

205. β -Aroylpropionic Acids. Part XI.* The Action of Grignard Reagents on Phenylsuccinic Anhydride.

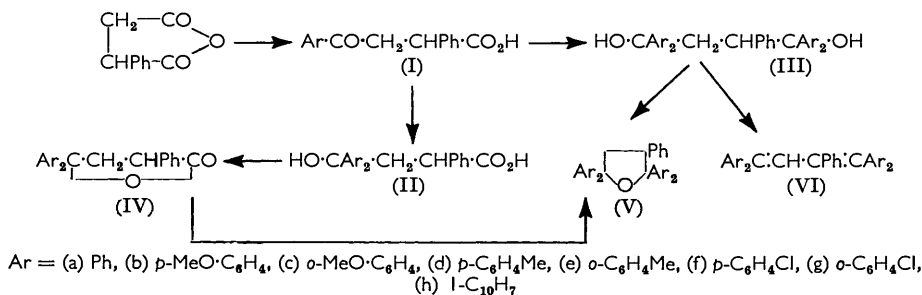
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Arylmagnesium halides with phenylsuccinic anhydride give β -aroyl- α -phenylpropionic acid (I), $\gamma\gamma$ -diaryl- γ -hydroxy- α -phenylbutyric acid (II), isolated as its lactone (IV), and a neutral product from which a tetrahydrofuran (V) has been isolated. The same products are obtained when the anhydride is replaced by the β -aroyl- α -phenylpropionic acid corresponding to the Grignard reagent. However, arylmagnesium halides with β -aroyl- α -phenylpropionic esters or with diethyl phenylsuccinate give 3 : 3-diaryl-1-phenylprop-2-ene-1-carboxylic acids.

Propene-acids isomerise irreversibly to the lactones.

PREVIOUS work on methylsuccinic anhydride¹ has been extended to phenylsuccinic anhydride. Contrary to Weizmann *et al.*,² phenylmagnesium bromide with phenylsuccinic anhydride gave the lactone (IVa) and the furan (Va), but naphthylmagnesium bromide gave the keto-acid (Ih) and the lactone (IVh).

Similarly, when one or two mols. of *o*- or *p*-methoxyphenyl-, *o*- or *p*-tolyl-, or *o*- or *p*-chlorophenyl-magnesium bromide reacted with phenylsuccinic anhydride they gave the β -aroyl- α -phenylpropionic acid (I), the $\gamma\gamma$ -diaryl- γ -hydroxy- α -phenylbutyric acid (II) [isolated as its lactone (IV)], and a neutral product, from which a 2 : 2 : 5 : 5-tetra-aryl-tetrahydro-3-phenylfuran (V) was isolated (see Table I).



However, although the neutral product isolated in the former case, gave analytical figures corresponding to 1 : 1 : 4 : 4-tetra-*p*-methoxyphenyl-2-phenylbuta-1 : 3-diene (VIb), its absorption spectrum (λ_{max} 291 m μ , ϵ 51,990) was different from that of 1 : 1 : 4 : 4-tetra-*p*-methoxyphenyl-but-1 : 3-diene,³ and this threw some doubt on its structure which needs further investigation.

The structure of the β -aroyl- α -phenylpropionic acids was confirmed by the fact that they gave pyrylium salts,⁴ and the β -benzoyl-, β -*p*-toluoyl-, and β -*p*-methoxybenzoyl-acids were identical with authentic specimens. The structure of the lactones and furans was established by identity with the products obtained when phenylsuccinic anhydride was replaced by β -aroyl- α -phenylpropionic acids (I). The lactones (IVa, d, and f) with arylmagnesium halides gave the 2 : 2 : 5 : 5-tetra-aryltetrahydro-3-phenylfurans (Va, d, and f, respectively).

When β -aroyl- α -phenylpropionic esters (VIIa, b, and c) were used instead of the

* Part X, *J.*, preceding paper.

¹ Baddar, El-Assal, and Habashi, *J.*, 1957, 1690.

² Weizmann, Blum-Bergmann, and Bergmann, *J.*, 1935, 1370.

³ Baddar and Sawires, *J.*, 1955, 4469.

⁴ Wali, Khalil, Bhatia, and Ahmad, *Proc. Indian Acad. Sci.*, 1941, **14**, A, 139; Desai and Wali, *ibid.*, 1937, **6**, A, 135.

When in this reaction phenylmagnesium bromide was treated with β -benzoyl- β -phenylpropionic acid even under more drastic conditions, the keto-acid was recovered unchanged.

Action of Grignard Reagents on γ -Diaryl- α -phenylbutyrolactones.—The experiment was

TABLE 2.

Compd.	M. p.	Solv. for cryst.*	Formula	Found (%)			Required (%)		
				C	H	Cl	C	H	Cl
Ib	149° ^a	A	C ₁₇ H ₁₆ O ₄	—	—	—	—	—	—
IVb	132	A	C ₂₄ H ₂₂ O ₄	76.4	5.8	—	77.0	5.9	—
VIb?	262	B	C ₃₆ H ₃₄ O ₄	82.6	6.1	—	82.3	6.2	—
Ic	152	A	C ₁₇ H ₁₆ O ₄	71.6	5.7	—	71.8	5.7	—
IVc	172	A	C ₂₄ H ₂₂ O ₄	76.9	5.9	—	77.0	5.9	—
Vc	208	B	C ₃₆ H ₃₆ O ₅	78.9	6.3	—	78.7	6.3	—
Id	151 ^b	A	C ₁₇ H ₁₆ O ₃	—	—	—	—	—	—
IVd	142	A	C ₂₄ H ₂₂ O ₂	83.8	6.3	—	84.2	6.5	—
Vd	228	B	C ₃₆ H ₃₆ O	89.9	7.2	—	89.7	7.1	—
Ie	116	A	C ₁₇ H ₁₆ O ₃	75.6	6.0	—	76.1	6.0	—
IVe	125	A	C ₂₄ H ₂₂ O ₂	84.1	6.5	—	84.2	6.5	—
Ve	Oil	—	—	—	—	—	—	—	—
If	160	A	C ₁₆ H ₁₅ O ₃ Cl	67.1	4.4	12.1	66.5	4.5	12.3
IVf	181	A	C ₂₂ H ₁₆ O ₂ Cl ₂	69.0	4.3	18.0	68.9	4.2	18.5
Vf	202	B	C ₃₄ H ₂₄ OCl ₄	69.0	4.1	23.8	69.1	4.1	24.1
Ig	112	A	C ₁₆ H ₁₅ O ₃ Cl	66.3	4.4	12.6	66.5	4.5	12.3
IVg	172	A	C ₂₂ H ₁₆ O ₂ Cl ₂	68.8	4.1	18.0	68.9	4.2	18.5
Vg	Oil	—	—	—	—	—	—	—	—
Ih	142	A	C ₂₀ H ₁₆ O ₃	78.7	5.2	—	78.9	5.3	—
IVh	211	A	C ₃₀ H ₂₂ O ₂	86.9	5.4	—	86.9	5.4	—
Vh	Oil	—	—	—	—	—	—	—	—

* A, Benzene—light petroleum (b. p. 40—60°). B, Acetic acid. ? Structure not rigidly established.

^a Identical with an authentic specimen (Allen and Frame, *Canad. J. Res.*, 1932, **6**, 605. ^b Identical with an authentic specimen (Desai *et al.*⁴).

TABLE 3.

Reactants			Products		
Ar in ArMgX	(g. = 1 mol.)	Keto-acid (g. = 1 mol.)	Unchanged keto-acid (g.)	Lactone (g.)	Neutral (g.)
Ph	7.5	Ia 10.5	2.0	IVa 2.5	Va 1.1
<i>p</i> -MeO·C ₆ H ₄	9.3	Ib 12.4	1.2	IVb 3.1	VIb(?) 2.5
<i>o</i> -MeO·C ₆ H ₄	9.3	Ic 12.4	2.6	IVc 3.8	Vc 2.2
<i>p</i> -C ₆ H ₄ Me	9.7	Id 13.4	3.8	IVd 4.1	Vd 1.9
<i>o</i> -C ₆ H ₄ Me	9.7	Ie 13.4	3.2	IVe 3.6	Ve 2.1
<i>p</i> -C ₆ H ₄ Cl	9.5	If 12.7	2.4	IVf 3.7	Vf 2.8
<i>o</i> -C ₆ H ₄ Cl	9.5	Ig 12.7	2.8	IVg 2.9	Vg 3.1
1-C ₁₀ H ₇	11.6	Ih 15.2	4.1	IVh 3.8	Vh 3.6

repeated in the usual manner with γ -diaryl- α -phenylbutyrolactones (1 mol.) instead of phenylsuccinic anhydride. The alkaline extract gave no precipitate on acidification, indicating the absence of acid. Only the neutral product was obtained, as in Table 4.

TABLE 4.

Reactants		Neutral product, g.
Ar in ArMgX, g.	Lactone (g. = 1 mol.)	
Ph	IVa 13.0	Va 10.2
<i>p</i> -C ₆ H ₄ Me	IVd 16.5	Vd 8.1
<i>p</i> -C ₆ H ₄ Cl	IVf 17.0	Vf 7.8

Action of Grignard Reagents on Ethyl β -Aroyl- α -phenylpropionate.—(i) *Action of phenylmagnesium bromide on ethyl γ -oxo- α -diphenylbutyrate.* The Grignard reagent [from bromobenzene (7.8 g., 1 mol.)] was added to a benzene solution (60 ml.) of ethyl γ -oxo- α -diphenylbutyrate (14.1 g., 1 mol.), and the mixture worked up as usual. The acid (ca. 2.4 g.), precipitated from the sodium hydroxide extract, crystallised from benzene—light petroleum (b. p. 40—60°) to give 1:3:3-triphenylprop-2-ene-1-carboxylic acid (VIIIa), m. p. 166° (Found: C, 83.9; H, 5.9. C₂₂H₁₈O₂ requires C, 84.0; H, 5.8%). It discharged the colour of alkaline potassium permanganate.

The neutral fraction (*ca.* 1.6 g.) was boiled with sodium hydroxide solution, then refluxed with glacial acetic acid for 1 hr., and left to crystallise, giving tetrahydro-2 : 2 : 3 : 5 : 5-penta-phenylfuran (Va), m. p. and mixed m. p. 180°.

(ii) A similar experiment with *p*-methoxyphenylmagnesium bromide and ethyl γ -*p*-methoxyphenyl- γ -oxo- α -phenylbutyrate gave, as acid fraction (*ca.* 2.6 g.), 3 : 3-di-*p*-methoxyphenyl-1-phenylprop-2-ene-1-carboxylic acid (VIIIb), m. p. 141° [from benzene-light petroleum (b. p. 40–60°)] (Found: C, 77.3; H, 6.0. C₂₄H₂₂O₄ requires C, 77.0; H, 5.9%). It discharged the colour of alkaline potassium permanganate.

The neutral fraction (*ca.* 2.0 g.) gave the same product, m. p. and mixed m. p. 262°, as in the case of phenylsuccinic anhydride.

(iii) A similar experiment with *p*-chlorophenylmagnesium bromide and ethyl γ -*p*-chlorophenyl- γ -oxo- α -phenylbutyrate gave 3 : 3-di-*p*-chlorophenyl-1-phenylprop-2-ene-1-carboxylic acid (*ca.* 1.6 g.) (VIIIc), m. p. 200° [from benzene-light petroleum (b. p. 40–60°)] (Found: C, 68.8; H, 4.4; Cl, 18.3. C₂₂H₁₆O₂Cl₂ requires C, 68.9; H, 4.2; Cl, 18.5%) (discharged the colour of alkaline potassium permanganate), and tetrahydro-2 : 2 : 5 : 5-tetra-*p*-chlorophenyl-3-phenylfuran (Vf) (*ca.* 2.1 g.), m. p. and mixed m. p. 202°.

Action of Grignard Reagents on Diethyl Phenylsuccinate.—Similar experiments with 2 mols. of the Grignard reagent and diethyl phenylsuccinate (1 mol.) gave the same propene-acids (cf. Table 5).

TABLE 5.

Reactants			Products			
Ar in ArMgX, g. = 2 mols.		Et ₂ phenyl- succinate (g.)	Propene acid, g.		Neutral, g.	
Ph	15.7	12.5	VIIIa	1.5	Va	2.5
<i>p</i> -MeO·C ₆ H ₄	18.6	12.5	VIIIb	1.2	VIIb	0.9?
<i>p</i> -C ₆ H ₄ Cl	19.0	12.5	VIIIc	0.8	Vf	1.0

Isomerisation of the Propene-acids to the Lactones.—When 1 : 3 : 3-triphenyl-, 3 : 3-di-*p*-methoxyphenyl-1-phenyl-, and 3 : 3-di-*p*-chlorophenyl-1-phenyl-prop-2-ene-1-carboxylic acid were dissolved in the least amount of boiling concentrated hydrochloric acid-acetic acid (1 : 1 v/v) and refluxed for 6 hr., they were converted almost quantitatively into the lactones, identified by their m. p.s and mixed m. p.s.

$\alpha\gamma\gamma$ -Triphenyl-, $\gamma\gamma$ -di-*p*-methoxy-phenyl- α -phenyl-, and $\gamma\gamma$ -di-*p*-chlorophenyl- α -phenyl-butyrolactone were unaffected when similarly treated.

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