326. *The Catalysed Reactions of Simple Aromatic Compounds with Ethylenic Systems. Part I. αβ-Unsaturated Ketones.*

By J. F. J. Dippy and A. L. L. Palluel.

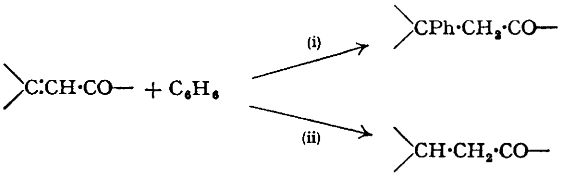
Three distinct processes may occur when an αβ-unsaturated ketone and a benzenoid compound are brought together in the presence of anhydrous aluminium chloride: (i) addition at the ethylenic link, the aromatic residue becoming attached to the β-carbon, (ii) hydrogenation of the ethylenic link, and (iii) replacement of an existing aryl group at the β-carbon of the ketone by an aromatic residue from the benzenoid reactant. Unsaturated ketones used successfully have been benzylideneacetophenone and its nuclear-substituted derivatives, β-phenylcrotonophenone, naphthylacrylophenone, and mesityl oxide, whilst the reactive benzenoid components were benzene, toluene, chlorobenzene, and bromobenzene.

This investigation extends the scope of the results provided by earlier workers, and leads to certain generalisations regarding the effect of the constitution of the unsaturated ketone on the incidence of the above-mentioned processes.

The aluminium chloride is considered to enable the unsaturated ketone to function as an electrophilic reagent for the purpose of aromatic substitution. Molecular compounds of unsaturated ketone and aluminium chloride have been isolated, the constitutions of which are taken into account in the mechanism proposed.

The addition of benzenoid compounds to ethylenic systems in the presence of anhydrous aluminium chloride has long been available as a synthetical method although limited in application. Among the compounds which have received attention have been unsaturated acids and ketones in which the ethylenic link is conjugated with the carboxyl or the carbonyl group.

In the reaction of an αβ-unsaturated ketone with benzene or a suitable monosubstituted benzene, serving as solvent, in the presence of anhydrous aluminium chloride, saturation of the ethylenic link occurs by the alternatives, (i) addition of an aryl group at the β- and hydrogen at the α-carbon atom, or (ii) hydrogenation (the hydrogen atoms being made available by the solvent present in large excess). The nature of the groups contained in the unsaturated ketone seems to determine which process predominates, although in one specific type we have demonstrated that both reactions occur:



The saturated product from either addition will undergo a further reaction (iii) which apparently is slower and leads to the stepwise replacement of aryl groups at the β-position of the ketone by aryl groups supplied by the excess of solvent.

These generalisations rest partly on evidence already recorded. The first such experimental observation appears to have been made by Vorländer and Friedberg (*Ber.*, 1923, **56**, 1144) who added benzene to benzylideneacetophenone; then Hurd (*J. Amer. Chem. Soc.*, 1925, **47**, 2777) showed that benzene and anisole could be added to keten (several such reactions with keten have been reported subsequently). Later, Fuson and his co-workers (*ibid.*, 1934, **56**, 687, 1241, 2103; 1935, **57**, 2208) furnished many instances of aromatic addition, accompanied by replacement, in αβ-unsaturated ketones, and claimed that both processes were reversible. The following kind of observation has been made in many cases:

$$C_6H_5{\cdot}CH{:}CH{\cdot}COR \xrightarrow{2C_6H_5X} (X{\cdot}C_6H_4)_2CH{\cdot}CH_2{\cdot}COR$$

$$X{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COR \xrightarrow{2C_6H_6} (C_6H_5)_2CH{\cdot}CH_2{\cdot}COR$$

In a similar reaction involving benzene and *p*-bromobenzylidenequinaldine, bromobenzene was identified as a product (Fuson *et al.*, *ibid.*, **1933**, **55**, 3799) but the fates of displaced groups in reactions of αβ-unsaturated ketones have not been established as yet. The replacement process (iii), implicit in the above reactions, involves aryl groups only : where alkyl groups occupy the β-position the change is not observed. It is noteworthy that replacement of R, which occupies a terminal position adjacent to carbonyl, does not occur, whether it be alkyl or aryl. Our investigation reinforces and extends these conclusions, and the recent work of Colonge and Pichat (*Bull. Soc. chim.*, 1949, Jan., p. 177; May, p. 142) also gives valuable confirmation of several features. These authors showed, for instance, that in aluminium chloride-catalysed reactions of benzene, toluene, and anisole with methyl ketones containing alkyl-substituted vinyl groups, addition occurred at the β-position and along customary lines (often giving very good yields), but there was no case where subsequent replacement took place.

The incidence of addition process (i) or (ii) seems to be confined to specific categories of unsaturated ketones. Thus in the system $CR'R''{:}CH{\cdot}CO{\cdot}$ where R′ and R″ are H–H, alkyl–H, alkyl–alkyl, or aryl–H, process (i) occurs exclusively. On the other hand process (ii), *i.e.*, exclusively hydrogenation, takes place in the system where both R′ and R″ are aryl (Fuson *et al.*, *loc. cit.*). A position intermediate between these extremes is represented by the system in which R′ = alkyl and R″ = aryl, as we have shown that dypnone, $CPhMe{:}CH{\cdot}COPh$, undergoes both kinds of reaction concurrently. It would appear from the above that, as the bulk of the group situated at the β-position increases, the hydrogenation process is favoured at the expense of the other addition process, so much so that where R′ and R″ are represented by two aryl groups the addition of a further aromatic nucleus to the β-position is so inhibited as to become negligible. Of course, bulk is not likely to be alone responsible, as changes in groups are accompanied by changes in polar influences.

An interesting reaction is provided by the addition of benzene to cinnamylideneacetophenone; this gives βδδ-triphenylvalerophenone, *i.e.*, two benzene molecules have added across the ethylenic bonds of the unsaturated ketone.

The effect of changing the character of the benzenoid reactant (always a liquid and in large excess) has also been examined by us. We found that apart from benzene, the liquids toluene, chlorobenzene, and bromobenzene gave addition; no success was met when anisole, nitrobenzene, ethyl benzoate, or pyridine was used, and iodobenzene and dimethylaniline underwent independent chemical changes under the standardised experimental conditions.

The orienting influence of the substituent in the benzenoid compound is significant; in successful additions and replacements the *p*-position of the entering ring is the point of attachment. A striking claim is that of Fuson and his co-workers (*loc. cit.*) who record that chlorobenzene reacts with *m*-chlorobenzylideneacetophenone to give ββ-di-*p*-chlorophenylpropiophenone. It is interesting, however, that when we treated the same ketone with unsubstituted benzene the addition reaction alone took place.

Our experimental procedure approximates to that described by Shildneck (*Org. Synth.*, **17**, 51—53) although in the first place we examined a number of factors which might have called for modification. We confirmed that the optimum proportion of catalyst was 2—2·5 mols. (with respect to the ketone) except in one case. The introduction of dry hydrogen chloride was not generally found necessary or advantageous; moreover, raising the temperature was without effect, every successful reaction proceeding at room temperature. We, also, showed that stannic chloride, a weaker electron acceptor, was of no catalytic value, and in this connexion it is significant that Colonge and Pichat (*loc. cit.*) found boron trifluoride ineffective in their work.

Unsaturated ketone.	Benzenoid compound.	Products.
$CMe_2{:}CH{\cdot}COMe$	PhCl	$p\text{-}C_6H_4Cl{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe$
$CHPh{:}CH{\cdot}COPh$	PhMe	$(p\text{-}C_6H_4Me)_2CH{\cdot}CH_2{\cdot}COPh$
,, ...	PhCl	$p\text{-}C_6H_4Cl{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$ & $(p\text{-}C_6H_4Cl)_2CH{\cdot}CH_2{\cdot}COPh$
,, ...	PhBr	$p\text{-}C_6H_4Br{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$
$m\text{-}C_6H_4Cl{\cdot}CH{:}CH{\cdot}COPh$	C_6H_6	$m\text{-}C_6H_4Cl{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$
$CPhMe{:}CH{\cdot}COPh$	C_6H_6	$CHPhMe{\cdot}CH_2{\cdot}COPh$ & $CPh_2Me{\cdot}CH_2{\cdot}COPh$
$CHPh{:}CH{\cdot}CH{:}CH{\cdot}COPh$	C_6H_6	$CHPh_2{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$
$\beta\text{-}C_{10}H_7{\cdot}CH{:}CH{\cdot}COPh$	C_6H_6	$CHPh_2{\cdot}CH_2{\cdot}COPh$

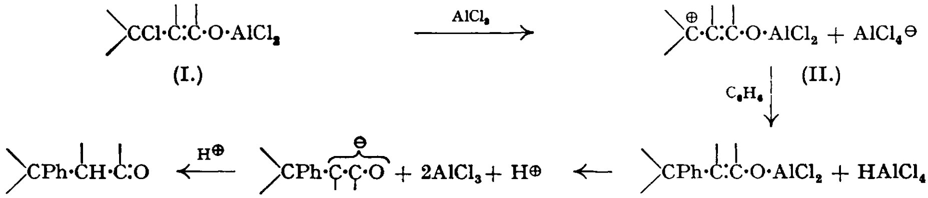
The annexed table summarises our results. The entry of aryl groups at the β-position relative to carbonyl in αβ-unsaturated ketones has been demonstrated experimentally in some cases (Fuson *et al.*, and Colonge and Pichat, *locc. cit.*) by oxidative degradation. Moreover, certain of the products, *e.g.*, benzylacetone, obtained in Colonge and Pichat's work possessed constitutions which were beyond doubt. For ββ-di-*p*-chlorophenylpropiophenone and 4 : 4-di-*p*-chlorophenylbutan-2-one, we have confirmed the β-orientation by oxidation with alkaline permanganate; we have simultaneously proved attachment at the *p*-position in the case of reactions with chlorobenzene, since in both cases *pp'*-dichlorobenzophenone was produced. Furthermore, benzophenone was formed in the oxidation of βδδ-triphenylvalerophenone.

In the reaction of naphthylacrylophenone with benzene to give ββ-diphenylpropiophenone, a high-boiling liquid residue recovered from the excess of benzene doubtless contained the displaced naphthyl group. It had an odour reminiscent of that of naphthalene but no solid component was recovered, and attempted conversion into a picrate was unsuccessful, signifying that aluminium chloride had reacted further with the naphthalene residue.

In the case of benzylideneacetophenone the reaction with chlorobenzene was arrested at the addition stage, *i.e.*, to give β-*p*-chlorophenyl-β-phenylpropiophenone. The second stage was reached by further treatment of the product, and it is noteworthy that whilst the first stage takes five hours, the second stage requires seventeen hours for completion.

In all experiments, whether addition occurred or not, there was always darkening of the liquid mixture and as a rule a light-coloured solid was formed. In two cases these solids have been isolated, and analyses show them to be equimolecular compounds of the unsaturated ketone with aluminium chloride. After storage they react to completion with the benzenoid solvent, although only after introduction of one further molecular proportion of aluminium chloride; thus it seems that the formation of a binary complex with the unsaturated ketone is not the sole function of the catalyst (it had already been found that 2—2·5 moles of aluminium chloride was essential for the success of reactions conducted without interruption). The 1 : 1 molecular composition of the complex in the case of cinnamylideneacetophenone points to the association of aluminium chloride with the carbonyl group rather than with the ethylenic linkage exclusively. It is noteworthy that lately Dilks, Eley, and Sheppard (*Trans. Faraday Soc.*, 1950, **46**, 261) have also demonstrated the 1 : 1 composition of some compounds of simple ketones with aluminium chloride (see also Thomas, " Anhydrous Aluminium Chloride in Organic Chemistry," 1941, pp. 50 and 51).

To account for the observed facts we submit that the co-ordination product $>\overset{\oplus}{C}\cdot\overset{|}{C}{:}\overset{|}{C}\cdot O\rightarrow\overset{\ominus}{A}lCl_3$, formed initially, gives the structure $>CCl\cdot\overset{|}{C}{:}\overset{|}{C}\cdot O\cdot AlCl_2$, by intramolecular rearrangement, a process favoured by the spatial considerations. Such a compound will require a further proportion of aluminium chloride in order to participate in an orthodox Friedel–Crafts reaction. Thus we favour the following mechanism for the addition process (i), as accounting best for the experimental observations :



The mechanism is thus one of initial production of a carbonium cation (II) in the aprotic solvent-reagent (in the case of cinnamylideneacetophenone the cation is mesomeric). It is recognised, however, that the second aluminium chloride molecule with hydrogen chloride, inevitably generated during reaction, would give rise to proton which is also effective in removing chlorine from the initial binary complex (I) to given the carbonium ion (II). The lack of reactivity of nitrobenzylideneacetophenone (even with four molecular proportions of aluminium chloride), observed by us, is apparently caused by the inhibition of reaction between the binary complex and the second molecule of aluminium chloride, *i.e.*, the chlorine in the complex is held so firmly, in consequence of the strong electron attraction of nitroxyl ($-I$, $-T$), as to inhibit the formation of the carbonium cation.

We recognise that the mechanism advanced here for unsaturated ketones is a specific one, and cannot apply to similar additions involving alkenes, unsaturated acids, etc., which are known also to occur under Friedel–Crafts conditions; these are to be the subject of further inquiries.

It should be appreciated that the addition reactions discussed in this paper can be regarded as special instances of the Michael-type condensation in which the catalyst is acidic. Hauser and Breslow (*J. Amer. Chem. Soc.*, 1940, **62**, 2385) have claimed that their successful addition of ethyl malonate to ethyl benzylidenemalonate under the influence of boron trifluoride was the first example of an acid-catalysed Michael addition, but strictly speaking many instances were already known (in the sense described in this paper), some of the earliest being provided by Liebermann and Hartmann (*Ber.*, 1891, **24**, 2582; 1892, **25**, 957, 2124), Karsten (*Ber.*, 1893, **26**, 1579), and Eijkman (*Chem. Weekblad*, 1908, **5**, 655) who caused aromatic hydrocarbons to react with cinnamic acid under the influence of sulphuric acid or anhydrous aluminium chloride.

The mechanism advanced by Colonge and Pichat (*loc. cit.*) for the addition of benzenoid compounds to aliphatic unsaturated ketones involves initial addition of hydrogen chloride to the ethylenic link to give a saturated β-chloro-ketone; this is essentially the view advanced originally by Vorländer and Friedberg (*loc. cit.*). Presumably this implies electrophilic addition, a process which would be much inhibited by the neighbouring carbonyl group. It is true that Colonge and Pichat were able to make saturated ketones from such β-chloro-ketones by treatment with benzene and aluminium chloride, but this does not prove that saturated β-chloro-ketones are an essential step where the unsaturated ketone is used as starting material. We prefer to follow the principle that the system $>C{:}\underset{|}{C}{\cdot}\underset{|}{C}{:}O$ is essentially attractive to nucleophilic reagents. In this connexion it is noteworthy that in Colonge and Pichat's experiments attachment of benzene seems to occur less readily when methyl groups occupy the β-position, partially satisfying thereby the electron deficiency at that carbon atom.

In conclusion it is interesting that recently addition between benzene and acetylenic ketones under the influence of sulphuric acid has also been effected (Bickel and Fabens, *J. Amer. Chem. Soc.*, 1949, **71**, 1450).

A far better knowledge of the factors governing the replacement reaction, as distinct from the addition process, will be needed before an interpretation can be undertaken, and work on this matter involving unsaturated ketones, nitro-compounds, and carboxylic acids is in progress.

EXPERIMENTAL.

Unsaturated Ketones.—The benzylidene-ketones were prepared by the condensation of the aldehyde with the appropriate methyl ketone in the presence of 10% aqueous alcoholic sodium hydroxide.

In the condensation of β-naphthaldehyde and acetophenone in equimolecular proportions a very low concentration of sodium hydroxide was used in order to preclude the Cannizzaro reaction which this aldehyde so readily undergoes, as for instance with the 10% alkali solution. β-2-*Naphthylacrylophenone* recrystallised from alcohol in fine, colourless needles, m. p. 157—158° (yield, 60%) (Found: C, 87·4; H, 5·2. $C_{19}H_{14}O$ requires C, 88·3; H, 5·4%).

Reactions of Benzenoid Compounds with Unsaturated Ketones.—A solution of the unsaturated ketone in the benzenoid solvent was added gradually to a cooled suspension of anhydrous aluminium chloride (about 2·2 mols. with respect to the ketone) in a large excess of the same solvent. The temperature of the mixture was not allowed to rise above 20°. The suspension was stirred at room temperature until the precipitated aluminium chloride–unsaturated ketone complex had passed into solution and for 1 hour subsequently. The whole was then added to hydrochloric acid–ice, the organic layer washed with water, and excess of solvent removed by steam-distillation. The resultant crude crystalline product obtained on storage was often contaminated by gum (doubtless arising from polymerisation); much of this could usually be removed on a porous tile. Recrystallisation was usually effected from aqueous alcohol (charcoal). By this method we obtained a 78% yield of ββ-diphenylpropiophenone (m. p. 91—92°) from the benzene–benzylideneacetophenone reaction; under similar conditions benzylideneacetone gave a 70% yield of 4 : 4-diphenylbutan-2-one.

Two modifications of the above procedure—in one the aluminium chloride suspension is saturated with dry hydrogen chloride before addition of the unsaturated ketone, and in the other powdered aluminium chloride is added to a hydrogen chloride-saturated solution of the ketone—did not improve the yields or decrease the amount of gum.

Throughout our experiments it was generally found that where reaction failed to take place at room temperature and with 2·2 mols. of catalyst, the use of forcing conditions, *e.g.*, a higher proportion of catalyst and an elevated temperature, was also unavailing.

Details relating to the separate systems are as follows: *Mesityl oxide and chlorobenzene.* The intermediate complex did not separate as a solid, and the reaction was allowed to proceed for approximately 30 hours, whereupon a dark brown colour developed. The product was separated, together with the excess of solvent, by steam-distillation and was recovered as an oil (yield 62%); from it 4-p-*chlorophenyl*-4-*methylpentan*-2-*one semicarbazone* was prepared, crystallising from alcohol in colourless leaflets, m. p. 174—175° (Found: Cl, 12·7. $C_{13}H_{18}ON_3Cl$ requires Cl, 13·2%).

Benzylideneacetophenone and toluene. The residue from the ethereal extract of the crude reaction product (stirring for 2½ hours was needed) gave a paste when left in a vacuum-desiccator for 2 days. This paste, after being pressed on porous porcelain, crystallised from alcohol (charcoal) as fine needles, m. p. 77—78°, and is considered to be ββ-*di*-p-*tolylpropiophenone* (yield 28%) (Found: C, 87·5; H, 7·0. $C_{23}H_{22}O$ requires C, 87·9; H, 7·0%).

Benzylideneacetophenone and chlorobenzene. This reaction was arrested by pouring the reaction mixture into dilute hydrochloric acid after 5 hours. β-p-*Chlorophenyl-β-phenylpropiophenone* was recovered in the usual way and recrystallised from aqueous alcohol as colourless needles, m. p. 92—93° (yield 32%) (Found: C, 77·8; H, 5·5; Cl, 11·2. $C_{21}H_{17}OCl$ requires C, 78·6; H, 5·3; Cl, 11·1%).

When the reaction mixture above was given prolonged stirring (17 hours in all) the product was ββ-di-*p*-chlorophenylpropiophenone, m. p. 120—121° (59% yield) (previously obtained by Fuson *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 687, with m. p. 120—121°). Oxidation of this product with alkaline permanganate (5 hours) gave *pp*′-dichlorobenzophenone, m. p. 143—144°, in good yield.

A similar oxidation of 4 : 4-di-*p*-chlorophenylbutan-2-one, obtained by the reaction of chlorobenzene with benzylideneacetone, also gave *pp*′-dichlorobenzophenone.

Benzylideneacetophenone and bromobenzene. The product, recovered after 7 hours' stirring, was regarded as β-p-*bromophenyl-β-phenylpropiophenone.* It recrystallised from aqueous alcohol in colourless needles, m. p. 105—106° (yield, 50%) (Found: C, 69·3; H, 4·7; Br, 21·2. $C_{21}H_{17}OBr$ requires C, 69·0; H, 4·7; Br, 21·9%). A similar reaction, allowed to continue for 50 hours, yielded an impure product which gave indications of being an intractable mixture of the mono- and di-bromo-substituted saturated ketones.

m-*Chlorobenzylideneacetophenone and benzene.* Addition of dry hydrogen chloride was found advantageous in this experiment. The yellow solid intermediate did not dissolve even after 21 hours' stirring at room temperature and subsequent warming during 7 hours gradually to 70°. After working up and recrystallisation of the solid product from alcohol β-m-*chlorophenyl-β-phenylpropiophenone*, m. p. 71—72°, separated (Found: C, 78·0; H, 5·3; Cl, 11·4. $C_{21}H_{17}OCl$ requires C, 78·6; H, 5·3; Cl, 11·1%). The yield was 1·2 g. from 4 g. of unsaturated ketone, and 3 g. of the latter were recovered.

β-Phenylcrotonophenone (dypnone) and benzene. This reaction occupied 22 hours and two products were separated. The first was recovered from the steam-distillate as a colourless solid, after removal of the excess of solvent. Recrystallisation from alcohol gave β-phenylbutyrophenone as colourless leaflets, m. p. 73—74° (Wohler, *Amer. Chem. J.*, 1904, **31**, 655, records m. p. 74°) (Found: C, 85·4; H, 7·2. Calc. for $C_{16}H_{16}O$: C, 85·7; H, 7·2%). The second product was obtained from the ethereal extract of the residue after steam-distillation; recrystallisation of the crude solid from alcohol gave ββ-diphenylbutyrophenone as fine needles, m. p. 100—102° (Wohler, *loc. cit.*, gave m. p. 103°), the identity being confirmed by preparation of the oxime, m. p. 162° (Wohler, *loc. cit.*, gave m.p. 163°).

Cinnamylideneacetophenone and benzene. This reaction (which required 6 hours for completion) gave βδδ-*triphenylvalerophenone* which recrystallised from aqueous alcohol (charcoal) in fine needles, m. p. 114—115° (yield, 46%) (Found: C, 88·9; H, 6·5. $C_{29}H_{26}O$ requires C, 89·2; H, 6·7%). Oxidation with alkaline permanganate yielded benzophenone.

The attempted addition of benzene to cinnamylideneacetone (4·8 g.) was unsuccessful. The intermediate was a brownish paste in contrast to the red solid formed by cinnamylideneacetophenone. After 30 hours' stirring the mixture was worked up as usual and a yellow oil (5 g.) was obtained which failed to give any ketone derivative.

β-Naphthylacrylophenone and benzene. A somewhat larger proportion of catalyst (three mols.) was found necessary in order to achieve complete dissolution of the primary addition complex. The reaction was allowed to proceed for 30 hours, and after separation and purification ββ-diphenylpropiophenone was obtained in 60% yield, having m. p. and mixed m. p. 91—92°.

Unsuccessful attempts were made to effect reaction between benzylideneacetophenone and iodobenzene, anisole, ethyl benzoate, nitrobenzene, dimethylaniline, naphthalene (in carbon disulphide), and pyridine, and also between *m*-nitrobenzylideneacetophenone and benzene, despite prolonged stirring, the addition of up to four molecular proportions of aluminium chloride, and eventual heating.

Isolation and Composition of Intermediate Molecular Compounds.—The anhydrous aluminium chloride employed in all experiments described heretofore was supplied either by British Drug Houses Ltd., or Imperial Chemical Industries Limited, but the specimen used for the preparation of intermediate molecular compounds was freshly prepared from hydrogen chloride and aluminium foil. After purification by sublimation it was stored in a desiccator and shown by analysis to be pure.

A solution of the unsaturated ketone (0·05 mole) in carbon disulphide was added with rapid stirring to a fine suspension of the aluminium chloride (0·0125 mole) in the same medium. The mixture was stirred for 1 hour, then filtered out of contact with moist air, and the solid intermediate product so obtained washed with dry carbon disulphide.

The intermediates formed by benzylidene- and cinnamylidene-acetophenone could be kept for day without deterioration in a vacuum-desiccator.

Analyses.—(i) A weighed sample of the intermediate in a small glass tube was immersed in an excess of acidified silver nitrate solution contained in a stoppered (ground-glass) flask; this was heated at 100° for 1 hour and the precipitated silver chloride washed with alcohol and ether in turn, dried, and weighed. (ii) The intermediate was hydrolysed as described above, and the chlorine content determined by the Volhard method. (iii) A weighed sample of the intermediate was hydrolysed with dilute acid at 100°, organic matter was removed from the cooled solution, and the aluminium content determined by the "oxine" method.

Inaccuracies should be attributed to factors such as slight lack of homogeneity of the sample and the rapid effect of moisture. The data, however, demonstrate beyond reasonable doubt a 1 : 1 molecular composition in each case. The following results are recorded: Benzylideneacetophenone *intermediate.* Found: Cl, 30·1 (gravimetric), 31·4 (volumetric); Al, 8·3. $C_{15}H_{12}O,AlCl_3$ requires Cl, 30·1; Al, 7·9%. Cinnamylideneacetophenone *intermediate.* Found: Cl, 30·4 (gravimetric); Al, 8·4. $C_{17}H_{14}O,AlCl_3$ requires Cl, 29·0; Al, 7·4%.

Reaction of the Benzylideneacetophenone–Aluminium Chloride Intermediate with Benzene.—(i) A suspension of the intermediate (3 g.) in benzene (80 ml.) was stirred for 7 hours at room temperature and then set aside for several weeks. No change was observed and the original unsaturated ketone was recovered unchanged. (ii) A suspension of the complex (6 g.) and aluminium chloride (3·5 g., 1·5 mols.) in benzene was stirred at room temperature; a homogeneous solution was obtained after 3 hours. The product isolated was ββ-diphenylpropiophenone (4 g.), m. p. and mixed m. p. 91—92°. (iii) Reaction with 0·5 mol. of aluminium chloride did not occur.

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CHELSEA POLYTECHNIC, LONDON, S.W.3

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