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TEMPERATURE CONTROLLED SELECTIVITY IN METHYLCYCLOPENTANE CARBONYLATION IN HF-SbF_5

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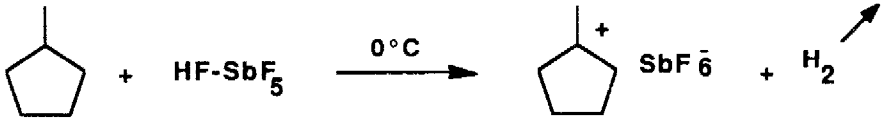
Summary: Protolytic ionization of methylcyclopentane in HF-SbF_5, followed by carbonylation at atmospheric pressure yields either methyl cyclopentane- or cyclohexaneoxocarbenium ions depending on the reaction temperature. An example of kinetic versus thermodynamic control.

The acid catalysed synthesis of carboxylic acids and esters from olefins, CO and water, known as the Koch-Haaf reaction[1] comprises a reversible key step in which carbocations react with CO. Since the pionneering work of Olah and his group , twenty years ago, an alternative route of preparation of carbocations is known : the protolytic ionization of alkanes in superacid medium.[2] Earlier reports on direct carbonylation of alkanes in HF-SbF_5, including the reactions of propane,[3] C_6 cycloalkanes,[4] C_5–C_8 alkanes[5] and adamantane,[6] show that the selectivity of this reaction is often limited by the usual side reactions of carbocations such as isomerisation and cracking. In this paper we show how the temperature of the carbonylation step can drastically change the selectivity in the C_6 cycloalkane system.

When methylcyclopentane (29 mmol) is added to HF-SbF_5 (380 mmol-7.8 mmol SbF_5) at 0°C, a two phase system results in which the ionization of the alkane takes place with hydrogen evolution over a 6 hour period.



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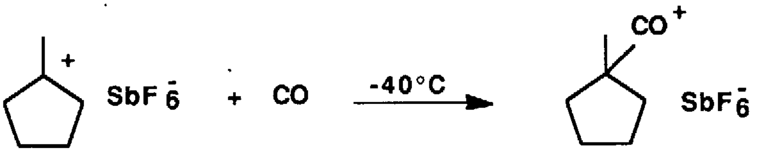
This protolytic ionisation step which has been studied in detail in the case of isobutane[7-8] is rather slow at 0° in this acidity range. The activation energy of this process under these conditions has been estimated as 18 $Kcal.mol^{-1}$.

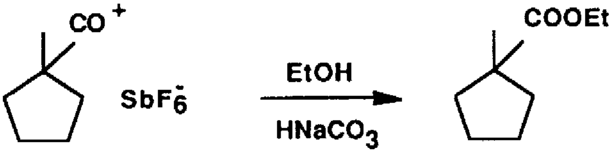
Carbonylation at -40°C

When after a variable time of reaction, the solution is cooled to -40° and carbon monoxide is bubbled through the solution (220 ml min^{-1}) the initial methylcyclopentyl carbocations yield quantitatively the corresponding oxocarbocations.



1 1a

When after 6 hours the solution is quenched in $HNaCO_3$/EtOH, after the usual work-up, ethyl methylcyclopentanecarboxylate 1b is obtained in an 80% yield based on SbF_5 (a small amount of cyclohexanone, stable under the reaction conditions, was used throughout this work as internal standard for GC analysis).



1a 1b

Figure 1 shows the yield dependence on time of reaction (i.e. time of activation at 0° C followed by carbonylation 1 hour at -40°C) and illustrates the slow ionization of the tertiary hydrocarbon in this weak superacid.[3]

Carbonylation at 0°C

When carbon monoxide was bubbled from the start, during 6 hours, through the HF-SbF_5 solution containing methylcyclopentane at 0°C, quenching the resulting solution as above yielded 90% of ethyl cyclohexanecarboxylate 2b (in a yield of 60% based on SbF_5), in fair agreement with the early findings of Paatz and Weisgerber.[4] The variation of the distribution of the oxo ions in the superacid solution versus time was followed by withdrawing and quenching aliquots, as described above. The product distribution versus time is shown on figure 2.

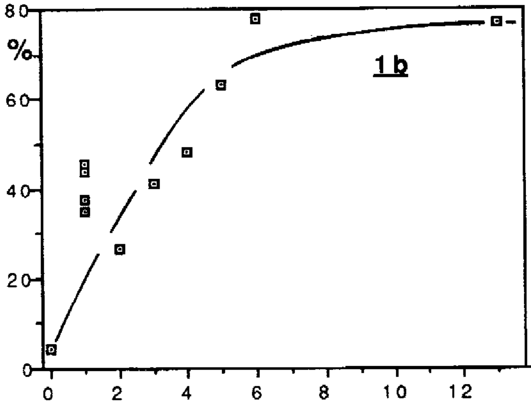


Fig.1: Yield in ester versus time of reaction at 0°C, carbonylation at -40°C. Selectivity in **1b**: > 98%

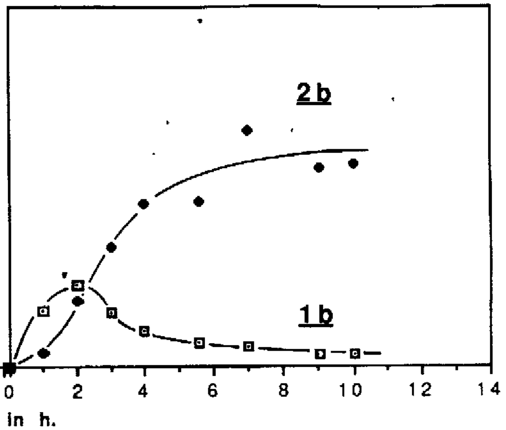
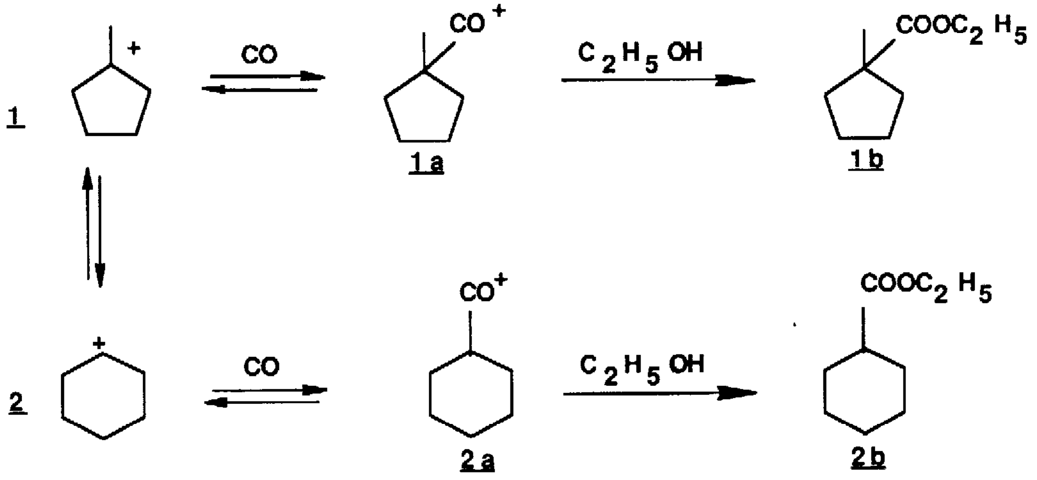


Fig.2: Yield in esters versus time of reaction at 0°C(ionization and carbonylation)



As expected ion **1a** is obtained first by protolytic cleavage of the tertiary C-H bond of methylcyclopentane and carbonylation. At 0°C however, the rate of decarbonylation of **1a** is not negligible and the competing pathway of isomerisation **1** → **2** despite unfavourable thermodynamics (10 Kcal.mol^{-1} difference in ground state between tertiary and secondary carbocations) yields the secondary cyclohexyl ion **2** which has a much higher affinity for carbon monoxide. A difference of 7 Kcal.mol^{-1} in activation energy for decarbonylation of secondary and tertiary oxo ions has been estimated by Hogeveen.[9] Thus in the temperature range where decarbonylation of **2a** is slow, the solution is enriched in cyclohexyl oxocarbenium ions at the expense of ion **1a**. These results should also be compared to those obtained by anodically assisted carbonylation of cyclohexane in HSO_3F-H_2O, yielding exclusively cyclohexanecarboxylic acid.[10]

On the other hand, the formation of the methylcyclopentyl ion **1** in the presence of excess methylcyclopentane induces two side reactions which could be followed by G.C. analysis of the hydrocarbon phase : isomerization of methyl cyclopentane to cyclohexane and ring opening.

- The isomerization reaction of the C_6 cycloalkanes in the presence of solid superacids has been described by us earlier.[11] At 0°C the thermodynamic equilibrium favoring cyclohexane is reached in 90 minutes. However this reaction has a negligible influence on the carbonylation reaction as the ionization of cyclohexane is very slow at this temperature.

- The ring opening of methyl cyclopentane via β-scission of the 3-methyl cyclopentylium ion is also very slow in this acidity[12] and temperature range. It is at the origin, via protonation and hydride transfer reactions, of the isomeric hexanes which appear in the hydrocarbon phase.

Whereas this carbonylation reaction of alkanes can be attractive on the basis of high selectivities it must be stressed that the conversion in the superacid is limited by the SbF_5 content responsible for its acidity. As the reaction proceeds, the formation of the SbF_6^- counterion decreases the acidity as well as the reaction rates.

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