23. *Preparation of* cyclo*Pentenones from the Products of Interaction of Acid Chlorides and Olefins.*

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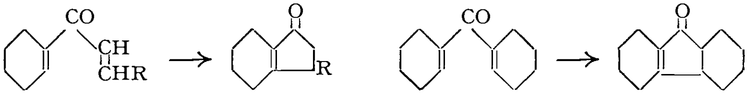
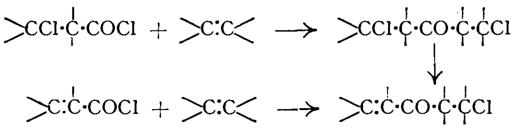
Ethylene readily combines with acid chloride–aluminium chloride complexes in solution in ethylene chloride or methylene chloride to provide 2-chloroethyl ketones and their products of dehydrochlorination. The products of interaction of *cyclo*hexene and the chlorides of β-chloropropionic, crotonic, and *cyclo*hex-1-enecarboxylic acid severally afford *cyclo*pentenones by the action of phosphoric acid in solution in formic acid (98%).

Recently, Braude and Coles (*J.*, 1952, 1430) have shown that the three divinyl ketones (I, II, and III), which they prepared by direct alkenylation with lithium alkenyls (*J.*, 1950, 2012, 2014), afford the *cyclo*pentenone derivatives (IV, V, and VI) by the action of phosphoric acid in formic acid. Interaction of olefins and acid chlorides and anhydrides through the agency of aluminium chloride affords ready access to ββ′-dichloro-ketones and the corresponding vinyl ketones resulting from monodehydrochlorination; the reaction can be formulated:



(I; R = H) (II; R = Me) (IV; R = H) (V; R = Me) (III) (VI)



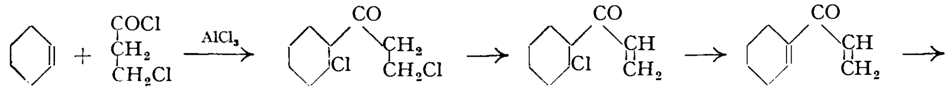
$$>\mathrm{CCl{\cdot}\overset{|}{\underset{|}{C}}{\cdot}COCl} + >\mathrm{C{:}C}< \longrightarrow >\mathrm{CCl{\cdot}\overset{|}{\underset{|}{C}}{\cdot}CO{\cdot}\overset{|}{\underset{|}{C}}{\cdot}\overset{|}{\underset{|}{C}}Cl}$$

$$\downarrow$$

$$>\mathrm{C{:}\overset{|}{C}{\cdot}COCl} + >\mathrm{C{:}C}< \longrightarrow >\mathrm{C{:}\overset{|}{C}{\cdot}CO{\cdot}\overset{|}{\underset{|}{C}}{\cdot}\overset{|}{\underset{|}{C}}Cl}$$

We now report that these products, though prevented by the incursion of polymerisation from being a convenient source of divinyl ketones, can provide *cyclo*pentenones by the action of phosphoric acid in formic acid; (IV, V, and VI) have been prepared in this way. The preparation of (IV) is formulated below; (V) and (VI) were similarly obtained from the products of interaction of *cyclo*hexene and the chlorides of crotonic and *cyclo*hex-1-enecarboxylic acid respectively.

To obtain optimum yields of halogenated ketones on interaction of acid halides and olefins in the presence of aluminium chloride, Catch, Elliot, Hey, and Jones (*J.*, 1948, 278) used no solvent other than the acyl halide itself. Since vigorous agitation was essential, excess of the acyl halide was used in reactions in which, when molar quantities of the reagents were used, stirring was difficult; poorer yields were obtained by earlier investigators employing inert diluents such as petroleum or carbon disulphide. These diluents are poor solvents for the polar complexes obtained by combination of acid and aluminium chlorides and since methylene and ethylene chlorides have proved to be valuable solvents for the conventional Friedel–Crafts ketone synthesis in the aromatic series, we have employed them in the aliphatic series. With ethylene, the best yields were obtained in the absence of hydrogen chloride and in the presence of a small excess of aluminium chloride and are given in the Table. The theoretical volume of ethylene was readily absorbed in each instance but simultaneous formation of vinyl ketones, which became more important with rise in temperature (Wieland and Beltog, *Ber.*, 1922, **55**, 2246) and on storage of the reaction mixture, prevented quantitative production of 2-chloroethyl ketones. Similarly, interaction of *cyclo*hexene and the chlorides of β-chloropropionic, crotonic, and *cyclo*hex-1-enecarboxylic acid severally afforded mixtures which contained less chlorine than is required for the products of addition. These mixtures are not readily dehydrochlorinated and unlike 2-chloro*cyclo*hexyl methyl ketone (Christ and Fuson, *J. Amer. Chem. Soc.*, 1937, **59**, 893) contain chlorine after distillation from anhydrous sodium carbonate. The results are summarised in the Table. Both before and after distillation from sodium carbonate, these mixtures evolve hydrogen chloride by the action of phosphoric acid in formic acid (98%) at 90° and afford *cyclo*pentenone derivatives. We are indebted to Dr. E. A. Braude for providing samples of the dinitrophenylhydrazones of the *cyclo*pentenones (IV and V).



(IV)

Interaction of ethylene and $R\cdot COCl$–$AlCl_3$ *in methylene and ethylene chlorides at* —5°.

R·COCl	Product	Yield (%)	B. p./mm.	Chlorine (%) Found	Chlorine (%) Reqd.
$CH_3\cdot COCl$	$CH_3\cdot CO\cdot CH_2\cdot CH_2Cl$	40 (40)	46°/14	33·1	33·3
$CH_2Cl\cdot COCl$	$CH_2Cl\cdot CO\cdot CH_2\cdot CH_2Cl$	83 (45)	68°/0·2	50·0	50·3
$CH_3\cdot CHCl\cdot COCl$	$CH_3\cdot CHCl\cdot CO\cdot CH_2\cdot CH_2Cl$	78 (60)	62°/1	46·2	45·8
$CH_2Cl\cdot CH_2\cdot COCl$	$CH_2\cdot Cl\cdot CH_2\cdot CO_2\cdot CH_2\cdot CH_2Cl$	53 (30)	78°/0·8	46·1	45·8

Interaction of cyclo*hexene and* $R\cdot COCl$–$AlCl_3$ *in methylene and ethylene chlorides at* —5°.

R·COCl	Cl (%) before distn.	Cl (%) theor.	Cl (%) after distn.
$CH_3\cdot COCl$	21·8	22·1	0
$C_6H_9\cdot COCl$	12·0	15·8	Not distilled
$CH_3\cdot CH{:}CH\cdot COCl$	10·6	19·1	8·4
$CH_2Cl\cdot CH_2\cdot COCl$	29·0	34·0 (dichloride) 20·6 (monochloride)	13·4

Since aryl vinyl ketones and aryl 2-chloroethyl ketones readily afford indanones by the action of aluminium chloride–hydrogen chloride, we have attempted, though without success, to apply this reagent to the preparation of the above *cyclo*pentenones.

EXPERIMENTAL

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : *11-Decahydrofluorenone.*—1-Anilino*cyclo*hexanecarboxylic acid (40 g.), obtained from *cyclo*hexanone as described by Walther and Hubner (*J. pr. Chem.*, 1916, **93**, 124) and Betts, Muspratt, and Plant (*J.*, 1927, 1312), provided a mixture of aniline and *cyclo*hex-1-enecarboxylic acid when melted and then strongly heated under reduced pressure. The mixture was shaken with dilute hydrochloric acid and methylene chloride, and the lower layer was extracted with sodium carbonate solution; on acidification, the alkaline extracts afforded a colourless oil which was extracted with methylene chloride, dried (Na_2SO_4), and distilled; *cyclo*hex-1-enecarboxylic acid (8 g.), b. p. 246—248°, m. p. 33°, was obtained and this afforded the corresponding acid chloride (9 g.), b. p. 202—204° (Kenner and Wain, *Ber.*, 1939, **72**, 456) by the action of thionyl chloride. The acid chloride (9 g.) was added to a suspension of finely powdered aluminium chloride (15 g. > 1 mol.) in methylene chloride (50 ml.), and the liquid phase was decanted from undissolved aluminium chloride and filtered through a plug of

glass wool into a reaction vessel from which atmospheric moisture was excluded. The solution was vigorously stirred, at −10°, and *cyclo*hexene (6 g., 1·2 mols.) was added during 25 minutes, and the mixture, the temperature of which was not allowed to exceed −5°, was stirred for a further 10 minutes and then poured into dilute hydrochloric acid and ice. The organic layer was dried (K_2CO_3), and methylene chloride was removed at 0° under reduced pressure; the residue was a pale brown viscous oil (10 g.) (Found: Cl, 12·0. Calc. for $C_{13}H_{17}OCl$: Cl, 15·8%). This product (5 g.) was heated with phosphoric acid (4 g.) and formic acid (98%; 8 g.) at 90° for 18 hours under nitrogen; hydrogen chloride was evolved and the product was poured into water and extracted with ether (2 × 30 ml.); the extract was dried (K_2CO_3) and distilled. The required decahydrofluorenone (2·5 g.), b. p. 126—127°/0·1 mm., and m. p. 20° [m. p. 25° after crystallisation from light petroleum (b. p. 0—40°)], formed an oxime, m. p. 133—134°; Braude and Coles (*loc. cit.*) record m. p.s 26° and 133—134° respectively.

4 : 5 : 6 : 7-*Tetrahydro*-3-*methylindanone*.—Crotonyl chloride (10·4 g.) was added to a suspension of aluminium chloride (20 g.) in methylene chloride; the solution was decanted from undissolved aluminium chloride, then cooled to −10°, and *cyclo*hexene (8·2 g.) was gradually added. Working up as in the previous case gave a dark material (14 g.) (Found: Cl, 10·6. Calc. for $C_{10}H_{15}OCl$: Cl, 19·0%) which was distilled from anhydrous sodium carbonate (2—3 g.) and provided a mixture (8 g.), b. p. 80—110°/0·25 mm. (Found: Cl, 8·4%). [In another experiment this mixture was fractionally distilled, providing a fraction (1 g.), b. p. 65—68°/0·25 mm., which was probably *cyclo*hex-1-enyl propenyl ketone, b. p. 64—65°/0·3 mm. (Braude and Coles, *J.*, 1952, 1430), and a residue which polymerised.] The mixture (7 g.) was heated with phosphoric acid (3 g.) and formic acid (98%; 8 g.) at 80—90° for 4 hours under nitrogen; hydrogen chloride was evolved. The product, worked up as described above, gave the indanone (4 g.), b. p. 130°/16 mm. It formed a semicarbazone which separated from aqueous methanol in prisms, m. p. 219° (decomp.) [Braude and Coles, *loc. cit.*, give m. p. 214—217° (decomp.)], and a 2 : 4-dinitrophenylhydrazone, m. p. 246°; the m. p. was not depressed on admixture of the sample with the 2 : 4-dinitrophenylhydrazone described by Braude and Coles, *loc. cit.*, who give m. p. 246—248°.

4 : 5 : 6 : 7-*Tetrahydroindanone*.—β-Chloropropionyl chloride (12·7 g.) was gradually added to a suspension of powdered aluminium chloride (20 g.) in methylene chloride (100 ml.). The solution was decanted from undissolved aluminium chloride and cooled to −10°; *cyclo*hexene (8·2 g.) was added at such a rate (during 30 min.) that the temperature of the reaction mixture did not exceed −5°. The product was worked up as above and provided a residue (13 g.) (Found: Cl, 29·0. Calc. for $C_9H_{14}OCl_2$: Cl, 34·0%) after evaporation of methylene chloride. Distillation from anhydrous sodium carbonate afforded a fraction (7 g.), b. p. 105—115°/15 mm. (Found: Cl, 13·4. Calc. for $C_9H_{13}OCl$: Cl, 20·6%). (Fractional distillation of this product in another experiment effected polymerisation.) The product (5 g.), together with phosphoric acid (2 g.) and formic acid (98%; 6 g.), was kept at 90° for 3 hours under nitrogen. Hydrogen chloride was evolved and the product was worked up as above. The required indanone (4 g.), b. p. 126—128°/15 mm. (Braude and Coles, *loc. cit.*, give b. p. 126—128°/14 mm.), formed a dinitrophenylhydrazone which crystallised from benzene in orange plates, m. p. 243—244°, and did not, by admixture, depress the m. p. of the 2 : 4-dinitrophenylhydrazone described by Braude and Coles, *loc. cit.*, who give m. p. 235—238°. In a further experiment, the product (17 g.) of the Friedel–Crafts reaction was allowed to react with phosphoric acid (8 g.) in formic acid (98%; 16 g.) and afforded the required indanone (4·5 g.).

Interaction of Acid Chlorides and Ethylene in Methylene or Ethylene Chloride as Solvent.—The acid chloride (0·25 mole) was added to a suspension of finely powdered aluminium chloride (0·30 mole) in solvent (150 ml.). The solution was decanted from undissolved aluminium chloride, and poured through a plug of glass wool into the reaction vessel which was cooled in a freezing mixture. Dry ethylene was passed into the agitated solution at −10°; absorption was rapid and ceased when ethylene (5·5 l.) has been absorbed. The temperature of the reaction mixture was not allowed to exceed −5°. The product was then poured into dilute hydrochloric acid and ice, and the organic layer was dried (Na_2SO_4) and distilled under reduced pressure. The best yields (see Table) of the 2-chloroethyl ketones were usually obtained (*a*) when the reaction mixtures were not freed from undissolved aluminium chloride and (*b*) when the reaction mixtures were freed from hydrogen chloride by a stream of dry nitrogen before ethylene was introduced. The yields given in parentheses in the Table were obtained by Catch, Elliot, Hey, and Jones (*loc. cit.*).

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