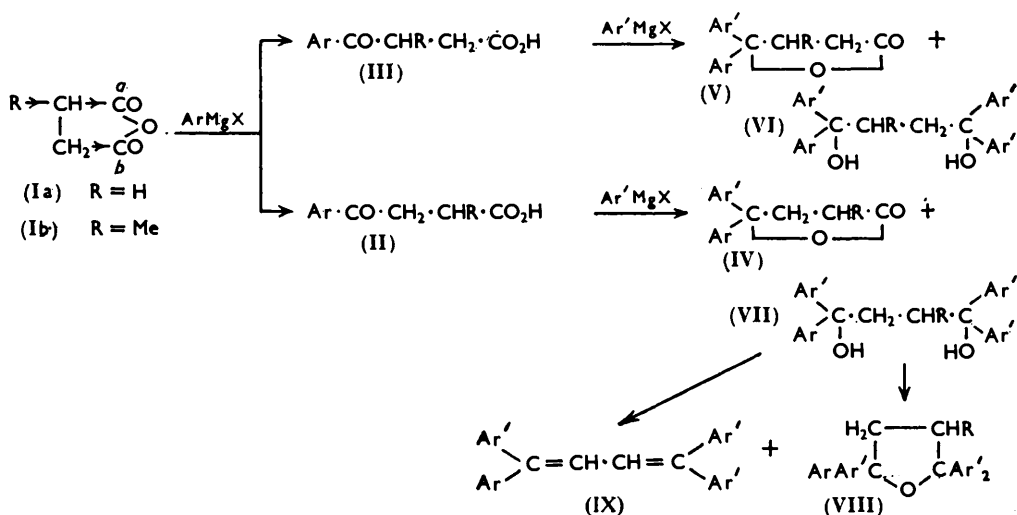
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Arylmagnesium halides with succinic anhydride give β -aroylpropionic (II) and $\gamma\gamma$ -diaryl- γ -hydroxybutyric acid, isolated as its lactone (IV), and a neutral product from which a tetrahydrofuran (VIII) is isolated. When β -aroylpropionic acids were used instead of succinic anhydride, the neutral product contained a tetrahydrofuran or a buta-1 : 3-diene (IX).

The reaction with methylsuccinic anhydride gives a mixture of β -aroyl- α - (II) and - β -methylpropionic acid (III), $\gamma\gamma$ -diaryl- α - (IV) and - β -methylbutyrolactone (V), and a neutral product containing a tetrahydrofuran (VIII).

However, β -aroyl- and β -aroyl- α -methyl-propionic esters give 3 : 3-diaryl- and 3 : 3-diaryl-1-methyl-prop-2-ene-1-carboxylic acid (XI), respectively, with a neutral product containing a tetrahydrofuran and/or a buta-1 : 3-diene.

PREVIOUS work (Part IV*) on the reaction of arylmagnesium halides with succinic anhydride has been extended to methylsuccinic anhydride and β -aroyl- α -methylpropionic acids and their esters, in order to obtain further insight into the mechanism. 2 : 5-Dimethoxyphenyl- or 2-methoxy-1-naphthyl-magnesium iodide with succinic anhydride



gave a mixture of the β -aroylpropionic acid (II; R = H) and $\gamma\gamma$ -diaryl- γ -hydroxybutyric acid, isolated as its lactone (IV; R = H). In the former case a neutral product was also obtained, from which the furan (VIII; R = H) was isolated. However, with methylsuccinic anhydride phenyl-, *p*-tolyl-, *p*-methoxyphenyl-, α -naphthyl-, *o*-methoxyphenyl-, or 2 : 5-dimethoxyphenyl-magnesium halide gave β -aroyl- α - (II; R = Me) and - β -methylpropionic acid (III; R = Me) and $\gamma\gamma$ -diaryl- α - (IV; R = Me) and - β -methylbutyrolactone (V; R = Me). In the last two cases both lactones were obtained pure, together with a tetrahydrofuran (VIII; R = Me). However, in the other cases either an inseparable mixture of lactones or the α -methyl lactone only was obtained; no tetrahydrofuran or buta-1 : 3-diene was isolated from the neutral fraction (see Tables). The structure of the α -methylbutyrolactone (IV; R = Me) was established by its identity with the product obtained by the action of Grignard reagent on the corresponding β -aroyl- α -methylpropionic acid (II; R = Me).

* Parts IV-VI, *J.*, 1955, 456, 2199, 4469.

However, when β -aroyl- or β -aroyl- α -methyl-propionic esters were used, 3:3-diaryl- (XI; R = H) or 3:3-diaryl-1-methylprop-2-ene-1-carboxylic acids (XI; R = Me) were obtained instead of the corresponding lactones (IV; R = H and Me, respectively).

TABLE 1. Reactions of Grignard compounds ArMgX (2 mols.) with succinic (Ia) or methylsuccinic anhydride (Ib).

Ar Anhydride (Ia)	Yields* (%) of products					
	(II)	(III)	(IV)	(V)	(VIII)	(IX)
2:5-(MeO) ₂ C ₆ H ₃	25.2		25.1		0.7	
2:1-MeO·C ₁₀ H ₆	31		1.1			
„ (1 mol.)	31					
Anhydride (Ib)						
Ph	11.8 ^a	2.5 ^a	4.2			
<i>p</i> -C ₆ H ₄ Me	9.6 ^a	3.7 ^a	1.1			
<i>o</i> -MeO·C ₆ H ₄	3.4	1.4	5.4 ^a	1.5	6.0	
„ (1 mol.)	5.5	2.1	6.3 ^a	1.5		←Oil→
2:5-(MeO) ₂ C ₆ H ₃	3.0 ^a	10.9 ^b	4.4 ^a	1.2	2.2	
<i>p</i> -MeO·C ₆ H ₄	2.7 ^a	8.9 ^b		←7.3→ ^c		←?→ ^c
1-C ₁₀ H ₇	9.4 ^a	15.7 ^b	2.2			

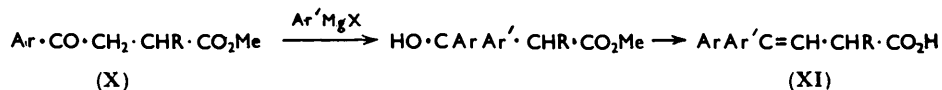
* Yields are calculated on the crude product unless stated as (a) pure product, (b) oil, or (c) semi-solid.

TABLE 2. Reactions of Grignard compounds Ar'MgX (2 mols.) with β -aroylpropionic acids (II) or (III) or their esters (X).

Ar'	R	Reactant	Yields* (%) of products					
			(II) ^d	(IV)	(V)	(VIII)	(IX)	(XI)
2:5-(MeO) ₂ C ₆ H ₃	II H	2:5-(MeO) ₂ C ₆ H ₃	56 ^d	9.0		2.3		
<i>o</i> -MeO·C ₆ H ₄	II H		52 ^d	Trace			←(VIIa)→	
„	II H	2:1-MeO·C ₁₀ H ₆	64 ^d					2.0
„	II H	2:5-MeO·C ₆ H ₃ Ph	48 ^d	6.1			←Mixed→	
„	II H	A †	70 ^d	4.9		4.6		
„	II H	2:5-MeO·C ₆ H ₃ Me	76 ^d	8.6		3.5		
„	II H	2:5-MeO·C ₆ H ₃ Cl	64 ^d	5.8		5.5		
„	II Me	<i>o</i> -MeO·C ₆ H ₄	30 ^d	18.6			←Trace→	
2:5-(MeO) ₂ C ₆ H ₃	II Me	2:5-(MeO) ₂ C ₆ H ₃	66	10.8				
Ph	II Me	Ph	34	10.0				
<i>p</i> -C ₆ H ₄ Me	II Me	<i>p</i> -C ₆ H ₄ Me	56	8.8				
„	III Me	„	36		11.8 ^b			
<i>p</i> -MeO·C ₆ H ₄	II Me	<i>p</i> -MeO·C ₆ H ₄	46	4.7			←?→	
1-C ₁₀ H ₇	II Me	1-C ₁₀ H ₇	60	3.4				
2:5-(MeO) ₂ C ₆ H ₃	X H	2:5-(MeO) ₂ C ₆ H ₃				3.2		16.5
<i>o</i> -MeO·C ₆ H ₄	X H	2:5-MeO·C ₆ H ₃ Ph					←Mixture→	15.8
„	X H	2:5-MeO·C ₆ H ₃ Me				0.8		3.2
„ (1 mol.)	X H	„				1.6		18.1
„	X H	2:5-MeO·C ₆ H ₃ Cl				4.6		19.2
Ph	X Me	Ph					←Mixed→	16.4
2:5-(MeO) ₂ C ₆ H ₃	X Me	2:5-(MeO) ₂ C ₆ H ₃				4.9		21.4

* Cf. Table 1; (d) Recovered. † 2:5-(MeO)₂C₆H₃·C₆H₄·OMe-*p*.

The isomerisation of $\gamma\gamma$ -di-*o*-methoxyphenyl- α -methyl-, $\gamma\gamma$ -di-2:5-dimethoxyphenyl-, and $\gamma\gamma$ -di-2:5-dimethoxyphenyl- α -methyl-butyrolactone with boiling concentrated hydrochloric acid¹ gave the corresponding 3:3-diarylprop-2-ene-1-carboxylic acids (XI), identical



with those obtained from the esters. The structures of the propene acids, 1:1:4:4-tetra-arylbutadienes, and 2:2:5:5-tetra-aryltetrahydrofurans were confirmed by their absorption spectra (see following paper).

Geometrical isomerism is possible among the buta-1:3-dienes and propene acids in

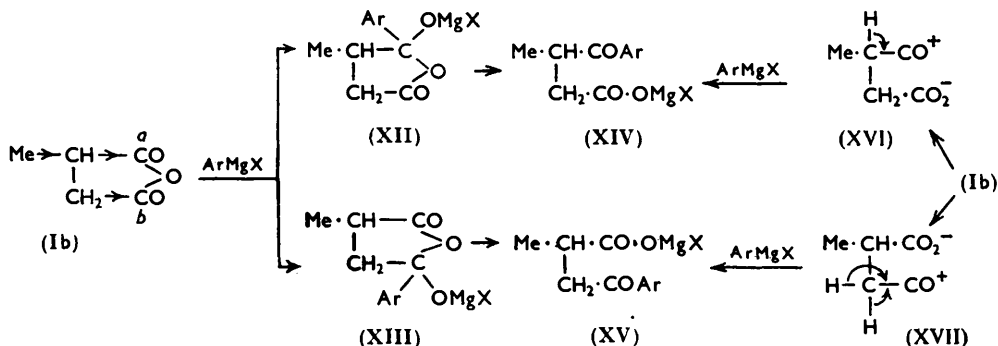
¹ Baddar and El-Assal, *J.*, 1951, 431.

which Ar and Ar' are not identical, but the configurations of the products now described cannot at present be determined.

The results (see Table) show that the highest yields of lactones and furans or butadienes are obtained when *o*-methoxyphenylmagnesium halide reacts with a β -*o*-methoxyaroyl-propionic acid. This confirms Baddar and El-Assal's previous assumption.¹

The non-reactivity of β -2-methoxy-1-naphthoylpropionic acid towards Grignard reagents (see Table) may be due to steric factors, caused by the additional ring,² which inhibits formation of the co-ordination complex.¹

The formation of the α -methyl-acids (II; R = Me) and the α -methyl-lactones (IV; R = Me) in greater proportion than the β -methyl-isomers (III and V; R = Me, respectively) could be attributed either to steric^{2,3} or to polar factors. Steric effects may be the main factor operating with bulky groups, such as phenyl.^{3a}



Thus, if the reaction takes place by addition to the carbonyl group,⁴ then carbon atom (b) will be more deficient in electrons than carbon atom (a), and, therefore, the Grignard reagent will add preferentially to the former, to give (XV). However, if the reaction takes place by the opening of the anhydride ring,⁵ to give the two ions (XVI) and (XVII), then ion (XVII) will be formed to a greater extent, owing to hyperconjugation, leading to the predominant formation of the α -methyl-acid. Whether the methyl group operates by a steric or a polar effect is left for further investigation.

EXPERIMENTAL

β -2 : 5-Dimethoxybenzoyl- α -methylpropionic Acid.—(i) A solution of ω -bromo-2 : 5-dimethoxyacetophenone⁶ (5.4 g.) in dry benzene (30 ml.) was gradually added to a mixture of sodium ethoxide (from 0.5 g. of sodium in 12.5 ml. of alcohol) and methyl malonate (3.8 g.), and the mixture was worked up as described by Mayer and Stamm.⁷ The product was hydrolysed with 5% alcoholic potassium hydroxide (1.5 hours' refluxing), and the resulting acid (ca. 2.5 g.) was crystallised from acetic acid, to give α -2 : 5-dimethoxyphenacyl- α -methylmalonic acid, m. p. 164—165° (gas evolution) (Found : C, 57.0; H, 5.6; OMe, 21.1. $\text{C}_{14}\text{H}_{16}\text{O}_7$ requires C, 56.8; H, 5.4; OMe, 20.9%). When this acid (1.0 g.) was heated at 205—210° for 30 min., then extracted with sodium carbonate solution (charcoal), and reprecipitated, it gave β -2 : 5-dimethoxybenzoyl- α -methylpropionic acid (ca. 0.5 g.), m. p. 116.5—118° (from benzene) (Found : C, 61.8; H, 6.2; OMe, 25.9. $\text{C}_{13}\text{H}_{16}\text{O}_6$ requires C, 61.9; H, 6.3; OMe, 24.6%).

(ii) The product (ca. 8.5 g., 66%), m. p. 102—112°, from methylsuccinic anhydride (6.0 g.),

² Fieser and Newman, *J. Amer. Chem. Soc.*, 1936, **58**, 2376; Newman and Orchin, *ibid.*, 1938, **60**, 586; Newman, *ibid.*, p. 1368; Newman and Orchin, *ibid.*, 1939, **61**, 244; Newman and Wise, *ibid.*, 1941, **63**, 2109.

³ (a) Weizmann, Blum-Bergmann, and Bergmann, *J.*, 1935, 1370; (b) Newman, *J. Amer. Chem. Soc.*, 1937, **59**, 1003; Newman and McCleary, *ibid.*, 1941, **63**, 1542; Newman and Muth, *ibid.*, 1950, **72**, 5191.

⁴ Geissman and Morris, *ibid.*, 1941, **63**, 1111.

⁵ Cf. Newman and Lord, *ibid.*, 1944, **66**, 733.

⁶ Bost and Howe, *ibid.*, 1951, **73**, 5864.

⁷ Mayer and Stamm, *Ber.*, 1923, **56**, 1424.

p-dimethoxybenzene (6.9 g.), and aluminium chloride (13.5 g., 2 mols.) in nitrobenzene (50 ml.), after being kept at room temperature overnight,^{8,9} was repeatedly crystallised from benzene, to give *β*-2 : 5-dimethoxybenzoyl-*α*-methylpropionic acid, m. p. 116.5—118° alone or mixed with a specimen prepared by the above method. The *methyl ester*, prepared by methanol and hydrogen chloride and crystallised from light petroleum (b. p. 40—60°), had m. p. 70—71° (Found: C, 63.3; H, 7.1; OMe, 33.3. C₁₄H₁₄O₅ requires C, 63.2; H, 6.8; OMe, 34.9%). Evaporation of the benzene mother-liquor from the first crystallisation left an oil (*ca.* 1.6 g.), which was probably the *β*-methyl-acid. With *s*-tetrachloroethane as a medium, the product (1.8 g., 14%) was a mixture of the *α*-methyl-acid (*ca.* 1.3 g.) and its *β*-methyl isomer (0.3 g.).

2-Methoxyacetophenone.—A mixture of 2-hydroxyacetophenone (10 g.), dimethyl sulphate (16 ml.), anhydrous potassium carbonate (37 g.), and dry acetone (100 ml.) was refluxed for 12 hr., then worked up as usual. 2-Methoxyacetophenone was obtained as a pale yellow oil, b. p. 245—246°/760 mm. Tahara¹⁰ gives b. p. 240°/712 mm.

ω-Bromo-2-methoxyacetophenone.—This was prepared by a method similar to that reported for *ω*-bromo-2 : 5-dimethoxyacetophenone. The unstable oily product was immediately used without purification in the following experiment.

β-o-Methoxybenzoyl-α-methylpropionic Acid.—To a suspension of diethyl sodiomethylmalonate [from finely powdered sodium (0.6 g.) and methylmalonate (4.7 g.) in ether (10 ml.)], crude *ω*-bromo-*o*-methoxyacetophenone (6 g.) was gradually added with occasional shaking, and the mixture left for 1—2 hr., then worked up as usual. The product was repeatedly extracted with boiling light petroleum (b. p. 40—60°), and the combined extracts were concentrated. The ester which crystallised was repeatedly crystallised from benzene—light petroleum (b. p. 40—60°), to give *diethyl α-o-methoxyphenacyl-α-methylmalonate*, m. p. 89—90° (Found: C, 63.7; H, 6.8. C₁₇H₂₂O₆ requires C, 63.4; H, 6.8%).

Hydrolysis of this ester with 5% alcoholic potassium hydroxide solution (1.5 hours' refluxing) gave an acid, which was heated with dilute hydrochloric acid on a boiling-water bath till bubbling ceased (several hr.). The product was then dissolved in ether and extracted with sodium carbonate solution (charcoal). The semi-solid acid (*ca.* 1.3—1.5 g.) precipitated on acidification was methylated with dimethyl sulphate, potassium carbonate, and acetone. The ester was distilled in a vacuum (b. p. 186—190°/12 mm.), then hydrolysed with 5% alcoholic potassium hydroxide. The acid, crystallised from benzene—light petroleum (b. p. 40—60°), gave *β-o-methoxybenzoyl-α-methylpropionic acid*, m. p. 96—97° (Found: C, 65.2; H, 6.2; OMe, 13.8. C₁₃H₁₄O₄ requires C, 64.9; H, 6.3; OMe, 14.0%).

Methylation with dimethyl sulphate was essential, since the product was a mixture of *β-o*-methoxy- and *β-o*-hydroxy-benzoyl-*α*-methylpropionic acid, the latter being predominant. The *hydroxy-acid* was obtained (m. p. 158.5—159.5°) by fractional crystallisation of the mixture from benzene (Found: C, 63.8; H, 5.8. C₁₁H₁₂O₄ requires C, 63.5; H, 5.8%). It gave a red colour with ferric chloride. The formation of this acid may be due to partial demethylation during heating with hydrochloric acid.

Action of 2 : 5-Dimethoxyphenylmagnesium Iodide on Succinic Anhydride, β-2 : 5-Dimethoxybenzoylpropionic Acid, and its Methyl Ester.—(i) An ethereal solution of 2 : 5-dimethoxyphenylmagnesium iodide [from 2-iodo-1 : 4-dimethoxybenzene¹¹ (26.4 g.) and magnesium (2.6 g.) in ether (40 ml.)] was added dropwise during 20 min. to a boiling benzene solution (100 ml.) of succinic anhydride (5 g.), and the experiment was carried out in a manner similar to that adopted in Part IV. The solid (A), insoluble in sodium carbonate, was filtered off and dried (*ca.* 4.5 g.). Repeated crystallisation from ethanol gave *γ-gamma-di-2 : 5-dimethoxyphenylbutyrolactone*, m. p. 139—140° (Found: C, 67.0; H, 6.15; OMe, 33.9. C₂₀H₂₂O₆ requires C, 67.0; H, 6.15; OMe, 34.6%).

The cold sodium carbonate solution gave on acidification an oily acid (B) (*ca.* 3.0 g.), which was methylated with methyl iodide and potassium carbonate in acetone (12 hours' refluxing). The ester was hydrolysed with 5% alcoholic potassium hydroxide, and the acid was crystallised from benzene, to give *β*-2 : 5-dimethoxybenzoylpropionic acid, m. p. 106—107°, undepressed on admixture with an authentic specimen.¹²

The oil (C) left on evaporation of the ether—benzene mixture was dissolved in hot alcohol,

⁸ Baddar, Fahim, and Fleifel, *J.*, 1955, 3302.

⁹ Baddar, Fahim, and Fleifel, *J.*, 1955, 2199.

¹⁰ Tahara, *Ber.*, 1892, 25, 1308.

¹¹ Kauffmann and Fritz, *Ber.*, 1908, 41, 4415.

¹² Dalal and Nargund, *J. Indian Chem. Soc.*, 1937, 14, 406.

and the solvent left to evaporate slowly. The precipitated product (D) (*ca.* 0.2 g.) was refluxed with glacial acetic acid (1.5 hr.), then repeatedly crystallised from the same solvent to give 2 : 2 : 5 : 5-tetra-(2 : 5-dimethoxyphenyl)tetrahydrofuran, m. p. 202—203° (Found : C, 70.3; H, 6.5; OMe, 37.1. $C_{28}H_{40}O_8$ requires C, 70.1; H, 6.5; OMe, 40.2%).

(ii) The experiment was repeated with β -2 : 5-dimethoxybenzoylpropionic acid (12 g.) to give a lactone (A) (1.7 g.), unchanged γ -keto-acid (6.7 g.), and a tetrahydrofuran (D) (0.7 g.).

(iii) The reaction between 2 : 5-dimethoxyphenylmagnesium iodide (2 mols.) and methyl β -2 : 5-dimethoxybenzoylpropionate (5 g.; 1 mol.) was carried out as described in Part IV. The acid (3.0 g.) extracted with sodium hydroxide solution was crystallised from light petroleum (b. p. 40—60°), to give 3 : 3-di-(2 : 5-dimethoxyphenyl)prop-2-ene-1-carboxylic acid, m. p. 134—136° (Found : C, 66.9; H, 6.15; OMe, 32.5. $C_{20}H_{22}O_6$ requires C, 67.0; H, 6.15; OMe, 34.6%). It discharged the colour of alkaline potassium permanganate.

The viscous oil (C) was treated as usual, to give β -2 : 5-dimethoxybenzoylpropionic acid (*ca.* 0.4 g.), and a solid (D) (0.4 g.) which, crystallised from acetic acid, gave 2 : 2 : 5 : 5-tetra-(2 : 5-dimethoxyphenyl)tetrahydrofuran, m. p. and mixed m. p. 202—203°.

Isomerisation of $\gamma\gamma$ -Di-2 : 5-dimethoxyphenylbutyrolactone.—The lactone was refluxed for 3 hr. with concentrated hydrochloric acid, and worked up as described by Baddar and El-Assal.¹ Crystallisation of the product from benzene—light petroleum (b. p. 40—60°) gave 3 : 3-di-(2 : 5-dimethoxyphenyl)prop-2-ene-1-carboxylic acid, m. p. and mixed m. p. 135—136°.

Unless otherwise stated, the following Grignard reactions were carried out as described in the above experiment.

Action of 2-Methoxy-1-naphthylmagnesium Iodide on Succinic Anhydride.—(i) The Grignard reagent [from 1-iodo-2-methoxynaphthalene (25.6 g., 2 mols.) in ether (50 ml.) and benzene (50 ml.)] was refluxed for 5 hr. with a benzene solution (100 ml.) of succinic anhydride (4.5 g.; 1 mol.). The acid (*ca.* 0.5 g.) precipitated on decomposition of the mixture was filtered off and mixed with the same acid (B) (3 g.) obtained from the carbonate solution. On crystallisation from benzene, β -2-methoxy-1-naphthylpropionic acid was obtained in colourless needles, m. p. 135—136°, undepressed on admixture with an authentic specimen.¹³

The lactone (A) (*ca.* 0.2 g.) was first crystallised from glacial acetic acid, then repeatedly from benzene, to give $\gamma\gamma$ -di-(2-methoxy-1-naphthyl)butyrolactone, m. p. 236—238° (Found : C, 78.6; H, 5.6; OMe, 16.1. $C_{28}H_{22}O_4$ requires C, 78.4; H, 5.6; OMe, 15.6%).

The neutral solid (C) (8.5 g.) was identified as nerolin.

(ii) When 1 mol. of the Grignard reagent was used (3 hours' refluxing) the only products were the γ -keto-acid (*ca.* 4.0 g.) and nerolin (2.6 g.).

Action of o-Methoxyphenylmagnesium Bromide on β -2-Methoxy-1-naphthylpropionic Acid.—The product from the Grignard reagent [from *o*-bromo-anisole (7.3 g., 2 mols.)] and β -2-methoxy-1-naphthylpropionic acid (5 g.) contained the unchanged acid (*ca.* 3.2 g.) and a neutral brown oil (C). The latter was digested with alcohol, and the insoluble product (D) (*ca.* 0.2 g.) was refluxed with glacial acetic acid, then crystallised from the same solvent, to give 4-(2-methoxy-1-naphthyl)-1 : 1 : 4-tri-*o*-methoxyphenylbuta-1 : 3-diene, m. p. 195—196° (Found : C, 82.5; H, 5.9; OMe, 22.2. $C_{28}H_{22}O_4$ requires C, 81.8; H, 6.1; OMe, 23.5%).

The alcoholic mother-liquor, when kept, deposited a colourless product (*ca.* 0.4 g.) which, crystallised from ethanol, then repeatedly from benzene—light petroleum (b. p. 40—60°), had m. p. 161—162° (Found : C, 76.0; H, 6.2; OMe, 19.3. $C_{29}H_{28}O_5$ requires C, 76.3; H, 6.1; OMe, 20.4%). Analysis and absorption spectrum gave some evidence that it might be γ -hydroxy-*o*-methoxy- γ -(2-methoxy-1-naphthyl)phenylbutyrophene.

Action of o-Methoxyphenylmagnesium Bromide on β -2-Methoxy-5-phenylbenzoylpropionic Acid and its Methyl Ester.—(i) The alkaline extract of the product from the Grignard reagent [from *o*-bromoanisole (6.6 g., 2 mols.)] and the acid¹⁴ (5 g., 1 mol.) contained the unchanged keto-acid (*ca.* 2.4 g.) and a lactone (*ca.* 0.4 g.). The latter compound was repeatedly crystallised from ethanol, to give γ -*o*-methoxyphenyl- γ -(4-methoxy-3-diphenyl)butyrolactone, m. p. 162—163° (Found : C, 76.4; H, 5.8; OMe, 17.4. $C_{24}H_{22}O_4$ requires C, 77.0; H, 5.9; OMe, 16.0%). The neutral product (D) (*ca.* 0.3 g.) was refluxed with glacial acetic acid to give an inseparable mixture, m. p. 176—178° (cleared at 185°).

(ii) The reaction between *o*-methoxyphenylmagnesium bromide (7.6 g., 2 mols.) and the ester (6 g., 1 mol.) gave a semi-solid acid (*ca.* 2.6 g.), which was repeatedly crystallised from

¹³ Short, Stromberg, and Wiles, *J.*, 1936, 319.

¹⁴ Fieser and Bradsher, *J. Amer. Chem. Soc.*, 1936, 58, 1738.

benzene–light petroleum (b. p. 40–60°) to give 3-(4-methoxy-3-diphenyl)-3-*o*-methoxyphenylprop-2-ene-1-carboxylic acid, m. p. 140–142°, depressed to 122–125° on admixture with the above keto-acid (Found : C, 76.2; H, 5.6; OMe, 16.0. $C_{24}H_{22}O_4$ requires C, 77.0; H, 5.9; OMe, 16.0%). It discharged the colour of alkaline potassium permanganate.

The neutral oily product (C) was treated as usual to give the γ -keto-acid (0.2 g.) and an inseparable mixture (0.7 g.).

Action of o-Methoxyphenylmagnesium Bromide on β-2-Methoxy-5-p-methoxyphenylbenzoylpropionic Acid.—The acid product from the interaction between the Grignard reagent [from *o*-bromoanisole (5.4 g., 2 mols.)] and the keto-acid⁹ (4.5 g., 1 mol.) contained the unchanged acid (3 g.) and a lactone (A) (ca. 0.3 g.). Crystallisation of the lactone from ethanol gave γ -(4 : 4'-dimethoxy-3-diphenyl)- γ -*o*-methoxyphenylbutyrolactone, m. p. 170–171° (Found : C, 74.4; H, 6.0; OMe, 23.2. $C_{25}H_{24}O_6$ requires C, 74.2; H, 6.0; OMe, 23.1%).

The neutral semi-solid (D) (ca. 0.4 g.) was refluxed with glacial acetic acid, then repeatedly crystallised from the same solvent, to give 5-(4 : 4'-dimethoxy-3-diphenyl)tetrahydro-2 : 2 : 5-tri-*o*-methoxyphenylfuran, m. p. 202–203° (Found : C, 77.1; H, 6.3; OMe, 24.4. $C_{30}H_{38}O_6$ requires C, 77.7; H, 6.3; OMe, 25.7%).

Action of o-Methoxyphenylmagnesium Bromide on β-2 : 5-Dimethoxybenzoylpropionic Acid.—The reaction between the Grignard reagent [from *o*-bromoanisole (7.9 g., 2 mols.)] and the keto-acid (5 g., 1 mol.) gave traces of a lactone, which could not be identified, and the unchanged keto-acid (ca. 2.6 g.). The neutral solid (D) (ca. 0.5 g.) was repeatedly crystallised from benzene, to give 4-(2 : 5-dimethoxyphenyl)-1 : 1 : 4-tri-*o*-methoxyphenylbutane-1 : 4-diol, m. p. 219–220° (Found : C, 72.9; H, 6.6; OMe, 25.6; active H, 0.36. $C_{33}H_{36}O_7$ requires C, 72.8; H, 6.6; OMe, 28.5; active H, 0.37%).

Refluxing this diol with glacial acetic acid gave an inseparable mixture.

Action of o-Methoxyphenylmagnesium Bromide on β-2-Methoxy-5-methylbenzoylpropionic Acid and its Methyl Ester.—(i) The Grignard reagent [from *o*-bromoanisole (8.5 g., 2 mols.)] with this acid (5 g., 1 mol.) gave recovered keto-acid (3.2 g.) and γ -(2-methoxy-5-methylphenyl)- γ -*o*-methoxyphenylbutyrolactone, m. p. 149–150° (from ethanol) (Found : C, 72.7; H, 6.6; OMe, 19.9. $C_{19}H_{20}O_4$ requires C, 73.1; H, 6.4; OMe, 17.1%). The neutral solid (D) (ca. 0.4 g.) was fractionally crystallised from acetic acid, to give tetrahydro-5-(2-methoxy-5-methylphenyl)-2 : 2 : 5-tri-*o*-methoxyphenylfuran, m. p. 233–234° (Found : C, 77.5; H, 6.6; OMe, 21.6. $C_{33}H_{34}O_6$ requires C, 77.6; H, 6.7; OMe, 24.3%).

(ii) The reaction between the above Grignard reagent (1 mol.) and the ester (6 g., 1 mol.) gave an acid (ca. 2.0 g.), which was repeatedly crystallised from benzene–light petroleum (b. p. 40–60°) to give 3-(2-methoxy-5-methylphenyl)-3-*o*-methoxyphenylprop-2-ene-1-carboxylic acid, m. p. 114.5–115.5° (Found : C, 73.6; H, 6.6; OMe, 18.0. $C_{18}H_{20}O_4$ requires C, 73.1; H, 6.4; OMe, 17.1%). It decolorised alkaline potassium permanganate.

The neutral oil (C) gave the γ -keto-acid (ca. 2 g.) and tetrahydro-5-(2-methoxy-5-methylphenyl)-2 : 2 : 5-tri-*o*-methoxyphenylfuran (ca. 0.2 g.), m. p. and mixed m. p. 234–235°.

When 2 mols. of the Grignard reagent were used, no propene acid was isolated. The solid (ca. 1.9 g.), m. p. 210–220°, precipitated on decomposition of the Grignard complex, was crystallised successively from acetic acid, acetone, and acetic acid, to give 4-(2-methoxy-5-methylphenyl)-1 : 1 : 4-tri-*o*-methoxyphenylbuta-1 : 3-diene, m. p. 176–177°, depressed to 170° on admixture with the corresponding tetrahydrofuran (Found : C, 79.8; H, 6.7; OMe, 23.9. $C_{33}H_{32}O_4$ requires C, 80.5; H, 6.5; OMe, 25.2%).

From the neutral oil (C), tetrahydro-5-(2-methoxy-5-methylphenyl)-2 : 2 : 5-tri-*o*-methoxyphenylfuran (ca. 0.1 g.), m. p. and mixed m. p. 233–234°, was isolated.

Action of o-Methoxyphenylmagnesium Bromide on β-5-Chloro-2-methoxybenzoylpropionic Acid and its Methyl Ester.—(i) *o*-Methoxyphenylmagnesium bromide [from *o*-bromoanisole (8 g., 2 mols.)] reacted with the keto-acid (5 g., 1 mol.), to give γ -(5-chloro-2-methoxyphenyl)- γ -*o*-methoxyphenylbutyrolactone (0.4 g., crude), m. p. 153–154° (from ethanol) (Found : C, 64.8; H, 4.9; Cl, 10.2; OMe, 19.0. $C_{18}H_{17}O_4Cl$ requires C, 65.0; H, 5.1; Cl, 10.6; OMe, 18.9%), and 5-(5-chloro-2-methoxyphenyl)tetrahydro-2 : 2 : 5-tri-*o*-methoxyphenylfuran (0.6 g.; crude), m. p. 250–251° (from acetic acid) (Found : C, 72.4; H, 5.8; Cl, 6.3; OMe, 19.6. $C_{28}H_{31}O_6Cl$ requires C, 72.4; H, 5.8; Cl, 6.7; OMe, 23.4%). The product contained unchanged keto-acid (ca. 3.2 g.).

(i) The Grignard reagent [from *o*-bromoanisole (9 g., 2 mols)] reacted with the ester (6 g., 1 mol.) as usual, and the solid (1.2 g.) precipitated on decomposition was found to be the above

tetrahydrofuran, m. p. and mixed m. p. 250—251°. The semi-solid acid (*ca.* 2 g.) was digested with light petroleum (b. p. 40—60°), then fractionally crystallised from benzene—light petroleum (b. p. 40—60°), to give two types of crystal which were mechanically separated. The predominant fraction, m. p. 120—122° (cleared at 136°), was repeatedly crystallised from the same solvent to give 3-(5-chloro-2-methoxyphenyl)-3-*o*-methoxyphenylprop-2-ene-1-carboxylic acid, m. p. 142—143° (shrinking at 140°) (Found: C, 64.9; H, 5.2; Cl, 10.4; OMe, 19.4. $C_{18}H_{17}O_4Cl$ requires C, 65.0; H, 5.1; Cl, 10.6; OMe, 18.9%). It decolorised alkaline potassium permanganate.

The neutral product (D) was triturated with benzene, then crystallised from glacial acetic acid to give another crop of the tetrahydrofuran. The benzene was evaporated, and the remaining viscous oil was dissolved in ethanol, and left to evaporate slowly. The precipitated product (*ca.* 0.4 g.) was crystallised from benzene—light petroleum (b. p. 50—60°), and the predominant crystals were mechanically separated (*ca.* 0.1 g.), then recrystallised from the same solvent to give colourless crystals, m. p. 125—126°, probably γ -(5-chloro-2-methoxyphenyl)- γ -hydroxy-*o*-methoxy- γ -*o*-methoxyphenylbutyrophenone (Found: C, 68.5; H, 5.9; Cl, 7.6; OMe, 20.6. $C_{25}H_{25}O_6Cl$ requires C, 68.1; H, 5.7; Cl, 8.1; OMe, 21.1%). This structure was supported by absorption spectra, but its full establishment was left for further investigation.

Action of Phenylmagnesium Iodide on Methylsuccinic Anhydride.—(i) Phenylmagnesium iodide [from iodobenzene (26.8 g., 2 mols.)] was added to methylsuccinic anhydride (7.5 g., 1 mol.), and worked up. The acid precipitated on acidification of the carbonate solution was crystallised from acetic acid, to give β -benzoyl- α -methylpropionic acid (1.0 g.), m. p. 140°, undepressed on admixture with an authentic specimen.⁷ The aqueous mother-liquor gave, on concentration, a viscous oil, which was crystallised from light petroleum (b. p. 40—60°) to give the β -methyl-isomer (*ca.* 0.2 g.), m. p. and mixed m. p. 56—58°. The mixture of lactones (A) (2.8 g.) was repeatedly crystallised from methyl alcohol to give α -methyl- $\gamma\gamma$ -diphenylbutyrolactone, m. p. and mixed m. p. 117—118°. The neutral oil (C) contained diphenyl. Isomerisation of the above lactone with concentrated hydrochloric acid was attempted unsuccessfully (5 hours' refluxing).

Action of Phenylmagnesium Iodide on β -Benzoyl- α -methylpropionic acid and its Methyl Ester.—(i) Phenylmagnesium iodide [from iodobenzene (12.6 g., 2 mols.)] reacted with the keto-acid (6 g., 1 mol.) to give a lactone (*ca.* 0.8 g.) and unchanged keto-acid (*ca.* 2.0 g.). Crystallisation of the lactone from methanol gave α -methyl- $\gamma\gamma$ -diphenylbutyrolactone, m. p. 117—118° (Found: C, 81.2; H, 6.2. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.3%).

The neutral product (D) was freed from iodobenzene and diphenyl by heating in a vacuum (b. p. 110—120°/4 mm.). The residue was crystallised from methanol to give the lactone.

(ii) Reaction between the Grignard reagent [from iodobenzene (14.2 g., 2 mols.)] and methyl β -benzoyl- α -methylpropionate (7 g., 1 mol.) gave an acid (*ca.* 3 g.), which was repeatedly crystallised from light petroleum (b. p. 40—60°), to give 1-methyl-3:3-diphenylprop-2-ene-1-carboxylic acid, m. p. 103—104° (*ca.* 0.6 g.) (Found: C, 81.3; H, 6.5. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.3%). It decolorised alkaline potassium permanganate. The neutral material (D) failed to give a pure product.

*Action of *p*-Tolylmagnesium Iodide on Methylsuccinic Anhydride.*—*p*-Tolylmagnesium iodide [from *p*-iodotoluene (28.6 g., 2 mols.)] with methylsuccinic anhydride (7.5 g., 1 mol.) gave a lactone and a mixture of keto-acids. The lactone was distilled at 255—265°/2 mm. (*ca.* 1 g.), then repeatedly crystallised from benzene—light petroleum (b. p. 40—60°) to give α -methyl- $\gamma\gamma$ -di-*p*-tolylbutyrolactone, m. p. and mixed m. p. 125—126°. The mixed acids were extracted with cold benzene, and the insoluble fraction was crystallised from glacial acetic acid to give α -methyl- β -*p*-toluoylpropionic acid, m. p. and mixed m. p. 169—170°⁷ (*ca.* 1.3 g.). Evaporation of the benzene extract left an oil, which was distilled at 180—190°/2 mm. (*ca.* 1.2 g.) and crystallised from benzene—light petroleum (b. p. 40—60°) to give the β -methyl isomer (*ca.* 0.5 g.), m. p. and mixed m. p. 62—64°. The neutral semi-solid (C) gave di-*p*-tolyl¹⁵ (from acetic acid), m. p. and mixed m. p. 119—120°.

*Action of *p*-Tolylmagnesium Iodide on α -Methyl- and β -Methyl- β -*p*-toluoylpropionic Acid.*—(i) The Grignard reagent [from *p*-iodotoluene (21.2 g., 2 mols.)] with α -methyl- β -*p*-toluoylpropionic acid (10 g., 1 mol.) gave the unchanged keto-acid (*ca.* 5.5 g.) and a lactone (A) (*ca.* 1.2 g.). The latter, crystallised from benzene—light petroleum, gave α -methyl- $\gamma\gamma$ -di-*p*-tolylbutyrolactone, m. p. 125—126° (Found: C, 81.8; H, 7.4. $C_{19}H_{20}O_2$ requires C, 81.4; H, 7.1%). The neutral product (D) contained di-*p*-tolyl.

¹⁵ Ullmann and Meyer, *Annalen*, 1904, **332**, 44.

(ii) The experiment was repeated with the β -methyl-keto-acid, to give the corresponding lactone (ca. 1.6 g.), b. p. 215—225°/3 mm.

Action of o-Methoxyphenylmagnesium Bromide on Methylsuccinic Anhydride.—(i) The Grignard reagent [from *o*-bromoanisole (24.6 g., 2 mols.)] with methylsuccinic anhydride (7.5 g., 1 mol.) gave a mixture of lactones (ca. 2.2 g.) and of keto-acids (ca. 1.7 g.). Trituration of the lactones with cold ethanol left an insoluble fraction (ca. 1.1 g.), which on repeated crystallisation from the same solvent gave $\gamma\gamma$ -di-*o*-methoxyphenyl- α -methylbutyrolactone, m. p. and mixed m. p. 126.5—127.5°. The crystals (ca. 0.3 g.), precipitated on slow evaporation of the alcohol used in trituration, were repeatedly crystallised from methanol, to give $\gamma\gamma$ -di-*o*-methoxyphenyl- β -methylbutyrolactone, m. p. 128—129°, depressed to 100° on admixture with a specimen of the above α -methyl isomer (Found: C, 73.3; H, 6.4; OMe, 20.8. $C_{19}H_{20}O_4$ requires C, 73.1; H, 6.4; OMe, 19.9%).

The mixture of keto-acids was fractionally crystallised from benzene-light petroleum to give β -*o*-methoxybenzoyl- α -methylpropionic acid, m. p. 96—97°, undepressed on admixture with an authentic specimen (p. 1693). Concentration of the mother-liquor followed by dilution with light petroleum and repeated crystallisation of the precipitated product from light petroleum (b. p. 40—60°) gave β -*o*-methoxybenzoyl- β -methylpropionic acid, m. p. 55—57° (clear at 58°), depressed to 47° on admixture with the α -methyl acid (Found: C, 64.9; H, 6.4; OMe, 13.4. $C_{12}H_{14}O_4$ requires C, 64.9; H, 6.3; OMe, 14.0%).

The neutral product (D) was refluxed with glacial acetic acid, filtered off (ca. 2 g.), then crystallised from benzene to give tetrahydro-2 : 2 : 5 : 5-tetra-*o*-methoxyphenyl-3-methylfuran, m. p. 222—223° (Found: C, 77.4; H, 6.6; OMe, 23.9. $C_{23}H_{24}O_8$ requires C, 77.6; H, 6.7; OMe, 24.3%).

(ii) When the experiment was repeated with 1 mol. of the Grignard reagent, the neutral product (ca. 1.0 g.) was an oil.

Action of o-Methoxyphenylmagnesium Bromide on β-o-Methoxybenzoyl-α-methylpropionic Acid.—*o*-Methoxyphenylmagnesium bromide [from *o*-bromoanisole (3.5 g., 2 mols.)] and β -*o*-methoxybenzoyl- α -methylpropionic acid (2 g., 1 mol.) gave recovered γ -keto-acid (ca. 0.6 g.) and a lactone (ca. 0.5 g.). The latter was repeatedly crystallised from ethanol, to give $\gamma\gamma$ -di-*o*-methoxyphenyl- α -methylbutyrolactone, m. p. 126.5—127.5° (Found: C, 72.8; H, 6.3; OMe, 22.0. $C_{19}H_{20}O_4$ requires C, 73.1; H, 6.4; OMe, 19.9%). There was insufficient of the neutral solid (D), m. p. 200—208°, for identification.

Isomerisation of γγ-Di-o-methoxyphenyl-α-methylbutyrolactone.—Isomerisation of the lactone with concentrated hydrochloric acid as usual gave a product, m. p. 134—137°, which was repeatedly crystallised from benzene-light petroleum to give 3 : 3-di-*o*-methoxyphenyl-1-methyl-prop-2-ene-1-carboxylic acid, m. p. 139—140° (Found: C, 73.4; H, 6.4; OMe, 21.05. $C_{19}H_{20}O_4$ requires C, 73.1; H, 6.4; OMe, 19.9%). It decolorised alkaline potassium permanganate.

Action of p-Methoxyphenylmagnesium Bromide on Methylsuccinic Anhydride.—*p*-Methoxyphenylmagnesium bromide [from *p*-bromoanisole (24.6 g., 2 mols.)] with methylsuccinic anhydride (7.5 g., 1 mol.) gave a mixture of keto-acids, and an oily lactone (ca. 1.5 g.) which failed to solidify even after distillation at 250—260°/3 mm. (ca. 0.6 g.). The keto-acids (ca. 2.0 g.), repeatedly crystallised from acetic acid, gave β -*p*-methoxybenzoyl- α -methylpropionic acid (ca. 0.4 g.), m. p. 143—144°, undepressed on admixture with an authentic specimen.¹⁶ Evaporation of the acetic acid mother-liquor left a viscous oil (ca. 1.3 g.) which gave a semicarbazone, m. p. 180°, undepressed on admixture with a specimen of the semicarbazone of the β -methyl acid, kindly provided by A. M. Fleifel.⁸ The semi-solid (D) failed to solidify even after passing through an alumina column.

Action of p-Methoxyphenylmagnesium Bromide on β-p-Methoxybenzoyl-α-methylpropionic Acid.—*p*-Methoxyphenylmagnesium bromide [from *p*-bromoanisole (12.6 g., 2 mols.)] and β -*p*-methoxybenzoyl- α -methylpropionic acid (7.5 g., 1 mol.) gave a lactone (ca. 0.5 g.), which failed to solidify, and the unchanged keto-acid (ca. 3.5 g.). The neutral semi-solid (C) failed to give a crystalline product.

Action of α-Naphthylmagnesium Bromide on Methylsuccinic Anhydride.— α -Naphthylmagnesium bromide [from α -bromonaphthalene (27.4 g., 2 mols.)] was refluxed with methylsuccinic anhydride (7.5 g., 1 mol.) for 5 hr., and worked up. The alkaline extract gave a lactone (ca. 2.0 g.), and a semi-solid mixture of the keto-acids. The lactone was repeatedly crystallised from methanol, to give α -methyl- $\gamma\gamma$ -di-1-naphthylbutyrolactone, m. p. and mixed m. p.

¹⁶ Mitter and De, *J. Indian Chem. Soc.*, 1939, **16**, 200.

166—167°. The keto-acids were repeatedly crystallised from benzene, to give α -methyl- β -1-naphthoylpropionic acid¹⁷ (*ca.* 1.5 g.), m. p. and mixed m. p. 122—123°. Evaporation of the benzene mother-liquor left a semi-solid (*ca.* 2.5 g.), which failed to solidify or give a crystalline semicarbazone. However, it gave 1-naphthoic acid on oxidation with potassium permanganate,⁹ and so was probably β -methyl- β -1-naphthoylpropionic acid. The neutral product (D) contained naphthalene.

Action of α -Naphthylmagnesium Bromide on α -Methyl- β -1-naphthoylpropionic Acid.—The Grignard reagent [from α -bromonaphthalene (3.42 g., 2 mols.)] and the keto-acid (2 g., 1 mol.) gave unchanged keto-acid (*ca.* 1.2 g.), and a lactone (A) (*ca.* 0.1 g.), which was crystallised from methanol to give α -methyl- $\gamma\gamma$ -di-1-naphthylbutyrolactone in colourless crystals, m. p. 166—167° (Found: C, 84.5; H, 5.7. $C_{25}H_{20}O_2$ requires C, 85.2; H, 5.7%).

Action of 2:5-Dimethoxyphenylmagnesium Iodide on Methylsuccinic Anhydride.—The Grignard reagent [from 2-iodo-1:4-dimethoxybenzene¹¹ (23.0 g., 2 mols.)] and methylsuccinic anhydride (5 g., 1 mol.) gave mixtures of lactones (*ca.* 3.7 g.) and of keto-acids (2.8 g.). The lactones were crystallised from ethanol, to give $\gamma\gamma$ -di-(2:5-dimethoxyphenyl)- α -methylbutyrolactone, m. p. and mixed m. p. 149—150°. Concentration of the alcoholic mother-liquor precipitated two crops. The first crop, m. p. 120—128°, was rejected. The second crop, m. p. 115—117° (*ca.* 0.3 g.), was fractionally crystallised from methanol to give a crop, m. p. 120—125° (rejected), and a second crop (*ca.* 0.2 g.), m. p. 137—139°. This was repeatedly crystallised from the same solvent to give $\gamma\gamma$ -di-(2:5-dimethoxyphenyl)- β -methylbutyrolactone, m. p. 139—140°, depressed to 120—125° on admixture with the α -methyl isomer (Found: C, 67.4; H, 6.3. $C_{21}H_{24}O_6$ requires C, 67.7; H, 6.5%).

The mixture of keto-acids was proved by ferric chloride test to contain a demethylated product, so it was methylated with methyl iodide, potassium carbonate, and acetone. Hydrolysis of the ester (5% alcoholic potassium hydroxide) gave a semi-solid which, crystallised from benzene, gave β -2:5-dimethoxybenzoyl- α -methylpropionic acid (*ca.* 0.3 g.), m. p. and mixed m. p. 116.5—118°. Evaporation of the benzene mother-liquor gave an oily acid, probably a mixture of the α - and β -methyl-keto-acids, which failed to solidify or to give a solid semicarbazone.

The neutral solid (D) was refluxed with glacial acetic acid, which was then removed in a vacuum. The residue was crystallised from ethanol, then from benzene-light petroleum to give 2:2:5:5-tetra-(2:5-dimethoxyphenyl)tetrahydro-3-methylfuran, m. p. 153.5—154.5° (Found: C, 70.3; H, 6.5; OMe, 40.4. $C_{37}H_{42}O_9$ requires C, 70.4; H, 6.7; OMe, 39.4%). The alcohol used in trituration of the neutral product (C) slowly afforded a product (*ca.* 0.2 g.), which was repeatedly recrystallised from benzene-light petroleum to give colourless crystals, m. p. 152—153.5°, depressed to 130—140° when mixed with the above tetrahydrofuran. It was probably $\gamma\gamma$ -di-(2:5-dimethoxyphenyl)- γ -hydroxy-2:5-dimethoxy- α -methylbutyrophenone (Found: C, 68.8; H, 6.6; OMe, 34.05. $C_{29}H_{34}O_8$ requires C, 68.2; H, 6.7; OMe, 36.5%). Although its structure was supported by absorption spectrum, its complete elucidation was left for further investigation.

Action of 2:5-Dimethoxyphenylmagnesium Iodide on β -2:5-Dimethoxybenzoyl- α -methylpropionic Acid and its Methyl Ester.—(i) The Grignard reagent [from 2-iodo-1:4-dimethoxybenzene (10.5 g., 2 mols.)] and the keto-acid (5 g., 1 mol.) gave recovered keto-acid (*ca.* 3.3 g.) and a lactone (*ca.* 0.8 g.), m. p. 120—125°. Repeated crystallisation of the lactone from ethanol gave $\gamma\gamma$ -di-(2:5-dimethoxyphenyl)- α -methylbutyrolactone, m. p. 149—150° (Found: C, 67.8; H, 6.5; OMe, 33.1. $C_{21}H_{24}O_6$ requires C, 67.7; H, 6.5; OMe, 33.3%). The neutral product (D) contained *p*-dimethoxybenzene.

(ii) The Grignard reagent [from 2-iodo-1:4-dimethoxybenzene (10 g., 2 mols.)] and methyl β -2:5-dimethoxybenzoyl- α -methylpropionate (5 g., 1 mol.) gave an acid (*ca.* 3.5 g.), which was repeatedly crystallised from benzene-light petroleum to give 3:3-di-(2:5-dimethoxyphenyl)-1-methylprop-2-ene-1-carboxylic acid (0.4 g.), m. p. 152—153° (Found: C, 67.3; H, 6.5; OMe, 33.0. $C_{21}H_{24}O_6$ requires C, 67.7; H, 6.5; OMe, 33.3%). The neutral product (D) (*ca.* 0.6 g.) was filtered off from an oily fraction, and refluxed with glacial acetic acid, which was then removed under reduced pressure. The residue was crystallised from benzene-light petroleum to give 2:2:5:5-tetra-(2:5-dimethoxyphenyl)tetrahydro-3-methylfuran, m. p. and mixed m. p. 153.5—154.5°.

Isomerisation of $\gamma\gamma$ -Di-(2:5-dimethoxyphenyl)- α -methylbutyrolactone.—The lactone was

¹⁷ Haworth, *J.*, 1932, 1125.

isomerised by concentrated hydrochloric acid. Crystallisation of the product from benzene-light petroleum gave 3:3-di-(2:5-dimethoxyphenyl)-1-methylprop-2-ene-1-carboxylic acid, m. p. and mixed m. p. 153—154°.

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