435. *Aliphatic Friedel–Crafts Reactions. Part V.*[1] *Further Acylations of Cyclopentene, Cyclohexene, and Cycloheptene.*

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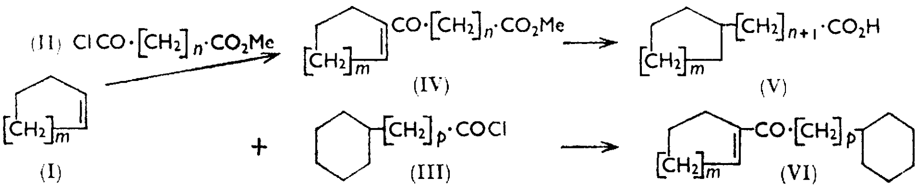
Cyclopentene, cyclohexene, and cycloheptene have been acylated by using the acid chloride–aluminium chloride complexes in methylene chloride to provide, after distillation from sodium carbonate, unsaturated ketones (IV and VI). Reduction of the ketone (IV) provides a route to cycloalkanecarboxylic acids (V) of various chain lengths.

Further studies have been carried out of the preparative usefulness of the acylation of olefins by Baddeley's modification [2] of Perrier's method [3] for the Friedel–Crafts reaction. This paper is concerned with the interaction of the cycloalkenes (I; $m = 1$—3) (*a*) with the half-ester chlorides of succinic and glutaric acid (II; $n = 2$ and 3), providing the cycloalkenyl keto-esters (IV) which, after hydrogenation followed by Clemmensen reduction, can provide the cycloalkanecarboxylic acids (V), and (*b*) with the cyclohexylalkanoyl chlorides (III; $p = 0$—3), leading to the cycloalkenyl cyclohexylalkyl ketones (VI).

In general, the products were high-boiling (>150°/15 mm.), and, in contrast to earlier work,[4] chlorine-free products could not be obtained by simple fractionation; purification was effected, where necessary, through the semicarbazone although this step is not essential if the product is required for further synthesis.



For example, cyclohexene reacted readily with the complex of 2-methoxycarbonylpropionyl chloride (II; $n = 2$) with aluminium chloride in methylene chloride at −5°, to

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[1] Part IV, Jones and Taylor, *J.*, 1961, 1345.
[2] Baddeley, *J.*, 1949, S99.
[3] Perrier, *Bull. Soc. chim. France*, 1903, **31**, 859.
[4] Jones and Taylor, *J.*, 1959, 4017.

provide, after distillation from anhydrous sodium carbonate, the ketone (IV; $m = n = 2$) containing 1·0% of chlorine which was completely removed only by formation and subsequent regeneration of the semicarbazone. Hydrogenation, followed by Clemmensen reduction, provided γ-cyclohexylbutyric acid (V; $m = n = 2$).

The cyclohexanecarbonyl chloride (III; $p = 0$)–aluminium chloride complex in ethylene chloride did not react with a cycloalkene at the expected temperature, but at 45° a reaction set in leading to mixed products which are now under investigation. A high reaction temperature favours polymerisation and the formation of saturated products, whilst too low a temperature may produce the chloro-ketone.[5] The γ-cyclohexylbutyryl chloride (III; $p = 3$)–aluminium chloride complex in methylene chloride did not undergo the expected reaction with a cycloalkene, but preferentially cyclised to α-decalone in low yield.

Infrared and ultraviolet absorption spectra provided convenient methods for diagnosis of the products. The presence of small amounts of saturated ketone in some of the products was indicated by the C=O stretching band at about 1710 cm.$^{-1}$ in addition to the C=O stretching band of the αβ-unsaturated ketone at about 1670 cm.$^{-1}$. The ultraviolet absorption maxima and extinction coefficients of ketones similar to those that we have prepared are known.[6] Our absorption maxima are in good agreement with these, but extinction coefficients are lower unless the ketone is purified through the semicarbazone.

Our results are summarised in the Table.

Interaction of cycloalkenes with acylating agents at 10° (unless otherwise stated).

Reactants		Products	Yield (%)
Cyclopentene with	$MeO_2C{\cdot}[CH_2]_3{\cdot}COCl$ *	$C_5H_7{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO_2Me$	53
,, ,,	$C_6H_{11}{\cdot}CH_2{\cdot}COCl$	$C_5H_7{\cdot}CO{\cdot}CH_2{\cdot}C_6H_{11}$	57
,, ,,	$C_6H_{11}{\cdot}[CH_2]_2{\cdot}COCl$	$C_5H_7{\cdot}CO{\cdot}[CH_2]_2{\cdot}C_6H_{11}$	56
Cyclohexene with	$MeO_2C{\cdot}[CH_2]_2{\cdot}COCl$ †	$C_6H_9{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2Me$	41
,, ,,	$MeO_2C{\cdot}[CH_2]_3{\cdot}COCl$	$C_6H_9{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO_2Me$	40
,, ,,	$C_6H_{11}{\cdot}CH_2{\cdot}COCl$	$C_6H_9{\cdot}CO{\cdot}CH_2{\cdot}C_6H_{11}$	48
,, ,,	$C_6H_{11}{\cdot}[CH_2]_2{\cdot}COCl$	$C_6H_9{\cdot}CO{\cdot}[CH_2]_2{\cdot}C_6H_{11}$	43
Cycloheptene with	$MeO_2C{\cdot}[CH_2]_2{\cdot}COCl$	$C_7H_{11}{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2Me$	50
,, ,,	$MeO_2C{\cdot}[CH_2]_3{\cdot}COCl$	$C_7H_{11}{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO_2Me$	40
,, ,,	$C_6H_{11}{\cdot}CH_2{\cdot}COCl$	$C_7H_{11}{\cdot}CO{\cdot}CH_2{\cdot}C_6H_{11}$	43
,, ,,	$C_6H_{11}{\cdot}[CH_2]_2{\cdot}COCl$	$C_7H_{11}{\cdot}CO{\cdot}[CH_2]_2{\cdot}C_6H_{11}$	45

* At 0°. † At −5°.

EXPERIMENTAL

Light absorption was determined for ethanol solutions.

Reaction of Acid Chlorides with Olefins.—The acid chloride (0·10 mole) was added to a suspension of finely powdered aluminium chloride (0·15 mole) in methylene or ethylene chloride (80 ml.). The resulting complex was decanted from the excess of aluminium chloride and poured through a plug of glass wool into a cooled beaker. The olefin (0·10 mole) in methylene or ethylene chloride (30 ml.) was then added dropwise, with stirring, at a rate that maintained the required temperature. The mixture was kept for 5 min., then poured into dilute hydrochloric acid and ice. The organic layer was separated, washed with water, and 10% sodium carbonate solution, and dried (Na_2SO_4). The solvent was removed, and the residue twice distilled from anhydrous sodium carbonate (0·10 and 0·02 mole, respectively).

γ-Methoxycarbonylbutyryl Chloride and Cyclopentene.—The reaction, carried out as above at 0°, provided cyclopentenyl 3-methoxycarbonylpropyl ketone (10·5 g.), b. p. 146—148°/12 mm. (containing 0·7% of chlorine), $\lambda_{\max.}$ 2385 Å (ε 9100) (English and Dayan [7] report $\lambda_{\max.}$ 2400 Å), $\nu_{\max.}$ 1740s (ester C=O stretching), 1666s (αβ-unsaturated C=O stretching), 1613w cm.$^{-1}$ (C=C

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[5] See Baddeley, *Quart. Rev.*, 1954, **8**, 355.

[6] Heilbron, Jones, Toogood, and Weedon, *J.*, 1949, 1827.

[7] English and Dayan, *J. Amer. Chem. Soc.*, 1950, **72**, 4187.

stretching). The ketone gave a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 146°, $\lambda_{\text{max.}}$ 3765 Å (ε 29,000) (Found: C, 54·4; H, 5·4; N, 14·8. $C_{17}H_{20}N_4O_6$ requires C, 54·3; H, 5·3; N, 14·9%), and a *semicarbazone* (from aqueous ethanol), m. p. 131° (Found: C, 56·7; H, 7·6; N, 16·4. $C_{12}H_{19}N_3O_3$ requires C, 56·9; H, 7·5; N, 16·6%).

Cyclohexylacetyl Chloride and Cyclopentene.—The reaction at 10° provided *cyclohexylmethyl cyclopentenyl ketone* (11·0 g.), b. p. 127—130°/7 mm. (containing no chlorine), $\lambda_{\text{max.}}$ 2390 Å (ε 9600), $\nu_{\text{max.}}$ 1667s, 1615w, and 1715w cm.$^{-1}$ (C=O stretching in a saturated ketone, present as impurity) (unspecified assignments here and below are as stated in the preceding paragraph). The ketone gave a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 128°, $\lambda_{\text{max.}}$ 3780 Å (ε 28,000) (Found: C, 61·1; H, 6·35. $C_{19}H_{24}N_4O_4$ requires C, 61·3; H, 6·45%), and a *semicarbazone* (from aqueous ethanol), m. p. 193°, $\lambda_{\text{max.}}$ 2650 Å (ε 27,000) (Found: C, 67·2; H, 9·3. $C_{14}H_{23}N_3O$ requires C, 67·5; H, 9·2%). The ketone was hydrogenated in the presence of palladium in ethanol to provide cyclohexylmethyl cyclopentyl ketone, which formed a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 78°, $\lambda_{\text{max.}}$ 3640 Å (ε 23,900) (Found: C, 60·7; H, 6·9. $C_{19}H_{26}N_4O_4$ requires C, 60·9; H, 6·95%), and a *semicarbazone* (from aqueous ethanol), m. p. 147°, $\lambda_{\text{max.}}$ 2290 Å (ε 14,400) (Found: C, 66·9; H, 9·7. $C_{14}H_{25}N_3O$ requires C, 66·9; H, 10·0%).

β-*Cyclohexylpropionyl Chloride and Cyclopentene.*—The reaction at 10° provided 2-*cyclohexylethyl cyclopentenyl ketone* (11·5 g.), b. p. 172—175°/13 mm. (containing 1·0% of chlorine), $\lambda_{\text{max.}}$ 2385 Å (ε 10,300), $\nu_{\text{max.}}$ 1668s and 1616w cm.$^{-1}$ [2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 144°, $\lambda_{\text{max.}}$ 3780 Å (ε 31,000) (Found: C, 62·0; H, 6·5; N, 14·7. $C_{20}H_{26}N_4O_4$ requires C, 62·2; H, 6·7; N, 14·5%); *semicarbazone* (from methanol), m. p. 170°, $\lambda_{\text{max.}}$ 2640 Å (ε 24,000) (Found: C, 68·1; H, 9·5. $C_{15}H_{25}N_3O$ requires C, 68·4; H, 9·5%)].

β-*Methoxycarbonylpropionyl Chloride and Cyclohexene.*—The reaction at −5° provided methyl γ-cyclohexenyl-γ-oxobutyrate (8·0 g.), b. p. 148—151°/6 mm. (containing 1·0% of chlorine), $\lambda_{\text{max.}}$ 2330 Å (ε 6000) (English and Dayan [7] report 2340 Å), $\nu_{\text{max.}}$ 1743s, 1668s, and 1639w cm.$^{-1}$ [2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 104°, $\lambda_{\text{max.}}$ 3760 Å (ε 30,800) (Found: C, 54·0; H, 5·2; N, 14·6. $C_{17}H_{20}N_4O_6$ requires C, 54·3; H, 5·3; N, 14·9%); semicarbazone (from ethanol), m. p. 146° (English and Dayan [7] record m. p. 147—148°), $\lambda_{\text{max.}}$ 2625 Å (ε 21,600)]. Steam-distillation of the semicarbazone with twice its weight of phthalic anhydride regenerated, almost quantitatively, the pure ketone, $\lambda_{\text{max.}}$ 2330 Å (ε 9500).

The ketone was hydrogenated in the presence of palladium in ethanol to provide methyl γ-cyclohexyl-γ-oxobutyrate which gave a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 110°, $\lambda_{\text{max.}}$ 3610 Å (ε 22,400) (Found: C, 53·8; H, 5·8; N, 15·0. $C_{17}H_{22}N_4O_6$ requires C, 54·0; H, 5·8; N, 14·8%), and a *semicarbazone* (from aqueous ethanol), m. p. 141°, $\lambda_{\text{max.}}$ 2290 Å (ε 11,300) (Found: C, 56·8; H, 8·5. $C_{12}H_{21}N_3O_3$ requires C, 56·5; H, 8·2%). This ketone (3·0 g.) was reduced by zinc amalgam (9 g.) in refluxing ethanol (20 ml.) and concentrated hydrochloric acid (20 ml.) for 1 hr.; more hydrochloric acid (20 ml.) was added later and refluxing continued for 5 hr. The resulting solution was poured into water and extracted with ether. The extract was dried (Na_2SO_4) and distilled, giving a non-ketonic ester (2·5 g.), b. p. 100—105°/6 mm., that was hydrolysed in alcoholic potassium hydroxide to γ-cyclohexylbutyric acid (1·0 g.), b. p. 126—128°/5 mm. (Found: Equiv., 172. Calc. for $C_9H_{17}{\cdot}CO_2H$: Equiv., 170).

γ-*Methoxycarbonylbutyryl Chloride and Cyclohexene.*—The reaction at 10° provided methyl δ-cyclohexenyl-δ-oxovalerate (8·5 g.), b. p. 154—157°/10 mm. (containing 2·0% of chlorine), $\lambda_{\text{max.}}$ 2330 Å (ε 8300) (English and Dayan [7] report 2340 Å), $\nu_{\text{max.}}$ 1738s, 1667s, and 1638w cm.$^{-1}$ [2,4-dinitrophenylhydrazone (from ethanol), m. p. 134° (English and Dayan [7] record m. p. 133°), $\lambda_{\text{max.}}$ 3760 Å (ε 30,600); *semicarbazone* (from aqueous ethanol), m. p. 112°, $\lambda_{\text{max.}}$ 2620 Å (ε 26,700) (Found: C, 58·1; H, 7·8. $C_{13}H_{21}N_3O_3$ requires C, 58·4; H, 7·9%)]. The ketone was hydrogenated as above to provide methyl δ-cyclohexyl-δ-oxovalerate [2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 98°, $\lambda_{\text{max.}}$ 3610 Å (ε 22,000) (Found: N, 14·1. $C_{18}H_{24}N_4O_6$ requires N, 14·3%)].

Cyclohexylacetyl Chloride and Cyclohexene.—The reaction at 10° provided cyclohexenyl cyclohexylmethyl ketone (10·0 g.), b. p. 172—175°/12 mm. (containing 1·4% of chlorine), $\lambda_{\text{max.}}$ 2330 Å (ε 7900), $\nu_{\text{max.}}$ 1666s, 1639w, and 1712w cm.$^{-1}$ (C=O stretching in a saturated ketone, present as impurity). The ketone gave a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 143°, $\lambda_{\text{max.}}$ 3780 Å (ε 27,800) (Found: C, 62·0; H, 6·7. $C_{20}H_{26}N_4O_4$ requires C, 62·2; H, 6·7%), and a *semicarbazone* (from aqueous ethanol), m. p. 180°, $\lambda_{\text{max.}}$ 2625 Å (ε 21,900) (Found: C, 68·2; H, 9·4. $C_{15}H_{25}N_3O$ requires C, 68·4; H, 9·5%). Hydrogenation as above provided cyclohexyl cyclohexylmethyl ketone, which formed a 2,4-*dinitrophenylhydrazone* (from ethanol),

m. p. 129°, $\lambda_{max.}$ 3630 Å (ε 22,100), and a semicarbazone (from light petroleum), m. p. 187° (Nazarov and Bakhmutskaya [8] record m. p. 186°), $\lambda_{max.}$ 2290 Å (ε 13,500).

β-*Cyclohexylpropionyl Chloride and Cyclohexene*.—The reaction at 10° provided cyclohexenyl 2-cyclohexylethyl ketone (9·5 g.), b. p. 142—146°/6 mm. (containing 1·5% of chlorine), $\lambda_{max.}$ 2330 Å (ε 6800), $\nu_{max.}$ 1668s, 1638w, and 1716w cm.$^{-1}$ (C=O stretching in a saturated ketone); this gave a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 140°, $\lambda_{max.}$ 3750 Å (ε 27,600) (Found: C, 62·8; H, 7·2. $C_{21}H_{28}N_4O_4$ requires C, 63·0; H, 7·0%).

β-*Methoxycarbonylpropionyl Chloride and Cycloheptene*.—The reaction at 10° provided methyl γ-cycloheptenyl-γ-oxobutyrate (10·5 g.), b. p. 136—140°/9 mm. (containing 1·5% of chlorine), $\lambda_{max.}$ 2365 Å (ε 6700), $\nu_{max.}$ 1740s, 1667s, 1634w, and 1715 cm.$^{-1}$ (C=O stretching in a saturated ketone). The ketone gave a *semicarbazone* (from aqueous ethanol), m. p. 176°, $\lambda_{max.}$ 2660 Å (ε 17,000) (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%), and on hydrogenation as above methyl γ-cycloheptyl-γ-oxobutyrate which formed a *semicarbazone* (from aqueous ethanol), m. p. 139°, $\lambda_{max.}$ 2290 Å (ε 13,500) (Found: C, 58·2; H, 8·7. $C_{13}H_{23}N_3O_3$ requires C, 58·0; H, 8·55%). The saturated ketone was hydrolysed with alcoholic potassium hydroxide to provide *γ-cycloheptyl-γ-oxobutyric acid* (Found: Equiv., 196. Calc. for $C_{10}H_{17}O{\cdot}CO_2H$: Equiv., 198), which formed a *semicarbazone* (from aqueous ethanol), m. p. 157°, $\lambda_{max.}$ 2260 Å (ε 13,000) (Found: C, 56·3; H, 8·0. $C_{12}H_{21}N_3O_3$ requires C, 56·5; H, 8·2%).

γ-*Methoxycarbonylbutyryl Chloride and Cycloheptene*.—The reaction at 10° provided the unsaturated ketone (9·0 g.), b. p. 154—156°/7 mm. (containing 1·0% of chlorine), $\lambda_{max.}$ 2370 Å (ε 7300), $\nu_{max.}$ 1740s, 1665s, and 1635w cm.$^{-1}$, that gave a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 137°, $\lambda_{max.}$ 3775 Å (ε 28,800) (Found: C, 56·3; H, 5·7; N, 14·0. $C_{19}H_{24}N_4O_6$ requires C, 56·4; H, 5·9; N, 13·9%), and a *semicarbazone* (from aqueous ethanol), m. p. 143° $\lambda_{max.}$ 2650 Å (ε 23,100) (Found: C, 59·6; H, 8·3. $C_{14}H_{23}N_3O_3$ requires C, 59·8; H, 8·2%).

Cyclohexylacetyl Chloride and Cycloheptene.—The reaction at 10° provided the cycloheptenyl ketone (9·5 g.), b. p. 148—151°/5 mm. (containing 1·9% of chlorine), $\lambda_{max.}$ 2365 Å (ε 5000), $\nu_{max.}$ 1667s, 1639w, and 1714w cm.$^{-1}$ (C=O stretching in a saturated ketone). This gave a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 117°, $\lambda_{max.}$ 3775 Å (ε 25,100) (Found: C, 63·0; H, 7·0. $C_{21}H_{28}N_4O_4$ requires C, 63·0; H, 7·0%), and a *semicarbazone* (from aqueous ethanol), m. p. 168°, $\lambda_{max.}$ 2650 Å (ε 18,000) (Found: C, 69·0; H, 9·6. $C_{16}H_{27}N_3O$ requires C, 69·3; H, 9·8%), and was hydrogenated as above to cycloheptyl cyclohexylmethyl ketone, which formed a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 105°, $\lambda_{max.}$ 3630 Å (ε 23,900) (Found: C, 62·5; H, 7·3. $C_{21}H_{30}N_4O_4$ requires C, 62·7; H, 7·5%).

β-*Cyclohexylpropionyl Chloride and Cycloheptene*.—The reaction at 10° provided cycloheptenyl 2-cyclohexylethyl ketone (10·5 g.), b. p. 165—169°/6 mm. Steam-distillation of the derived *semicarbazone* (37%), m. p. 173° (from methanol), $\lambda_{max.}$ 2650 Å (ε 19,500) (Found: C, 69·8; H, 9·8. $C_{17}H_{29}N_3O$ requires C, 70·1; H, 10·0%), with twice its weight of phthalic anhydride regenerated, almost quantitatively, the pure ketone, $\lambda_{max.}$ 2360 Å (ε 9,700), $\nu_{max.}$ 1667s and 1640w cm.$^{-1}$. This gave a 2,4-*dinitrophenylhydrazone* (from ethanol), m. p. 114°, $\lambda_{max.}$ 3760 Å (ε 30,800) (Found: C, 63·6; H, 7·1. $C_{22}H_{30}N_4O_4$ requires C, 63·8; H, 7·25%).

γ-*Cyclohexylbutyryl Chloride and Cyclopentene* (*or Cyclohexene, or Cycloheptene*).—The reaction at 10° provided α-decalone (15%), b. p. 150°/9 mm. The product had negligible light absorption between 2300 and 2400 Å, and the infrared spectrum had a band at 1709s cm.$^{-1}$ (C=O stretching in a saturated ketone). The ketone gave a 2,4-dinitrophenylhydrazone (from ethanol), m. p. 220—222° (Wilds and Nelson [9] record m. p. 224°), $\lambda_{max.}$ 3650 Å (ε 20,300).

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[8] Nazarov and Bakhmutskaya, *Zhur. obshchei Khim.*, 1949, **19**, 1777.

[9] Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5360.