The Catalysed Reactions of Simple Aromatic Compounds with Ethylenic Systems. Part III. Substituted Acrylic Acids.*

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The studies recorded in Part II * of this series have been extended to the behaviour of further substituted acrylic acids with benzene in the presence of anhydrous aluminium chloride as catalyst, and the results are presented in summarised form. Moreover, the reaction of phenylated aliphatic acids with chlorobenzene, a related problem, has been examined. An interpretation of the addition and replacement reactions is offered.

The first systematic examination of the reactions of unsaturated acids (including substituted cinnamic acids) with benzene under the influence of anhydrous aluminium chloride was by Eijkman (*Chem. Weekblad*, 1907, **4**, 727; 1908, **5**, 655). Addition of an aryl group fron the solvent to the ethylenic linkage was reported in most cases, and with αβ-unsaturated acids this occurred at the β-carbon, except in the cases of ββ-dimethyl- and α-phenyl-acrylic acids, where α-addition was claimed. It has since been shown (Hoffman, *J. Amer. Chem. Soc.*, 1929, **51**, 2542; Bergmann, Taubadel, and Weiss, *Ber.*, 1931, **64**, 1493) that the phenyl*iso*valeric acid obtained by Eijkman from ββ-dimethylacrylic acid is actually the product of β-aryl addition, and similar additions have since been demonstrated by Smith and Pritchard (*J. Amer. Chem. Soc.*, 1940, **62**, 771) with *ψ*-cumene, hemimellitene, *p*-xylene, and mesitylene ($AlCl_3$). In their experiment Bergmann *et al.* (*loc. cit.*) reported a second acid product, but using milder conditions we have obtained only a high yield of β-phenyl*iso*valeric acid (Expt. 1, see Table).

On the other hand, Eijkman's claim of α-aryl addition in the reaction of α-phenylacrylic (atropic) acid with benzene has been confirmed by us, but only by using his experimental conditions (Expt. 4); the slow reaction encountered here contrasts with the readiness of addition of benzene to the β-phenyl isomer (see Dippy and Young, *J.*, 1952, 1817). This is, therefore, the only substantiated instance of *α-aryl addition* in a reaction of this kind.

Addition of benzene to β-methyl-β-phenylacrylic acid to give ββ-diphenylbutyric acid in fair yield was reported by Bergmann, Taubadel, and Weiss (*loc. cit.*) using the conditions of Eijkman. In our experiment (Expt. 3), however, hydrogen transfer occurred chiefly, with some evidence of benzene addition (cf. the reaction of CPhMe=CH·COPh with benzene; Dippy and Palluel, *J.*, 1951, 1415); thus it appears that the dominating process here depends on the experimental conditions. It is noteworthy, also, that where *two* aryl groups occupy the β-position, hydrogen transfer occurs exclusively, ββ-diphenylpropionic acid thus being obtained in fair yield from ββ-diphenylacrylic acid (Expt. 2). A similar observation was made by Alexander, Jacoby, and Fuson (*J. Amer. Chem. Soc.*, 1935, **57**, 2208) who obtained ββ-diphenylpropionic acid on treating β-*p*-chlorophenylcinnamic acid with benzene ($AlCl_3$). This tendency to favour hydrogen transfer as the total bulk of the β-substituents increases may be interpreted in terms of steric hindrance, *i.e.*, the introduction of any other adduct than hydrogen is inhibited by a primary steric effect.

Fuson, Kozacik, and Eaton (*J. Amer. Chem. Soc.*, 1933, **55**, 3799) treated both *o*- and *p*-chlorocinnamic acid with benzene and chlorobenzene ($AlCl_3$) and recorded that, where benzene was used, the product was ββ-diphenylpropionic acid from both acids, whilst with chlorobenzene ββ-di-*p*-chlorophenylpropionic acid was obtained. With each of the chloro-substituted cinnamic acids, therefore, not only had the usual β-aryl additon occurred, but, also, the existing chlorophenyl group had been replaced by an aryl group supplied by the solvent; some confirmation of this was provided by Pfeiffer, Jenning, and Stöcker (*Annalen*, 1949, **563**, 73). The experiments of Fuson *et al.* (*loc. cit.*, 1933) represented the first examples of this type of replacement involving acids, although the general feature had previously been reported. Such reactions were designated by Fuson and his co-workers as

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* Part II, *J.*, 1952, 1817.

the "reversible addition of an aromatic compound to a conjugated system" and this description has been used by later authors referring to this kind of process. To derive more information concerning the behaviour of acids of this type under such conditions, the reactions of *p*-methyl-, *p*-methoxy-, *o*-chloro-, and *m*-nitro-cinnamic acid with benzene ($AlCl_3$) have been examined by us; our aim, where possible, was to arrest the reactions at the addition stage.

Reactions of substituted acrylic acids with benzene.

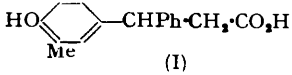
Expt. no.	Unsaturated acid [1]	Reaction procedure [2]	Product	Yield (%)	Type of reaction
1	$CMe_2=CH\cdot CO_2H$	(b)	$CMe_2Ph\cdot CH_2\cdot CO_2H$	94	*β*-Aryl addition
2	$CPh_2=CH\cdot CO_2H$	(b)	$CHPh_2\cdot CH_2\cdot CO_2H$	55	Hydrogen transfer
3	$CMePh=CH\cdot CO_2H$	(b)	$CHMePh\cdot CH_2\cdot CO_2H$ (some evidence of $CMePh_2\cdot CH_2\cdot CO_2H$)	42	Principally hydrogen transfer
4	$CH_2=CPh\cdot CO_2H$	[3]	$CMePh_2\cdot CO_2H$	*ca.* 10	*α*-Aryl addition
5	,,	(a)	None	—	None
6	*p*-$C_6H_4Me\cdot CH=CH\cdot CO_2H$	(b)	$CHPh_2\cdot CH_2\cdot CO_2H$	75	*β*-Aryl addition with replacement
7	,,	(a)	$CHPh_2\cdot CH_2\cdot CO_2H$	100	
8	*o*-$C_6H_4Cl\cdot CH=CH\cdot CO_2H$	(a)	*cis*-*o*-$C_6H_4Cl\cdot CH=CH\cdot CO_2H$	38	*trans*–*cis*-Isomerisation
9	,,	(c)	*o*-$C_6H_4Cl\cdot CHPh\cdot CH_2CO_2H$	[6]	*β*-Aryl addition
10	,,	[4]	*o*-$C_6H_4Cl\cdot CHPh\cdot CH_2CO_2H$	18	
11	*p*-$MeO\cdot C_6H_4\cdot CH=CH\cdot CO_2H$	(b)	*cis*-*p*-$MeO\cdot C_6H_4\cdot CH=CH\cdot CO_2H$	[6]	*trans*–*cis*-Isomerisation
12	,,	(b) [5]	$HO\cdot C_6H_3Me\cdot CHPh\cdot CH_2\cdot CO_2H$	29	*β*-Aryl addition with isomeric rearrangement

[1] All cinnamic acids were ordinary *trans*-modifications. [2] Reaction procedures (a), (b), (c), and (d) refer to experimental conditions established in Part II of this series. [3] Using the procedure of Eijkman (*loc. cit.*). [4] Using the procedure of Fuson, Kozacik, and Eaton (*J. Amer. Chem. Soc.*, 1933, **55**, 3799). [5] Larger proportion of catalyst. [6] High losses on recrystallisation.

The production of ββ-diphenylpropionic acid ("addition plus replacement" reaction) from *p*-methylcinnamic acid and benzene ($AlCl_3$) (Expts. 6 and 7) was in accordance with expectation since it compares with replacement of the *p*-tolyl group in an analogous unsaturated ketone (Eaton, Black, and Fuson, *J. Amer. Chem. Soc.*, 1934, **56**, 687); application of milder conditions (Expt. 7), however, failed to give the product of intermediate addition. It is noteworthy that whereas replacement of *p*-tolyl by phenyl is effected readily, replacement of phenyl by *p*-tolyl under the same experimental conditions (cf. Dippy and Young, *loc. cit.*) does not occur. Since the primary addition product is presumably the same in each case, this difference in behaviour seems to be a function of the two benzenoid solvents in the replacement process.

In the reaction between *o*-chlorocinnamic acid and benzene ($AlCl_3$), Fuson and his collaborators (*loc. cit.*, 1933) did not isolate an addition product, and, in our attempt to achieve this, under mild conditions [procedure (a), Expt. 8], *cis*-*o*-chlorocinnamic acid was produced (see Dippy, McGhie, and Young, *Chem. and Ind.*, 1952, 195). Nevertheless, the simple adduct, β-*o*-chlorophenyl-β-phenylpropionic acid was obtained by alternative procedures (Expts. 9 and 10); no replacement product arose in these experiments.

When *p*-methoxycinnamic acid was treated with benzene ($AlCl_3$) (Expt. 11), a solid separated on addition of the catalyst, from which a small quantity of a very labile acid, considered to be *cis*-*p*-methoxycinnamic acid, was isolated. The experiment was repeated with a higher proportion of catalyst (Expt. 12), and an acid was then recovered which was ***not*** identical with β-*p*-methoxyphenyl-β-phenylpropionic acid (obtained from anisole and cinnamic acid), although of the same m. p. and equivalent weight. From a consideration of the strength of this acid and those of acids of related constitution, the compound under review was assigned the constitution (I), a product of isomeric rearrangement. The following approximate values of dissociation constant (10^5K) were determined conductimetrically in water at 25°: $Ph_2CH\cdot CH_2\cdot CO_2H$, 3·2; *p*-$MeO\cdot C_6H_4\cdot CHPh\cdot CH_2\cdot CO_2H$, 3·0; the acid (I), 2·15. The low value in the last case excludes the possibility of there having been α-aryl addition because the nearer is the situation of phenyl to carboxyl the stronger is the acid (cf. $Ph_2CH{\cdot}CO_2H$, 11·15 × 10^{-5}); thus a ββ-diarylpropionic system is indicated for the acid (I). Moreover, it can be expected that *p*-hydroxyl will be more effective than *p*-methoxyl in depressing acid strength, and that the existence of *m*-methyl will reduce *K* still further (see Dippy, *Chem. Rev.*, 1939, **25**, 151).



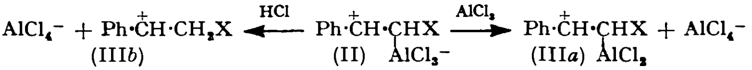
(I)

With *m*-nitrocinnamic acid no reaction took place. Since in this case aluminium chloride separated as a complex with the acid, reaction was attempted with a large excess of catalyst, but without result.

The use of anhydrous stannic chloride and titanium tetrachloride as catalysts was explored with cinnamic acid and benzene as reactants to no effect, although aluminium bromide gave an excellent yield of ββ-diphenylpropionic acid.

The mode of addition with substituted acrylic acids, as with αβ-unsaturated ketones (Dippy and Palluel, *loc. cit.*), is best regarded as nucleophilic attachment of the aromatic addendum to the carbon atom carrying the positive charge in a carbonium cation (III*a* or *b*) derived from the unsaturated acid under the influence of aluminium chloride. Normally this atom is the β-carbon in consequence of the polar character of carboxyl (−*I* − *M*). Nevertheless, one exceptional case of α-aryl attachment occurs, *viz.*, when atropic acid is used; this must be ascribed to the strong electron-release capacity (+*M*) of the phenyl group which at the α-position competes so effectively with the influence of carboxyl as to alter the polarity of the ethylene link. In other unsaturated acids under review phenyl, carried by the β-carbon, serves to augment the polarising influence of carboxyl; the β-carbon in such a case has therefore a relatively low electron density and so β-aryl orientation occurs, as the proposed mechanism (below) serves to ensure.

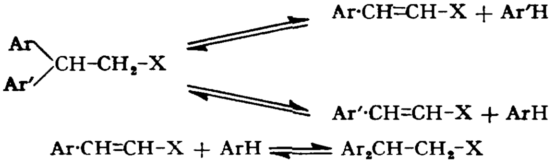
In the following scheme the promotion of a reactive cation is illustrated in terms of cinnamic acid (X represents the carboxyl group which has undergone reaction with aluminium chloride, an excess of which has been provided):



$$\mathrm{AlCl_4^-} + \underset{\text{(III}b\text{)}}{\mathrm{Ph{\cdot}\overset{+}{C}H{\cdot}CH_2X}} \xleftarrow{\mathrm{HCl}} \underset{\text{(II)}}{\mathrm{Ph{\cdot}\overset{+}{C}H{\cdot}\underset{AlCl_3^-}{C}HX}} \xrightarrow{\mathrm{AlCl_3}} \underset{\text{(III}a\text{)}}{\mathrm{Ph{\cdot}\overset{+}{C}H{\cdot}\underset{AlCl_3}{C}HX}} + \mathrm{AlCl_4^-}$$

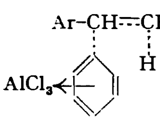
The use of hydrogen chloride as an alternative to aluminium chloride in the production of the cation from (II) is justified since hydrogen chloride is inevitably present during reaction. In the unique case of atropic acid the β-carbon atom becomes associated with the aluminium chloride, and here, therefore, the reactive centre of the eventual cation is the α-carbon atom.

The replacement reaction of the kind involved in the conversion of *p*-methylcinnamic acid into ββ-diphenylpropionic acid is not unusual. It was encountered in the reaction of cinnamic acid with chlorobenzene (Dippy and Young, *loc. cit.*) and by Fuson, Kozacik, and Eaton (*loc. cit.*) with chlorocinnamic acids and benzene. Probably the first case of this type of reaction was the conversion of ω-*p*-chlorobenzylidenequinalidine into 2-(2 : 2-diphenylethyl)quinoline by means of benzene and aluminium chloride (Hoffman, Farlow, and Fuson, *J. Amer. Chem. Soc.*, 1933, **55**, 2000). Other examples have since come to light involving unsaturated ketone, stilbene, and lepidine systems (Fuson *et al.*, *ibid.*, 1934, **56**, 687, 1241, 2103; 1936, **58**, 1979; Fuson and Cooke, *J. Amer. Chem. Soc.*, 1951, **73**, 3515; Dippy and Palluel, *loc. cit.*). It has been shown that in such reactions addition first occurs to give a saturated compound, followed by the slower replacement process, although so far only unsubstituted aryl (usually phenyl) or halogenophenyl groups have shown themselves capable of entering or of being withdrawn in this process (see Dippy and Young, *loc. cit.*). In all cases, a large excess of benzenoid solvent (ArH) is used, and this effects a favourable displacement of the following addition–elimination equilibria (first proposed by Fuson and his collaborators):



$$\mathrm{Ar{\cdot}CH{=}CH{-}X + ArH \rightleftharpoons Ar_2CH{-}CH_2{-}X}$$

It is significant that we have been unable to observe exchange of aryl groups in the case of diphenylacetic acid and chlorobenzene, whereas, on the other hand, γγ-diphenyl-*n*-butyric acid in the same medium has yielded γγ-di-*p*-chlorophenyl-*n*-butyric acid. Further, replacement of the phenyl group by chlorophenyl could not be effected with (i) phenylacetic acid, (ii) deoxybenzoin, or (iii) β-phenylpropionic acid. These observations when added to the available information seem to imply that exchange occurs only with *gem*-diaryl groups and that these must occupy a position not less remote (from X) than the β-position. The need for a *gem*-diaryl system is possibly connected with the need for stabilisation of the ethylenic link (for which the residual aryl group provides) in the elimination process which, in the transition state (IV), might be represented as inset, where the electron-deficient $AlCl_3$ engages in a π-bond with an aryl group, the eventual withdrawal of which is effected, accompanied by loss of hydrogen (as proton) from the α-position. The replacement of aryl groups in γγ-diphenylbutyric acid might involve an elimination of proton from either α- or β-carbon atom, as the system is capable of three-carbon prototropy.



(IV)

EXPERIMENTAL

Reactions of Substituted Acrylic Acids with Benzene.—*ββ-Dimethylacrylic* (*3-methylbut-2-enoic*) *acid.* Procedure (b). ββ-Dimethylacrylic acid (20 g.), benzene (400 ml.), and aluminium chloride (50 g.) gave β-phenyl*iso*valeric acid (33·0 g.), m. p. 57—58° after recrystallisation from aqueous ethanol (Hoffman, *loc. cit.*, records m. p. 57·5—58·5°) (Found : equiv., 178. Calc. for $C_{11}H_{14}O_2$: equiv., 178) (anilide, m. p. 121°; Hoffman, *loc. cit.*, gives m. p. 122—123°).

β-Methyl-β-phenylacrylic (*3-phenylbut-2-enoic*) *acid.* Procedure (b). This acid (4 g.), benzene (100 ml.), and aluminium chloride (6 g.) yielded β-phenyl-*n*-butyric acid (1·7 g.), b. p. 142°/1 mm.; slow evaporation of a solution in light petroleum (b. p. 100—120°) gave crystals, m. p. 37° (Eijkman, *loc. cit.*, gives m. p. 37—38°, b. p. 140—145°/3 mm.) (Found : equiv., 165. Calc. for $C_{10}H_{12}O_2$: equiv., 164). A further acid fraction (0·3 g.), b. p. 180—190°/2 mm. (equiv., 193), could not be crystallised (probably β-phenyl-*n*-butyric acid mixed with some ββ-diphenyl-*n*-butyric acid).

ββ-Diphenylacrylic acid. Procedure (b). ββ-Diphenylacrylic acid (0·9 g.), benzene (10 ml.), and aluminium chloride (1 g.) yielded ββ-diphenylpropionic acid (0·5 g.), m. p. and mixed m. p. 156° (Pfeiffer and de Waal, *Annalen*, 1935, **520**, 185, give m. p. 154—155°).

α-Phenylacrylic acid (method of Eijkman, *loc. cit.*). α-Phenylacrylic acid (0·5 g.), benzene (3·3 ml.), and aluminium chloride (0·5 g., 1·1 mols. with respect to the acid) after 3 weeks gave a crude product (0·21 g.) from which αα-diphenylpropionic acid, m. p. 172°, was obtained by recrystallisation from aqueous ethanol [the structure of this acid has been fully established and the m. p. 173° recorded by Thörner and Zincke (*Ber.*, 1878, **11**, 1993), Bateman, and Marvel (*J. Amer. Chem. Soc.*, 1927, **49**, 2917), and Ziegler and Schnell (*Annalen*, 1924, **437**, 243)].

No reaction occurred by use of procedure (a).

p-*Methylcinnamic acid.* Procedure (b). *p*-Methylcinnamic acid (4 g.), benzene (100 ml.), and anhydrous aluminium chloride (6 g.) gave ββ-diphenylpropionic acid (4·2 g.), m. p. 156°. The same result was obtained with procedure (a).

o-*Chlorocinnamic acid.* Procedure (a). Ordinary *o*-chlorocinnamic acid (4·5 g.), benzene (90 ml.), and aluminium chloride (6 g.) gave *cis*-*o*-chlorocinnamic acid [recrystallised from benzene–light petroleum (b. p. 100—120°)], m. p. 128—129° (Stoermer *et al.*, *Ber.*, 1911, **44**, 637, record m. p. 127°) (1·7 g.) (Found : C, 59·8; H, 4·0; Cl, 19·4. Calc. for $C_9H_7O_2Cl$: C, 59·2; H, 3·9; Cl, 19·4%) (amide, m. p. 114°; Stoermer, *loc. cit.*, gives m. p. 112°). This acid decolorised cold aqueous alkaline potassium permanganate and produced an odour of aromatic aldehyde on warming. Exposure of a solution in acetic acid to ultraviolet light (*ca.* 20 hr.) raised the m. p. of the acid by 20—40°.

o-Chlorocinnamic acid (0·2 g.) and benzene by the method of Fuson, Kozacik, and Eaton (*loc. cit.*) did not yield the expected ββ-diphenylpropionic acid but instead β-o-*chlorophenyl*-β-*phenylpropionic acid* (0·05 g.) which recrystallised from aqueous ethanol in colourless needles, m. p. 133° (Found : C, 70·2; H, 5·0. $C_{15}H_{13}O_2Cl$ requires C, 69·1; H, 5·0%). (The presence of chlorine was demonstrated qualitatively, as in other similar cases described in this paper.) This acid is so sparingly soluble in water that the determination of its strength in this medium led only to a very approximate value of K of the order 2×10^{-5} which, however, suffices (on comparison with the known data for reference acids in water) to demonstrate that both aryl groups are carried by the β-carbon atom.

Procedure (c), applied to the same quantities of reactants as in (a) above, gave crude β-*o*-chlorophenyl-β-phenylpropionic acid (5·5 g.) but recrystallisation losses were high.

p-*Methoxycinnamic acid.* Procedure (b). *p*-Methoxycinnamic acid (2·25 g.), benzene (55 ml.), and aluminium chloride (3 g.) were used. A bright yellow intermediate separated which remained after warming to 45° and stirring at intervals over 2 days at room temperature. The solid recovered after pouring on ice was treated with concentrated hydrochloric acid to give a pale-yellow viscous oil (2 g.) from which a somewhat pasty solid, m. p. 48—52°, was obtained after crystallisation from benzene–light petroleum (b. p. 60—80°) (Roth and Stoermer, *Ber.*, 1913, **46**, 260, give the m. p. of *cis*-*p*-methoxycinnamic acid as 66°). Slow evaporation of a solution in the same solvent during several weeks in ordinary light gave the normal *trans*-*p*-methoxycinnamic acid, m. p. and mixed m. p. 168°.

Procedure (b) was repeated, except that a much higher proportion of aluminium chloride was used. *p*-Methoxycinnamic acid (1·2 g.), benzene (40 ml.), and aluminium chloride (4·3 g., *ca.* 5 mols. with respect to the acid) gave a crude colourless product (0·5 g.) which on crystallisation twice from benzene–light petroleum (b. p. 100—120°) and twice from aqueous acetic acid gave colourless needles, m. p. 123° (10^5K, 2·15) to which the constitutionβ-4 -*hydroxy*-3-*methylphenyl*-β-*phenylpropionic acid* is assigned [admixed m. p. 96—106° with β-*p*-methoxyphenyl-β-phenylpropionic acid (Dippy and Young, *loc. cit.*), m. p. 122°; 10^5K, 3·0] (Found: C, 74·4; H, 6·3%; equiv., 256. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%; equiv., 256).

Reaction between γγ-Diphenyl-n-*butyric acid and Chlorobenzene.*—The procedure followed was that employed by Dippy and Young (*loc. cit.*) for the reaction between ββ-diphenylpropionic acid and chlorobenzene. From γγ-diphenylbutyric acid (2 g.), chlorobenzene (240 ml.), and aluminium chloride (11 g.) a yellow oil (2·6 g.) was obtained which on esterification gave ***methyl* γγ-*di*-p-*chlorophenylbutyrate*** (1·46 g.), a pale-yellow viscous liquid, b. p. 203—207°/5 mm. (Found: C, 63·7; H, 5·4. $C_{17}H_{16}O_2Cl_2$ requires C, 63·2; H, 5·0%). Direct fractional distillation of the crude acid product gave γγ-di-*p*-chlorophenylbutyric acid as an uncrystallisable pale-brown gum, b. p. 220—230°/3 mm.; oxidation of this with potassium permanganate yielded 4 : 4′-dichlorobenzophenone, m. p. 142—143° (Eaton, Black, and Fuson, *loc. cit.*, give 142—143°).

By a similar procedure (i) phenylacetic acid, (ii) diphenylacetic acid, (iii) β-phenylpropionic acid, and (iv) deoxybenzoin were treated, in turn, with chlorobenzene but no exchange of aryl groups was observed, *i.e.*, the starting material was recovered unchanged in each case.

The materials used in the course of this investigation were prepared by established methods except for the following, where adaptations were made.

ββ-*Diphenylacrylic Acid.*—Ethyl β-hydroxy-ββ-diphenylpropionate (5 g., 1 mol.), phosphoric oxide (3·28 g., 1·25 mol.), and benzene (15 ml.) were refluxed for 3 hr. (cf. Kon and Nargund, *J.*, 1932, 2461), whereupon ββ-diphenylacrylic acid was obtained (2·5 g.), having m. p. 161° (Rupe, *Annalen*, 1913, **395**, 136, reported m. p. 162°). Subsequent reduction with Raney nickel in aqueous alkali (cf. Papa, Schwenk, and Breiger, *J. Org. Chem.*, 1949, **14**, 366) gave ββ-diphenylpropionic acid, m. p. 156°.

γγ-*Diphenyl*-n-*butyric Acid.*—This was obtained by a Stobbe condensation. Diethyl succinate (13 g.), benzophenone (9·1 g.), and potassium *tert.*-butoxide gave a product which upon decarbethoxylation yielded a mixture of γγ-diphenylbutyrolactone and γγ-diphenylvinylacetic acid (Johnson, Petersen, and Schneider, *J. Amer. Chem. Soc.*, 1947, **69**, 74). To this, potassium iodide (1·03 g.) and red phosphorus (3 g.) were added, followed by phosphoric acid (*d* 1·75) (35 ml.) and water (5 ml.), and the mixture was refluxed for 6 hr. The whole was diluted with water and extracted with ether; the extract was washed with sodium hydrogen sulphite solution and water, and from it, after drying, pale brown crystals (9·3 g.) were recovered. These after recrystallisation from methanol and then light petroleum (b. p. 80—100°) gave γγ-diphenyl-*n*-butyric acid in colourless needles (4·7 g.), m. p. 105° (Ziegler, *Annalen*, 1929, **473**, 25, gives m. p. 105°) (Found: C, 79·9; H, 6·5%; equiv., 237. Calc. for $C_{16}H_{16}O_2$: C, 80·0; H, 6·7%; equiv., 240). A much poorer yield was given by the Arndt–Eistert process.

We are indebted to Mr. J. W. Laxton and Mr. L. G. Bray for the measurement of the strengths of the acids reported here. These determinations were made by a conductivity method already described (*J.*, 1954, 1470) and results refer to aqueous solution at 25°.

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