334. *The Catalysed Reactions of Simple Aromatic Compounds with Ethylenic Systems. Part II.* Cinnamic Acid.*

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The experimental conditions for the addition of benzene, toluene, anisole, fluorobenzene, chlorobenzene, and bromobenzene to cinnamic acid under the influence of anhydrous aluminium chloride have been investigated. The aromatic residue provided by the solvent is added at the β-carbon of the unsaturated acid in all cases, leading mostly to substantial yields of ββ-diphenylpropionic acids with the substituent in the *p*-position (uncertainty existing in the case of toluene). With chlorobenzene alone reaction proceeds further to give ββ-di-*p*-chlorophenylpropionic acid whereby the original phenyl group has been replaced by chlorophenyl. The same product was also obtained by the action of chlorobenzene on the unsubstituted diphenylpropionic acid, and, in this case, the fate of the displaced phenyl groups was established by the isolation of benzene.

ADDITION of simple aromatic compounds to unsaturated carboxylic acids in the presence of acid catalysts has been the subject of inquiry by several workers, most attention having been directed to long-chain aliphatic compounds. In a review of cases where anhydrous aluminium chloride was the catalyst, Thomas (" Anhydrous Aluminium Chloride in Organic Chemistry," 1941, pp. 468—469) observes that, except in the reactions with oleic acid, the reports are scanty and often contradictory; in some cases identification of the products is not completely satisfactory and, furthermore, the yields and the experimental conditions are often not recorded.

In the present paper, therefore, some catalysed reactions of cinnamic acid with simple aromatic compounds are reported. Cinnamic acid was first used in reactions of this kind by Liebermann and Hartmann (*Ber.*, 1891, **24**, 2582; 1892, **25**, 957, 2124); both the *trans*- and the *cis*-acid were treated with phenols, benzene, and *m*-xylene in the presence of concentrated sulphuric acid, leading to addition of the aryl group to the β-carbon of the acid. Karsten (*Ber.*, 1893, **26**, 1579) obtained similar results with toluene; Eijkman (*Chem. Weekblad*, 1907, **4**, 727; 1908, **5**, 655) in a systematic examination of the reactions of various unsaturated acids and lactones, with benzene (and, in a few cases, with toluene), using anhydrous aluminium chloride as catalyst, also reported that cinnamic acid and benzene gave ββ-diphenylpropionic acid, and Wislicenus and Eble (*Ber.*, 1917, **50**, 250) obtained this acid by similar means in almost quantitative yield at room temperature. Nevertheless, Marcusson (*Z. angew. Chem.*, 1920, **33**, 234) denied the occurrence of such reactions in systems where the double bond is adjacent to the carboxyl group, suggesting that, in these acids, the catalyst does not add to the double bond, thereby precluding condensation with benzene. Eijkman's general findings for cinnamic acid, however, have been confirmed by Pfeiffer and Waal (*Annalen*, 1935, **520**, 185), Koelsch *et al.* (*J. Amer. Chem. Soc.*, 1943, **65**, 59), Allen and Gates (*ibid.*, p. 422), and Dey and Ramanathan (*Proc. Nat. Inst. Sci. India*, 1943, **9**, 193), all using anhydrous aluminium chloride as the catalyst, and by Simons and Archer (*J. Amer. Chem. Soc.*, 1939, **61**, 1521) with anhydrous hydrogen fluoride. Widely varying reaction conditions and yields were recorded by these workers, so we sought to determine the most favourable method as well as to confirm that addition of the aryl group occurs exclusively at the β-position. The effect of using monosubstituted derivatives of benzene in place of benzene was also investigated, and our results are summarised in the Table.

The results for Expt. 1 agree in every respect with those of Wislicenus and Eble and of Eijkman (*locc. cit.*). The only product isolated by fractional crystallisation was ββ-diphenylpropionic acid. Since this acid is of synthetic value, we compared the effectiveness of Wislicenus and Eble's procedure with that of Pfeiffer and Waal (*loc. cit.*, and quoted in Shirley's " Preparation of Organic Intermediates," 1951, p. 137) (Expt. 2 in the Table).

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* Part I, *J.*, 1951, 1415.

The yields by the two processes were similar, but only $1\frac{1}{2}$ hours is required for completion of reaction in Expt. 1 as against 12 hours in Expt. 2.

Expt. no.	Benzenoid addendum	Procedure (see p. 1819)	Product	Yield (pure), %
1	C_6H_6	(*a*)	$CHPh_2{\cdot}CH_2{\cdot}CO_2H$	87
2	C_6H_6	*	$CHPh_2{\cdot}CH_2{\cdot}CO_2H$	91
3	PhCl	(*c*)	$p\text{-}C_6H_4Cl{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$	51
4	PhCl	(*d*)	$(p\text{-}C_6H_4Cl)_2CH{\cdot}CH_2{\cdot}CO_2H$	22
5	PhBr	(*d*)	$p\text{-}C_6H_4Br{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$	5
6	PhF	(*d*)	$p\text{-}C_6H_4F{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$	30
7	PhOMe	(*b*)	$p\text{-}C_6H_4(OMe){\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$	37
8	PhMe	(*a*)	$C_6H_4Me{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$	44
9	PhMe	(*b*)	$C_6H_4Me{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$	37

* By the procedure of Pfeiffer and Waal (*loc. cit.*).

The experimental details given by Marcusson (*loc. cit.*) for αβ-unsaturated acids are vague and his failure to obtain normal addition products could have been due to the use either of too high a reaction temperature, or of too little or too much catalyst. It is known that high temperatures promote cyclisation of these products of addition: *e.g.*, Koelsch *et al.* (*loc. cit.*) obtained 39% of 3-phenylindanone by heating cinnamic acid with benzene and 3·3 mols. of aluminium chloride for five hours. Eijkman first used an elevated temperature (*loc. cit.*, 1907) whereby he obtained indifferent results, but later (*loc. cit.*, 1908) claimed better success with milder conditions. Again, Schmidt (*J. Amer. Chem. Soc.*, 1930, **52**, 1172) found that the production of phenylstearic acid, by heating oleic acid and benzene in the presence of aluminium chloride, proceeded most favourably when equimolecular amounts of oleic acid and catalyst were used; excessive amounts of catalyst, or prolonged heating, gave products having low neutralization equivalents, but, on the other hand, with less than 0·33 mol. of catalyst little reaction occurred. Our own experience is similar because, in the presence of about 0·6 mol. of the catalyst, benzene does not add to cinnamic acid even after several days. There are indications that the aluminium chloride first added reacts with the carboxyl group leading to hydrogen chloride, and involving two molecular proportions of cinnamic acid and one of aluminium chloride.

The best conditions for promotion of the addition of a simple aromatic compound to cinnamic acid in the presence of aluminium chloride to give a ββ-diarylpropionic acid thus appear to be (i) the use of rather more than one mol. of the catalyst relative to the unsaturated acid (in practice, 1·5—2 mols. of technical anhydrous aluminium chloride is used, the reaction being cooled until addition of the catalyst is complete), and (ii) a relatively low reaction temperature (normally, the reaction mixtures are kept at room temperature, except where halogenated benzenes are used).

Anhydrous boron trifluoride was found to be ineffective as catalyst, recalling that Colonge and Pichat (*Bull. Soc. chim.*, 1949, Jan., p. 177; May, p. 142) showed boron trifluoride to be of no use in catalysing additions of benzenoid compounds to unsaturated ketones.

When cinnamic acid was treated with an excess of a *mono-substituted benzene* in the presence of anhydrous aluminium chloride (procedures *a*, *b*, and *c*) addition again occurred (Expt. 3 and 5—9), a *p*-substituted ββ-diphenylpropionic acid being produced. With cinnamic acid and chlorobenzene, however, we have succeeded in isolating also a *pp*′-disubstituted ββ-diphenylpropionic acid, in which an aryl group derived from the solvent has replaced the β-phenyl group of the initial addition product. For the addition reaction the conditions used by Wislicenus and Eble (*loc. cit.*) with benzene were ineffective, but when the reaction mixture was kept at 30—45° for one hour after introduction of the catalyst [procedure (*c*)], normal addition took place giving β-*p*-chlorophenyl-β-phenylpropionic acid. The product of subsequent replacement, *i.e.*, ββ-di-*p*-chlorophenylpropionic acid, was then obtained by prolonging the reaction for 2—3 days [procedure (*d*), Expt. 4]. It is noteworthy in this connection that Fuson, Kozacik, and Eaton (*J. Amer. Chem. Soc.*, 1933, **55**, 3799) with chlorocinnamic acids and chlorobenzene also used an elevated temperature in obtaining the product of replacement, whereas Allen and Gates (*loc. cit.*) secured only partial addition of bromobenzene to cinnamic acid at room temperature.

We also obtained ββ-di-*p*-chlorophenylpropionic acid from chlorobenzene and ββ-diphenylpropionic acid at room temperature in the presence of a large excess of aluminium chloride (*ca.* 10 mols.) with added hydrogen chloride. This is consistent with the results of Fuson and his co-workers with αβ-unsaturated ketones (*J. Amer. Chem. Soc.*, 1934, **56**, 687, 1241, 2103) where the step-wise nature of the addition and replacement reactions of Friedel–Crafts type was first demonstrated. Furthermore, we have established the fate of the displaced phenyl groups in the foregoing reaction by isolating benzene from the residual solvent after removal of the resultant acid. The only evidence concerning this aspect of the general problem hitherto provided was that of Fuson, Kozacik, and Eaton (*loc. cit.*) who identified bromobenzene in the solvent layer from the reaction between *p*-bromobenzylidenequinaldine and benzene by its conversion into a Grignard compound followed by treatment with phenyl *iso*cyanate to give benzanilide as the final product.

With fluorobenzene and bromobenzene we isolated β-*p*-fluoro- and β-*p*-bromo-phenyl-β-phenylpropionic acids but not the products of subsequent replacement. Anisole is added at the same temperature as benzene; no replacement of the phenyl group took place even after 3 days.

It was expected that toluene would react at least as readily as benzene. Addition alone has been shown to ensue, β-phenyl-β-tolylpropionic acid being obtained in good yield (Expt. 8) but apparently consisting of an intractable mixture of isomerides. Under conditions designed to promote the formation of the ultimate replacement product (Expt. 9) cinnamic acid and toluene yielded the same acid mixture although in diminished yield and accompanied by tars. Under similar conditions *p*-xylene gave evidence of some addition but phenylxylylpropionic acid could not be isolated.

Addition of the aryl group to the β-carbon atom in these reactions is consistent with the well-known additions to acrylic acid which do not conform to the Markownikoff rule on account of the strong polar influence of carboxyl group adjacent to the double bond. In cinnamic acid the opposing ambipolar phenyl group is a secondary influence on orientation of the addendum. This reaction has been described by Fuson, Kozacik, and Eaton (*loc. cit.*) as " a reversible Friedel–Crafts addition," and they suggest that the explanation of the replacement product should also involve equilibria of this kind. It is significant, however, that all recorded cases of this replacement involve the *gem*-diaryl group, and more investigation is needed on this and other aspects of the problem before any certain light can be shed on the course followed by either of the processes.

EXPERIMENTAL

Reactions of Benzenoid Compounds with Cinnamic Acid. Methods of Procedure.—Pure, dry reagents were employed throughout and the anhydrous aluminium chloride, of commercial quality (supplied by British Drug Houses Ltd., and Imperial Chemical Industries Limited), was stored in sealed bottles; different samples were given batch numbers, and, as far as possible, related experiments were conducted with catalyst of one batch. The reactions were carried out in all-glass apparatus under anhydrous conditions. The following procedures were employed:

(*a*) (Cf. Wislicenus and Eble, *loc. cit.*) The acid was stirred with excess of the benzenoid solvent, cooled to 0—5°, and powdered anhydrous aluminium chloride (about 1·8 mols. with respect to the acid) added in portions to the mixture, the temperature not rising above 10°. After 1 hour's stirring the whole was poured on crushed ice and hydrochloric acid to halt the reaction.

(*b*) As in (*a*), but after addition of the catalyst, the mixture was kept at room temperature for 2—3 days with stirring at intervals.

(*c*) As in (*a*), but after addition of the catalyst, the mixture was warmed to 30—45° for 1 hour, then poured directly on ice and hydrochloric acid.

(*d*) As in (*c*), but, after the heating, the mixture was set aside at room temperature for 2—3 days with occasional stirring.

Isolation of the Acid Product.—The reaction mixture produced by any of the above procedures was usually almost black and contained undissolved aluminium chloride. After the reaction had been halted, the mixture was stirred for at least 10 minutes to hydrolyse any catalyst complexes. The pale yellow solvent layer then usually separated sharply, and after its removal the aqueous acid layer was extracted twice with further solvent. The pooled extracts were washed twice with water, and the solvent was removed in steam (this is preferable to alkaline extraction of the solvent which tends to produce emulsions). The residue from the steam-distillation (usually brown) was dissolved in hot aqueous sodium carbonate, and the solution was filtered (if much solid remained) and clarified with charcoal. The deposit from the acidified filtrate was filtered off or extracted with ether. A high yield of almost colourless crude acid (*ca.* 90%) was obtained as a rule, but purification of this was mostly difficult. Several crystallisations were usually necessary (the acids tending to separate as oils); in obstinate cases, the acid was purified by distillation of the methyl ester.

Confirmation of Identity.—Equivalents were determined by direct titration (on the semi-micro-scale) with barium hydroxide solution. The presence of halogen was shown by application of the calcium oxide incineration test. Oxidation to the corresponding benzophenone was usually effected by boiling 1 g. of the acid for 6 hours with aqueous potassium permanganate (4 g. in 80 ml. of water), whereupon the ketone was recovered by steam-distillation.

Cinnamic Acid and Benzene.—*Procedure* (*a*). Cinnamic acid (15 g.), benzene (220 ml.), and aluminium chloride (25 g.) were used. As the catalyst was added the mixture became bright yellow and later dark brown, the acid dissolved, and hydrogen chloride was evolved. After working up, the eventual aqueous sodium carbonate extract was acidified, and the precipitate, on recrystallisation from ethanol, gave ββ-diphenylpropionic acid (20 g., 87%) in fine needles, m. p. 155° (Pfeiffer and Waal, *loc. cit.*, give m. p. 154—155°) (Found: equiv., 225. Calc. for $C_{15}H_{14}O_2$: equiv., 226). No other product could be isolated. The identity of the acid was confirmed by preparation of the amide, m. p. 125°, and by admixed m. p. with an authentic sample synthesised by an unambiguous route *via* a Reformatsky condensation.

By the method of Pfeiffer and Waal (loc. cit.). Cinnamic acid (15 g.) and benzene (180 ml.) were stirred together and cooled to $<10°$. Anhydrous aluminium chloride (6 g.) was added, and the mixture kept at 10—15° for 10 hours (with stirring), a further 24 g. of aluminium chloride being added, in four equal portions during this time (making a total of 30 g. of the catalyst, *i.e.*, about 2·2 mols. with respect to the acid). The whole was then poured into 300 ml. of water and 60 ml. of hydrochloric acid, and the mixture well shaken. The benzene was removed in steam, and the pale-brown, granular residue, after being heated with 600 ml. of water, was dissolved in aqueous sodium carbonate, and the solution was filtered. Acidification gave a precipitate which, after treatment again with water (600 ml.), gave ββ-diphenylpropionic acid (21 g., *i.e.*, 91%).

Procedure (*b*), *except that* 6 *days' storage was allowed.* Cinnamic acid (5 g.), benzene (70 ml.), and aluminium chloride (2·8 g., *ca.* 0·6 mol. with respect to the acid) yielded cinnamic acid (3·5 g.) as the only product.

Cinnamic Acid and Chlorobenzene.—*Procedure* (*c*). Cinnamic acid (10 g.), chlorobenzene (130 ml.), and aluminium chloride (16·5 g.) were used. As the temperature was raised, after addition of the catalyst, vigorous evolution of hydrogen chloride occurred at about 11°. The product was worked up by the standard method and separated as an oil which was then extracted with benzene. The residue from the dried extract crystallised from light petroleum (b. p. 100—120°) (11·6 g.; m. p. 82—83°), and a further 4·15 g. were recovered from the mother-liquor. Recrystallisations from both light petroleum (b. p. 100—120°) and aqueous ethanol gave β-*p*-chlorophenyl-β-phenylpropionic acid, m. p. 95° (Bergmann *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 1612, record m. p. 108°) (Found: C, 69·1; H, 5·2; Cl, 13·5%; equiv., 258. Calc. for $C_{15}H_{13}O_2Cl$: C, 69·1; H, 5·1; Cl, 13·6%; equiv., 261). The orientation was confirmed by oxidation (of 2 g.) with aqueous potassium permanganate to 4-chlorobenzophenone (0·30 g.), m. p. 73—74° (Schaum and Unger, *Z. anorg. Chem.*, 1924, **132**, 90, give m. p. 75·5—76°).

Procedure (*a*). Cinnamic acid alone was recovered.

Procedure (*d*). This was applied to the same quantities. The crude product (18·9 g.), isolated as usual, was thrice recrystallised from ethanol, to give ββ-di-(*p*-chlorophenyl)propionic acid as prisms (3·0 g.), m. p. 189—190° (Fuson *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 3799, give m. p. 188—189°) (Found: equiv., 291. Calc. for $C_{15}H_{12}O_2Cl_2$: equiv., 295). From the mother-liquor, more of the acid (1·3 g.) was recovered. Oxidation of the acid (1 g.) with aqueous potassium permanganate gave 4 : 4′-dichlorobenzophenone (0·5 g.), m. p. 145° (Cook and Chambers, *J. Amer. Chem. Soc.*, 1921, **43**, 334, give m. p. 146°).

Cinnamic Acid and Bromobenzene.—*Procedure* (*d*). Cinnamic acid (5 g.) was treated with bromobenzene (80 ml.) and aluminium chloride (8·25 g.). On warming, after addition of the catalyst at 4°, no evolution of hydrogen chloride was perceptible until about 12°. The crude product was isolated by the standard method, using ether-extraction in the final stage, and consisted of a yellow oil containing some solid (8·7 g.). Treatment with ethanol gave crystals (3·3 g.) which on recrystallisation twice from light petroleum (b. p. 100—120°)–benzene gave small colourless prisms (1·5 g.), m. p. 116—118°. Four further recrystallisations from aqueous ethanol containing a little acetic acid gave β-*p*-bromophenyl-β-phenylpropionic acid (0·5 g.), m. p. 130—130·5° (Found : C, 58·3; H, 4·2; Br, 26·5%; equiv., 303. Calc. for $C_{15}H_{13}O_2Br$: C, 59·0; H, 4·3; Br, 26·2%; equiv., 305) (cf. Allen and Gates, *loc. cit.*, m. p. 107—108°). From the mother-liquors impure acid (1·65 g.) was obtained. Oxidation of this material with aqueous potassium permanganate gave *p*-bromobenzophenone, m. p. 76—77° (cf. Schöpff, *Ber.*, 1891, **24**, 3766, m. p. 79—80°).

Cinnamic Acid and Fluorobenzene.—Procedure (*d*). From cinnamic acid (2 g.), fluorobenzene (25 ml.), and aluminium chloride (3·3 g.), appreciable evolution of hydrogen chloride occurred during the addition of the catalyst. The acid product was isolated as usual and extracted with ether, giving a pale-yellow, viscous oil (3·25 g.). Recrystallisations from benzene–light petroleum (b. p. 60—80°) gave β-*p*-fluorophenyl-β-phenylpropionic acid (1 g.) as prisms, m. p. 111° (Bergmann *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 1612, give m. p. 118°) (Found : C, 73·7; H, 5·0%; equiv., 244. Calc. for $C_{15}H_{13}O_2F$: C, 73·7; H, 5·4%; equiv., 244). Oxidation with aqueous potassium permanganate gave an extremely volatile, colourless ketone (m. p. 46°) in small yield, probably *p*-fluorobenzophenone (Koopal, *Rec. Trav. chim.*, 1915, **34**, 115, records m. p. 52°).

Cinnamic Acid and Anisole.—Procedure (*b*). From cinnamic acid (2·5 g.), purified anisole (35 ml.), and aluminium chloride (4·2 g.), the product (4·7 g.) was isolated by the normal method and after recrystallisations from benzene–light petroleum (b. p. 100—120°) gave β-*p*-methoxyphenyl-β-phenylpropionic acid in prisms (1·6 g.), m. p. 122° (Bergmann *et al.*, *loc. cit.*, give m. p. 122°); the m. p. was raised to 128—129° by drying over phosphoric oxide at 110° (Found : C, 74·9; H, 5·2%; equiv., 262, 264. Calc. for $C_{16}H_{16}O_3$: C, 75·0; H, 6·3%; equiv., 256). Further acid (1·1 g.) was recovered from the mother-liquors. No product was isolated when this acid was oxidised by aqueous potassium permanganate.

Cinnamic Acid and Toluene.—Procedure (*a*). Cinnamic acid (5 g.), toluene (70 ml.), and aluminium chloride (8·3 g.) became dark brown, and hydrogen chloride was evolved at about 8°. The crude acid product (8·9 g.), isolated by the usual method, with ether-extraction in the last stage, was recrystallised twice from ethanol and once from light petroleum (b. p. 100—120°) and had m. p. 129° (1·5 g.), a further 2·6 g. (m. p. 118°) being recovered from the mother-liquors. β-Phenyl-β-*o*-, -*m*-, and -*p*-tolylpropionic acid melt at 129°, 109°, and 140° respectively according to von Braun, Manz, and Reinsch (*Annalen*, 1929, **468**, 277). In an attempt further to purify the phenyltolylpropionic acid the *methyl* ester (1·8 g.; b. p. 185—187°/5 mm.; from 2·6 g. of acid) was prepared (Found : C, 80·5; H, 7·3. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%). The acid (0·83 g.) obtained by hydrolysis of the ester (0·84 g.) on recrystallisation successively from ethanol, aqueous acetic acid, and light petroleum (b. p. 100—120°) had m. p. 123° (Found : equiv., 244. Calc. for $C_{16}H_{16}O_2$: equiv., 240). The orientation is uncertain since oxidation under three different conditions failed to yield an identifiable product.

It is likely that some migration of the methyl group had occurred under the influence of the catalyst, leading to an intractable mixture of isomers. The preparation of the addition product was repeated, and after several recrystallisations a specimen of the same acid, m. p. 120° (equiv., 246), was obtained.

Procedure (*b*).—Half the quantities of the foregoing reactants, when poured on ice–hydrochloric acid, yielded a tarry product. The whole was worked up by the normal method and the crude acid obtained as a colourless solid (2·7 g.), m. p. 110°; after recrystallising once from alcohol, this yielded colourless crystals (1·5 g.), m. p. 120°. Further purification through the methyl ester (0·92 g.), b. p. *ca.* 180°/3 mm., led to a specimen (0·35 g.), m. p. 122—123° (mixed m. p. with a specimen from the preceding experiment, 122—123°).

Cinnamic Acid and Benzene in the Presence of Anhydrous Boron Trifluoride.—Cinnamic acid (5 g.) was added to benzene (150 ml.) saturated with dry boron trifluoride (*ca.* 6 g. of BF_3, 2·7 mols. with respect to the acid). The whole was well shaken; the solution became yellow but there was no temperature rise. Next morning the mixture was poured into ice–water, and the solvent layer then washed with water and extracted twice with sodium carbonate solution. The extract on acidification yielded cinnamic acid (3·8 g.).

Reaction of ββ-*Diphenylpropionic Acid with Chlorobenzene.*—ββ-Diphenylpropionic acid (2 g.) was dissolved in chlorobenzene (300 ml.) and stirred with powdered anhydrous aluminium chloride (12 g., *ca.* 10 mols.), and dry hydrogen chloride gas passed in to saturation (20 minutes). After 20 hours with occasional stirring, the mixture (almost black) was thoroughly mixed with ice and hydrochloric acid. The crude product (2 g.), isolated in the usual manner, was thrice recrystallised from ethanol, to give ββ-di-*p*-chlorophenylpropionic acid (0·35 g.), m. p. and mixed m. p. 190° (Found : equiv., 293. Calc. for $C_{15}H_{12}O_2Cl_2$: equiv., 295). Further acid (0·13 g.) was recovered from the mother-liquor.

The above experiment was repeated with 10 g. of ββ-diphenylpropionic acid. After removal of the eventual acid product with aqueous sodium carbonate, the solvent layer was washed twice with water, dried ($CaCl_2$), and distilled. The first fraction (1·9 ml.), b. p. 79·2—79·5°/760 mm., was identified as benzene by conversion into *m*-dinitrobenzene. The distillation apparatus incorporated a heated 2-ft. column of Fenske helices with a total-condensation, variable take-off head of Whitmore and Lux pattern. Its efficiency for the object in hand was initially demonstrated by the successful fractionation of a prepared mixture of purified benzene (16 ml.) and chlorobenzene (484 ml.). From this, benzene (9·1 ml.) was recovered as a first fraction, b. p. 79·7—80·0°/760 mm. (all b. p.s recorded here have been corrected to 760 mm. pressure).

The chlorobenzene used for these experiments was purified by refluxing it with anhydrous aluminium chloride, washing, drying, and fractionation.

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