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FRIEDEL–CRAFTS CYCLISATION—VI[1]

POLYPHOSPHORIC ACID-CATALYSED REACTIONS OF CROTONOPHENONES AND CHALCONES

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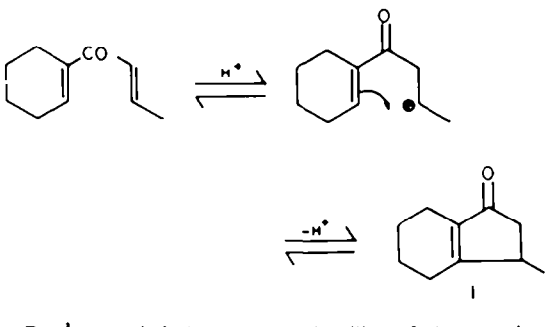
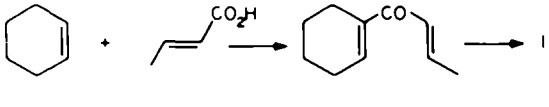
Abstract—Polyphosphoric acid-catalysed cyclisation of derivatives of crotonophenone and chalcone is shown to be a general reaction which occurs without migration of aryl substituents evident with other Friedel–Crafts catalysts. Two other reactions, however, may intervene: hydrogenation and α-carbonyl cleavage. Thus 4-bromochalcone gives 3 - (*p* - bromophenyl) - 1 - phenylpropan - 1 - one, 3 - (*p* - bromophenyl)indan - 1 - one and some benzoic acid. A mechanism for the cyclisation is discussed in comparison with those reported for cyclisations of α,β-unsaturated esters and divinyl ketones. The formation of intermediate Wheland complexes is predicted to be conrotatory.

Intramolecular alkylation of α,β-unsaturated carbonyl compounds catalysed by polyphosphoric acid (PPA) has been much less utilised and studied than the corresponding intramolecular acylation, although both processes can constitute alternative procedures for obtaining the same cyclic ketones.

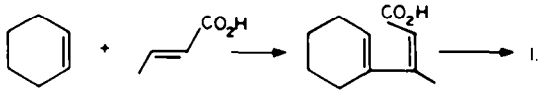
Cyclisations of various divinyl or vinyl allyl ketones by means of PPA and related catalysts such as phosphoric and formic acid mixtures, to give cyclopentenone derivatives have been reported by several groups of workers.[2] Braude and Coles[2a] formulated a mechanism for these reactions in which the PPA behaved as a protonating agent towards the unsaturated α-carbon atom in the first step:



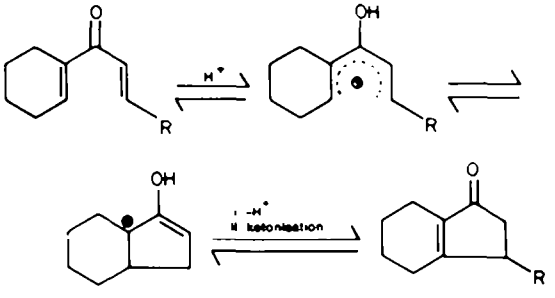
Dev[3] extended the scope and utility of the reaction such that, in a one-pot synthesis, PPA was caused to catalyse both intermolecular acylation of cyclohexene by various α,β-unsaturated acids and the cyclisation of the resulting α,β-unsaturated ketones to form derivatives of tetrahydroindan-1-one. For instance crotonic acid and cyclohexene gave a 56% yield of 3 - methyl - 4,5,6,7 - tetrahydroindan - 1 - one, 1:



Cyclopentene reacted similarly. In these reactions Dev tacitly assumed that the overall process was one of intermolecular acylation followed by intramolecular alkylation. However, an alternative process is one of intermolecular alkylation followed by intramolecular acylation and this cannot be overlooked. In the aforementioned experiment the product is the same and hence the pathways indistinguishable by product analysis:



Another possibility is that the reaction is a concerted cycloaddition but the extreme polarity of the reagents renders this less likely. Dev pointed out that in cyclisations of divinyl ketones, the far more basic carbonyl oxygen atom is likely to be protonated in PPA and the mechanism (slightly modified) was formulated:

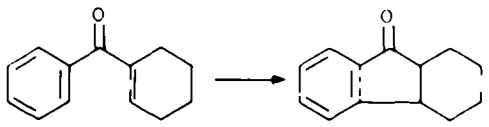


It was also stated that free phosphorus pentoxide, believed to be contained in PPA, could be envisaged as the active cyclising agent presumably by behaving as a Lewis acid towards the carbonyl O atom.

Conia and Leriverend reported extensive studies of the cyclisation of α,β-unsaturated esters in PPA to derivatives of cyclopentenone.[4] These reactions were remarkable because the alcohol-derived alkyl chain migrated, sometimes with rearrangement, to the carbonyl C atom prior to cyclisation. Loss of water lead to a divinyl ketone which then cyclised normally (Scheme 1). They first proposed that a molecule of PPA behaves in the Lewis sense and forms a complex with the carbonyl O atom which persists until it is hydrolysed during workup.

All the above reactions were those where both β-C atoms forming the new covalent bond were olefinic. Shotter, Williams and Johnson[5] described a short series of PPA-catalysed unsaturated ketone cyclialkylations in which one of the β-C atoms was aromatic. However, all the aryl groups were polynuclear and their studies were

concerned with the competition between 5-ring and 6-ring ketone formation. To our knowledge there is one record in the literature of the use of PPA to catalyse the cyclialkylation of an unsaturated ketone at a phenyl β-C atom and that is the conversion of 1-benzoylcyclohexene, 2, to 1,2,3,4,4a,9a - hexahydrofluoren - 9 - one, 3, in a 65% yield.[1]



2 3

Table 1. Reactions of α,β-unsaturated ketones in PPA at 136° for 0.5 hr.
(i) Derivatives of 1,3-diphenylpropen-1-one (chalcones)

Substituents	Products, yield % (*ind* = indan-1-one)	m.p.	anal. of new compound or lit. m.p. C	H	X	MW (Rast)
none	3-phenyl*ind*, 31-50[a]	78°	lit.[8] 78°			
3'methyl	6-methyl-3-phenyl*ind*, 37	92-3°	lit.[9] 93-4°			
	4-methyl-3-phenyl*ind*, 30[b]	62-4°	86.40	6.30	—	208
4'-methyl	5-methyl-3-phenylind, 65[c]	89-90°	85.90	6.30	—	154
3'chloro	6-chloro-3-phenyl*ind*, 8[d]	94°	—	—	14.90	252
	4-chloro-3-phenyl*ind*, 3[e]	oil b.p. 140-150°/0.5 mm, new cpd.				
	starting compound, 8					
4-methyl	3-(*p*-tolyl)*ind*, 12[f]	82°	86.30	6.15	—	212
	starting cpd., 20					
4'-chloro	5-chloro-3-phenyl*ind*, 29[g]	127-8°	73.80	4.95	13.50	191
	p-chlorobenzoic acid, 26	242°[a]				
3-bromo	3-(*m*-bromophenyl)*ind*, 17[h]	116-7°	62.90	3.80	28.20	254
	3-(*m*-bromophenyl)-1-phenyl-propan-1-one, 7[a]	82-3°	62.40	4.55	28.00	288
4-bromo	3-(*p*-bromophenyl)*ind*, 10	59-60°	lit.[10] 61°			
	3-(*p*-bromophenyl)-1-phenyl-propan-1-one, 35[a]	68-9°	lit.[11] 69°			
	benzoic acid, 6					
4-chloro	3-(*p*-chlorophenyl)*ind*, 23[a]	78°	74.00	4.95	14.60	245
	benzoic acid, 7					
	starting cpd., 10					
2',4'-dimethyl	5,7-dimethyl-3-phenyl*ind*, 73	103-4°	lit.[12] 101°			
	starting cpd., 2					
2',5'-dimethyl	4,7-dimethyl-3-phenyl*ind*, 87	91-3°	lit.[12] 94-5°			
3',5'-dimethyl	4,6-dimethyl-3-phenyl*ind*, 67	76-7°	lit.[9] 77.5°			
β-phenyl	no reaction					
β-methyl	3-methyl-3-phenyl*ind*,[i]	oil b.p. 150-160°/1 mm, lit.[13] 197-9°/16 mm				
	starting cpd., combined yield, 32	oil, forms inseparable mixture				

(ii) Derivatives of 1-phenylbut-2-ene-1-one (crotonophenones)

none	3-methyl*ind*, 48	oil b.p. 100-110°/3 mm, lit.[14] 108-110°/4 mm
	butyrophenone, 3	oil Identified by IR spectrum
p-methyl	3,5-dimethyl*ind*, 62[j]	oil b.p. 83-6°/0.3 mm, lit.[15] 113-5°/3 mm
	p-methylbutyrophenone, 1	oil Identified by IR spectrum
	starting cpd., 2	
o-methyl	3,7-dimethyl*ind*, 24[k]	oil b.p. 75-7°/0.3 mm, C, 82.65; H, 7.45%
β-methyl	3,3-dimethyl*ind*, 65	oil b.p. 69-78°/0.4 mm, lit.[16] 115-7°/18 mm
p-methoxy	5-methoxy-3-methyl*ind*, 45	50-1°[l] lit.[17] 50-1°

[a] Mixed m.p. with authentic compound undepressed.

[b] Assigned by difference and by IR spectrum: ν(C=O), 1712 cm^{-1} (5-ring ketone); ν (3 adj. arom. H), 804 cm^{-1}. Recrystallised from ethanol/water and is the more soluble isomer.

[c] Needles (methanol). Chromic acid gave 2-benzoyl-4-methylbenzoic acid m.p. 147-8° (lit.[18] 149-150°).

[d] Fibrous needles (light petroleum). IR spectrum: ν(C=O), 1722 cm^{-1} (5-ring ketone); ν (2 adj. arom. H), 828 cm^{-1}; ν (isolated arom. H), 904 cm^{-1}.

[e] Insufficient for analysis. IR spectrum: ν(C=O), 1722 cm^{-1} (5-ring ketone); ν (3 adj. arom. H), 806 cm^{-1}.

[f] Recrystallised from methanol. IR spectrum: ν(C=O), 1713 cm^{-1} (5-ring ketone). Chromic acid gave *o*-(*p*-toluyl)benzoic acid m.p. and mixed m.p. 138-9°.

[g] Needles (cyclohexane). Chromic acid gave 2-benzoyl-4-chlorobenzoic acid m.p. 181° (lit.[19] 180.5).

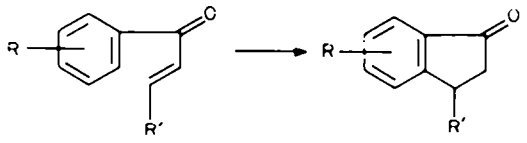
[h] Prisms (cyclohexane). Chromic acid gave *o*-(*m-bromobenzoyl*)*benzoic acid* m.p. 167° (methanol/water) (Found: Br, 27.00%; M, 267. $C_{14}H_9BrO_3$ requires: Br, 26.25%; M, 305). This was almost certainly the impure uncharacterised acid m.p. 156° obtained by the bromination of *o*-benzoylbenzoic acid.[20]

[i] Inseparable mixture (fractional distillation and prep. scale glc). Detected by IR spectroscopy which indicated an approx. equimolar mixture.

[j] 2,4-DNP derivative m.p. 224-5° (lit.[15] 226-7).

[k] 2,4-*DNP derivative* m.p. 250-0.5°, red (ethanol). (Found: N, 16.35%. $C_{17}H_{16}N_4O_4$ requires: N, 16.45%).

The experiments described in this publication show that this reaction is a general one for the formation of indan-1-one derivatives and, although other catalysts have been used for this purpose, PPA has the considerable advantage of not causing unwanted isomerisations such as nuclear Me[6] or Br[7] migration which has been observed with aluminium chloride. Furthermore, some cyclisations have been successful where other catalysts have failed. All the reactions studied were of the type:



and are summarised in Table 1. Two new side reactions were observed: these were hydrogenation of the double bond in the starting compound by an unknown source and α-CO cleavage to form an aromatic acid. Both of these reactions were evident with nuclearly halogenated ketones (Table 1). In some experiments the formation of water-soluble pyrylium salts was observed and this will form the subject of a future report. After separation, all the cyclic ketones were readily recognised by their characteristic carbonyl absorption in the infrared at 1710–22 cm^{-1} and absorptions due to aromatic substitution patterns proved extremely useful.

The following are supplementary observations to those recorded in Table 1.

Chalcone. Several runs were conducted on this ketone to establish the approximate optimum conditions. The highest yield of 3-phenylindan-1-one was 50% obtained by heating 0.01 mole of chalcone in 50 cm^3 of PPA at 136° for 0.5 hr. The same conditions were then employed in all the other experiments. Bruce, Sorrie and Thompson[21] reported that a 60% yield of 3-phenylindan-1-one was obtained by heating chalcone with a molten mixture of aluminium chloride and sodium chloride at 180°. Although this experiment was repeated several times, a yield of no more than 20% was obtained in this laboratory.

3'-Methylchalcone. Both ortho and para cyclisation occurred. The isomeric indan-1-ones were separated by fractional crystallisation from ethanol/water in which the 6-methyl isomer is less soluble and, in a second experiment, by preparative scale GLC.

4'-Methylchalcone. This gave a 65% yield of 5-methyl-3-phenylindan-1-one whereas the sodium chloride/aluminium chloride method gave only 20%.

3'-Chlorochalcone. The isomeric indan-1-ones obtained and some starting compound were readily separated by preparative scale GLC.

4-Methylchalcone. This cyclised with difficulty and a considerable quantity of a yellow water-soluble pyrylium derivative was formed.

4'-Chlorochalcone. Cleavage to *p*-chlorobenzoic acid competed seriously with cyclisation.

4-Bromochalcone. This cyclised normally without any sign of bromine migration. The sodium chloride/aluminium chloride method gave a mixture of 3-(*m*-bromophenyl)indan-1-one with very little of the *p*-bromo isomer. The m.p. of this mixture was about 110°. The table shows that two side reactions were evident in the PPA-catalysed reaction.

3-Bromochalcone. This also cyclised without bromine migration but a hydrogenation product, 3-(*m*-bromophenyl)-1-phenylpropan-1-one, accompanied the main product. An authentic specimen of this new compound was prepared by hydrogenating 3-bromochalcone over Raney nickel. The source of hydrogen in the PPA-catalysed reaction has not been identified. In Part V we reported a PPA-catalysed dehydrogenation.[1]

4-Chlorochalcone. This ketone was partly cleaved to benzoic acid but a 23% yield of 3-(*p*-chlorophenyl-indan-1-one was obtained. The latter was a new compound and its identity was checked by the method of mixed melting points with an authentic specimen prepared by a different method (Experimental).

Dimethylchalcones. The three isomers (Table 1) cyclised normally in good yields. Auwers and Risse were unable to cyclise 2',4'-dimethylchalcone by treatment with aluminium chloride in carbon disulphide or by the sodium chloride/aluminium chloride method but prepared the expected indan-1-one by intramolecular acylation.[12]

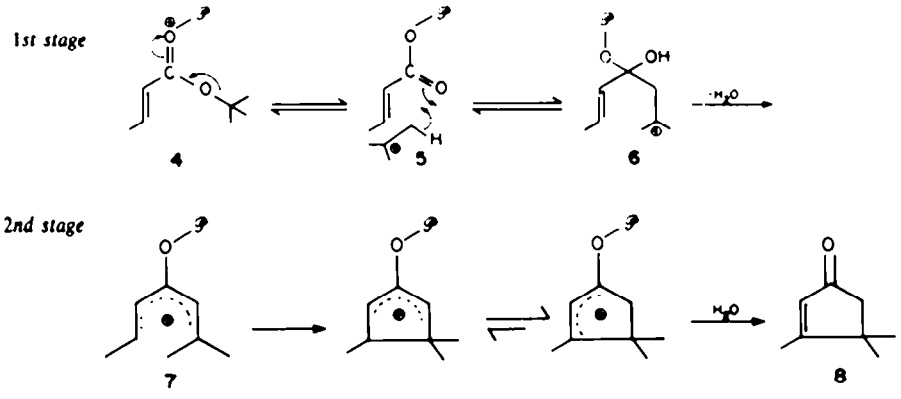
Crotonophenone and p-methylcrotonophenone gave the expected indan-1-ones but hydrogenation was a minor side reaction.

o-Methylcrotonophenone. This formed 3,7-dimethylindan-1-one. Chio Jen *et al.*[22] claimed it was formed by the PPA-catalysed action of crotonic acid on toluene. This structure was corrected to 3,5-dimethylindan-1-one by Kemp and Spanswick[15] who repeated the previous workers' experiment. Tada *et al.*[23] prepared (S)-3,7-dimethylindan-1-one by the degradation of a natural product. The structure appears to have been proved beyond doubt by NMR evidence but no elemental analysis was given. Thus, our unambiguous synthesis constitutes the first method by means of which the racemic compound has been obtained.

p-Methoxycrotonophenone. A 45% yield of 5-methoxy-3-methylindan-1-one was obtained. Dev[24] indirectly reported that cyclisation did not occur in PPA, since when anisole was treated with crotonic acid in PPA, *p*-methoxycrotonophenone (80%) was the sole product.

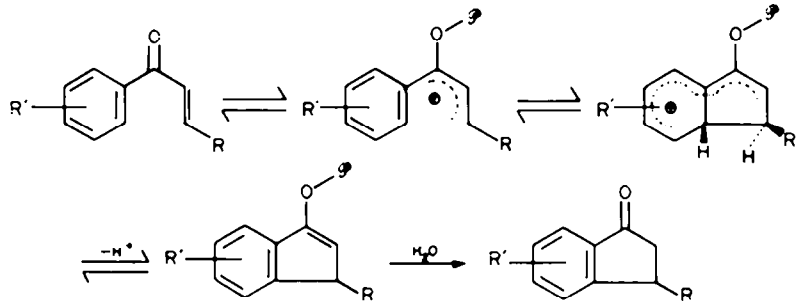
It is pertinent to recall Conia and Leriverend's proposed mechanism for PPA-catalysed reactions of α,β-unsaturated esters[4] before discussing that of α,β-unsaturated ketones. This was formulated as a process occurring in two stages each consisting of a number of smaller steps (Scheme 1). In the first stage the ester complex, **4**, underwent alkyl oxygen fission in the highly polar medium to form the charged mixed anhydride, **5**, together with a carbonium ion which may rearrange. Next the latter nucleophilically attacked the carbonyl carbon atom by a complex mechanism to give the species, **6**, which dehydrated to the ketone complex, **7**. In the second stage this complex cyclised accompanied by a double-bond shift and gave, after hydrolysis accomplished during work-up, the cyclopentenone, **8**.

In the present case of alkenyl aryl ketones the mechanism proposed corresponds closely to Conia and Leriverend's second stage. This is shown in Scheme 2 and differs only in so far as aromatic substitution is depicted instead of vinylic substitution. However, it can equally be used to explain Braude and Coles's cyclisation of divinyl ketones.[25a] The step common to all these reactions is essentially the electrocyclisation of a pentadienyl cation, a conrotatory process. In the present example the first post-cyclisation species is a Wheland complex with the two protons at the ends of the newly formed bond probably existing in a trans configuration.



(℘ represents a molecule of complexed PPA).

Scheme 1. Cyclisation of α,β-unsaturated esters (after Conia and Leriverend[4])



Scheme 2. Cyclisation of alkenyl aryl ketones in PPA

With regard to the role of PPA as a catalyst we recognise that proton and Lewis acid behaviour are competing processes. Kurzanov *et al.* showed that when vinyl allyl ketones are cyclised in deuterated PPA, deuterium is incorporated at C-3 in the allyl chain.[25] Although this shows that PPA is a good protonating agent, the situation is somewhat different here since the allyl double bond is not conjugated and therefore not deactivated by the CO group.

EXPERIMENTAL

GLC was effected on a Wilkins Aerograph Autoprep 705 instrument fitted with a 50 × 3/8 in. column packed with chromosorb W silicone gum SE 30 and used at 250–300° for quantitative analyses and for the preparation of specimens. The following technique for monitoring and rapidly identifying substances as they were eluted from the column was developed. A warmed rock salt plate was placed directly in the stream of hot gas emerging from the column. This produced an even coating of eluent on the plate and remained liquid in most cases for a melt IR spectrum to be determined. A series of such plates were prepared so that each component of a mixture could be impingement-coated separately.

Preparation of unsaturated ketones. These were prepared by Claisen–Schmidt reactions, except of those described below, and had physical properties in accord with those described in the literature.

β-Phenylchalcone was available from previous work.[26]

o-Methylcrotonophenone was prepared as follows. *o*-Bromotoluene (34.2 g, 0.2 mol) was converted into the Grignard reagent by treating it in ether with Mg (4.86 g, 0.2 mol). Dry $CdCl_2$ (18.3 g, 0.1 mol) was added portionwise until the soln no longer gave a positive test with Michler's ketone. The ether was evaporated in N_2 and benzene (25 cm^3) was added. To this a soln of crotonyl chloride (20.9 g, 0.2 mol) in benzene (25 cm^3) was added dropwise. The soln was heated under reflux for 1 hr and then left overnight. It was poured into ice-dil. HCl mixture, and the organic layer was separated, washed with water, dried ($MgSO_4$) and distilled *in vacuo*. The fraction b.p. 110–130°/3.0 mm (2.5 g, 8%) was used in the cyclisation experiments. It appeared to contain a small amount of ethyl crotonate which, however, was not expected to interfere. A small sample was oxidised with 50% HNO_3 aq which afforded *o*-toluic acid m.p. and mixed m.p. 102°.

Crotonophenone, *p*-methylcrotonophenone and β-methylcrotonophenone were prepared by standard Friedel–Crafts reactions between the appropriate acid chlorides and aromatic hydrocarbons.

p-Methoxycrotonophenone was prepared by the method of Dev.[24]

PPA-catalysed cyclisations. PPA (50 cm^3) was heated in a vapour bath at 136° (ethylbenzene) and the ketone (0.01 mol) was stirred in until the mixture appeared homogenous. Heating was continued without stirring for a further 0.5 hr. The products were poured into ice-water and the mixture was extracted with ether. The largely fluorescent aqueous layers were rejected but the ether extracts were washed with several portions of water. In some runs the ether layer was given a prior wash with dilute alkali to extract organic acids which were recovered by acidification. After drying ($MgSO_4$) the solvent was removed and the residue distilled *in vacuo*. Where organic acids had not been previously removed they appeared, when present, as sublimates in the condenser at this stage. After the removal of any crystalline material for separate examination, the oily distillates were separated into their components by means of preparative scale GLC. Solids thus obtained were further purified by recrystallisation from an appropriate solvent (Table 1).

Cyclisations in a mixture of sodium chloride and aluminium chloride

General directions. Unless otherwise stated these were performed by the method described by Bruce *et al.*[21] A mixture of $AlCl_3$ (10 g) and NaCl (2 g) was heated to 140°. The unsaturated ketone (2 g) was stirred into the melt at such a rate that the heat

of the reaction raised the temp. to 180°. This temp. was held for a further 2 min. After pouring ice-dil. HCl the products were worked up in the usual way and separated from tar by distillation *in vacuo*.

4-*Bromochalcone*. The pale yellow distillate, b.p. 160°/1.5 mm, (0.9 g) crystallised on trituration. This was shown to be a mixture containing mainly 3 - (*m* - bromophenyl)indan - 1 - one and a little 3 - (*p* - bromophenyl)indan - 1 - one by comparison of its IR spectrum with the spectra of the pure components prepared by the PPA method. Repeated recrystallisation gave mixed crystals of constant m.p. 107–9° (ethanol/water). The combined yield was 45%.

3-*Bromochalcone*. The fraction b.p. 120°/0.5 mm solidified to needles of 3 - (*m* - bromophenyl)indan - 1 - one m.p. and mixed m.p. 116–7° (cyclopexane/light petroleum) (0.1 g, 5%).

4-*Chlorochalcone*, 4-*methylchalcone*, 3-*methoxychalcone and* 4-*nitrochalcone*. No crystalline products were obtained from these reactions. The products were largely high boiling tars. 4-Nitrochalcone gave a mass of expanded charcoal. The experiment with 4-methylchalcone was repeated at a lower temp. (110°) without success.

Chalcone. This reaction was conducted under a variety of conditions including those used by Bruce *et al.* but in no case did the yield of 3 - phenylindan - 1 - one approach the 60% yield reported by these workers.[21] The following procedure gave the highest yield. An intimate mixture of NaCl and $AlCl_3$ (in the ratio 1/5 w/w) was prepared by gently fusing and then allowing to solidify. The powdered catalyst (24 g) was mixed with chalcone (3 g, 0.014 mol) and the temp. raised to 136° by means of an external vapour bath (ethylbenzene) and was held for 10 min. After working up, the products were distilled and the fraction b.p. 150–200°/2 mm (0.6 g, 20%) formed a solid which on recrystallisation was shown to be mainly 3 - phenylindan - 1 - one m.p. and mixed m.p. 77–8° (EtOH). An IR spectrum of the mother liquors revealed the presence of at least three other carbonyl containing compounds.

4'-*Methylchalcone*. The pale yellow fraction b.p. 150–200°/0.7 mm was triturated with MeOH and gave 5 - methyl - 3 - phenylindan - 1 - one m.p. and mixed m.p. 89–90° (MeOH), (0.4 g, 20%).

Reference compounds

3 - (p - *Chlorophenyl)indan* - 1 - *one*. This was prepared from *β* - (*p* - chlorophenyl) - *β* - phenylhydracrylic acid, itself prepared by a Reformatskii reaction in a manner analogous to that described[27] as follows. The acid (2 g, 0.0072 mol) was stirred with H_2SO_4 for 0.5 hr and then poured into ice-water and extracted with ether. The ether layer was washed with several portions of Na_2CO_3 aq and then the solvent was evaporated. The residue was crystallised from EtOH by dissolving at a temp. of no more than 40° and then chilling to −10°. This gave yellow needles of 3 - (p - *chlorophenyl)ind*-1-*one* m.p. 143–4° (darkens). It was decomposed in boiling alcohol but was stable in hot AcOH and gave a deep green soln in H_2SO_4. ν(C=O), 1718 cm^{-1} (5-ring ketone). (Found: C, 74.65; H, 4.10; Cl, 14.70; MW, 220. $C_{15}H_9ClO$ requires: C, 74.85; H, 3.75; Cl, 14.75%; MW, 240.5). The *oxime* formed lemon-yellow crystals m.p. 138–40° and gave a red soln in H_2SO_4. (Found: N, 6.10; MW, 248. $C_{15}H_{10}ClNO$ requires: N, 5.50%; MW, 255.5). The chloro derivative was obtained by first decolourising a soln of the indone in CCl_4 by a stream of Cl_2, evaporating the solvent and the dehydrochlorinating the residue by boiling with EtOH/AcOH. The cooled soln deposited orange-yellow fibres of 2 - *chloro* - 3 - (p - *chlorophenyl)ind* - 1 - *one* m.p. 172° (EtOH/AcOH), ν(C=O), 1733 cm^{-1} (α-halogeno 5-ring ketone). (Found: C, 64.85; H, 3.10; Cl, 24.60%; MW, 243. $C_{15}H_8Cl_2O$ requires: C, 65.45; H, 2.90; Cl, 25.80%; MW, 275). Hydrogenation of the parent indone over Raney nickel at atmospheric pressure gave the required 3 - (*p* - chlorophenyl)indan - 1 - one m.p. 78°.

When the above procedure was applied to the formation of the bromo analogue the following were obtained. 3 - (p - *bromophenyl)ind* - 1 - *one* m.p. 150–1° (dec), yellow needles (cyclohexane) which formed a green soln in H_2SO_4, ν(C=O), 1720 cm^{-1} (5-ring ketone). (Found: C, 63.15; H, 3.25; Br, 28.65; MW, 269. $C_{15}H_{11}BrO$ requires: C, 63.15; H, 3.15; Br, 28.05%; MW, 285). The *oxime* formed greenish yellow fibres (cyclohexane) and had m.p. 130–4° (Found: N, 4.50%; MW, 294. $C_{15}H_{10}BrNO$ requires: N, 4.65%; MW, 300). Bromination-dehydrobromination gave 2 - *bromo* - 3 - (p - *bromophenyl)ind* - 1 - *one* m.p. 183–5° as golden-yellow needles (EtOH/$CHCl_3$), ν(C=O), 1733 cm^{-1} (α-halogeno 5-ring ketone). (Found: C, 50.10; H, 2.20; Br, 44.70; MW, 296. $C_{15}H_8Br_2O$ requires: C, 49.45; H, 2.20; Br, 43.65%; MW, 364). Chromic acid oxidation of this dibromide gave *p*-bromobenzoic acid m.p. 252°. The *oxime* formed a lemon yellow crystalline powder m.p. 252–4° (dec) (EtOH/$CHCl_3$). (Found: N, 3.55%; MW, 348. $C_{15}H_9Br_2NO$ requires: N, 3.70%). Attempts to prepare the required indan-1-one by hydrogenating either of these two ind-1-ones over Raney nickel were unsuccessful.

3-Phenylindan-1-one was available from previous work.[28]

REFERENCES

[1]Part V. J. M. Allen, K. M. Johnston and R. G. Shotter, *Chem. & Ind.* 108 (1976).

[2a]E. A. Braude and J. A. Coles, *J. Chem. Soc.* 1430 (1952); [b]I. N. Nazarov and L. N. Pinkina, *Zh. Obschei Khim.* **18**, 675 *and* 681 (1948); [c]I. N. Nazarov and I. L. Kotlyarevskii, *Ibid.* 903 (1948).

[3]S. Dev, *J. Indian Chem. Soc.* **34**, 169 (1957).

[4]J.-M. Conia and M.-L. Leriverend, *Bul. Soc. Chim. Fr.* **8–9**, 2981, 2992 (1970).

[5]R. G. Shotter, K. M. Johnston and H. J. Williams, *Tetrahedron* **29**, 2163 (1973).

[6]G. Braddeley, G. Holt and S. Makar, *J. Chem. Soc.* 3289 (1952).

[7]P. J. de Valois, M. P. van Albada and J. U. Veenland, *Tetrahedron* **24**, 1835 (1968).

[8]E. P. Kohler, *Amer. Chem. J.* **31**, 649 (1904).

[9]P. Pfeiffer and E. E. Roos, *J. Prakt. Chem.* **159**, 13 (1941).

[10]C. F. H. Allen and J. W. Gates, Jr., *J. Am. Chem. Soc.* **65**, 422 (1943).

[11]J. R. Johnson, T. L. Jacobs and A. M. Schwartz, *Ibid.* **60**, 1885 (1938).

[12]K. von Auwers and E. Risse, *Liebigs Ann.* **502**, 282 (1933).

[13]C. F. Koelsch, H. Hochmann and C. Le Claire, *J. Am. Chem. Soc.* **65**, 59 (1943).

[14]R. T. Hart and R. F. Tebbe, *Ibid.* **72**, 3286 (1950).

[15]W. Kemp and J. Spanswick, *J. Chem. Soc.* Perkin I, 151 (1972).

[16]G. Baddeley and R. Williamson, *Ibid.* 4647 (1956).

[17]L. H. Conover, *J. Am. Chem. Soc.* **75**, 4017 (1953).

[18]M. Hayashi, S. Tsuruoka, I. Morokawa and H. Namikawa, *Bull. Chem. Soc. Japan* **11**, 184 (1936).

[19]G. Egerer and H. Meyer, *Monatsh.* **34**, 83 (1913).

[20]F. Kunckell and Knigge, *Ber. Dtsch. Chem. Ges.* **39**, 194 (1906).

[21]D. Bruce, A. Sorrie and R. Thomson, *J. Chem. Soc.* 2403 (1953).

[22]Chio Jen, Lin-Lin K'uang, Ying-Chun Lin, Chin-Shih Ma and Sheng Chin, *K'o Hsueh T'ung Pao* **17**(9), 412 (1966); *Chem. Abstr.* **66**, 37678 (1967).

[23]M. Tada, Y. Moriyama, Y. Tanahashi and T. Takahashi, *Tetrahedron Letters* 5251 (1972).

[24]S. Dev, *J. Indian Chem. Soc.* **33**, 703 (1956).

[25]D. N. Kursanov, Z. N. Parnes, I. I. Zaretskaya and I. N. Nazarov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 114 (1953).

[26]K. M. Johnston and R. G. Shotter, *J. Chem. Soc.* (C), 1703 (1966).

[27]J. F. Feeman and E. D. Amstutz, *J. Am. Chem. Soc.* **72**, 1526 (1950).

[28]R. G. Shotter and K. M. Johnston, *Tetrahedron* **30**, 4059 (1974).