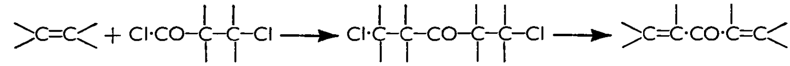
258. *Aliphatic Friedel–Crafts Reactions. Part IV.* The Preparation of Divinyl Ketones.*

By N. Jones and H. T. Taylor.

Ethylene or propene combines with an acyl chloride–aluminium chloride complex in methylene chloride to provide chloro-ketones, which on dehydrohalogenation afford divinyl ketones. Cyclisation of dipropenyl ketone gives 3,4-dimethylcyclopent-2-en-1-one.

The acylation of an olefin with a β-chloro-acid chloride, through the agency of aluminium chloride, readily affords 2,2′-dichlorodialkyl ketones, which on complete dehydrohalogenation provide divinyl ketones:



$$>C=C< + Cl\cdot CO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Cl \longrightarrow Cl\cdot\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Cl \longrightarrow >C=\overset{|}{C}\cdot CO\cdot\overset{|}{C}=C<$$

Di-2-chloroethyl ketone, prepared by interaction of ethylene and β-chloropropionyl chloride,[1] when distilled from anhydrous sodium carbonate, provides divinyl ketone. Attempts to effect dehydrohalogenation by *NN*-dimethylaniline,[2] aluminium chloride, or alcoholic potassium hydroxide resulted in polymerisation. Divinyl ketone readily polymerises [3] and was identified by quantitative hydrogenation to diethyl ketone.

Reaction of ethylene with crotonoyl chloride, or of propene with β-chloropropionyl chloride, provides propenyl vinyl ketone, dehydrohalogenation taking place during the reaction if carried out at 25—30°. The formation of a divinyl ketone is readily detected by the lachrymatory properties and the odour produced. Propene and crotonoyl chloride provide dipropenyl ketone.

Propene is less reactive towards an acid chloride–aluminium chloride complex in methylene or ethylene chloride than is ethylene. Higher reaction temperatures (25—30°) are required, and the reaction is indefinite in that absorption of propene does not stop after one mol. has been absorbed.[4] n-Propyl iodide did not react with the acetyl chloride–aluminium chloride complex at 40° after one hour, but isopropyl bromide afforded the expected methyl propenyl ketone.

On treatment with phosphoric acid and 98% formic acid,[5] divinyl ketone and vinyl propenyl ketone polymerise, but dipropenyl ketone yields 3,4-dimethylcyclopent-2-en-1-one; this on hydrogenation provided 3,4-dimethylcyclopentanone.

---

* Part III, preceding paper.

[1] Baddeley, Taylor, and Pickles, *J.*, 1953, 124.

[2] B.P. 459,537/1937.

[3] Nazarov, numerous papers, *Bull. Acad. Sci. U.S.S.R.*, 1947 onwards.

[4] See Thomas, " Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publ. Inc., New York, 1942.

[5] Nazarov and Burmistrova, *Bull. Acad. Sci. U.S.S.R.*, **1947**, 51.

Our various results are summarised in the Table.

Interaction of olefin with acetylating agent, at 25—30° unless otherwise stated.

Reactants		Product	Yield (%)
$CH_2:CH_2$	$Cl·CH_2·CH_2·COCl$	$(CH_2:CH)_2CO$	35[a]
,,	$CH_3·CH:CH·COCl$	$CH_2:CH·CO·CH:CHMe$	52
$Me·CH:CH_2$	AcCl	$Me·CH:CH·COMe$ }	40
,,	Ac_2O	$Cl·CHMe·CH_2·COMe$ }	
,,	$CH_3·CH:CH·COCl$	$(Me·CH:CH)_2CO$	40
,,	$Cl·CH_2·CH_2·COCl$[b]	$CH_2·CH·CO·CH:CHMe$	45
,,	$MeO_2C·[CH_2]_2·COCl$	$Me·CH:CH·CO·[CH_2]_2·CO_2Me$	35
Pr^nI	AcCl[c]	—	0
Pr^iBr	AcCl[c]	$MeCH:CH·COMe$	43

[a] After distillation from Na_2CO_3. [b] At 35°. [c] At 40°.

EXPERIMENTAL

Propene and Acetyl Chloride.—Powdered aluminium chloride (0·60 mole) was added with stirring to acetyl chloride (0·50 mole) in methylene chloride (200 ml.). The acetyl chloride–aluminium chloride complex was decanted from the excess of chloride into the reaction vessel, and dry propene was passed into the stirred solution at 25—30° (no reaction occurred at 0°). A slow, steady absorption occurred, which slackened but did not cease after 12 l. had been absorbed. The mixture was poured into dilute hydrochloric acid and ice, the organic layer separated and dried (Na_2SO_4), and the solvent removed. Distillation of the residue (41 g.) gave methyl propenyl ketone (4 g.), b. p. 103°, which afforded a 2,4-*dinitrophenylhydrazone*, m. p. 156—157° (Found: N, 21·0. $C_{11}H_{12}N_4O_4$ requires N, 21·2%), and 2-chloroethyl methyl ketone (15 g.), b. p. 123—125° (Found: Cl, 29·0. Calc. for C_5H_9ClO: Cl, 29·4%), together with higher-boiling material (20 g.). Distillation of 2-chloroethyl methyl ketone from anhydrous sodium carbonate gave methyl propenyl ketone, which was hydrogenated to methyl propyl ketone (2,4-dinitrophenylhydrazine, m. p. 144°).

Acetic anhydride (0·50 mole) and aluminium chloride (1·1 mole) provided identical products.

Propene and Crotonoyl Chloride.—Crotonoyl chloride (0·25 mole) and aluminium chloride (0·30 mole) were treated as above; absorption of propene proceeded readily at 25°, ceasing sharply after 6 l. The product, isolated as above, was dipropenyl ketone (11 g.), b. p. 62—63°/16 mm. (Found: C, 85·3; H, 9·0. Calc. for $C_7H_{10}O$: C, 85·5; H, 9·1%). A sample (1·50 g.) in ethanol (10 ml.) absorbed hydrogen (596 ml. corr. to S.T.P. Calc. for $C_7H_{10}O$: 2 mol., 611 ml.) in the presence of palladium). The reduced product gave a semicarbazone, m. p. and mixed m. p. 132°.

3,4-*Dimethylcyclopent*-2-*en*-1-*one*.—Dipropenyl ketone (10 g.) was added to a solution of phosphoric acid (8 g.) in 98% formic acid (16 g.), and the mixture was kept at 90° for 4 hr. under nitrogen, then poured into water and extracted with ether. After the solvent had been removed, distillation gave 3,4-dimethylcyclopent-2-en-one (6 g.), b. p. 70°/12 mm. [2,4-*dinitrophenylhydrazone*, m. p. 210—212° (Found: C, 53·6; H, 4·9; N, 19·6. $C_{13}H_{14}N_4O_4$ requires C, 53·8; H, 4·8; N, 19·4%)]. The product (2·0 g.) in ethanol (10 ml.) absorbed hydrogen (410 ml. corr. to S.T.P. Calc. for $C_7H_{10}O$: 1 mol., 403 ml.) in the presence of palladium (0·1 g.). The reduced product, 3,4-dimethylcyclopentanone gave a 2,4-*dinitrophenylhydrazone*, m. p. 140° (Found: C, 53·1; H, 5·5; N, 19·6. $C_{13}H_{16}N_4O_4$ requires C, 53·4; H, 5·5; N, 19·4%), and a *semicarbazone*, m. p. 221° (Found: C, 56·2; H, 9·3; N, 24·6. $C_8H_{13}N_3O$ requires C, 56·5; H, 8·8; N, 24·8%).

Attempted cyclisation of divinyl ketone to yield cyclopentenone and of propenyl vinyl ketone to yield a methylcyclopentenone resulted in polymerisation.

Propene and β-Chloropropionyl Chloride.—β-Chloropropionyl chloride (0·25 mole) and aluminium chloride (0·30 mole) were treated as in the previous experiment. Absorption was slow and, at 35°, 6 l. were absorbed in 1 hr. The mixture was decomposed and distillation of the product gave propenyl vinyl ketone (10·5 g.), b. p. 57—58°/16 mm. (Found: C, 74·8; H, 8·25. Calc. for C_6H_8O: C, 75·0; H, 8·3%). A sample (2·50 g.) in ethanol (20 ml.) absorbed hydrogen (1065 ml., corr. to S.T.P. Calc. for C_6H_8O: 2 mol., 1080 ml.) in the presence of palladium. The reduced product, ethyl propyl ketone, gave a 2,4-dinitrophenylhydrazone, m. p. 132°.

Propene and β-Methoxycarbonylpropionyl Chloride.—β-Methoxycarbonylpropionyl chloride

(0·25 mole) and aluminium chloride (0·30 mole) were treated as above. Absorption of propene was rapid at 25° and almost ceased after 6 l. The product, isolated as above, provided methyl 4-oxohept-5-enoate (14 g.), b. p. 105°/10 mm. A sample (2·00 g.) in ethanol (10 ml.) absorbed hydrogen (300 ml. corr. to S.T.P. Calc. for $C_8H_{12}O_3$: 1 mol., 290 ml.) in the presence of palladium. The reduced product gave a semicarbazone, m. p. and mixed m. p. 108° (Found: N, 19·2. Calc. for $C_9H_{17}N_3O_3$: N, 19·5%).

Ethylene and β-Chloropropionyl Chloride.—β-Chloropropionyl chloride (0·25 mole) and aluminium chloride (0·30 mole) were treated with ethylene as described by Baddeley, Taylor, and Pickles.[1] The product, di-2-chloroethyl ketone (16 g.), was distilled rapidly from an excess of anhydrous sodium carbonate, giving divinyl ketone, b. p. 30°/16 mm. (7·5 g.). A sample (2·00 g.) in ethanol (10 ml.) absorbed hydrogen (1080 ml. corr. to S.T.P. Calc. for C_5H_6O: 2 mol., 1092 ml.). The product, dipropyl ketone, readily gave a 2,4-dinitrophenylhydrazone, m. p. 156°.

Ethylene and Crotonoyl Chloride.—Crotonoyl chloride (0·25 mole) and aluminium chloride (0·30 mole) were treated as in the reaction with propene. Absorption of ethylene occurred readily at 25—30° and almost ceased after 12 l. Distillation of the residue provided propenyl vinyl ketone (12·5 g.), b. p. 57°/16 mm., identical with that obtained in the reaction with propene.

n-Propyl Iodide and Acetyl Chloride.—Acetyl chloride (0·25 mole) was added to a suspension of aluminium chloride (0·30 mole) in methylene chloride (100 ml.). The complex was decanted from excess of chloride, and n-propyl iodide (0·25 mole) was added at 40°, some evolution of hydrogen chloride and hydrogen iodide occurring, but not vigorously. After 3 hr. the mixture was decomposed, the organic layer dried (Na_2SO_4), and the solvent removed. The residue was propyl iodide. In the presence of excess of aluminium chloride (0·10 mole), iodine was liberated and a product (6·5 g.), b. p. −40°, was collected in a carbon dioxide–methanol trap. The product (propane) did not decolorise bromine water.

Isopropyl Bromide and Acetyl Chloride.—To the acetyl chloride–aluminium chloride complex (0·25 mole) .as above, isopropyl bromide (0·25 mole) was added slowly at room temperature; little reaction occurred. At 40°, hydrogen bromide was copiously evolved and reaction was complete after 1 hr. The mixture was poured into dilute hydrochloric acid and ice, the organic layer separated and dried (Na_2SO_4), and the solvent removed. Distillation of the residue gave methyl propenyl ketone (9 g.), b. p. 48°/15 mm. (2,4-dinitrophenylhydrazone, m. p. 157°).

We thank Dr. G. Baddeley for his interest.

LANCHESTER COLLEGE OF TECHNOLOGY, COVENTRY. [*Received, September 5th,* 1960.]