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FRIEDEL-CRAFTS CYCLISATION—IV[1]

INTRAMOLECULAR VS INTERMOLECULAR ACYLATION WITH β-ARYL DERIVATIVES OF PROPIONYL CHLORIDE IN AROMATIC SUBSTRATES

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Abstract—Studies on the aluminium chloride-catalysed behaviour of β-phenylpropionyl, β,β-diphenylpropionyl, and β,β,β-triphenylpropionyl chlorides in anisole and some other aromatic stubstrates under standardised conditions are discussed. β,β-Diphenylpropionyl chloride gave yields of up to 27% 3-phenylindan-1-one in anisole and is one of the most easily cyclised acid chlorides so far reported. β,β,β-Triphenylpropionyl is less easily cyclised in anisole to 3,3-diphenylindan-1-one and its transformation product 2,3-diphenylind-1-one. The expected open-chain ketone is completely decomposed into products of αβ-ketonic cleavage and a subsequent redox reaction. Differences in ratios of intermolecular to intramolecular acylation (now called o/c ratios) are discussed.

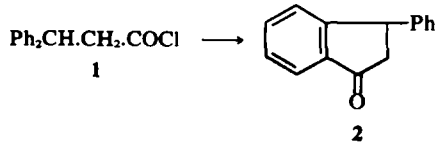
In benzene, β-bis-(*p*-chlorophenyl)propionyl chloride gave, in addition to the previously noted β-bis-(*p*-chlorophenyl)propiophenone (48%), the folloowing compounds: 6-chloro-3-(*p*-chlorophenyl)indan-1-one (4%) (the intramolecular acylation product), β-(*p*-chlorophenyl)-β-phenylpropiophenone (2·3%), β,β-diphenylpropiophenone (0·5%), 3-(*p*-chlorophenyl)-indan-1-one (5·2%). The transformation processes are discussed. Aluminium chloride-catalysed β-aryl exchange in acid chlorides is reported for the first time, but β-aryl exchange does not occur in β,β-(or 3,3-)di-aryl derivatives of indan-1-one.

Many reports exist of the cyclisation of β-phenylpropionyl chloride but very few studies have been made of such reactions conducted under specifically competitive conditions which allow the intramolecular process (cyclic ketone formation) to compete with an intermolecular one (open-chain ketone formation). All the reactions studied here were of this competitive kind and measurements were made of ratios of open-chain to cyclic ketones in the products (now called o/c ratios).

Buu-Hoï *et al*[2] treated β-phenylpropionyl chloride with 1·2 molecular proportions of aluminium chloride in anisole at room temp for 24 hr and obtained an o/c ratio of 90/0. Unfortunately, the concentration of anisole was not stated clearly because, although two different concentrations of aromatic substrates were used in a long series of experiments, they did not state which was applicable to their anisole experiments. For this reason and to make precise comparisons with our other experiments we have repeated their work using modified conditions and have summarised the results in Table 1A.

These confirm the previous workers' finding[2] that no cyclic ketone was formed from this acid chloride in anisole notwithstanding our improved analytical techniques. Furthermore, the increase in the yield of open-chain ketone obtained by raising the temperature from 21° to 80° indicates the insignificance of competing processes.

Under the same conditions, β,β-diphenylpropionyl chloride, **1**, gave some 3-phenylindan-1-one, **2**: at 80° the o/c ratio was 95/4 and at 22° the o/c ratio was 69/27 (Table 1B, experiments 3 and 4). In a third experiment (No 5) the concentration of anisole was reduced to one molecular proportion, a large excess of catalyst was used and the mixture was heated at 80° for 1 hr. The yield of cyclic ketone (4·7%) was almost the same as in experiment 3. The remarkable ease with which β,β-diphenylpropionyl chloride cyclises appears to be surpassed by only α,α,β,β-tetramethyl-β-phenylpropionyl chloride which gave a quantitative yield of cyclic ketone in anisole.[3] Also shown in Table 1B are the results of using mesitylene and toluene as aromatic substrates and, as expected, the decreased activity of these towards electrophiles enhances the yields of cyclic ketones.



1 **2**

In order to compare the behaviour of β,β,β-triphenylpropionyl chloride, **3**, with that of the other acid chlorides, a series of experiments was conducted with the acid chloride in anisole. These are summarised in Table 2 and Scheme 1.

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Table 1.

Expt. No.	Reagents	Conditions	Products* % Open Chain	Cyclic ketone
A	*Reactions of β-Phenylpropionyl Chloride*			
1	Anisole (41·6 mol) + $AlCl_3$ (1 mol)	1 hr at 80°	93	Nil
2	Anisole (41·6 mol) + $AlCl_3$ (1 mol)	1 hr at 21°	85	Nil
B	*Reactions of β,β-Diphenylpropionyl Chloride*			
3	Anisole (41·6 mol) + $AlCl_3$ (1 mol)	1 hr at 80°	95	4
4	Anisole (41·6 mol) + $AlCl_3$ (1 mol)	1 hr at 22°	68·7	26·8
5	Anisole (1 mol) $AlCl_3$ (excess)	1 hr at 80°	93·5	4·7
6	Mesitylene (20 mol) $AlCl_3$ (excess)	1 hr at 80°	48 (+8% recovered acid)	23
7	Toluene (20 mol) $AlCl_3$ (excess)	1 hr at 80°	Nil (+17% recovered acid)	78·7

*Analysed by preparative-scale glc.

Table 2. Aluminium Chloride-Catalysed Reactions of β,β,β-Triphenylpropionyl Chloride in Anisole[a]

Products	Yield[d]% in Exp. No. 8	9	10	11	Remarks
Open-chain ketone and cleavage products					
Open-chain ketone, **6**	nil	nil	nil	nil	
p-Methoxyacetophenone	11·7	57	69	8·5	
Triphenylcarbinol	82	51	85	8	
Triphenylmethane	1·25	5	8	3·5	reduction
p-Tritylanisole	nil	18·9	nil	nil	
Cyclisation products					
3,3-Diphenylindan-1-one	4·3	trace	nil	51·6	
2,3-Diphenylind-1-one	1·45	nil	nil	4·0	oxidation + rearragement
Recovered acid	nil	nil	nil	3·3	
Open/cyclic ketone percentages[b]	83/6	76/0	93/0	12/58[c]	
Conditions					
Catalyst (mol. props.)	2	1	1	1	
Anisole (mol. props.)	16	41·8	41·8	1	
CS_2 (5-fold dilution)	no	no	no	yes	
Temp	100°	80°	22°	21°	
Time (hr)	½	1	1	2	

[a] See also experimental.
[b] Calculated as explained in text.
[c] Calculated as explained in text and corrected for recovered acid.
[d] Based on a maximum theoretical yield of 100% for each cleavage fragment.

The numerous products were isolated by means of preparative-scale GLC and were of two kinds: (a) those formed by cyclisation of the acid chloride and subsequent reactions namely 3,3-diphenylindan-1-one, **4**, and 2,3-diphenylind-1-one, **5**, and (b) those formed from the expected hypothetical open-chain ketone, **6**, namely the αβ-ketone cleavage fragments: p-methoxyacetophenone, triphenylcarbinol, triphenylmethane and p-tritylanisole, **7**.

The yields of these products enabled the hypothetical o/c ratios to be calculated. Thus, in order to calculate the hypothetical yield of open-chain ketone the sum of the yields of the non-ketonic cleavage fragments and the sum of the yields of the ketonic fragments were determined separately. Where a discrepancy occurred between these figures, the *higher* of the two sums was confidently taken to be equal to the yield of open-chain ketone. The yield of cyclic ketone was taken to be the sum of the yields of 3,3-diphenylindan-1-one and 2,3-diphenylind-1-one.

In the first experiment (No 8) forcing conditions were

employed and, in view of the aforementioned observations on the behaviour of β,β-diphenylpropionyl chloride, these were expected to favour open chain ketone formation. The o/c ratio was 83/6 showing that some cyclisation was possible even in an excess of anisole. Experiments Nos 9 and 10 were performed under the same conditions as experiments Nos 3 and 4 respectively involving β,β-diphenylpropionyl chloride. In the first of these the acid chloride was treated with an excess of anisole and one molecular proportion of catalyst for 1 hr at 80°. The o/c ratio was 76/0 whilst the corresponding o/c ratio for β,β-diphenylpropionyl chloride was 95/4. In an otherwise similar experiment (No 10) but with the temperature kept at 22° the o/c ratio was 93/0 (for β,β-diphenylpropionyl chloride it was 69/27). These facts clearly show that β,β,β-triphenylpropionyl chloride is less easily cyclised than β,β-diphenylpropionyl chloride and in this respect more closely resembles β-phenylpropionyl chloride.

The enhanced intramolecular activity of β,β-diphenylpropionyl chloride compared with the monophenyl derivative may not be due entirely to the statistical factor. Mutual electronic activation of the two phenyl rings (which can adopt an approximately coplanar conformation) may operate. The reduced intramolecular activity of β,β,β-triphenylpropionyl chloride relative to the diphenyl derivative, may be attributed not only to the primary (bulk) steric effect, but also to the secondary steric effect. Mutual electronic activation is prevented because the phenyl rings cannot adopt a coplanar conformation but exist in the well-known propellor conformation. Bothorel has measured the angle between the planes of benzene rings (φ) in diphenylmethane (φ = 30·5°) and in triphenylmethane (φ = 59°).[4]

In a fourth experiment (No 11) the temperature was kept at 21° for 2 hr and one molecular proportion of both anisole and catalyst were used and in order to render the conditions similar to those traditionally employed in Friedel-Crafts syntheses, a 5-fold dilution with carbon disulphide was used. The o/c ratio became 12/58 and the greatly enhanced yield of cyclic ketone is in accordance with the well-known technique of dilution with an inert solvent to expedite monomolecular cyclisations. It is concluded therefore that where β,β,β-triphenylpropionyl chloride is employed as a potential acylating agent (or where it can be formed *in situ* e.g. from phenylpropioloyl chloride and benzene[5]) cyclisation will be a major competing process.

2,3-Diphenylind-1-one arises from 3,3-diphenylindan-1-one presumably by a dehydrogenation-rearrangement process. It is proposed that a hydride ion is first abstracted yielding the carbonium ion **8**, which then rearranges with the elimination of a proton:

The hydride ion abstraction by the triphenylmethyl carbonium ion, the species first formed by the αβ-cleavage of the expected open-chain ketone, **6**, would explain the formation of triphenylmethane.

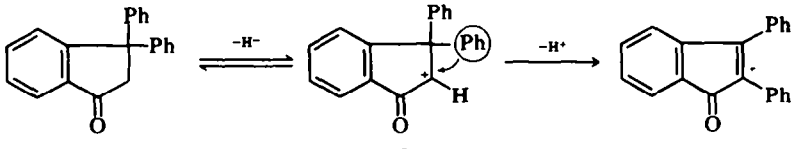
However, not all triphenylmethyl carbonium ions react in this manner since the isolation of triphenylcarbinol indicates that some survive and react with water which is employed to quench the reaction. Furthermore, in one instance, some of the triphenylmethyl carbonium ion was trapped out by anisole to form *p*-tritylanisole. These deductions are supported by the fact that in two experiments (Nos 8 and 11) the yields of triphenylmethane were almost equal to those of 2,3-diphenylind-1-one. In a separate quantitative experiment, an equimolecular mixture of 3,3-diphenylindan-1-one and triphenylcarbinol (a source of triphenylmethyl carbonium ions) was heated with aluminium chloride at 100° for ½hr. Analysis of the products by means of preparative scale GLC showed that 17% of the carbinol had been reduced to triphenylmethane and that 20% of the indanone had been oxidised to 2,3-diphenylind-1-one. No reaction occured if the catalyst was omitted.

With regard to the secondary redox reactions that occur in some experiments, since Moureu *et al.* reported that 3,3-diphenylindan-1-one was converted in low yield into 2,3-diphenylind-1-one by heating alone,[6] it was necessary to establish that this reaction did not occur during analysis.

The series of acid chlorides arranged in order of decreasing ease of cyclisation proposed by Buu-Hoï *et al.*[2] may now be extended to β,β-diphenylpropionyl > γ-phenylbutyryl > β,β,β-triphenylpropionyl ~ β-phenylpropionyl ~ β-p-tolylpropionyl > 1-naphthylacetyl > β-*p*-chlorophenylpropionyl.

Finally, in order to assess the ease of cyclisation at a deactivated aryl nucleus, aluminium chloride-catalysed reactions of β-bis-(*p*-chlorophenyl)-propionyl chloride, **9**, in benzene were re-investigated. A 50% yield of the open chain ketone, β-bis-(*p*-chlorophenyl)propiophenone, **10**, had been reported but no other product was isolated.[7] Analysis of the products by means of preparative scale GLC indeed gave a 48% yield of the open chain ketone, **10**, but there was also isolated a 4% yield of 6-chloro-3-(*p*-chlorophenyl)indan-1-one, **11**. In addition to the cyclic ketone, products formed by stepwise aryl exchange were β-(*p*-chlorophenyl)-β-phenylpropiophenone, **12**, (2·3%), β,β-diphenylpropiophenone, **13**, (0·5%) and 3-(*p*-chlorophenyl)indan-1-one, **14**, (5·2%).

The aluminium chloride-catalysed reversible conversion of β-bis-(*p*-chlorophenyl)-propiophenone, **10**, into β,β-diphenyl-propiophenone, **13**, when treated with benzene has been reported[8] but the present work shows that this proceeds via the mono-exchanged product, β-(*p*-



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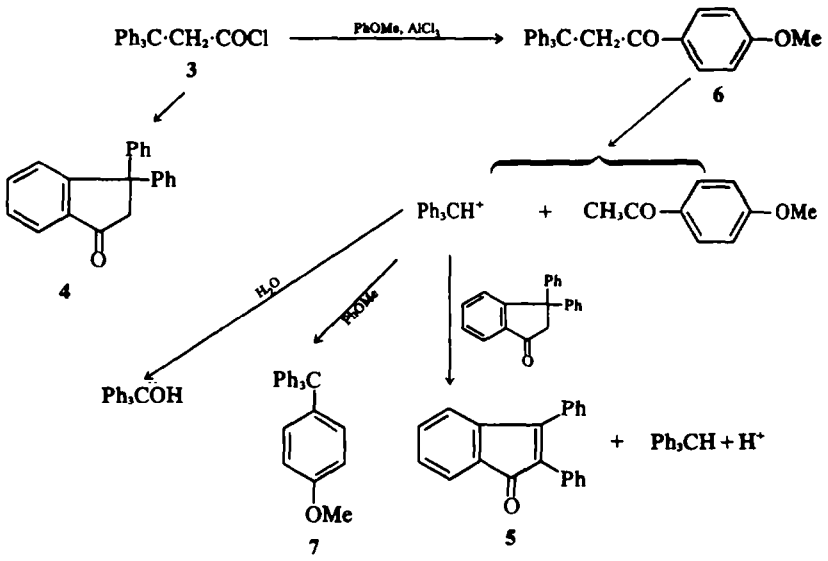
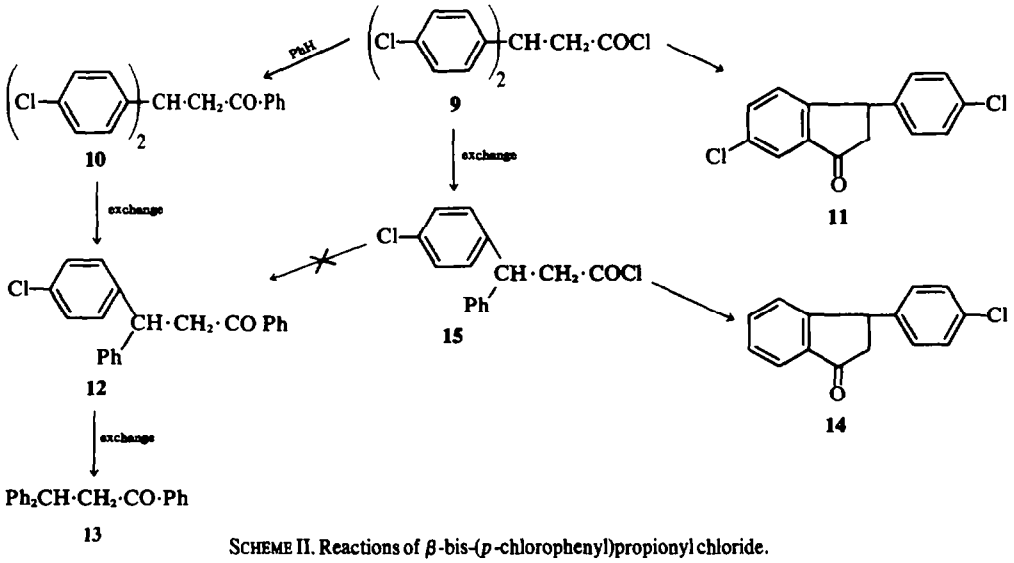


SCHEME I. Reactions of β,β,β-triphenylpropionyl chloride in anisole.

chlorophenyl)-β-phenylpropiophenone, **12**, not previously noted.

The formation of 3-(*p*-chlorophenyl)indan-1-one, **14**, occurred by a type of Friedel–Crafts reaction not previously noted: that is by β-aryl exchange in an acid chloride. It must be formed in this way since cyclisation occurred at the *introduced* phenyl group (in **15**). β-Aryl exchange is well-known to occur in β,β-diaryl derivatives of propionic acid[9] and propiophenone.[10] Since the introduced nucleus is not deactivated, cyclisation is able to proceed at a faster rate and correspondingly the acylation of benzene is much diminished so that the formation of β-(*p*-chlorophenyl)-β-phenylpropiophenone, **12**, is believed not to have occurred in this way but as indicated in the previous paragraph. Support for such rapid cyclisation of **15** comes also from the absence of 3-phenylindan-1-one. This shows that cyclisation of the mono-exchanged acid chloride, **15**, intervenes before a second chlorophenyl group can be replaced by a phenyl group. The absence of 3-phenylindan-1-one also shows that β-aryl exchange does not occur with β,β-(or 3,3-)diaryl derivatives of indan-1-one. We attribute this to the fact that the rigid 5-ring structure prevents nucleophilic attack by the aromatic substrate because a coplanar transition state is prevented.

These proposed reactions are summarised in Scheme II.



SCHEME II. Reactions of β-bis-(*p*-chlorophenyl)propionyl chloride.

The calculation of the o/c ratio was complicated by the intervention of β-aryl exchange in the acid chloride. However, it was small enough to ignore. In this case, the yield of open-chain ketone was taken to be the sum of the yields of the three derivatives of propiophenone. The yield of directly cyclised acid chloride is equal to the yield of 6-chloro-3-(*p*-chlorophenyl)-indan-1-one, **11**, and this gave an o/c ratio of 51/4 uncorrected for recovered acid.

We have previously noted that when cinnamoyl[11] or phenylpropioloyl[5] chlorides were used in attempted Friedel–Crafts ketone syntheses, derivatives of indan-1-one were obtained instead. The ease of cyclisation of the acid chlorides described above supports our view that the cyclic ketones had arisen by the prior addition of aromatic substrates to the unsaturated acid chlorides and this was followed by intramolecular acylation. We have now studied the alternative mode of formation of cyclic ketones, that is, by the cyclialkylation of αβ-unsaturated ketones which we find much more difficult to achieve.

EXPERIMENTAL

GLC was effected on a Wilkins Aerograph Autoprep 705 instrument with a 50′ × ⅜″ column packed with Chromosorb W silicone gum SE30 and used at 250 – 300°. Quantitative analyses of small aliquots (0·01 g) of product mixtures were obtained by comparison of peak areas with those given by standard mixtures. Identification of the components of mixtures was achieved by chromotography on a larger scale (0·1 g – 1 g) and examining the eluted components by the method of mixed melting points and by comparison of IR spectra with those of authentic compounds. A technique which often gave excellent spectra was to allow the eluates from the GLC apparatus to impinge directly on rock-salt plates and then to measure the spectra whilst the substances remained supercooled. IR spectra were measured on a Perkin–Elmer Infracord 137 spectrometer. Analytical data were determined by Dr. Strauss of Oxford. Molecular weights were obtained by the Rast method.

Preparation of reagents. $AlCl_3$ was a commercial specimen finely powdered and of high activity (May and Baker). Aromatic substrates and solvents were purified by standard techniques. Acid chlorides were prepared from acids by Watson's method.[12] β-Phenylpropionic acid was a commercial specimen. β,β-Diphenylpropionic acid[9] and β,β,β-triphenylpropionic acid[13] were prepared by literature methods.

β-Bis-(p-chlorophenyl)propionic acid. The procedure described by Dippy and Young[9] for the preparation of β-(*p*-chlorophenyl)-β-phenylpropionic acid gave this acid instead. Cinnamic acid (10 g, 0·073 mole) and chlorobenzene (130 cm^3) were treated with $AlCl_3$ (16·5 g, 0·124 mole) below 10°. After the addition was completed, the temp was raised to 45° for 1 hr and then the mixture was worked up in the usual way. The products were extracted with Na_2CO_3 aq which gave an oil on acidification. The oil was dissolved in hot EtOH and on cooling deposited crystals (3·3 g, 15%) of β-bis-(*p*-chlorophenyl) propionic acid which was repeatedly recrystallised from light petroleum–benzene mixture until its m.p. was 188–9° (lit.[9] 189–190°). Its purity was checked by conversion of a small portion into the *methyl ester* which after the removal of unchanged acid was analysed by GLC without further purification. Only one peak was obtained. The ester had m.p. 60–1° (MeOH/water). (Found: C, 62·05; H, 4·80; M, 245. $C_{16}H_{14}Cl_2O_2$ requires: C, 62·15; H, 4·55%, M, 309).

Reactions of acid chlorides

β-Phenylpropionyl chloride in anisole, Experiments 1 *and* 2. The acid chloride (from 1·5 g of acid, 0·01 mole) in anisole (44·8 g, 0·416 mole) was stirred with $AlCl_3$ (1·335 g, 0·01 mole) at 21° for 1 hr (Experiment 1) or at 80° for 1 hr (Experiment 2). After working up in the usual way the crystalline product was β-phenylethyl *p*-methoxyphenyl ketone, m.p. and mixed m.p. 97° (lit.[14] 97°) (EtOH) (2·03 g, 85% in experiment 1) (2·24 g, 93% in experiment 2). In each case the crude products were shown to be free from indan-1-one by GLC.

β,β-Diphenylpropionyl chloride in anisole, toluene and mesitylene, Experiment 3. The acid chloride (from 0·2 g of acid, 0·000885 mole) in anisole (4 g, 0·037 mole) was stirred with $AlCl_3$ (0·118 g, 0·000885 mole) for 1 hr at 22°. The products were worked up in the usual way, extracted with Na_2CO_3 aq, and the neutral fraction after removing anisole by steam distillation was separated into its components by means of preparative scale GLC at 275°. There were obtained (calculated from peak areas): 3-phenylindan-1-one, m.p. and mixed m.p. 77°, (lit.[15] 78°) (EtOH) (0·0493 g, 26·8%) and β,β-diphenyl-*p*-methoxypropiophenone, m.p. 118° (lit.[16] 118°) (EtOH) (0·1919 g, 68·7%). The alkaline extract gave recovered β,β-diphenylpropionic acid (0·008 g, 4%).

Experiment 4. As Experiment 3 but with the temp kept at 80° for 1 hr. The products contained 3-phenylindan-1-one (0·0069 g, 3·8%) and β,β-diphenyl-*p*-methoxypropiophenone (0·2658 g, 95·0%). There was no recovered acid.

Experiment 5. The acid chloride (from 0·6 g of acid, 0·00245 mole) was heated with anisole (0·27 g, 0·00245 mole) and $AlCl_3$ (1 g, 0·0075 mole) at 80° for 1 hr and then worked up as in Experiment 3. The products contained 3-phenylindan-1-one (0·024 g, 4·7%) and β,β-diphenyl-*p*-methoxypropiophenone (0·726 g, 93·5%).

Experiment 6. This was the same as Experiment 5 but anisole was replaced by toluene (4·5 g, 0·049 mole). The products contained 3-phenylindan-1-one (0·4 g, 78·7%) and recovered acid (0·1 g, 17%).

Experiment 7. This was the same as Experiment 5 but anisole was replaced by mesitylene (5·9 g, 0·049 mole). The products contained 3-phenylindan-1-one (0·116 g, 22·8%), and β,β-diphenylpropionylmesitylene, m.p. 79° (lit.[17] 82°) (cyclohexane) (0·384 g, 47·7%). The mixed m.p. of these two ketones was depressed to 45°. The alkaline extract gave recovered acid (0·05 g, 8%).

β,β,β-Triphenylpropionyl chloride in anisole, Experiments 8–11. The molecular proportions, conditions used and products are listed in Table 2. The weights of acid chloride (weighed as acid) used were Experiment 8: 0·7 g; Experiment 9: 1·51 g; Experiment 10: 0·5 g; Experiment 11: 0·5 g. The same general techniques were used as in previous experiments. The physical properties of the products isolated were (in order of appearance from GLC): *p*-methoxyacetophenone m.p. and mixed m.p. 38°, triphenylmethane m.p. and mixed m.p. 95° (EtOH), triphenylcarbinol m.p. and mixed m.p. 162° (EtOH), 3,3-diphenylindan-1-one m.p. and mixed m.p. 134° (EtOH), 2,3-diphenylind-1-one m.p. and mixed m.p. 152° (MeOH), *p*-tritylanisole m.p. and mixed m.p. 200–1°.

Experiment 12, *β-Bis-(p-chlorophenyl)propionyl chloride in benzene.* The acid chloride (2 g, 0·006 mole) was stirred with benzene (6 g, 0·077 mole), and $AlCl_3$ (0·8 g, 0·006 mole) at 21° until the evolution of HCl ceased, then at 80° for 1 hr. After working up in the usual way, the Na_2CO_3 extracts gave β-bis-(*p*-chlorophenyl)-propionic acid (0·2 g, 12%) m.p. and mixed m.p. 188–9° (lit.[9] 189–90°). The distilled neutral products, b.p. 208–280°/0·9 mm, contained (in order of appearance by preparative scale GLC):

(i) 3-(*p*-chlorophenyl)indan-1-one m.p. and mixed m.p. 77–8° (0·081 g, 5·2%).

(ii) 6-chloro-3-(*p*-chlorophenyl)indan-1-one m.p. and mixed m.p. 116° (ethanol) (lit.[7] 117–8°) (0·070 g, 4·0%).

(iii) β,β-diphenylpropiophenone m.p. and mixed m.p. 94–5° (lit.[18] 96°) (0·009 g, 0·5%).

(iv) β-(*p*-chlorophenyl)-β-phenylpropiophenone m.p. and mixed m.p. 89° (lit.[10] 92–3°) (0·047 g, 2·3%).

(v) β-bis-(*p*-chlorophenyl)propiophenone, m.p. 120–121° (lit.[7] 120–1°), (needles from ethanol) 1·093 g, 48·2%).

Experiment 13, *Aluminium chloride-catalysed oxidation of* 3,3-*diphenylindan-1-one by triphenylcarbinol.* An equimolar mixture of these three compounds was heated on a water bath for ½hr. The dark orange melt was worked up in the usual way and the organic products were separated by preparative scale GLC into (in order of appearance):

(i) triphenylmethane m.p. and mixed m.p. 95° (EtOH; 17%)

(ii) triphenylcarbinol m.p. and mixed m.p. 162° (EtOH; 78%)

(iii) 3,3-diphenylindan-1-one m.p. and mixed m.p. 134° (EtOH; 74%)

(iv) 2,3-diphenylind-1-one m.p. and mixed m.p. 152° (20%).

When the experiment was repeated without the catalyst, the reagents were recovered quantitatively.

Experiment 14. *Action of heat on* 3,3-*diphenylindan-1-one.* This was heated to 275° by passage through a GLC column and was recovered unchanged.

Reference compounds. Indan-1-one[19] m.p. 42° (lit.[19] 42°); *p*-tritylanisole[20] m.p. 200-1° (lit.[21] 197·5–199°) and *o*-(*p*-chlorobenzoyl)benzoic acid m.p. 149° (lit.[22] 150-1°) were prepared by standard methods.

β,β-Diphenylpropiophenone, β-(*p*-chlorophenyl)-β-phenylpropiophenone and 6-chloro-3-(*p*-chlorophenyl)indan-1-one were prepared by J. F. Jones of this laboratory using standard methods.

Preparation of 3-(p-*chlorophenyl*)*indan-1-one.* Cinnamoyl chloride (10 g, 0·06 Mole) was dissolved in a mixture of chlorobenzene (7 g, 0·062 mole) and CS_2 (100 cm^3) and then $AlCl_3$ (10 g, 0·075 mole) was added. The temp was raised from 20° to the b.p. during 1 hr and allowed to reflux for a further 4 hr. After working up in the usual way the products were chromatographed on alumina (Brockman activity no. 1) and eluted with a mixture of benzene and light petroleum (50/50). On partial evaporation the main fraction gave 3-(p-*chlorophenyl*)*indan-1-one*, (5 g, 34%). This was recrystallised from EtOH (charcoal) then light petroleum and had m.p. 78°. $\bar{\nu}$, 1715 cm^{-1} (5-ring ketone). (Found: C, 74·00; H, 4·95; Cl, 14·60; M, 245. $C_{15}H_{11}ClO$ requires: C, 74·25; H, 4·55; Cl, 14·6%; M, 242·5). Oxidation with chromic acid/acetic acid at 100° for 5 hr gave *p*-chlorobenzoic acid m.p. and mixed m.p. 244° (purified by sublimation) and *o*-(*p*-chlorobenzoyl)benzoic acid m.p. and mixed m.p. with a specimen prepared by standard method 149° (lit.[22] 150–1°).

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