β-*Aroylpropionic Acids. Part IV.* The Action of Grignard Reagents on Succinic Anhydride : β-Aroylpropionic Acids and their Esters.*

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[Reprint Order No. 5035.]

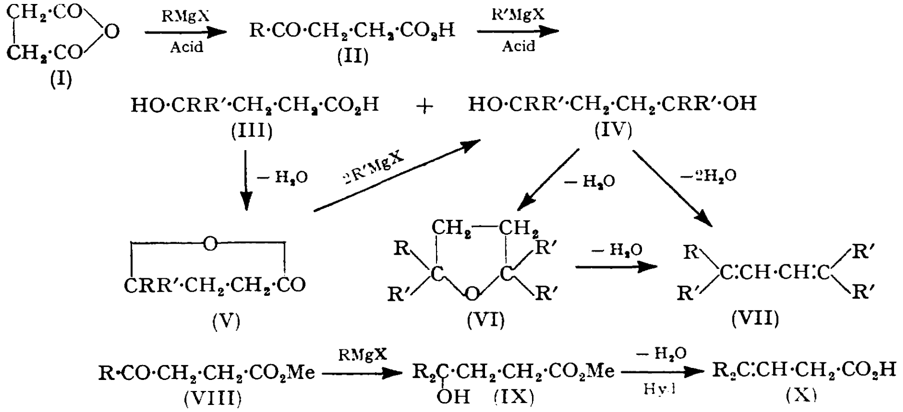
Arylmagnesium halides react with succinic anhydride (I) to give a mixture containing a β-aroylpropionic acid (II), a γγ-diaryl-γ-hydroxybutyric acid (III), and a neutral product from which a tetrahydrofuran (VI) or a buta-1 : 3-diene (VII) are isolated. The same products are obtained when succinic anhydride is replaced by the β-aroylpropionic acid corresponding to the Grignard reagent.

However, when arylmagnesium halides react with β-aroylpropionic esters, they give 3 : 3-diarylprop-2-ene-1-carboxylic acids instead of γγ-diaryl-γ-hydroxybutyric acids.

Identical lactones are obtained either by the interaction of R'MgX and $R\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$ or of RMgX and $R'\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$.

Ethylmagnesium iodide reacts with β-aroylpropionic acids to give γ-aryl-γ-ethylbutyrolactones.

Baddar and El-Assal (Part II *) reported that, although reaction between succinic anhydride and *o*-methoxyphenylmagnesium bromide gave γγ-di-*o*-methoxyphenylbutyrolactone (V; R = R' = *o*-$MeO\cdot C_6H_4$), yet *p*-methoxyphenylmagnesium iodide afforded β-*p*-methoxybenzoylpropionic acid. Newman and Wise (*J. Amer. Chem. Soc.*, 1941, **63**, 2109) obtained similar results from the reaction between *o*-methoxyphenylmagnesium bromide or other arylmagnesium halides and naphthalic anhydride. We therefore studied the effect of the nature and the position of substituents on the course of this reaction.



When phenyl-, *p*-methoxyphenyl-, *o*-methoxyphenyl-, *o*-ethoxyphenyl-, or *o*-tolylmagnesium halide reacted with succinic anhydride, it gave a mixture of β-aroylpropionic acid (II), a γγ-diaryl-γ-hydroxybutyric acid (III) [isolated as its lactone (V)], and a neutral product from which a 2 : 2 : 5 : 5-tetra-aryltetrahydrofuran (VI) or a 1 : 1 : 4 : 4-tetra-arylbuta-1 : 3-diene (VII) were isolated. The same products were obtained when succinic anhydride was replaced by β-aroylpropionic acids. Lactones (V; R = R' = Ph, and R = R' = *o*-$MeO\cdot C_6H_4$) with the corresponding arylmagnesium halides gave 2 : 2 : 5 : 5-tetra-aryltetrahydrofurans (VI; R = R' = Ph, and R = R' = *o*-$MeO\cdot C_6H_4$, respectively). However, when β-aroylpropionic esters were used, 3 : 3-diarylprop-2-ene-1-carboxylic acids (X) were obtained. The reaction between β-aroylpropionic acids ($R\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$) and Grignard reagents (R'MgX) gave lactones (V) identical with those obtained from $R'\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$ and RMgX. Ethylmagnesium halide reacted with β-benzoylpropionic and β-*o*-methoxybenzoylpropionic acid to give the lactones

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* Parts II and III, *J.*, 1951, 431; 1954, 4538.

(V; R = Ph, R′ = Et) and (V; R = *o*-MeO·C_6H_4, R′ = Et), respectively, the latter in greater proportion. The above results are summarised in the Table.

Grignard reagent (2 mols.)	Reactant and subst.	Product, %,* of type :				
		(II)	(V)	(VI)	(VII)	(X)
R = Ph	I	25·3	10·9—12·6	0·8	—	—
R′ = Ph	II; R = Ph	54 (r)	6·7	2·4	—	—
R′ = Ph (4 mols.)	V; R = R′ = Ph	—	—	2·9 (pure)	—	—
R = Ph	VIII; R = Ph	—	—	1·8 (pure)	—	24·2
R = *p*-MeO·C_6H_4	I	28·9	10·0	←2·1 (crude)→		—
R′ = ,,	II; *p*-MeO·C_6H_4	72 (r)	4·2	—	6·5 (pure)	—
R = ,,	VIII; ,,	—	—	←1·5→		18·6 §
R = *o*-MeO·C_6H_4	I	18·8	25·2	1·2 (pure)	—	—
R′ = ,,	II; *o*-MeO·C_6H_4	23 (r)	28·0	8·4	—	—
R′ = ,, (4 mols.)	V; ,,	—	—	15·0	—	—
R = ,,	VIII; ,,	—	—	15·0	—	33·5
R = *o*-EtO·C_6H_4	I	15·8	7·6—9·2	2·7	—	—
R = *o*-Me·C_6H_4	I	18·2	6·4	†	†	—
R′ = Ph	II; *o*-MeO·C_6H_4	28 (r)	10·8	†	†	—
R′ = *o*-MeO·C_6H_4	II; Ph	35 (r)	10·9	5·3	—	—
R′ = ,,	II; *o*-EtO·C_6H_4	38 (r)	5·6	—	4·5	—
R′ = *o*-EtO·C_6H_4	II; *o*-MeO·C_6H_4	28 (r)	5·3	—	6·4	—
R′ = Et	II; Ph	35 (r)	9·3	‡	‡	—
R′ = Et	II; *o*-MeO·C_6H_4	25 (r)	18·3	‡	‡	—

* The yields are calculated on the crude product unless otherwise stated; (r) = recovered.

† The neutral portion was an oil which failed to solidify.

‡ The neutral products were mixtures which could not be adequately separated by fractional distillation.

§ When 4 mols. of the Grignard were used no propene acid was obtained, and the neutral portion gave 2·3% of (pure) butadiene and 0·9% of unidentified material.

The structure of the two buta-1 : 3-dienes (VII; R = *o*-EtO·C_6H_4, R′ = *o*-MeO·C_6H_4) and (VII; R = *o*-MeO·C_6H_4, R′ = *o*-EtO·C_6H_4) was confirmed by their absorption spectra being identical with that of 1 : 1 : 4 : 4-tetra-*p*-methoxyphenylbuta-1 : 3-diene (VII; R = R′ = *p*-MeO·C_6H_4) ($\lambda_{max.}$ = 335, 334, and 363 mμ, respectively), and different from that of the tetrahydrofurans (VI; R = R′ = Ph, R = R′ = *o*-MeO·C_6H_4, R = R′ = *o*-EtO·C_6H_4, and R = Ph, R′ = *o*-MeO·C_6H_4), which closely resemble that of diphenylmethane [$\lambda_{max.}$ = 259, 277, 274, 273(279), and 262 mμ, respectively]. The buta-1 : 3-diene (VII; R = R′ = Ph) exhibits $\lambda_{max.}$ at 343 mμ (Alberman *et al.*, *J.*, 1952, 3284).

The relatively high yield of the lactone obtained from the action of Grignard reagents on β-*o*-methoxybenzoylpropionic acid is therefore readily interpreted as explained by Baddar and El-Assal (*loc. cit.*). However, the exceptionally high yield of the lactone obtained from β-*o*-methoxybenzoylpropionic acid and *o*-methoxyphenylmagnesium halide may be due to the reactivity of the Grignard reagent caused by the co-ordination of the ethereal oxygen with the magnesium atom in the same molecule.

EXPERIMENTAL

The procedure described in the first experiment was adopted with slight modification in the remaining experiments.

Action of Phenylmagnesium Iodide on Succinic Anhydride, β-Benzoylpropionic Acid, Methyl β-Benzoylpropionate, and γγ-Diphenylbutyrolactone.—(i) An ethereal solution (40 ml.) of phenylmagnesium iodide (from iodobenzene; 20·4 g., 1 mol.) was added dropwise (20 min.) to a boiling solution of succinic anhydride (10 g., 1 mol.) in dry, thiophen-free benzene (200 ml.). The mixture was refluxed for a further 3 hr., left overnight at room temperature, and then treated with dilute sulphuric acid. The ether–benzene layer was extracted with sodium hydroxide solution, and the alkaline solution (charcoal) was cooled and acidified. The precipitated acids (*ca.* 5·4 g.) were refluxed with benzene for 1·5—2 hr., solvent was removed, and the semi-solid residue was extracted with cold sodium carbonate solution. The insoluble viscous oil (A) (*ca.* 0·6 g.) solidified on trituration with cold alcohol. On crystallisation from benzene–light petroleum (b. p. 40—60°), γγ-diphenylbutyrolactone was obtained, of m. p. 90·5—91·5° undepressed on admixture with an authentic specimen prepared by Stobbe's reaction (cf. Johnson *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 74) (Found: C, 80·0; H, 5·7%; *M*, 200. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·9%; *M*, 238).

The sodium carbonate solution gave on acidification an acid (B) (*ca.* 4·2 g.), which on crystallisation from benzene–light petroleum (b. p. 40—60°) gave β-benzoylpropionic acid, m. p. and mixed m. p. 115—116°. The neutral product in the ether–benzene layer was refluxed for 1—2 hr. with 20% sodium hydroxide solution to remove any lactone. The insoluble semi-solid (C) was converted into a solid (D) (0·2 g.) on trituration with cold alcohol or extraction with hot light petroleum (b. p. 40—60°). It was refluxed with acetic acid for 1 hr., then allowed to crystallise, giving tetrahydro-2 : 2 : 5 : 5-tetraphenylfuran, m. p. 180° (Found : C, 88·4; H, 6·4%; *M*, 328. Calc. for $C_{28}H_{24}O$: C, 89·3; H, 6·4%; *M*, 376). Komppa and Rohrmann (*Annalen*, 1934, **509**, 259) and Valeur (*Compt. rend.*, 1903, **136**, 695) gave m. p. 180° and 182°, respectively. The experiment was repeated with β-benzoylpropionic acid and γγ-diphenylbutyrolactone, and the results are tabulated below :

		Products, g.		
PhMgX, mols.	Reactant (R = R′ = Ph)	Keto-acid (B) (II; R = Ph)	Lactone (A) (V; R = R′ = Ph)	Neutral (D) (R = R′ = Ph)
2	I (10 g.)	4·5	2·6—3·0	0·3
2	II (10 g.)	4·8 (r) *	0·9	0·5 †
3	V (2 g.)	—	—	0·8 ‡

* (r) = recovered.

† M. p. 150—155°, raised by repeated extraction with light petroleum (b. p. 40—60°) to 175—180°. On crystallisation from acetic acid two types of crystals were obtained, which were mechanically separated. The main product was recrystallised from the same solvent to give (VI; R = R′ = Ph), identified by m. p. and mixed m. p. The minor product (trace) melted at 210—225° and was not sufficient for identification.

‡ The reaction mixture was refluxed for 6 hr., and the neutral product (D) was proved to be the tetrahydrofuran (VI; R = R′ = Ph) by m. p. and mixed m. p. (Found : C, 88·8; H, 6·4%).

(ii) The reaction was repeated with phenylmagnesium iodide (2 mols.) and methyl β-benzoylpropionate (5 g.; 1 mol.). Acidification of the sodium hydroxide extract precipitated an acid (*ca.* 1·5 g.), which gave 3 : 3-diphenylprop-2-ene-1-carboxylic acid (X; R = Ph) (from dilute alcohol), m. p. 116—117°, depressed to 90° on admixture with β-benzoylpropionic acid (Found : C, 80·1; H, 5·7. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·9%). Johnson *et al.* (*loc. cit.*) gave m. p. 117·5—118·5°. Oxidation with alkaline potassium permanganate afforded benzophenone (cf. Baddar and El-Assal, *loc. cit.*).

The viscous oil (C) was refluxed with 20% sodium hydroxide solution, then treated with alcohol. The alkaline solution, on acidification, precipitated β-benzoylpropionic acid (1·2 g.). The neutral portion (D) (0·2 g.), m. p. 198—200°, which was probably the diol (cf. Wassermann and Kloetzel, *J. Amer. Chem. Soc.*, 1953, **75**, 3037; Valeur, *loc. cit.*), gave tetrahydro-2 : 2 : 5 : 5-tetraphenylfuran (from glacial acetic acid), m. p. and mixed m. p. 180°.

Action of o-*Methoxyphenylmagnesium Bromide on Succinic Anhydride,* β-o-*Methoxybenzoylpropionic Acid, and* γγ-*Di*-o-*methoxyphenylbutyrolactone.*—(i) The Grignard reagent from *o*-bromoanisole (18·7 g., 1 mol.) was treated with succinic anhydride (10 g., 1 mol.) in the usual manner. The alkaline extract contained γγ-di-*o*-methoxyphenylbutyrolactone (A) (*ca.* 4·0 g.) and β-*o*-methoxybenzoylpropionic acid (B) (*ca.* 1·7 g.) (cf. Baddar and El-Assal, *loc. cit.*). The neutral, sticky solid (C) was triturated with alcohol, the product (D) (*ca.* 2·0 g.), m. p. 110—116°, extracted with hot acetone (30—40 ml.), and the insoluble fraction was filtered off (*ca.* 0·4 g.), m. p. 274—276°. Crystallisation from nitrobenzene gave *tetrahydro-2 : 2 : 5 : 5-tetra-*o-*methoxyphenylfuran* (VI; R = R′ = *o*-C_6H_4·OMe), m. p. 287·5—288·5° (Found : C, 77·8; H, 6·7; OMe, 22·6. $C_{32}H_{32}O_5$ requires C, 77·4; H, 6·45; OMe, 25·5%). The acetone solution on cooling deposited a crystalline product, m. p. 104—108° (cleared at 150°; *ca.* 1·0 g.), which could not be purified by fractional crystallisation. It gave no derivative with 2 : 4-dinitrophenylhydrazine. The experiment was repeated under varying conditions, and also with β-*o*-methoxybenzoylpropionic acid and the lactone (V; R = R′ = *o*-MeO·C_6H_4) instead of succinic anhydride. The results are given below :

o-MeO·C_6H_4·MgX, mols.	Reactant (10 g.) (R = R′ = *o*-MeO·C_6H_4)	Keto-acid (B), g.	Lactone (A), g.	Neutral (D) Wt. (g.) and m. p.
2	I	3·9	7·5	2·9, 110—116°
2 *	I	3·9	3·0	4·0, 110—116
2	II	2·3 ‡	4·0	2·0, 220—250
4 †	V	—	—	2·5, 250—260

* Refluxed for 5 hr. instead of 3 hr. † Refluxed for 6 hr. instead of 3 hr., and the product insoluble in ether–benzene was filtered off (*ca.* 1·5 g.), combined with (D) (*ca.* 1·0 g.), and purified as usual. ‡ Recovered.

Action of o-*Methoxyphenylmagnesium Bromide on Methyl* β-o-*Methoxybenzoylpropionate.*—The Grignard reagent (from *o*-bromoanisole; 10·2 g., 2 mols.) was added to a benzene solution (60 ml.) of methyl β-*o*-methoxybenzoylpropionate (6 g., 1 mol.), and the reaction mixture worked up. The insoluble product (*ca.* 2·0 g.) (D′) had m. p. 230—250°. The acid (2·7 g.) precipitated from the sodium hydroxide extract crystallised from benzene–light petroleum (b. p. 40—60°) to give 3 : 3-di-*o*-methoxyphenylprop-2-ene-1-carboxylic acid, identical (m. p. and mixed m. p.) with an authentic specimen (cf. Baddar and El-Assal, *loc. cit.*).

A mixture of solids (D) (*ca.* 0·5 g.), m. p. 230—240°, and (D′) was extracted with boiling acetone. The insoluble fraction (*ca.* 2·0 g.), m. p. 255—260°, crystallised from nitrobenzene to give tetrahydro-2 : 2 : 5 : 5-tetra-*o*-methoxyphenylfuran, m. p. and mixed m. p. 287·5—288·5°.

Action of o-*Ethoxyphenylmagnesium Iodide on Succinic Anhydride.*—The precipitate obtained on acidification of the product of the reaction of the Grignard reagent (from *o*-iodophenetole; 49·6 g., 2 mols.) and succinic anhydride (10 g., 1 mol.) was dissolved in hot sodium carbonate solution, the hot solution filtered, and the crystalline sodium salt obtained on cooling was treated with acid. *γγ-Di-*o*-ethoxyphenylbutyrolactone* (V; R = R′ = *o*-C_6H_4·OEt) (*ca.* 2·5—3 g.; m. p. 148—150°), formed monoclinic crystals, m. p. 157—157·5°, from acetic acid (Found: C, 73·6; H, 6·7; OEt, 28·6. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·7; OEt, 27·6%).

On acidification the sodium hydroxide extract precipitated *β-*o*-ethoxybenzoylpropionic acid* (needles from benzene), m. p. 123—124° undepressed on admixture with a specimen prepared from β-*o*-hydroxybenzoylpropionic acid ethyl iodide and potassium carbonate in dry acetone (Found: C, 64·6; H, 6·2; OEt, 21·05. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3; OEt, 20·3%).

The neutral product (D) (1·5 g.) was repeatedly extracted with boiling light petroleum (b. p. 60—80°), refluxed with glacial acetic acid for 1 hr., and then dissolved in benzene, a little insoluble material being removed. The solution was diluted with light petroleum (b. p. 40—60°), to give 2 : 2 : 5 : *5-tetra-*o*-ethoxyphenyltetrahydrofuran*, m. p. 207·5—208·5° (Found: C, 77·8; H, 7·3. $C_{36}H_{40}O_5$ requires C, 78·3; H, 7·3%).

Use of 1 mol. of the Grignard reagent gave yields of lactone, keto-acid, and neutral material of 3·5, 3·5, and 0·2 g., respectively.

Action of p-*Methoxyphenylmagnesium Bromide on Succinic Anhydride and on* β-p-*Methoxybenzoylpropionic Acid.*—(i) The product from the reaction of the Grignard reagent from *p*-bromoanisole (18·7 g., 1 mol.) and a solution of succinic anhydride (10 g., 1 mol.) in benzene (200 ml.) contained γγ-di-*p*-methoxyphenylbutyrolactone, m. p. and mixed m. p. 107·5—108·5° (from ether) (cf. Johnson *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 513) (A) (0·8 g.), β-*p*-methoxybenzoylpropionic acid (B) (6·0 g.), and a neutral substance (D) (0·6 g.). A benzene solution of the neutral fraction (D) was passed on to alumina. Evaporation of the eluate obtained with benzene–ethyl acetate (1 : 1, vol.) and repeated crystallisation of the residue from benzene–light petroleum (b. p. 40—60°) gave 1 : 1 : 4 : 4-tetra-*p*-methoxyphenylbuta-1 : 3-diene, m. p. 203—204° undepressed by a specimen kindly supplied by Dr. Tadros (cf. Tadros *et al.*, *J.*, 1951, 2555) (Found: C, 80·6; H, 6·2; OMe, 23·0. Calc. for $C_{32}H_{30}O_4$: C, 80·3; H, 6·3; OMe, 25·9%).

(ii) With 2 mols. of the Grignard reagent, the yields of (A), (B), and (D) were 3·0, 6·0, and 1·0 g., respectively.

(iii) The Grignard reagent (18·0 g., 2 mols.) and β-*p*-methoxybenzoylpropionic acid (10 g., 1 mol.) gave a lactone (A) (0·6 g.), unchanged keto-acid (B) (7·2 g.), and 1 : 1 : 4 : 4-tetra-*p*-methoxyphenylbuta-1 : 3-diene (crude yield, 1·5 g.), m. p. and mixed m. p. 203—204°. The alcohol used in the trituration of the crude butadiene gave a trace of material identical with the specimen obtained by the action of Grignard reagent on the ester.

Action of p-*Methoxyphenylmagnesium Bromide on Methyl* β-p-*Methoxybenzoylpropionate.*—The Grignard reagent from *p*-bromoanisole (10·2 g., 2 mols.) was added to the ester (6 g., 1 mol.), and the reaction was carried out as usual. The semi-solid acid, after purification through the ester (1·5 g.) and crystallisation from light petroleum (b. p. 40—60°), gave 3 : 3-di-*p*-methoxyphenylprop-2-ene-1-carboxylic acid (X; R = R′ = *p*-C_6H_4·OMe), m. p. and mixed m. p. 86—87° (cf. Johnson *et al.*, *loc. cit.*). The neutral product (D) (*ca.* 0·2 g.), m. p. 190—222°, was not identified.

With 4 mols. of the Grignard reagent, no propene-acid was obtained. The neutral viscous oil (C) gave unidentified material (crude yield, 0·2 g.), m. p. 213—214°, and 1 : 1 : 4 : 4-tetra-*p*-methoxyphenylbuta-1 : 3-diene (crude yield, 0·5 g.), yellow crystals, m. p. 203—204° (from benzene–light petroleum).

Action of o-*Tolylmagnesium Iodide on Succinic Anhydride.*—The reaction between *o*-tolylmagnesium iodide (from *o*-iodotoluene; 21·8 g., 1 mol.) and succinic anhydride (10 g., 1 mol.)

gave *γγ-di-*o*-tolylbutyrolactone* (A) (V; R = R′ = o-C_6H_4Me) (crude yield, 0·5 g.), m. p. 138—139° (from light petroleum) (Found: C, 81·0; H, 6·8%; *M*, 248. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%; *M*, 266), *β-*o*-toluoylpropionic acid* (B) (crude yield, 3·5 g.), m. p. 104—105° (from benzene–light petroleum) (Found: C, 68·5; H, 6·1. $C_{11}H_{12}O_3$ requires C, 68·6; H, 6·3%), and a neutral portion (C) (1·4 g.) which failed to solidify and did not give a solid nitro-derivative.

When 2 mols. of the Grignard reagent were used, the amounts of the lactone (A), keto-acid (B), and neutral product (C) were 1·7, 3·5, and 3·0 g., respectively.

Action of o*-Methoxyphenylmagnesium Iodide on β-Benzoylpropionic Acid.*—The Grignard reagent (from o-iodoanisole; 26·4 g., 2 mols.) and a benzene solution (100 ml.) of β-benzoylpropionic acid (10 g., 1 mol.) gave crude o*-methoxy-γγ-diphenylbutyrolactone* (A) (V; R = Ph; R′ = o-C_6H_4·OMe) (*ca.* 1·8 g.), unchanged keto-acid (B) (3·5 g.), and a neutral product (D). The pure lactone (*ca.* 0·3 g.) had m. p. 73—74° [Found: C, 76·5; H, 5·9; OMe, 11·9%; *M* (Rast), 240. $C_{17}H_{16}O_3$ requires C, 76·1; H, 5·9; OMe, 11·5%; *M*, 268]. The neutral solid (D) (*ca.* 1·4 g.), m. p. 170—175° (clearing at 190°), was crystallised from glacial acetic acid, and the first crop, m. p. 200—204°, was recrystallised from the same solvent giving 2 : 2 : 5*-tri-*o*-methoxyphenyl-5-phenyltetrahydrofuran* (VI; R = C_6H_5, R′ = o-C_6H_4·OMe), m. p. 208—209° (Found: C, 80·1; H, 6·6; OMe, 18·8%; *M*, 470. $C_{31}H_{30}O_4$ requires C, 79·8; H, 6·4; OMe, 19·8%; *M*, 466). The second crop, m. p. 135—140° (cleared at 190°), could not be purified by fractional crystallisation. It failed to give either the unsaturation test (bromine) or a 2 : 4-dinitrophenylhydrazone.

*Action of Phenylmagnesium Iodide on β-*o*-Methoxybenzoylpropionic Acid.*—The reaction between phenylmagnesium iodide (from iodobenzene; 15·8 g., 2 mols.) and β-o-methoxybenzoylpropionic acid (8 g.; 1 mol.) gave o-methoxy-γγ-diphenylbutyrolactone (A) (crude yield, (1·1 g.), m. p. and mixed m. p. 73—74°, unchanged keto-acid (B) (2·2 g.), and a neutral portion (C) (*ca.* 1·0 g.). Fraction (C) remained liquid and was not identified.

Action of o*-Ethoxyphenylmagnesium Iodide on β-*o*-Methoxybenzoylpropionic Acid.*—The reaction between the Grignard reagent from o-iodophenetole (19·2 g., 2 mols.) and the keto-acid (8 g., 1 mol.) was carried out as usual. The neutral product (D′), precipitated on decomposition of the Grignard complex, was worked up with the remainder of (D) (see below). The viscous oily lactone (0·6 g.) after trituration with ether and crystallisation from methyl alcohol gave o*-ethoxy-*o′*-methoxy-γγ-diphenylbutyrolactone* (V; R = o-C_6H_4·OMe, R′ = o-C_6H_4·OEt), m. p. 122—123° (Found: C, 72·9; H, 6·4. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%).

The combined neutral product (D + D′) (*ca.* 0·5 g.) was boiled with 20% sodium hydroxide solution, and then crystallised from glacial acetic acid, giving 1 : 1 : 4*-tri-*o*-ethoxyphenyl-4-*o*-methoxyphenylbuta-*1 : 3*-diene* (VII; R = o-C_6H_4·OMe, R′ = o-C_6H_4·OEt), m. p. 195—196° (Found: C, 80·7; H, 6·8%; *M*, 601. $C_{35}H_{36}O_4$ requires C, 80·8; H, 6·9%; *M*, 520).

Action of o*-Methoxyphenylmagnesium Bromide on β-*o*-Ethoxybenzoylpropionic Acid.*—The Grignard reagent from o-bromoanisole (6·72 g., 2 mols.) and β-o-ethoxybenzoylpropionic acid (4 g., 1 mol.) gave a neutral portion (D) (*ca.* 0·4 g.) and o-ethoxy-$o′$-methoxy-γγ-diphenylbutyrolactone (crude yield, 0·3 g.), m. p. 122—123°, undepressed on admixture with an authentic specimen from the preceding experiment.

An acetone solution of solid (D), on cooling, deposited 4*-*o*-ethoxyphenyl-*1 : 1 : 4*-tri-*o*-methoxyphenylbuta-*1 : 3*-diene* (VII; R = o-C_6H_4·OEt, R′ = o-C_6H_4·OMe), m. p. 188—189° (after crystallisation from acetic acid) (Found: C, 80·4; H, 6·5. $C_{33}H_{32}O_4$ requires C, 80·5; H, 6·5%).

*Action of Ethylmagnesium Iodide on β-Benzoyl- and on β-*o*-Methoxybenzoyl-propionic Acid.*—(i) Reaction between ethylmagnesium iodide (from ethyl iodide; 17·5 g., 2 mols.) and β-benzoylpropionic acid (10 g., 1 mol.) gave γ-ethyl-γ-phenylbutyrolactone (A) (*ca.* 1·0 g.), unchanged keto-acid (B) (*ca.* 3·5 g.), and a neutral oil (*ca.* 1·4 g.) (C). The lactone (A) was a faintly yellow oil, b. p. 135—138°/2 mm., n_D^{27} 1·5250 (Found: C, 75·4; H, 7·4. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%). Johnson *et al.* (*J. Amer. Chem. Soc.*, 1947, **69**, 74) gave b. p. 135°/0·05 mm., n_D^{20} 1·5283. (ii) A similar experiment with ethylmagnesium iodide (from ethyl iodide; 12·0 g., 2 mols.) and β-o-methoxybenzoylpropionic acid (8·0 g., 1 mol.) gave *γ-ethyl-γ-*o*-methoxyphenylbutyrolactone* (crude yield, 1·5 g.), b. p. 155—158°/4 mm., n_D^{27} 1·5725 (Found: C, 70·8; H, 7·2; OMe, 14·6. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3; OMe, 14·1%), unchanged keto-acid (about 2·0 g.), and an oil (C) (about 1·3 g.) which was not identified.

The identification of all the constituents of the neutral mixtures in the above reactions is now in progress.

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[*Received, January 18th,* 1954.]