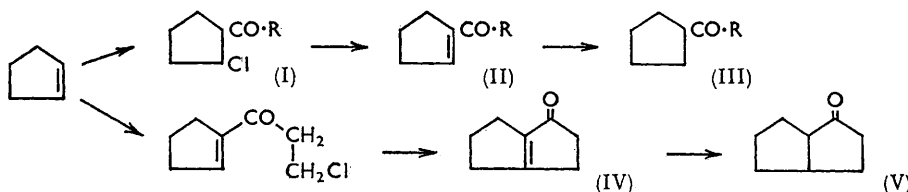


807. Aliphatic Friedel-Crafts Reactions. Part II.* The Acylation of Cyclopentene.

By N. JONES and H. T. TAYLOR.

Cyclopentene is readily acylated with acid chloride-aluminium chloride complex in methylene chloride to provide an alkyl (or aryl) cyclopentenyl ketone in good yield. The product of interaction of 2-chloropropionyl chloride and cyclopentene affords bicyclo[3,3,0]oct-1(5)-en-2-one on cyclisation.

By using Baddeley's modification¹ of Perrier's method² for the Friedel-Crafts reaction, a rapid homogeneous reaction is obtained, affording better yields than the more conventional technique in a solvent such as carbon disulphide. The acylation of ethylene and cyclohexene has been reported,^{3,4} and this communication reports the acylation of cyclopentene with a variety of acid chlorides providing, after slow distillation from sodium carbonate,⁵ the corresponding cyclopentenyl ketone (II). For comparison pent-1-ene has also been acetylated. The products have been quantitatively hydrogenated to the cyclopentyl ketones (III). Experimental procedure was simple and no precautions were taken against atmospheric moisture.



Cyclopentene readily reacts with acyl chloride-aluminium chloride complex in methylene chloride, the product containing some chlorine; improved yields are obtained at lower temperatures. Royals and Hendry⁶ noted that in the acetylation of cyclohexene, the use of acetic anhydride is preferable to acetyl chloride in that subsequent dehydrohalogenation is easier; this seems to be the case in the acetylation of cyclopentene. Nightingale *et al.*⁷ when preparing alkyl cyclohexenyl ketones observed persistent residual

* *J.*, 1958, 3922, should be regarded as Part I.

¹ Baddeley, *J.*, 1949, S 99.

² Perrier, *Bull. Soc. chim. France*, 1903, **31**, 859.

³ Baddeley, Taylor, and Pickles, *J.*, 1953, 124.

⁴ Taylor, *J.*, 1958, 3922.

⁵ Christ and Fuson, *J. Amer. Chem. Soc.*, 1937, **59**, 893.

⁶ Royals and Hendry, *J. Org. Chem.*, 1950, **15**, 1147.

⁷ Nightingale, Milberger, and Tomisek, *ibid.*, 1948, **13**, 357.

chlorine after complete distillation of the products from sodium carbonate. Stevens and Farkas⁸ isolated a little 4-chlorocyclohexyl methyl ketone when acetylating cyclohexene at low temperature in addition to the expected 1-chlorocyclohexyl methyl ketone; it is the former which is not readily dehydrochlorinated. The result can be explained by a carbonium ion mechanism.⁹ A chlorine-free product will remain colourless, and the presence of chlorine is indicated by the product's slowly darkening.^{7,10} Cyclopentenyl methyl ketone has been prepared previously, carbon disulphide being used as solvent.^{10,11}

Treatment of the product of interaction of cyclopentene and β -chloropropionyl chloride with phosphoric acid in formic acid¹² gave bicyclo[3,3,0]oct-1(5)-en-2-one (IV), quantitatively hydrogenated to bicyclo[3,3,0]octan-2-one¹³ (V). Cyclopentene and benzoyl chloride provide cyclopentenyl phenyl ketone,^{14,15} which was reduced to cyclopentyl phenyl ketone; the unsaturated ketone has been cyclised¹⁵ to 2,3-cyclopentanoindanone. The use of the ester chloride of a dibasic acid provides a route to acids of the type (III; R = $\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$).

Interaction of pent-1-ene and cyclopentene with acylating agents at 0°, unless otherwise stated.

| Acylating agent | Olefin | Product | Yield (%) |
|--|---------------------------|--|----------------------|
| Me·COCl | Pent-1-ene | Me·CO·C ₈ H ₉ | 43 |
| (Me·CO) ₂ O | " | | 46 |
| Me·COCl | Cyclopentene ^a | Me·CO·C ₈ H ₉ | 75(50 ^d) |
| " | " | | 68 |
| (Me·CO) ₂ O | " | Me·CO·C ₈ H ₉ | 52 |
| Et·COCl | " | | 67 |
| (Et·CO) ₂ O | " | Et·CO·C ₈ H ₇ | 50 |
| Pr·COCl | " | | 55 |
| Cl·[CH ₂] ₂ ·COCl | " | Pr·CO·C ₈ H ₇ | 57 |
| MeO ₂ C·[CH ₂] ₂ ·COCl | " | Cl·[CH ₂] ₂ ·CO·C ₈ H ₇ | 40 |
| Ph·COCl | " | MeO ₂ C·[CH ₂] ₂ ·CO·C ₈ H ₇ | 46 |
| | " | Ph·CO·C ₈ H ₇ | 62(53 ^e) |

^a At -15°. ^b At 25°. ^c At 15°. ^d See ref. 10. ^e See ref. 15.

EXPERIMENTAL

Reaction of Acid Chlorides or Anhydrides with Olefins.—The acid chloride (0.2 mole) or acid anhydride (0.2 mole) was added to a suspension of finely powdered aluminium chloride (0.25 or 0.45 mole, respectively) in methylene chloride (150 ml.) with shaking. The resulting complex was decanted from excess of aluminium chloride, and poured through glass-wool into a cooled beaker. The olefin (0.2 mole) in methylene chloride (50 ml.) was then added dropwise, with stirring, at a convenient rate to maintain the required temperature. The mixture was kept for 5 min., and the product was then poured into dilute hydrochloric acid and ice. The organic layer was separated and dried (Na₂SO₄), the solvent removed, and the residue slowly distilled from anhydrous sodium carbonate (0.15 mole); occasionally a second distillation was necessary.

Acetyl chloride and pent-1-ene at 0° provided hept-3-en-2-one (9.5 g.), b. p. 50—51°/12 mm. [semicarbazone, m. p. 152° (Eccott and Linstead¹⁶ record m. p. 152° for *cis*-form) (Found: N, 24.7. Calc. for C₇H₁₅ON₃: N, 24.9%)]. Acetic anhydride and pent-1-ene gave the same product (10.5 g.). A sample (1.74 g.) in ethanol (20 ml.) absorbed hydrogen (362 ml. corr. to S.T.P.; C₇H₁₂O requires 349) in the presence of palladium (0.1 g.). The reduced product, heptan-2-one, gave a 2,4-dinitrophenylhydrazone, m. p. 89° (Johnson and Hager¹⁷ record m. p. 89°).

⁸ Stevens and Farkas, *J. Amer. Chem. Soc.*, 1953, **75**, 3306.

⁹ Baddeley, *Quart. Rev.*, 1954, **8**, 355.

¹⁰ Rapson and Robinson, *J.*, 1935, 1285.

¹¹ Rosenfielder and Grisberg, *J.*, 1954, 2955.

¹² Braude and Coles, *J.*, 1952, 1430.

¹³ Linstead and Cook, *J.*, 1934, 946.

¹⁴ Fuson, Johnson, and Cole, *J. Amer. Chem. Soc.*, 1938, **60**, 1594.

¹⁵ Baker and Jones, *J.*, 1951, 787.

¹⁶ Eccott and Linstead, *J.*, 1930, 914.

¹⁷ Johnson and Hager, *Org. Synth., Coll. Vol. I*, 1st edn., p. 343.

Acetyl chloride and cyclopentene at -15° provided cyclopentenyl methyl ketone (16 g.), b. p. 168° [semicarbazone, m. p. 210° , and 2,4-dinitrophenylhydrazone, m. p. 203° (Heilbron *et al.*¹⁸ record m. p. 212° and 203° , respectively)]. Acetic anhydride and cyclopentene at 0° gave the same product (14.5 g.). A sample (1.256 g.) absorbed hydrogen (261 ml., corr. to S.T.P.; $C_7H_{10}O$ requires 256 ml.) in the presence of palladium. The reduced product, cyclopentyl methyl ketone, gave a semicarbazone, m. p. 145° (Bartlett and Rosenwald¹⁹ record m. p. $146-147^{\circ}$), and a 2,4-dinitrophenylhydrazone, m. p. 124° (Found: C, 53.5; H, 5.4; N, 19.0. Calc. for $C_{13}H_{16}O_4N_4$: C, 53.4; H, 5.5; N, 19.2%).

Propionyl chloride and cyclopentene at 0° provided cyclopentenyl ethyl ketone (13 g.), b. p. $60^{\circ}/15$ mm. [semicarbazone, m. p. 193° (Found: C, 59.6; H, 8.4; N, 23.0. Calc. for $C_9H_{15}ON_3$: C, 59.7; H, 8.3; N, 23.2%), and 2,4-dinitrophenylhydrazone, m. p. 210° (Found: C, 55.5; H, 5.3; N, 18.3. Calc. for $C_{14}H_{16}O_4N_4$: C, 55.3; H, 5.3; N, 18.4%)]. Propionic anhydride and cyclopentene at 0° gave the same product (14 g.). A sample (1.174 g.) absorbed hydrogen (206 ml., corr. to S.T.P.; $C_8H_{12}O$ requires 211 ml.). The reduced product, cyclopentyl ethyl ketone, gave a semicarbazone, m. p. 132° (Bedos²⁰ records m. p. 134°).

Butyryl chloride and cyclopentene at 0° provided cyclopentenyl propyl ketone (15.5 g.), b. p. 182° [2,4-dinitrophenylhydrazone, m. p. 164° (Found: C, 56.8; H, 5.7; N, 17.4. Calc. for $C_{15}H_{18}O_4N_4$: C, 56.6; H, 5.7; N, 17.6%)]. A sample (1.53 g.) absorbed hydrogen (239 ml. corr. to S.T.P.; $C_9H_{14}O$ requires 248 ml.). The reduced product, cyclopentyl propyl ketone gave a semicarbazone, m. p. 122° (Nazarov and Burmistrova²¹ record m. p. $123-124^{\circ}$).

2-Methoxycarbonylpropionyl chloride and cyclopentene gave cyclopentenyl 2-methoxycarbonyl ethyl ketone (16.5 g.), b. p. $135^{\circ}/15$ mm. [semicarbazone, m. p. 150° (Found: C, 55.4; H, 7.0; N, 17.4. Calc. for $C_{11}H_{17}O_3N_3$: C, 55.2; H, 7.1; N, 17.6%)]. A sample (1.67 g.) absorbed hydrogen (214 ml. corr. to S.T.P.; $C_{10}H_{14}O_3$ requires 205 ml.). Cyclopentyl 2-methoxycarbonyl ethyl ketone gave a semicarbazone, m. p. 122° (Found: C, 54.9; H, 7.8; N, 17.3. Calc. for $C_{11}H_{19}O_3N_3$: C, 54.8; H, 7.9; N, 17.4%).

Benzoyl chloride and cyclopentene provided cyclopentenyl phenyl ketone (21.3 g.), b. p. $140^{\circ}/12$ mm. [2,4-dinitrophenylhydrazone, m. p. 168° (Baker and Jones¹⁵ record m. p. $162-163^{\circ}$) and oxime, m. p. 140° (Smith and Scribner²² record m. p. $138-142^{\circ}$)]. A sample (1.87 g.) absorbed hydrogen (262 ml., corr. to S.T.P.; $C_{12}H_{12}O$ requires 243 ml.). Cyclopentyl phenyl ketone gave a 2,4-dinitrophenylhydrazone, m. p. $142-143^{\circ}$ (Nightingale and Maienthal²³ record m. p. $144.5-145.5^{\circ}$).

2-Chloropropionyl chloride and cyclopentene provided a product (12 g.), b. p. $108-112^{\circ}/12$ mm., which contained chlorine. It (5 g.) was added to a solution of phosphoric acid (3 g.) in 98% formic acid (6 g.), and the mixture kept at 90° under nitrogen for 12 hr. The mixture was then poured into water (100 ml.), and the organic material extracted with ether (2×25 ml.). The extracts were dried (Na_2SO_4) and, after removal of the ether, distillation of the residue gave bicyclo[3,3,0]oct-1(5)-en-2-one (4 g.), b. p. $87^{\circ}/12$ mm. [2,4-dinitrophenylhydrazone, m. p. 221° (decomp.) (Found: C, 55.3; H, 4.9; N, 18.7. Calc. for $C_{14}H_{14}O_4N_4$: C, 55.6; H, 4.6; N, 18.6%)]. A sample (1.01 g.) absorbed hydrogen (176 ml. corr. to S.T.P.; Calc. for $C_8H_{10}O$: 185 ml.). The reduced product, bicyclo[3,3,0]octan-2-one, gave a 2,4-dinitrophenylhydrazone, m. p. 112° after repeated crystallisation from ethyl acetate (Found: C, 55.1; H, 5.25; N, 18.5. Calc. for $C_{14}H_{16}O_4N_4$: C, 55.3; H, 5.30; N, 18.4%), and a semicarbazone, m. p. 181° (Found: N, 22.8. Calc. for $C_9H_{15}ON_3$: N, 23.2%) (Linstead and Cook¹³ record m. p.s 116° and 181° , respectively).

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¹⁸ Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 1827.

¹⁹ Bartlett and Rosenwald, *J. Amer. Chem. Soc.*, 1934, **56**, 1990.

²⁰ Bedos, *Compt. rend.*, 1949, **228**, 1441.

²¹ Nazarov and Burmistrova, *Bull. Acad. Sci. U.S.S.R.*, 1947, 51.

²² Smith and Scribner, *J. Amer. Chem. Soc.*, 1956, **78**, 3412.

²³ Nightingale and Maienthal, *ibid.*, 1950, **72**, 4823.