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Carbonylation of Cyclopentane in the Presence of Aprotic Organic Superacids

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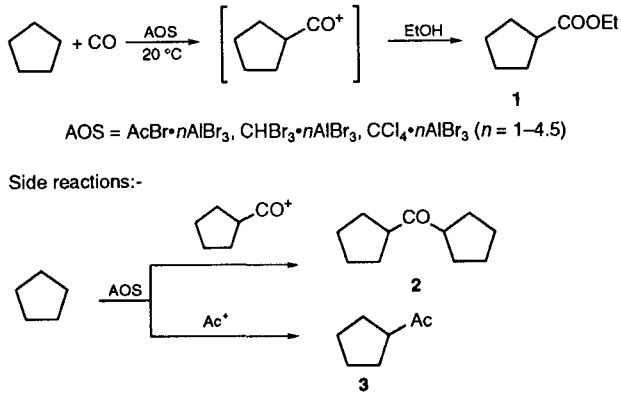
The systems MeCOBr·nAlBr$_3$ as well as CHBr$_3$·nAlBr$_3$ and CCl$_4$·nAlBr$_3$ (n=1–4.5) have been shown to initiate carbonylation of cyclopentane under mild conditions to give, after alcoholic work-up, the corresponding ester of cyclopentylcarboxylic acid with good yields and high selectivity.

The single-stage functionalization of alkanes and cycloalkanes is a promising approach to the direct synthesis of organic compounds from available hydrocarbons. This problem has therefore attracted great interest over the two last decades.[1]

We have already described two groups of aprotic organic superacids (AOS). Both of them, the acyl halide–aluminium halide superacids, RCOX·2A1X$_3$,[2] and the polyhalogenomethane–aluminium bromide systems, CBr$_4$·nAlBr$_3$, CHBr$_3$·nAlBr$_3$, (n=1, 2), CCl$_4$·2AlBr$_3$, CHCl$_3$·2AlBr$_3$,[3] were shown to exhibit high activity in low-temperature alkane transformations. The AOS of the first group have been used for alkane functionalization reactions such as ionic bromination,[4] acylation,[5] thioacylation[6] and arylacylation.[7] Bromination of alkanes and cycloalkanes by CHBr$_3$·2AlBr$_3$ has also been described.[2]

In continuation of these studies we now wish to report the carbonylation of cyclopentane with CO in the presence of both of these types of AOS under mild conditions. The carbonylation of C$_1$,[8] C$_3$,[9] C$_5$–C$_9$ alkanes,[10] cyclopentane, cyclohexane[11] and adamantane,[12] *etc.*, has been carried out directly with CO using proton superacids. However, in the presence of proton superacids the selectivity of carbonylation products is generally poor. In some reactions high CO pressure is used. Moreover, since the carbonylation of alkanes demands the participation of stoichiometric or even excessive amounts of toxic and expensive proton superacids, it is important to find simple and available initiators for this reaction.

The reactions of cyclopentane in the presence of AOS were carried out at room temperature under CO atmosphere without a solvent. The ester of cyclopentylcarboxylic acid **1** (Scheme 1) is formed in good yield and selectivity of 90–98% after ethanol work-up of the reaction mixture (Table 1). The yields of by-products **2**+**3** (AcBr·nAlBr$_3$) or **2** (polyhalogenomethane·nAlBr$_3$) are less than 1–5% and only reach 15% in run 12.



Scheme 1

In agreement with reported data on the activity of AcBr·nAlBr$_3$ systems,[2] the AcBr·AlBr$_3$ complex is inert while the AcBr·1.8AlBr$_3$ system is active in this reaction. The activity of the AcBr·nAlBr$_3$ systems increases with AlBr$_3$ concentration. The CHBr$_3$·nAlBr$_3$ and CCl$_4$·nAlBr$_3$ superacids are more effective and show activity in the presence of smaller quantities of AlBr$_3$. The total yield of carbonylation products (**1**+**2**) by CCl$_4$·4AlBr$_3$ reaches 1.5 mol per mol of AOS (run 12). This shows that the initiator works twice, being reduced on the first step to active CHX$_3$·nAlX$_3$; in its turn, the latter on reduction to CH$_2$X$_2$·nAlX$_3$ (X=Cl, Br) initiates the second reaction cycle. The capacity of CX$_4$·nAlX$_3$ systems to be reduced by alkanes to CH$_2$X$_2$·nAlX$_3$ has been shown.[3]

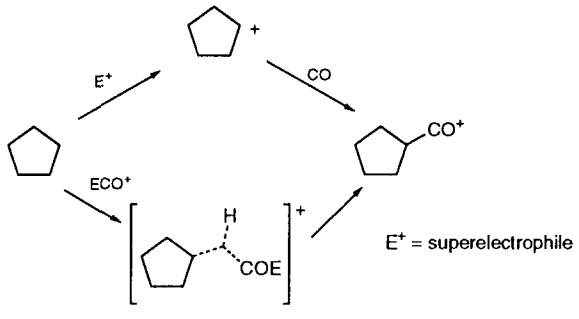
CH$_2$Br$_2$·nAlBr$_3$ (n=4) were found to be inactive under similar conditions as well as AlBr$_3$ alone.

Two mechanistic pathways have been proposed for proton superacid-initiated alkane (or cycloalkane) carbonylation and

Table 1 Cyclopentane carbonylation with CO in the presence of A·nAlBr$_3$.[a]

Run no.	A	n	Products, mol% from A		
			1	**2**	**3**
1	AcBr	1	0	0	0
2	AcBr	1,8	50	2	1
3	AcBr	2,7	66	1	1
4	AcBr	3,6	74	2	3
5	AcBr	4,5	95	1	1
6	CH_2Br_2	4	0	0	—
7	$CHBr_3$	1	52	1	—
8	$CHBr_3$	2	91	4	—
9[b]	$CHBr_3$	4	95	5	—
10	CCl_4	1	44	4	—
11	CCl_4	2	77	3	—
12	CCl_4	4	139	15	—

[a] Cyclopentane and AOS at molar ratio 10:1 were stirred without solvent in a closed glass flask under 1 atm CO at 20 °C for 4 h followed by EtOH work-up. The reaction mixture was then extracted with diethyl ether and washed and analysed by GLC and GLC–MS techniques. For NMR study the reaction mixture was worked-up with MeOH, extracted with CCl_4 and washed. Selected spectroscopic data: MS (m/z) for **1**: 69, 101, 41, 73, 97, 142 (M^+); for **2**: 69, 97, 41, 166 (M^+); for **3**: 43, 41, 69, 71, 112 (M^+), 68, 39, 97; for cyclo-C_5H_9COOMe: 87, 69, 41, 97, 100, 55, 128 (M^+); ^{1}H NMR δ 3.6 (MeO), 1.50 (CH_2). [b] Reaction time 2 h.



Scheme 2

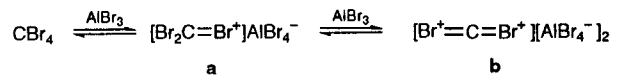
formylation. The first (Koch–Haaf reaction[13]) involves the generation of an alkyl cation from hydrocarbon *via* hydride abstraction by a superacid with subsequent acceptance of CO resulting in acylium cation formation. The second path implies the preliminary activation of CO by proton superacid to give HCO^+ cation or even $HCOH^{2+}$ dication.[14] The HCO^+ (or $HCOH^{2+}$) attacks hydrocarbon leading to carbonylation or formylation products. The second mechanism was proved for the reaction of adamantane with CO by labelling studies.[12]

For carbonylation of cyclopentane initiated by AOS both mechanisms could be proposed, Scheme 2.

The $MeC^+{=}O{\rightarrow}AlX_3$ species seem to play the role of key superelectophilic E^+ in the AcBr·nAlBr$_3$ systems.[2]

Passing to the second group of AOS it should be noted that the path involving hydride abstraction from propane by CCl_3^+ was proposed by Sommer and co-workers for carbonylation of propane in the presence of CCl_4 in HF–SbF_5 media.[9] Olah's doubts concerning the plausibility of this mechanism are based on ^{13}C NMR data for the CCl_3^+ cation[15] and consider the latter to be an electrophile of moderate strength only and so incapable of abstracting hydride ion from propane. Therefore, the participation of superelectrophiles $Cl_2C^+{-}Cl{\rightarrow}SbF_5$, or even Cl_2C^{2+}, was postulated for these reactions.[14]

According to recent AM1 and MNDO calculations,[16]



Scheme 3

following interaction of CBr_4 and $AlBr_3$[†] ionic complexes with positive charge on the bromine atoms can be generated, namely the bromenium cations **a** and dications **b**, Scheme 3.

To prove the possibility of CO activation by bromenium cations (or bromenium dications) and to choose between two alternative mechanisms of carbonylation (Scheme 2) needs special studies.

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[†] In these reactions CCl_4 and excess $AlBr_3$ tetrabromomethane is also formed due to halide exchange.