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# An Effective Formylation of Adamantane with CO Initiated by the Aprotic Organic Superacid $CBr_4{\bullet}2AlBr_3$ under Mild Conditions.

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**Abstract:** The reaction of adamantane with carbon monoxide at -45° ÷ +20°C over 0.5-2 h, catalyzed by the aprotic organic superacid $CBr_4{\bullet}2AlBr_3$, is described. The formylation of adamantane under CO atmosphere at 0 ÷ +20°C in the presence of methylcyclopentane as a source of hydride ion affords 1-adamantanecarbaldehyde (1) in yield 70-72% on adamantane for 1 h.

Induced by protic superacids reactions of alkanes and cycloalkanes with carbon monoxide proceed by two main pathways. The first involves the generation of a carbocation from a saturated hydrocarbon, followed by the carbon monoxide trapping with the formation of an acyl cation (The Koch-Haaf reaction).[1] Quenching of the acylium ion by water or alcohol gives the corresponding carboxylic acid or ester.[2] (Scheme 1)

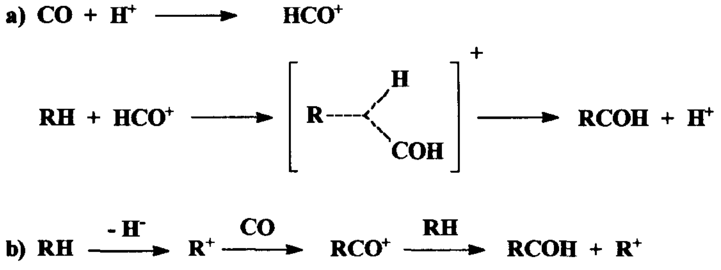
**Scheme 1**

$$RH + E^+ \xrightarrow{-H^-} RCO^+ \xrightarrow{R'OH} RCOOR'$$

In some cases, due to acylium intramolecular rearrangements, ketones can be obtained as major products.[2f] The second direction is the formylation reaction, proceeding via two different mechanisms. (Scheme 2a or 2b).

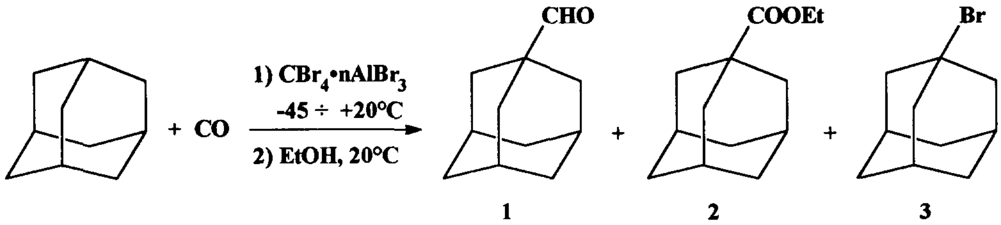
In contrast to the often observed Koch-Haaf reaction (Scheme 1), the second pathway (Scheme 2), involving insertion of the formyl cation into the hydrocarbon C-H bond (a)[3] or the two-stage process (b)[4] with intermolecular hydride ion abstraction from a parent hydrocarbon by the acylium cation, has been reported for adamantane only. However, all previous efforts to obtain the formylation product of adamantane (AdH) from AdCO+ or its various precursors in a proton superacid media,[3,4] or in the presence of $AlCl_3$,[5] under CO pressure (up to 80 atm for 4-10 h) were not effective. The yields of (1) amount to 0.2-21%.

Scheme 2



Now we report an effective formylation of AdH by aprotic organic superacid $CBr_4 \bullet 2AlBr_3$ in $CH_2Br_2$. The reactions of AdH were carried out under CO atmosphere at $-45 \div +20^0$C for 0.5-2 h. After work-up of the reaction mixture with alcohol the resulting products AdCHO (1), AdCOOEt (2) and AdBr (3) are formed with a ratio depending on the experimental conditions. (Scheme 3.)

Scheme 3

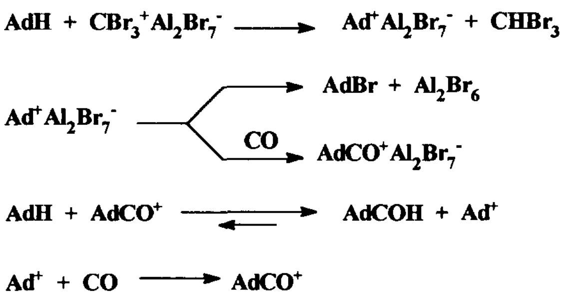


In a typical experiment, a mixture of anhydrous $AlBr_3$ (2 mmol) and $CBr_4$ (1 mmol) in 0.5 ml of $CH_2Br_2$ was stirred for 5-10 min. The flask with the homogeneous reaction mixture was cooled by liquid $N_2$, then AdH and methylcyclopentane were added. After cooling, the reaction flask was evacuated and connected with CO under atmospheric pressure, and stirred at a fixed temperature. Then the reaction mixture was worked-up with EtOH, the standard (undecan-2-on) was added, the mixture was poured into cold water, washed, extracted with ether and analyzed by GC and GC-MS.

Selected spectral data: MS, m/z (relative intensity) for 1: 164 ($M^+$, 25), 137 (5), 135 (100), 107 (24), 91 (33), 79 (45), 67 (39), 65 (21), ; for 2: 208 ($M^+$, 28), 180 (13), 163 (3), 136 (44), 135 (100), 107 (18), 93 (45), 91 (17), 79 (54), 67 (24).

It is important to note that under certain conditions (1) is a major reaction product. The sequence of reaction steps resulting in the formation of the observed products is outlined below (Scheme 4).

Scheme 4



The overall formylation reaction:

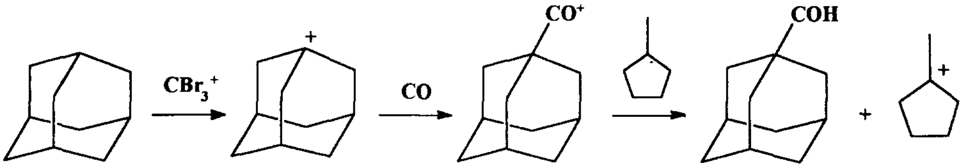
$$2AdH + 2CO + CBr_3^+Al_2Br_7^- \longrightarrow AdCHO + AdCO^+Al_2Br_7^- + CHBr_3$$

According to Scheme 4, the cation $CBr_3^+$ abstracts adamantane hydride ion to form $CHBr_3$ and $Ad^+$. The adamantyl cation adds either $Br^-$ to form (3), or carbon monoxide to give the 1-adamantanoyl cation, which then abstracts hydride ion from the second molecule of AdH to give (1) and a new adamantyl cation. In agreement with Scheme 4, the complete reduction of $CBr_4$ into $CHBr_3$ occurs in the course of the reaction. The functionalization of AdH by $CBr_4{\bullet}2AlBr_3$ effectively proceeds even at -45°C, with the overall yield of (1) +(2)+(3) being 73% (on the superacid) for 1 h. At -23°C the total yield (1)+(2)+(3) reaches 111%. At low temperature the addition of $Ad^+$ cation to $Br^-$ proceeds more rapidly than to CO molecule.

For instance, for 1 h the ratio [3]/[1]+[2] = 1.7; 1.4 at -45°C; and -23°C; respectively. At 0°C the reaction of $Ad^+$ with CO becomes dominant and the selectivity of formylation increases by one and even two orders, when the temperature is raised from -45°C to -23°C, and from -45°C to 0°C, respectively. At 0°C the yield of (1) reaches about 50% (on AdH and 183% on the superacid), and the selectivity of formylation increases up to 80%. We have shown that the yield of (1) could be increased up to 72% on AdH when the reaction is carried out in the presence of methylcyclopentane as an alternative donor of hydride ion for $AdCO^+$. In this case only a small amount of (2) and other by-products are formed after the usual alcohol work-up of the reaction mixture. So, the formation of (1) proceeds not only by Scheme 4, but probably also with the participation of methylcyclopentane (by Scheme 5).

This result can be interpreted as follows: although, the reaction of adamantane formylation is an exothermic one (equation 1), the step of hydride ion abstraction from AdH by $AdCO^+$ proceeds with consumption of 15.7 kcal/mol (equation 2). The calculations of the energies (in kcal/mol) for reactions 1-5 were carried out using the AM1 method and the reported data.[6] These calculations show that methylcyclopentane is the best donor of hydride ion among the hydrocarbons considered.

**Scheme 5**



[AdH] : [ $CBr_4$•$2AlBr_3$] : [cyclo$C_5H_9CH_3$] = 1 : 1 : 2; 20°C; 1 h; yield 72%

Equations 1 - 5

(1) AdH + CO $\longrightarrow$ AdCHO

-43.2 -5.7 -69.6 $\Delta H_f = -20.7$

$AdCO^+$ + RH $\longrightarrow$ AdCHO + $R^+$

(2) R=Ad $\Delta H_f = 15.7$

(3) R=cyclo-$C_6H_{11}$ $\Delta H_f = 17.0$

(4) R=i-Bu $\Delta H_f = 8.2$

(5) R=1-Me-cyclo-$C_5H_8$ $\Delta H_f = 5.5$

It is to be stressed that in the course of the reactions esters of cyclohexanecarboxylic acid and 1-methylcyclopentanecarboxylic acid are formed in very small amounts only. The main products of methylcyclopentane transformations are isomeric dimethyldecalenes. Thus, methylcyclopentane is a poor competitor for CO in comparison with adamantane.

In summary, we have observed the first example of an effective and selective formylation of the saturated hydrocarbon by CO under mild conditions.

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