257. *Aliphatic Friedel–Crafts Reactions. Part III.*[1] *The Acylation of Cycloheptene and Cyclo-octene.*

By N. Jones, H. T. Taylor, and (in part) E. Rudd.

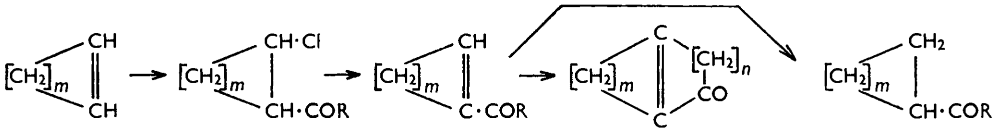
Cycloheptene and cyclo-octene are readily acylated with acid chloride–aluminium chloride complex in methylene chloride to provide, after distillation from sodium carbonate, an unsaturated ketone. The initial stages of Braude and Coles's azulene synthesis have been shortened.

This paper is one of a series on the preparative usefulness of the acetylation of olefins by the Friedel–Crafts method. The reaction has been less studied than the corresponding acylation of aromatic compounds. In every case, reactions do not proceed so clearly, the essential difference being the fate of the hydrogen chloride. Direct yields of chloride (I) or unsaturated ketone (II) depend mainly on the temperature, an increase favouring the olefin but at the expense of reduced overall yields (owing to polymerisation). The unsaturated product can be obtained (if not formed directly) by dehydrohalogenation of

---

[1] Part II, Jones and Taylor, *J.*, 1959, 4017.

the chloride with anhydrous sodium carbonate.[2] Preliminary calorimetric work shows that polymerisation of cycloheptene and cyclo-octene occurs more readily than of cyclohexene in the presence of aluminium chloride, and lower reaction temperatures for the acylation are preferable.



(I) (II) (III) (IV)

Cycloheptene and cyclo-octene have now been acylated with a variety of acyl halides, slightly lower yields being obtained (owing to polymerisation) than from cyclopentene[1] and cyclohexene.[3] Experimental technique was similar to that previously described. Friess and Pinson,[4] using the rather drastic conditions of Nenitzescu and Goranescu,[5] obtained only a mixture of 3- and 4-methylcyclohexane on attempted acetylation of cycloheptene: at lower temperatures, however, acetylcycloheptene was obtained when carbon disulphide was used as solvent.[6,7] Cycloheptene and cyclo-octene readily react with an acyl chloride–aluminium chloride complex in methylene chloride at —15° (in the case of the less reactive benzoyl chloride at 10—15°, and β-naphthoyl chloride did not react at 40°) to provide, after distillation from anhydrous sodium carbonate, the cycloalkenone (II). Most of these compounds have been quantitatively hydrogenated to the saturated ketones (IV).

Interaction of β-chloropropionyl chloride and cycloheptene, though prevented by the incursion of polymerisation from affording cycloheptenyl vinyl ketone, provides a product which, on treatment with 98% formic acid and phosphoric acid,[8] affords bicyclo[5,3,0]dec-1(7)-en-8-one [9,10] (III; $m = 5$, $n = 2$) shortening the initial stages of Braude and Coles's azulene synthesis.[10] Attempted cyclisation of the product of interaction of cycloheptene and γ-chlorobutyryl chloride to provide bicyclo[5,4,0]undec-1(7)-en-8-one (III; $m = 5$, $n = 3$) resulted in polymerisation.

Interaction of cycloalkenes with acylating agents at —15° unless otherwise stated.

Reactants		Product	Yield (%)
Cycloheptene	AcCl	C_7H_{11}·COMe	70
,, ...	Et·COCl	C_7H_{11}·COEt	58
,, ...	Pr^n·COCl —	C_7H_{11}·COPr^n	45
,, ...	MeO_2C·[CH_2]$_2$·COCl [a]	C_7H_{11}·CO·[CH_2]$_2$·CO_2Me	26
,, ...	BzCl [a]	C_7H_{11}·COPh	50
,, ...	β-$C_{10}H_7$·COCl [b]	—	0
,, ...	Cl·[CH_2]$_2$·COCl	C_7H_{11}·CO·[CH_2]$_2$·Cl	60
,, ...	Cl·[CH_2]$_3$·COCl	C_7H_{11}·CO·[CH_2]$_3$·Cl	54
Cyclo-octene	AcCl	C_8H_{13}·COMe	48
,, ...	BzCl	C_8H_{13}·COPh	33

[a] At 10°. [b] At 40°. [c] At 15°.

Cyclo-octene has been acetylated by Ruzicka and Boekenoogen,[11] using Darzens's method,[12] and they prepared the semicarbazone, m. p. 180°, of the reduced product,

---

[2] Christ and Fuson, *J. Amer. Chem. Soc.*, 1937, **59**, 893.
[3] Baddeley, Taylor, and Pickles, *J.*, 1953, 124.
[4] Friess and Pinson, *J. Amer. Chem. Soc.*, 1951, **73**, 3512.
[5] Nenitzescu and Goranescu, *Ber.*, 1936, **69**, 1820.
[6] Tamb and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1952, **74**, 2117.
[7] Rosenhelder and Guisberg, *J.*, 1954, 2955.
[8] Nazarov and Burmistrova, *Bull. Acad. Sci. U.S.S.R.*, 1947, 51.
[9] Islam and Raphael, *J.*, 1953, 2247.
[10] Braude and Coles, *Nature*, 1951, **168**, 879; *J.*, 1953, 2208.
[11] Ruzicka and Boekenoogen, *Helv. Chim. Acta*, 1931, **14**, 1319.
[12] Darzens, *Compt. rend.*, 1910, **150**, 707; **151**, 758.

cyclo-octyl methyl ketone. Reppe *et al.*[13] record the m. p. of the semicarbazone of cyclo-octenyl methyl ketone as 211°; we record the m. p. as 160° after repeated recrystallisation from ethanol, and agree with the m. p. of the derivative recorded by Ruzicka *et al.*

Our various results are summarised in the Table.

EXPERIMENTAL

Reaction of Acid Chlorides with Cycloalkenes.—The method was as described in Part II (0·20-molar scale).

Acetyl chloride and cycloheptene at −10° provided cycloheptenyl methyl ketone (19·6 g.), b. p. 210° [semicarbazone, m. p. 193° (Tamb and Szmuszkovicz[6] record m. p. 194—195°); 2,4-*nitrophenylhydrazone*, m. p. 173° (Found: N, 17·8. $C_{15}H_{18}N_4O_4$ requires N, 17·6%)]. A sample (2·40 g.) absorbed hydrogen (395 ml. corr. to S.T.P. Calc. for $C_9H_{14}O$: 1 mol., 389 ml.) in the presence of palladium. The reduced product, cycloheptyl methyl ketone gave a *semicarbazone*, m. p. 162° (Found: N, 21·2. $C_{10}H_{19}N_3O$ requires H, 21·3%), and a 2,4-*dinitrophenylhydrazone*, m. p. 195° (Found: N, 17·9. $C_{15}H_{20}N_4O_4$ requires N, 17·5%).

Propionyl chloride and cycloheptene at −10° gave cycloheptenyl ethyl ketone (19·0 g.), b. p. 220°, which gave a *semicarbazone*, m. p. 163° (Found: C, 63·0; H, 9·10; N, 20·0. $C_{11}H_{19}N_3O$ requires C, 63·2; H, 9·10; N, 20·1%). A sample (2·75 g.) absorbed hydrogen (410 ml. corr. to S.T.P. $C_{10}H_{16}O$ requires 1 mol., 405 ml.) in the presence of palladium. The reduced product, cycloheptyl ethyl ketone gave a 2,4-*dinitrophenylhydrazone*, m. p. 113° (Found: C, 57·3; H, 6·5; N, 16·7. $C_{16}H_{22}N_4O_4$ requires C, 57·5; H, 6·6; N, 16·8%).

Butyryl chloride and cycloheptene at −10° gave cycloheptenyl propyl ketone (15·0 g.), b. p. 233°, which gave a 2,4-*dinitrophenylhydrazone*, m. p. 123° (Found: C, 58·8; H, 6·28; N. 16·2. $C_{17}H_{22}N_4O_4$ requires C, 59·0; H, 6·4; N, 16·2%).

2-Methoxycarbonylpropionyl chloride and cycloheptene at 15° gave methyl γ-cyclohept-1-enyl-γ-oxobutyrate (10·5 g.), b. p. 162°/15 mm., which gave a *semicarbazone*, m. p. 176° (Found: C, 58·2; H, 7·8; N, 15·9. $C_{13}H_{21}N_3O_3$ requires C, 58·4; H, 7·9; N, 15·7%).

Benzoyl chloride and cycloheptene at 10° gave benzoylcycloheptene (20 g.), b. p. 178°/18 mm., which gave a *semicarbazone*, m. p. 172° (Found: C, 69·8; H, 7·3; N, 16·0. $C_{15}H_{19}N_3O$ requires C, 70·0; H, 7·4; N, 16·3%), and a 2,4-*dinitrophenylhydrazone*, m. p. 107° (Found: C, 63·0; H, 5·4; N, 14·5. $C_{20}H_{20}N_4O_4$ requires C, 63·2; H, 5·3; N, 14·7%).

β-Naphthoyl chloride and cycloheptene did not react during 1 hr. at temperatures up to 40°.

β-Chloropropionyl chloride and cycloheptene at −10° gave a product (38 g.) before distillation from sodium carbonate (Found: Cl, 20·22. Calc. for $C_{10}H_{16}Cl_2O$: Cl, 31·8. Calc. for $C_{10}H_{15}ClO$: C, 19·0%). Distillation from anhydrous sodium carbonate afforded a fraction (23 g.), b. p. 125°/15 mm. (Found: Cl, 7·8%). (Subsequent slow redistillation from sodium carbonate, followed by fractional distillation, effected polymerisation.) The product (21 g.), together with phosphoric acid (10 g.) and 98% formic acid (30 g.) was kept at 90° for 4 hr. under nitrogen. Hydrogen chloride was evolved, and the product was poured into water and extracted with ether (2 × 50 ml.). The extract was dried (Na_2CO_3) and after solvent removal gave bicyclo-[5,3,0]dec-1(7)-en-8-one (10 g.), b. p. 120°/15 mm. [semicarbazone, m. p. 238—240° (decomp.); 2,4-dinitrophenylhydrazone m. p. 228°; Braude and Coles[10] record m. p.s 238° and 226° respectively]. A sample (2·37 g.) absorbed hydrogen (364 ml. corr. to S.T.P. Calc. for $C_{10}H_{14}O$: 1 mol., 354 ml.) in the presence of palladium. The reduced product, bicyclo[5,3,0]dec-8-one gave a *semicarbazone*, m. p. 225° (Found: C, 63·4; H, 8·9; N, 20·3. $C_{11}H_{19}N_3O$ requires C, 63·2; H, 9·1; N, 20·1%), and a 2,4-*dinitrophenylhydrazone*, m. p. 190° (Found: C, 58·1; H, 6·1; N, 16·8. $C_{16}H_{20}N_4O_4$ requires C, 57·8; H, 6·0; N, 16·9%).

γ-Chlorobutyryl chloride and cycloheptene at −10° gave a product (40 g.) before distillation from sodium carbonate (Found: Cl, 18·9. Calc. for $C_{11}H_{18}Cl_2O$: Cl, 30·0. Calc. for $C_{11}H_{17}ClO$: C, 17·7%). Distillation from anhydrous sodium carbonate gave 3-*chloropropyl cycloheptenyl ketone* (Found: Cl, 17·9. $C_{11}H_{17}ClO$ requires Cl, 17·7%). The product (25 g.), together with phosphoric acid (12 g.) and 98% formic acid (36 g.), was kept at 90° for 6 hr. under nitrogen. Isolation of the product as above gave a tar which could not be distilled.

Acetyl chloride and cyclo-octene at −15° provided cyclo-octenyl methyl ketone (14·5 g.),

---

[13] Reppe, Schlichling, and Westphal, U.S.P. 2,759,926/1956.

b. p. 108°/12 mm., which gave a semicarbazone, m. p. 160° (Reppe *et al.*[13] record m. p. 211°) (Found: C, 63·0; H, 9·0; N, 21·0. Calc. for $C_{11}H_{19}N_3O$: C, 63·2; H, 9·1; N, 21·1%). A sample (2·6 g.) absorbed hydrogen (376 ml. corr. to S.T.P. Calc. for $C_{10}H_{16}O$: 1 mol., 383 ml.) in the presence of palladium. The reduced product, cyclo-octyl methyl ketone, gave a semicarbazone, m. p. 180° (Ruzicka and Boerkenoogen [11] record m. p. 180°).

Benzoyl chloride and cyclo-octene at 10° provided benzoylcyclo-octene (14 g.), b. p. 168°/15 mm., that gave an *oxime*, m. p. 123° (Found: C, 78·4; H, 8·25; N, 5·95. $C_{15}H_{19}NO$ requires C, 78·6; H, 8·3; N, 6·1%), and a 2,4-*dinitrophenylhydrazone*, m. p. 134° (Found: C, 63·6; H, 5·65; N, 14·5. $C_{21}H_{22}N_4O_4$ requires C, 64·0; H, 5·6; N, 14·2%).

We thank Mr. R. Muir (Courtaulds Ltd.) for a number of microanalyses.

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