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THE FRIEDEL-CRAFTS REACTION OF ACID CHLORIDES WITH ETHENE ; DI-ADDITION AND MOLECULAR REARRANGEMENT

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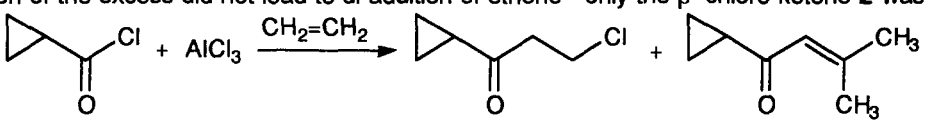
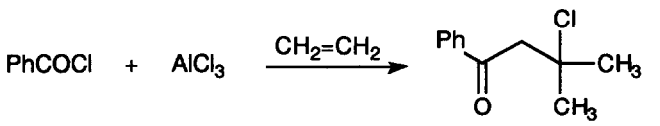
*Abstract - Acid chlorides, complexed with excess aluminium chloride, reacted with ethene to form 3-methyl-2-buten-1-ones, i.e. rearranged di-addition products having a terminal isoprenoid skeleton, together with the usual β-chloropropanones. The latter were the sole products in the absence of excess catalyst. Acid chlorides containing a suitably situated π-system underwent intramolecular cyclization, e.g. 2-phenylcyclopropanecarbonyl chloride (**10**) cyclized to 3,4-benzobicyclo[3.1.0]hexan-2-one (**11**).*

In the course of synthesising 3-chloro-1-cyclopropyl-1-propanone (**2**) by the reaction of equimolar quantities of cyclopropanecarbonyl chloride (**1**) and aluminium chloride with excess ethene, it was observed that, when the usual acylation procedure of employing an excess of Lewis acid (1.1 molar equivalent) was used, an additional product, containing an isoprenoid skeleton, 1-cyclopropyl-3-methyl-2-buten-1-one (**3**), was obtained in approximately 5% yield. Increasing the amount of aluminium chloride to 1.5 and 2.3 molar equivalents increased the yield to 36% and 49%, respectively. Further increases in the amounts of catalyst did not significantly increase the yield of enone **3**. Removal of excess catalyst by filtration before the passage of ethene suppressed the formation of 1-cyclopropyl-3-methyl-2-buten-1-one (**3**). 3-Chloro-1-cyclopropyl-1-propanone (**2**) is not an intermediate in the formation of the 2-buten-1-one **3** as a mixture of the former and aluminium chloride was unreactive with ethene. The excess catalyst must be present initially; later addition of the excess did not lead to di-addition of ethene - only the β-chloro ketone **2** was formed.



1 **2** **3**

In 1958, Matsumoto, Hata, and Nishida reported[1] that benzoyl chloride and ethene reacted in the presence of 1.5 molar equivalents of aluminium chloride to give 3-chloro-3-methylbutyrophenone (**4**). They did not comment on how the isoprenoid skeleton was formed except to suggest that one mole of acid chloride reacts with two moles of ethene. In the same year, Taylor[2] acylated ethene with maleic anhydride using 2.4 molar equivalents of aluminium chloride and isolated, after esterification, methyl 6-methyl-4-oxo-2,5-heptadieneoate (**5**). It was noted that two moles of ethene were absorbed before the reaction slackened[3]. More recently, in 1982, and again without comment, Condon *et al* [4] acylated ethene with *cis*-cyclopentane-1,2-dicarboxylic anhydride (**6**) and obtained *cis*- 2-(3-methyl-1-oxo-2-butenyl)cyclopentanecarboxylic acid (**7**).



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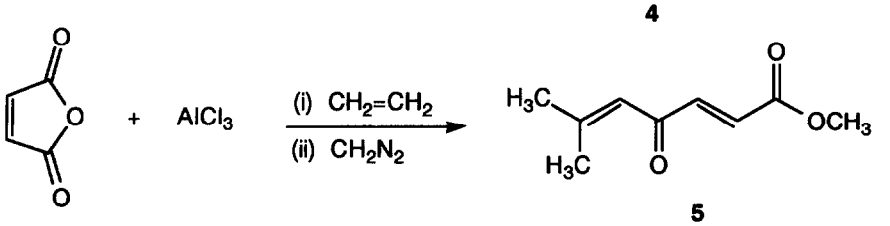

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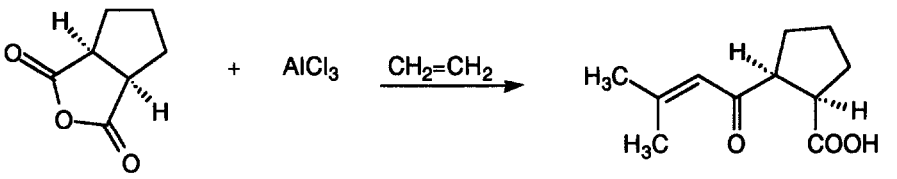

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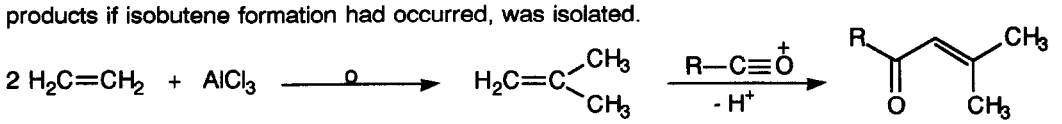
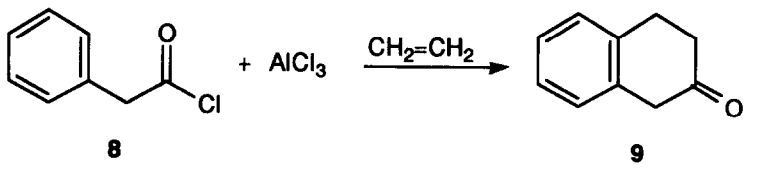
In a review, Groves[5] has commented that the products are, at least formally, derived from dimerization and rearrangement of ethene to isobutene, and reaction with the acylating species (scheme 1), In the present work, however, when ethene was passed through a suspension of aluminium chloride in deuteriochloroform, the Hmr spectrum of the resulting solution showed the ethene singlet at 5.14δ but no trace of the isobutene signal at 2δ. Also, phenylacetyl chloride (**8**) in the presence of aluminium chloride is known[6] to react with ethene to form 2-tetralone (**9**). When this reaction was now repeated using excess catalyst, 2-tetralone (**9**) was again the only product isolated. Neither 4,4-dimethyl-2-tetralone nor 4-methyl-1-phenyl-3-penten-2-one, probable products if isobutene formation had occurred, was isolated.



Scheme 1

2-Phenylcyclopropanecarbonyl chloride (**10**), with or without an excess of aluminium chloride, did not acylate ethene. Instead, its acylium ion cyclized to 3,4-benzobicyclo[3.1.0]hexan-2-one (**11**). Somewhat similarly, 2,2-dimethylpropanoyl chloride (**12**), although it formed the isoprenoid skeleton-containing 2,5,5-trimethyl-2-hexen-4-one (**14**) exclusively in the presence of aluminium chloride and ethene, most likely did not acylate ethene either but, rather, as Grundy *et al* have reported,[7] its acylium ion **13** underwent decarbonylation and deprotonation to form isobutene which reacted with the acylium ion **13** to form the observed product **14**. 2-Naphthoyl chloride (**15**), on the other hand, in the presence of 1.5 molar equivalents of aluminium chloride afforded 3-methyl-1-(2-naphthyl)-2-buten-1-one (**16**); with one molar equivalent of catalyst it gave 3-chloro-1-(2-naphthyl)-1-propanone (**17**).



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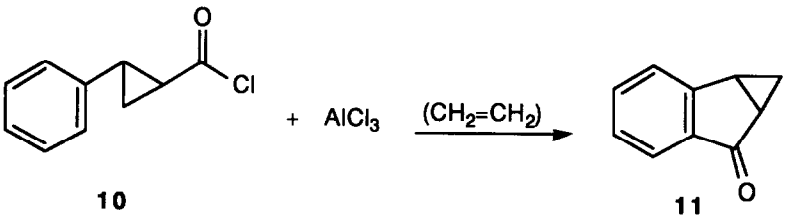

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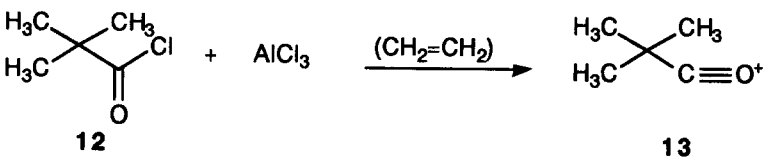

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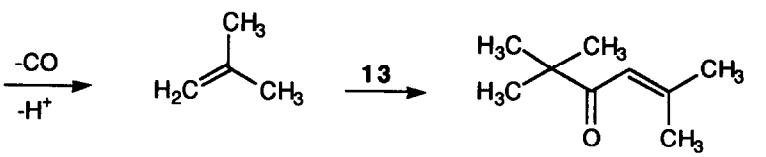

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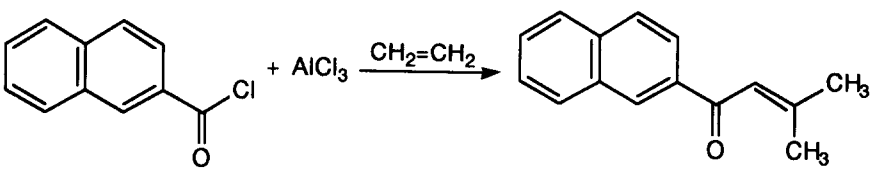

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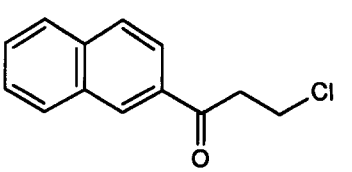

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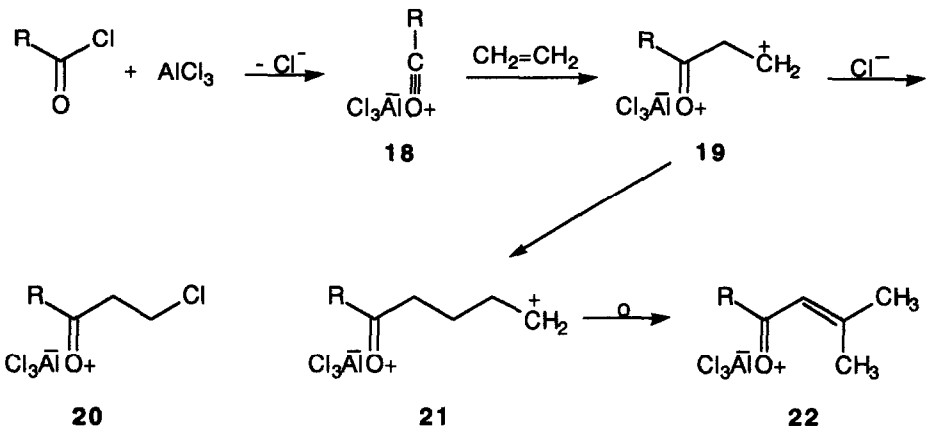
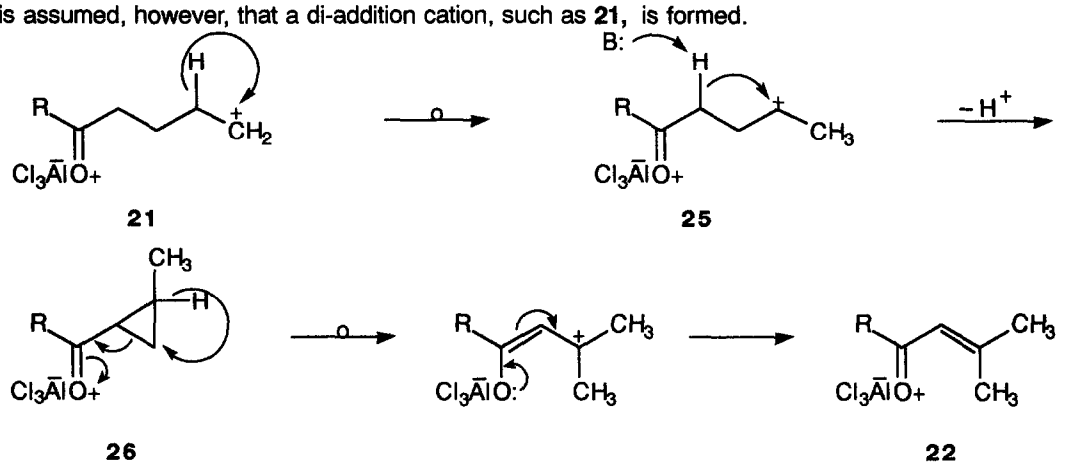


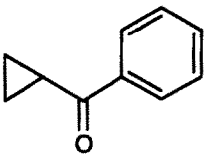
Scheme 2

Generally, it would appear (scheme 2) that the initial acylium ion **18** forms a carbocation **19** which may react intramolecularly with a suitably placed π-system as in, for example, compound **10**. Failing that, and in the absence of excess aluminium chloride, the cation reacts with chloride ion forming a β-chloro ketone **20**. However, when excess aluminium chloride is present, the cation would appear unable to compete with it for chloride ion and, instead, reacts intermolecularly with a second molecule of ethene to form a cation, formally of the type **21**, which rearranges to the observed isoprenoid skeleton-containing product **22**. Further support for the formation of the first two cations **18**, **19** was obtained by adding ethene, followed by benzene, to an equimolar solution of cyclopropanecarbonyl chloride (**1**) and aluminium chloride; a mixture of cyclopropyl phenyl ketone (**23**) and 1-cyclopropyl-3-phenyl-1-propanone (**24**) was obtained. This mixture could not be fractionated but its components were separated as their 2,4-dinitrophenylhydrazones. Repeating the reaction with an excess of catalyst gave a more complex mixture which could not be resolved. It is assumed, however, that a di-addition cation, such as **21**, is formed.



Scheme 3

To account for the rearranged product **22**, it is suggested (scheme 3) that an initial 1,2-



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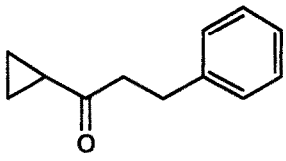

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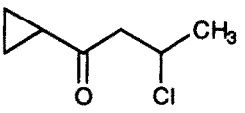

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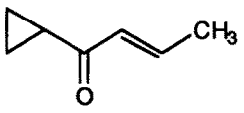

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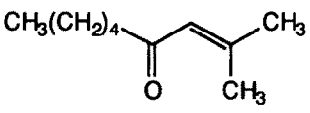

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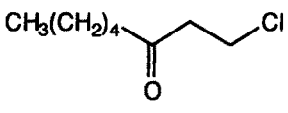

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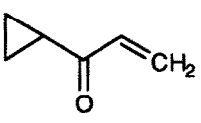

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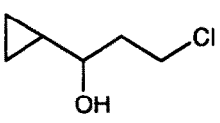

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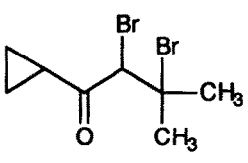

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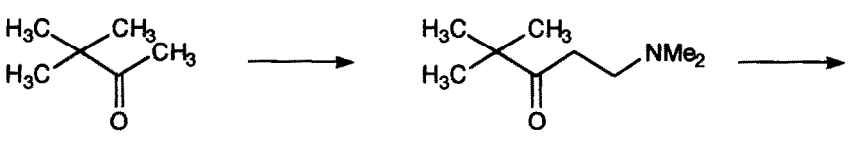

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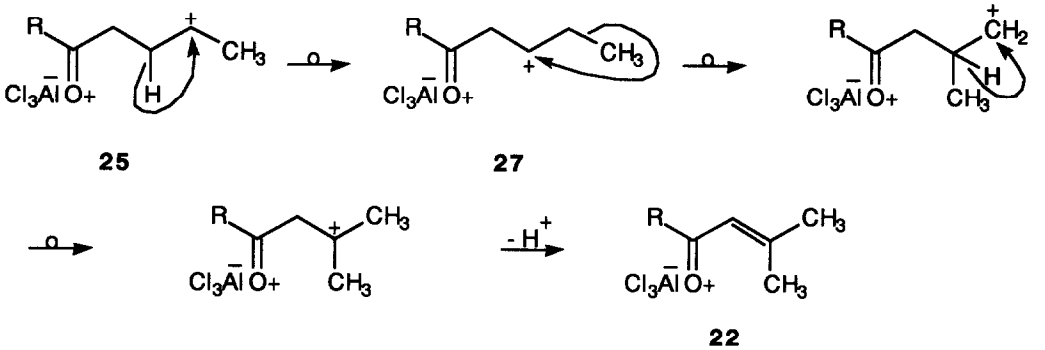
36 **37**

hydride shift converts the primary carbocation **21** into the secondary cation **25**. Then, loss of a proton from the carbon adjacent to the carbonyl group, followed by cyclization, would give a cyclopropyl carbonyl complex **26** which, after opening of the cyclopropane ring and a hydride shift , would form the complex **22** of the observed product. Alternatively, the cation **25** might undergo a second 1,2-hydride shift (scheme 4) to form the carbocation **27** which, after a 1,2-shift of its methyl group followed by a hydride shift and loss of a proton, would also form the complex **22**.



Scheme 4

Other typical Lewis acids, such as iron(III) chloride, boron trifluoride etherate, and titanium(IV) chloride failed to catalyse a reaction between cyclopropanecarbonyl chloride (**1**) and ethene. A molar equivalent of aluminium chloride plus 0.5 molar equivalent of zinc chloride or tin(IV) chloride afforded the β-chloro ketone **2** but not the di-addition compound **3**. Apparently, the acid chloride **1** complexes preferentially with aluminium chloride and the weaker Lewis acids, zinc chloride and tin(IV) chloride, are then unable to compete (scheme 2) with the initially formed carbocation **19** (R = cyclopropyl) for chloride ion.

The acylation of propene by cyclopropanecarbonyl chloride (**1**) in the presence of 1.5 molar equivalents of aluminium chloride did not lead to di-addition of propene. 3-Chloro-1-cyclopropyl-1-butanone (**28**), contaminated by 1-cyclopropyl-2-buten-1-one (**29**), was obtained. Purification attempts only served to increase the contamination and so the product was dehydrochlorinated by sodium acetate to the 2-buten-1-one **29**. The acid chloride reactant, on the other hand, may be extensively varied. In addition to the examples already mentioned, hexanoyl chloride, in the presence of two molar equivalents of aluminium chloride, gave a mixture of 2-methyl-2-nonen-4-one (**30**) and 1-chloro-3-octanone (**31**) in the ratio 2:3.

3-Chloro-1-cyclopropyl-1-propanone (**2**) was dehydrochlorinated to 1-cyclopropyl-2-propen-1-one (**32**) by sodium acetate and reduced to 3-chloro-1-cyclopropyl-1-propanol (**33**) by sodium borohydride. 1-Cyclopropyl-3-methyl-2-buten-1-one (**3**) was characterized as its 2,4-dinitrophenylhydrazone and dibromide **34**. Authentic 4,4-dimethyl-1-penten-3-one (**37**) was synthesised from the methyl iodide salt **36** of 4,4-dimethyl-1-(*N*,*N*-dimethylamino)-3-pentanone (**35**).

EXPERIMENTAL

Melting points were determined with a Reichert Thermovar hot-block and are uncorrected. Hmr spectra of all products were recorded at 60 MHz on a Perkin-Elmer R12B spectrometer in $CDCl_3$ solutions containing Me_4Si as an internal standard. Ir spectra were recorded on a Perkin-Elmer 337 spectrometer. Mass spectra were obtained with a VG Micromass 7070H spectrometer. Merck silica gel PF_{254} + 366 was used for preparative thin layer chromatography (PLC).

General procedure for Friedel-Crafts reactions. A solution of the acid chloride in CH_2Cl_2 was added dropwise to a suspension of $AlCl_3$ in CH_2Cl_2 and stirred for 15 min. Ethene was passed for 90 min. through the solution which was then poured on ice and aqueous HCl (10%) and extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was purified chromatographically.

3-Chloro-1-cyclopropyl-1-propanone (2). Cyclopropanecarbonyl chloride (**1**) (10.00 g; 0.096 mol) in CH_2Cl_2 (20 ml) and $AlCl_3$ (12.77 g; 0.096 mol) in CH_2Cl_2 (20 ml) reacted with ethene to give the *β–chloropropanone* **2** as an oil (8.46 g). Hmr δ 0.72-1.26 (m, CH_2CH_2), 1.77-2.24 (m, CH), 3.04 (t, J 7 Hz, 2-CH_2), 3.78 (t, J 7 Hz, 3-CH_2). Ir (neat) ν 1700 cm^{-1} (C=O). Found: C, 54.8; H, 6.9; Cl, 26.3. C_6H_9ClO requires: C, 54.4; H, 6.8; Cl, 26.7%.

1-Cyclopropyl-3-methyl-2-buten-1-one (3). Cyclopropanecarbonyl chloride (**1**) (10.00 g; 0.096 mol) in CH_2Cl_2 (20 ml) and $AlCl_3$ (14.03 g; 0.105 mol) in CH_2Cl_2 (20 ml) reacted with ethene to give the *buten-1-one* **3** (0.58 g.) and the β-chloropropanone **2** (6.96 g). The use of $AlCl_3$ (19.20 g; 0.144 mol) gave the butenone **3** (4.32 g) and the chloro ketone **2** (6.49 g); use of $AlCl_3$ (29.45 g; 0.221 mol) gave the butenone **3** (5.86 g), b.p. 46-8°C/10 torr. Hmr δ 0.65-1.29 (m, CH_2CH_2), 1.71-2.15 (m, cyclopropyl CH), 1.92 (d, J 1 Hz, CH_3), 6.36 (m, 2-CH). Ir (neat) ν 1670 cm^{-1} (C=O). The butenone **3** was converted into its *2,4-dinitrophenylhydrazone*, m.p. 164-5°C (EtOH). Found: C, 55.0; H, 5.1; N, 18.9. $C_{14}H_{16}N_4O_4$ requires: C, 55.3; H, 5.3; N, 18.4%. Hmr δ 0.67-1.38 (m, CH_2CH_2), 1.54-1.82 (m, cyclopropyl CH), 1.97 (d, J 1 Hz, *o*-H), 8.31 (q, J 3 and 10 Hz, *m*-H), 9.16 (d, 3 Hz, *m*-H), 11.96 (bs, NH).

Cyclopropanecarbonyl chloride (**1**) (1.00 g) in CH_2Cl_2 (10 ml) and $AlCl_3$ (1.28 g; 1 molar equiv.) and zinc chloride (0.66 g; 0.5 molar equiv.) in CH_2Cl_2 (20 ml) reacted with ethene to give 3-chloro-1-cyclopropyl-1-propanone (**2**) (0.45 g). Substitution of tin(IV) chloride for zinc chloride in the above reaction gave the chloropropanone **2** (0.57 g).

2,3-Dibromo-1-cyclopropyl-3-methyl-1-butanone (34). Br_2 (1.70 g) in CCl_4 (15 ml) was added dropwise to a solution of 1-cyclopropyl-3-methyl-2-buten-1-one (**3**) (1.305 g) in CCl_4 (20 ml). After 30 min., the solvent was removed and the residual oil was purified by column chromatography on silica gel, using light petroleum/Et_2O (4:1) as eluent, and gave the *dibromide* **34** (2.22 g) as an oil. Hmr δ 0.75-1.34 (m, CH_2CH_2),1.93-2.47 (m, cyclopropyl CH), 2.03 (s, Me), 2.05 (s, Me), 4.94 (s, CHBr). Ir (neat) ν 1710 cm^{-1} (C=O). Found: C, 33.7; H, 4.0; Br, 56.7. $C_8H_{12}Br_2O$ requires: C, 33.8; H, 4.3; Br, 56.3%.

1-Cyclopropyl-2-propen-1-one (32). A mixture of 3-chloro-1-cyclopropyl-1-propanone (**2**) (26.83 g) and NaOAc (16.86 g) in EtOH (40 ml) was heated under reflux for 13 h., diluted with H_2O and dried over anhydrous Na_2SO_4. Removal of the solvent and distillation of the residual oil gave the 2-propen-1-one[8] **32** as a colourless oil (13.71 g), b.p. 22-4°C/0.53 torr. Hmr δ

0.71-1.48 (m, CH_2CH_2), 1.92-2.40 (m, cyclopropyl CH), 5.88 (q, J 2 and 10 Hz, 3-CH), 6.35-6.62 (m, 2-CH, 3-CH).

3-Chloro-1-cyclopropyl-1-propanol (33). A solution of 3-chloro-1-cyclopropyl-1-propanone (**2**) (12.50 g) in EtOH (50 ml) was added dropwise to a suspension of $NaBH_4$ (7.00 g) in EtOH (100 ml), stirred overnight, poured into H_2O (100 ml), heated on a steam-bath for 1 h., cooled, and extracted with $CHCl_3$. The extract was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed and the residual oil was purified by column chromatography on silica gel, using light petroleum/Et_2O (3:2) as eluent, affording the *chloropropanol* **33** as an oil (11.15 g). Hmr δ 0.28–0.83 (CH_2CH_2), 0.85-1.16 (m, CH), 1.89-2.31 (m, 2-CH_2), 2.21 (bs, OH), 2.96-3.31 (m, 1-CH), 3.75 (t, J 7 Hz, 3-CH_2). Ir (neat) ν 3380 cm^{-1} (OH). Found: C, 53.3; H, 7.8; Cl, 26.2. $C_6H_{11}ClO$ requires: C, 53.5; H, 8.2; Cl, 26.3%.

Acetyl chloride (6.10 g) was added to a solution of the chloropropanol **33** (10.00 g) in Et_2O (100 ml) containing pyridine (6 g), heated under reflux for 2 h., poured into water, and extracted with $CHCl_3$. The extract was washed, dried, and chromatographed as above and afforded *1-acetoxy-3-chloro-1-cyclopropylpropane* as an oil (12.11 g). Hmr δ 0.22-0.67 (m, CH_2CH_2), 0.74-1.27 (m, CH), 2.10 (s, Ac), 2.02-2.36 (m, 2-CH_2), 3.64 (t, J 7 Hz, 3-CH_2), 4.49-4.73 (m, 1-CH). Ir (neat) ν 1740 cm^{-1} (C=O). Found: C, 55.0; H, 7 3; Cl, 20.5. $C_8H_{13}ClO_2$ requires: C, 54.4; H, 7.4; Cl, 20.1%.

1-Cyclopropyl-3-phenyl-1-propanone (24) and Cyclopropyl phenyl ketone (23). Cyclopropanecarbonyl chloride (**1**) (2.00 g) in CH_2Cl_2 (10 ml) and $AlCl_3$ (2.56 g; 1 molar equiv.) in CH_2Cl_2 (50 ml) was allowed to react with ethene for 60 min. Dry benzene (10 ml) was added and the solution was stirred for 3 h.. The usual work-up gave an oil which, after purification by column chromatography on silica gel, gave a mixture (1 35 g) which could not be fractionated. A sample (0.4 g) was treated with a solution of 2,4-dinitrophenylhydrazine (1.00 g) in MeOH (15 ml) containing H_2SO_4 (1 ml). The resulting precipitate was filtered off after 20 min., washed with a little MeOH, dried, and fractionated by PLC into two bands. The band with the larger R_F value afforded 1-cyclopropyl-3-phenyl-1-propanone 2,4-dinitrophenylhydrazone[9] (0.02 g), m.p. 156-7°C. Hmr δ 0.68-2.16 (m, cyclopropyl), 2.52-3.12 (m, 2-CH_2, 3-CH_2), 7.18-7.50 (m, Ar), 7.89 (d, J 9 Hz, 6'-H), 8.39 (q, J 3 and 9 Hz, 5'-H), 9.18 (d, J 3 Hz, 3'-H), 11.14 (bs, NH). Ms m/z 354 (M^+).

The other band afforded *cyclopropyl phenyl ketone 2,4-dinitrophenylhydrazone* (0.02 g), m.p. 215-7°C. Hmr δ 0.61-2.06 (m, cyclopropyl), 7.28-7.73 (m, 3-H, 4-H, 5-H of phenyl ring), 7.84-8.11 (m, 2-H, 6-H of phenyl ring), 8.22 (d, J 9 Hz, 6-H of nitrophenyl ring), 8.53 (q, J 3 and 9 Hz, 5-H of nitrophenyl ring), 9.29 (J 3 Hz, 3-H of nitrophenyl ring), 12.12 (bs, NH).

1-Cyclopropyl-2-buten-1-one (29). Cyclopropanecarbonyl chloride (**1**) (1.00 g) in CH_2Cl_2 (10 ml) and $AlCl_3$ (1.91 g; 1.5 molar equiv.) in CH_2Cl_2 (50 ml) reacted with propene and gave a viscous oil (6.72 g) which, after being column chromatographed on silica gel, afforded impure 3-chloro-1-cyclopropyl-1-butanone (**28**) (0.47 g). Hmr δ 0.63-1.38 (m, CH_2CH_2), 1.51 (d, J 7 Hz, CH_3), 1.78-2.33 (m, cyclopropyl CH), 2.86 (q, J 7 and 16 Hz, 2-CH), 3.22 (q, J 7 and 16 Hz, 2-CH), 4.54 (m, 3-CH). Ir (neat) ν 1695 cm^{-1} (C=O). A sample (0.30 g) was treated with NaOAc (0.30 g) in EtOH (10 ml), heated under reflux overnight, poured into water, and extracted with Et_2O. The extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by PLC, using light petroleum/Et_2O (9:1) as eluent, and gave 1-cyclopropyl-2-

buten-1-one[10] (**29**) as an oil (0.13 g). Hmr δ 0.65-1.42 (m, CH_2CH_2), 1.78-2.36 (m, CH), 1.95 (q, J 2 and 7 Hz, CH_3), 6.26 (q, J 2 and 17 Hz, 2-CH), 6.97 (q, J7 and 17 Hz, 3-CH). Ir (neat) ν 1685 cm^{-1}.

2-Tetralone (9). Phenylacetyl chloride (**8**) (2.00 g) in CH_2Cl_2 (20 ml) and $AlCl_3$ (2.59 g; 1.5 molar equiv.) in CH_2Cl_2 (50 ml) reacted with ethene to give an oil which was purified by column chromatography on silica gel followed by distillation and gave 2-tetralone[6] (**9**) (1.15 g), b.p. 121-2°C/6 torr.

3,4-Benzobicyclo[3.1.0]hexan-2-one (11). 2-Phenylcyclopropanecarbonyl chloride (**10**) (0.50 g) in CH_2Cl_2 (10 ml) and $AlCl_3$ (0.37 g; 1 molar equiv.) in CH_2Cl_2 (20 ml), on reaction with ethene, gave an oil which was purified by PLC, using light petroleum/Et_2O (7:3) as eluent, and afforded the 2-hexanone[11] **11** as an oil (0.29 g). Hmr δ 1.12-1.83 (m, CH_2), 2.37-2.74 (m, CH), 2.79-3.16 (m, CH), 7.18-8.08 (m, 4 H). Use of $AlCl_3$ (0.56 g; 1.5 molar equiv.) gave the hexanone **11** (0.12 g).

2,5,5-Trimethyl-2-hexen-4-one (14). 2,2-Dimethylpropanoyl chloride (**12**) (5.00 g) in CH_2Cl_2 (10 ml) and $AlCl_3$ (5.53 g) in CH_2Cl_2 (20 ml), on reaction with ethene at -78°C, gave the 4-hexen-3-one[7] **14** as an oil (1.27 g). Hmr δ 1.25 (s, Me_3C), 1.93 (d, J 1 Hz, (E)-CH_3), 2.15 (d, J 1 Hz, (Z)-CH_3), 6.39 (m, 4-CH).

4,4-Dimethyl-1-penten-3-one (37). A mixture of 2,2-dimethyl-3-butanone (25.00 g), dimethylamine hydrochloride (20.40 g), and paraformaldehyde (7.50 g) in 2-propanol (40 ml) containing conc. HCl (0.5 ml) was heated under reflux for 6 hr. Removal of the solvent gave a paste which was triturated with Et_2O. The resulting solid was added to aqueous NaOH (50%) and extracted with Et_2O. The extract was washed with H_2O and dried over anhydrous Na_2SO_4. Removal of the solvent and distillation of the residual oil afforded *4,4-dimethyl-1-(N,N-dimethylamino)-3-pentanone* (**35**) (22.53 g), b.p. 38-40°C/0.23 torr. Hmr δ 1.15 (s, Me_3C), 2.29 (s, Me_2N), 2.58-2.82 (m, CH_2CH_2) Found: C, 68.6; H, 12.2; N, 8.5. $C_9H_{19}NO$ requires: C, 68.7; H, 12.2; N, 8.9%.

Methyl iodide (11.31 g) was added to this pentanone **35** (10.00 g) stirring in an ice-bath. The resulting solid was triturated with Et_2O and afforded *4,4-dimethyl-1-(N,N,N-trimethylamino)-3-pentanone* (**36**) as a white solid (11.07 g). Hmr δ 1.15 (s, Me_3C), 2.80-2.94 (m, CH_2CH_2), 3.13 (bs, Me_3N). Found: C, 39.9; H, 7.6; I, 42.3; N, 4.6. $C_{10}H_{22}INO$ requires: C, 40.1; H, 7.4; I, 42.4; N, 4.7%.

The iodide **36** (3.00 g) and NaOAc (1.00 g) in MeOH (15 ml) were heated under reflux for 15 min., poured into H_2O, and extracted with CH_2Cl_2. The extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residual oil was purified by PLC and gave 4,4-dimethyl-1-penten-3-one[12] (**37**) as an oil (0.55 g). Hmr δ 1.12 (s, Me_3C), 5.72 (q, J 2 and 10 Hz, 3-CH_{cis}), 6.31 (q, J 2 and 17 Hz, 3-CH_{trans}), 7.00 (q, J 10 and 17 Hz, 2-CH).

3-Methyl-1-(2-naphthyl)-2-buten-1-one (16). 2-Naphthoyl chloride (1.00 g) in CH_2Cl_2 (10 ml) and $AlCl_3$ (1.05 g; 1.5 molar equiv.) reacted with ethene to give an oil which was purified by column chromatography on silica gel, using light petroleum/Et_2O (9.1) as eluent, and afforded the 2-buten-1-one **16** as an oil[13] (0.16 g). Hmr δ 2.07 (d, J 1 Hz, (E)-CH_3), 2.31 (d, J 1 Hz, (Z)-CH_3), 7.01 (m, 2-CH), 7.43-8 19 (m, Ar), 8.57 (m, 1'-H).

The use of $AlCl_3$ (0 7 g; 1 molar equiv) in this reaction gave an oil which was purified as

above, but using light petroleum/Et_2O (17:3) as eluent, and afforded 3-chloro-1-(2-naphthyl)-1-propanone[14] (**17**) as an oil (0.25 g). Hmr δ 3.57 (t, J 7 Hz, 2-CH_2), 4.01 (t, J 7 Hz, 3-CH_2), 7.37-8.23 (m, Ar), 8.52 (m, 1'-H).

2-Methyl-2-nonen-4-one (30). Hexanoyl chloride (2.00 g) in CH_2Cl_2 (15 ml) and $AlCl_3$ (1.98 g; 1 molar equiv.) in CH_2Cl_2 (20 ml) reacted with ethene to give 1-chloro-3-octanone[15] (**31**) as an oil (1.73 g). Hmr δ 0.58-1.94 (m, C_4H_9), 2.51 (t, J 7 Hz, 4-CH_2), 2.97 (t, J 7 Hz, 2-CH_2), 3.81 (t, J 7 Hz, 1-CH_2).

The use of $AlCl_3$ (2.97 g; 1.5 molar equiv.) and a reaction time of 8 h. gave an oil (2.66 g) which was fractionated by PLC, using light petroleum/Et_2O (9:1) as eluent. The band with the larger R_F value afforded 1-chloro-3-octanone[15] (**31**) as an oil (0.28 g). The other band gave 2-methyl-2-nonen-4-one[16] (**30**) as an oil (0.18 g). Hmr δ 0.63-2.10 (m, C_4H_9), 1.92 (d, J 1 Hz, (E)-CH_3), 2.18 (d, J 1 Hz, (Z)-CH_3), 2.46 (t, J 7 Hz, 5-CH_2), 6.13 (m, 3-CH).

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