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Carbonylation of Methylcyclopentane and Cyclohexane Initiated by the Aprotic Organic Superacid $CBr_4{\cdot}2AlBr_3$

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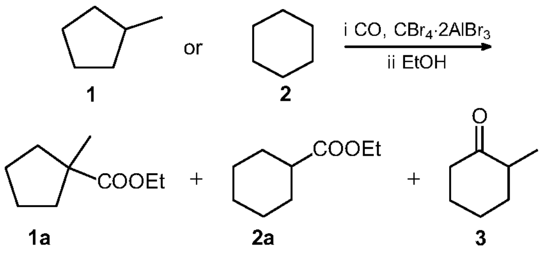
The aprotic organic superacid $CBr_4{\cdot}2AlBr_3$ initiates carbonylation of methylcyclopentane **1** and cyclohexane **2** with CO at atmospheric pressure with formation (after EtOH treatment) of various products in high yields depending on the conditions. The products are esters of 1-methylcyclopentanecarbonic (**1a**; at –45 °C) and cyclohexanecarbonic (**2a**; at 0°C) acids and 2-methylcyclohexanone (**3**; at –23 °C); the reaction mechanism is discussed.

SbF_5-based protic superacids have been widely used for single-stage functionalization of saturated hydrocarbons[1] including carbonylation with CO of C_1,[2] C_3,[3] C_5–C_9[4] alkanes, cyclopentane,[5] methylcyclopentane and cyclohexane,[5,6] adamantane,[7] *etc.* Methylcyclopentane **1** reacts with CO in the presence of HF–SbF_5 at 0 °C and atmospheric pressure for 4 h to produce after hydrolysis a 95% yield of a 9:1 mixture of cyclohexane- and 1-methylcyclopentanecarbonic acids.[5] The reaction with cyclohexane **2** is not effective:[5,6] under similar conditions the yield of cyclohexanecarbonic acid after 5 h is 11%.[5] Sommer has shown that the direction of carbonylation of **1** under the action of HF–SbF_5 depends on the temperature: at 0 °C an ester of the cyclohexane series is formed and one of the 1-methylcyclopentane series is formed at –40 °C.[6]

Aprotic organic superacids, namely, complexes of $AlHal_3$ with acylhalides[8] and polyhalogenomethanes[9] have been shown to be effective initiators for alkane and cycloalkane functionalization and, in particular, for cyclopentane carbonylation.[10]

In the present communication we report on the carbonylation of **1** and **2** in the presence of aprotic organic superacid $CBr_4{\cdot}2AlBr_3$ resulting in the formation of three different products depending on the reaction conditions (Scheme 1).

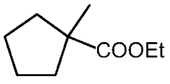
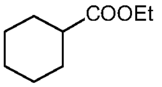
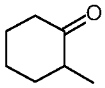
At –45 to 0 °C and atmospheric pressure both cycloalkanes



Scheme 1

react with CO to afford (after EtOH work-up) mainly one of two esters depending on the temperature and reaction time: **1a** at −45 °C independent of reaction time and at 0 °C for 15 min and **2a** at 0 °C for 4 h (Table 1). Under optimum conditions the maximum yields of **1a** and **2a** amount to more than 80%.[†] Formation of the third product, ketone **3**, is of special interest. It was not observed among the carbonylation products in the presence of HF–SbF_5,[5,6] but was found in the reaction of **2** with HCl–$AlCl_3$ at 150 atm CO.[11] In the presence of $CBr_4 \cdot 2AlBr_3$ ketone **3** is formed from **1** at −23 °C in 80% yield together with 74% of **1a**.[‡] The directions of the reactions of **1** and **2**, depending on the temperature, are in general similar.

Table 1 Carbonylation of methylcyclopentane and cyclohexane with CO in the presence of $CBr_4 \cdot 2AlBr_3$.[a]

Run	RH	T/°C, t/min	Yield (%) on $CBr_4 \cdot 2AlBr_3$[b]			1:2 Molar ratio
			 **1a**	 **2a**	 **3**	
1	Methylcyclo-	0, 15	55	14	30	0.18
2[c]	pentane **1**	0, 240	0	44	39	0.06
3		i 0, 240 ii −45, 120	0	42	33	0.05
4		−23, 240	74	< 1	80	9
5[d]		−45, 240	76	< 1	21	38
6		i −45, 240 ii 20, 60	0	45	29	0.07
7		0, 240 at 100 atm. CO	13	< 1	76	> 100
8	Cyclohexane **2**	0, 15	52	10	9	0.05
9		0, 240	3	82	18	0.06
10		i 0, 60 ii 0, 60 in Ar	0	32	14	0.09
11		−45, 15	55	4	1	< 0.01
12		−45, 60	83	5	1	< 0.01
13		−45, 240	78	< 1	< 1	< 0.01
14		−45, 60; and 0, 60 in Ar	0	8	3	0.09
15		i −45, 60 ii −23, 90 with **1**	59	5	40	0.97
16		0, 240 at 100 atm. CO	26	75	3	< 0.01

[a] In a typical experiment cycloalkane (6 mmol) was added to a mixture of CBr_4 (1 mmol) and $AlBr_3$ (2 mmol) in 0.5 ml of CH_2Br_2 cooled by liquid N_2. After evacuation the reaction flask was filled with CO under atmospheric pressure and stirred at fixed temperature. The reaction mixture was then worked-up by EtOH, a standard (mesitylene) was added, then the mixture was washed, extracted with ether and analysed by GC and GC-MS. For ^1H NMR measurements the reaction mixture was hydrolysed with water. The experiments 7 and 16 were carried out in a steel autoclave under stirring. [b] Selected spectral data: MS (m/z) for **1a**: 83, 55, 41, 29, 67, 115, 27, 141, 39, 156 (M^+); for **2a**: 83, 55, 101, 41, 156 (M^+), 29, 111, 88, 73, 128; for **3**: 68, 41, 56, 112, 69, 54, 84, 42, 27, 39; ^1H NMR: **1a** (acid) in [$^2H_6$]acetone (δ, ppm): 1.3 (s, Me), 1.5 (m, CH_2), 1.7 (m, CH_2), 2.1 (m, CH_2), 9.2 (s, COOH). Semicarbazone of **3**: m.p. 190 °C (lit. 189 °C[11b]). [c] Under similar conditions without CBr_4 **3** was the only reaction product (yield 8%). [d] Under similar conditions without CBr_4 carbonylation does not occur.

However, in contrast to the data for HF–SbF_5,[5,6] the reaction with **2** proceeds more effectively and selectively than with **1**. On the other hand, the yields of ketone **3** in reactions of **1** are markedly higher than with **2**.

Sommer has previously proposed a scheme for the carbonylation of **1** in an HF–SbF_5 medium with formation of $\mathbf{1}''$ at −40 °C and $\mathbf{2}''$ at 0 °C due to both kinetic and thermodynamic control of the chain of reversible reactions[6] $\mathbf{1}'' \leftrightarrows \mathbf{1}' \leftrightarrows \mathbf{2}' \leftrightarrows \mathbf{2}''$ (Scheme 2).

It follows from our data that $\mathbf{2}''$, which is the main product of these cycloalkane reactions at 0 °C, is not converted into $\mathbf{1}''$ on cooling to −45 °C (Table 1, run 3) and does not disappear on blowing argon through the reaction mixture (run 10), and thus the reverse decarbonylation reaction $\mathbf{2}'' \rightarrow \mathbf{2}'$ is absent. At 0 °C the initial carbonylation product of **2** is $\mathbf{1}''$ (run 8), *i.e.* the cation $\mathbf{2}'$ does not have time to add CO with formation of $\mathbf{2}''$, but rapidly isomerizes into the thermodynamically more stable $\mathbf{1}'$, which then adds CO to yield $\mathbf{1}''$. According to ref. 4, intramolecular transformations of carbocations, such as isomerizations and fragmentations, proceed more rapidly in comparison with their bimolecular reactions with CO. At the same time $\mathbf{1}''$, being the main carbonylation product at −45 °C, completely converts into $\mathbf{2}''$ at 0–20 °C under a CO atmosphere for 1–4 h. The $\mathbf{1}'' \leftrightarrows \mathbf{1}'$ equilibrium is quickly reached as it follows from an almost complete disappearance of carbonyl-containing products on displacement of CO with argon in the presence of $\mathbf{1}''$ (run 14). Note that carbonylation of **1** and **2** at 20 °C does not result in noticeable quantities of $\mathbf{1}''$ and $\mathbf{2}''$. It should be stressed that the $\mathbf{1} \leftrightarrows \mathbf{2}$ isomerization, caused by interconversion of carbenium ions $\mathbf{1}'$ and $\mathbf{2}'$, does not occur at −45 °C when $\mathbf{1}'$ rapidly captures CO with a shift of the $\mathbf{1}'' \leftrightarrows \mathbf{1}'$ equilibrium in the direction of $\mathbf{1}''$ (runs 5, 11–13).

Increasing CO pressure strongly affects the composition of products, speeding up the stage of CO addition to carbenium ions and blocking its elimination process. The only acyl

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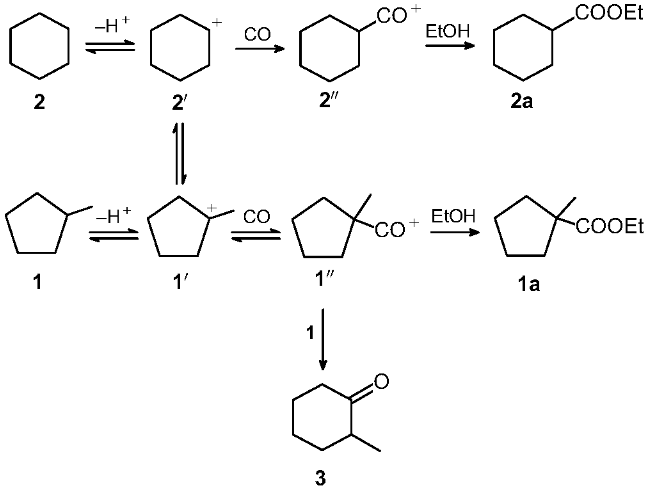
[†] In all cases the yields given are based on $CBr_4 \cdot 2AlBr_3$.

[‡] Note that in this case the total yield of carbonylation products exceeds 150% of initiator.



Scheme 2

cation formed from **1** at 0 °C and P_{CO} = 100 atm is **1′** due to suppression of the **1″**⇆**1′** stage (run 7, in contrast to run 2 at P_{CO} = 1 atm). The run 7 allows us exclude the alternative scheme of formation of **2a** by direct rearrangement of **1a**. With **2** as the starting hydrocarbon the rate of intermolecular reaction of the initially formed **2′** with CO leading to **2″** is probably even higher than that of isomerization of **2′** into **1′** with subsequent transformation into **1″** (run 16). At high CO pressure the isomerization of both cycloalkanes **2**⇆**1** is suppressed (*cf.* the [**1**]:[**2**] molar ratio in runs 16 and 9, 7 and 2).

Ketone **3** is simply the product of **1″** conversion in the presence of **1** under conditions under which the decarbonylation of **1″** is inhibited (runs 4 and 7). When in a CO atmosphere **1** is added to **1″** (initially prepared from **2**), **3** is also formed (run 15). Under similar conditions, but without **1**, the formation of **3** does not occur as well as from **1″** in the presence of such donors of hydride ion as isopentane, methylcyclohexane or butanal. Elucidation of the mechanism of formation of **3** needs further study.

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