Functionalization of saturated hydrocarbons by aprotic superacids

6.* Effective regioselective monoformylation of adamantane in the presence of a hydride ion donor

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The inefficient formylation of adamantane by CO initiated by superacid systems based on polyhalomethanes and aluminum halides becomes selective in the presence of methylcyclopentane and affords 1-adamantanecarbaldehyde in an almost quantitative yield under mild conditions.

Key words: functionalization of saturated hydrocarbons, formylation, adamantane, carbon monoxide, complexes of polyhalomethanes and aluminum halides, aprotic superacids, hydride ion donors, mass spectra.

The reactions of alkanes and cycloalkanes with carbon monoxide in the presence of protic[2—9] and aprotic[1,10,11] superacids follow two main pathways. One of them involves generation of a carbocation from alkane under the action of an electrophile, and addition of this cation to a CO molecule to give an acylium cation, according to the known Koch—Haaf reaction pattern.[12] Treatment of the reaction mixture containing an acylium salt with water or alcohol yields the corresponding acid or ester:

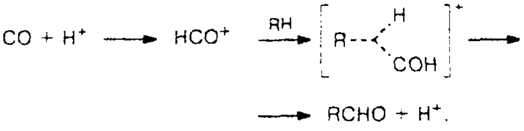
$$\mathrm{RH + E^+ \xrightarrow[-H^-]{} R^+ \xrightarrow{CO} RCO^+ \xrightarrow{R'OH} RCOOR'}. \quad (1)$$

In some cases, the acylium cation formed initially undergoes an intramolecular rearrangement to give ketones as the major products.[11]

The second route of the reactions of hydrocarbons with CO is formylation:

$$\mathrm{RH + CO \longrightarrow RCHO}. \quad (2)$$

This reaction can proceed by two alternative mechanisms. One of them can be described by the following reactions:



$$\mathrm{CO + H^+ \longrightarrow HCO^+ \xrightarrow{RH} \left[R{-}{-}\langle^{H}_{COH}\right]^+ \longrightarrow RCHO + H^+}. \quad (3a)$$

The second mechanism (3b) is a three-step process, in which the initially formed acylium cation abstracts a hydride ion from the alkane to give aldehyde and a new carbocation. The latter process is the rate-determining step of the reactions of saturated hydrocarbons with aprotic organic superacids $RCO^+Al_2X_7^-$.[13]

$$\mathrm{RH \xrightarrow{-H^-} R^+ \xrightarrow{CO} RCO^+ \xrightarrow{R'H} RCHO + R'^+}. \quad (3b)$$

Both formylation pathways have been confirmed previously.[7,8] However, unlike the carbonylation of alkanes and cycloalkanes according to reaction (1) which is encountered fairly frequently, formylation by reaction (2) has been described for only one saturated hydrocarbon, *viz.*, adamantane. Moreover, the formylation of adamantane in the presence of various protic superacids (with and without a solvent) or $AlCl_3$ (in CH_2Cl_2, P_{CO} = 80 atm, 0—30 °C, 4—20 h) gave 1-adamantanecarbaldehyde (1-AdCHO (**1**)) in a low yield (0.2—21%).[7—8] The reaction of adamantane with CO yielded mostly (60—75%) 1-adamantanecarboxylic acid resulting from the Koch—Haaf reaction and also a minor amount (2—7%) of 1-adamantanol.[7] Japanese authors, who have studied in detail the reactions of 1-AdOTf and other sources of the adamantyl cation (1-Ad^+) with CO and AdH catalyzed by trifluoromethanesulfonic acid (TfOH) at 30 °C in CCl_4, detected no compound **1** at all among the reaction products. Instead, after treatment of the reaction mixture with water, they isolated the homoadamantanol derivative (A)[9] as the major product in a yield of up to 70%.

When aldehyde **1** was used as the starting compound, it was completely converted into compound A and other products, which allowed the authors to conclude that this aldehyde is unstable under the conditions studied.[9]

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[*] For Part 5, see Ref. 1.

[†] Deceased.

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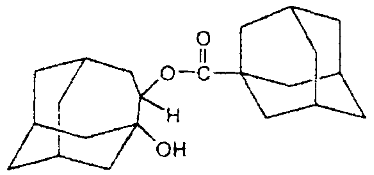
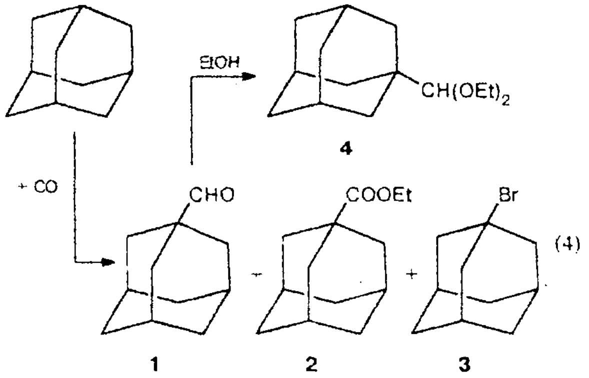


A

Results and Discussion

In this work, we report on efficient and selective formylation of adamantane under mild conditions (see Ref. 14). The reaction was carried out in CH_2Br_2 and in an atmosphere of CO for 0.5—2 h at −45—+20 °C. As catalysts we used aprotic superacid systems: $CBr_4 \cdot nAlX_3$, $CH_2Br_2 \cdot nAlX_3$ (n = 1, 2; X = Cl, Br),[15] $Br_2 \cdot 2AlBr_3$,[16] and $SOCl_2 \cdot 2AlBr_3$.[17] Treatment of the reaction mixture with ethanol afforded products **1**—**3**, whose ratio depended on the experimental conditions. In some cases, treatment of the reaction mixture with ethanol gave acetal **4** in addition to aldehyde **1**.



It follows from Table 1 that functionalization of adamantane through the action of $CBr_4 \cdot 2AlBr_3$ occurs even at −45 °C. However, only traces of AdCHO (**1**) are formed under these conditions. The major reaction products at −45 °C are AdCOOEt (**2**) and AdBr (**3**), which are formed in 72% overall yield based on the catalyst; the yield of bromide **3** is markedly larger than that of ester **2**. This indicates that at low temperatures, the reaction of adamantyl cation with the Br^- anion occurs more readily than that with CO. As the temperature is raised to −23 °C, the yield of compound **1** increases by an order of magnitude but still remains low. In this case, compounds **2** and **3** are still the major products of the transformation of adamantane. Their overall yield amounts to 68%, and the bromide predominates (Table 1, entry 3).

Table 1. Formylation of adamantane by CO in the presence of $CBr_4 \cdot nAlBr_3$ and $CH_2Br_2 \cdot nAlX_3$ (the time of the reaction was 1 h)

Entry	Catalyst (Cat)	[AdH] : [Cat]	T/°C	Composition of products (mol. %) based on AdH		
				1[a]	**2**	**3**
1	$CBr_4 \cdot 2AlBr_3$	4 : 1	−45	traces	6	12
2	$CBr_4 \cdot 2AlBr_3$	4 : 1	−23	2	10	16
3	$CBr_4 \cdot 2AlBr_3$	1 : 1	−23	1	28	40
4	$CBr_4 \cdot 2AlBr_3$	1 : 1	0	8	33	30
5	$CBr_4 \cdot 2AlBr_3$	4 : 1	0	45	2	6
6	$CBr_4 \cdot 2AlBr_3$	1 : 1	20	30	22, 10[b]	28
7	$CBr_4 \cdot AlBr_3$	2 : 1	0	32	3	3
8	$CBr_4 \cdot AlBr_3$	2 : 1	0	26[c]	1[c]	3[c]
9	$CH_2Br_2 \cdot 2AlBr_3$	1 : 1	20	57	0	0
10	$CH_2Br_2 \cdot 2AlCl_3$	1 : 1	20	36[c,d]	0	0

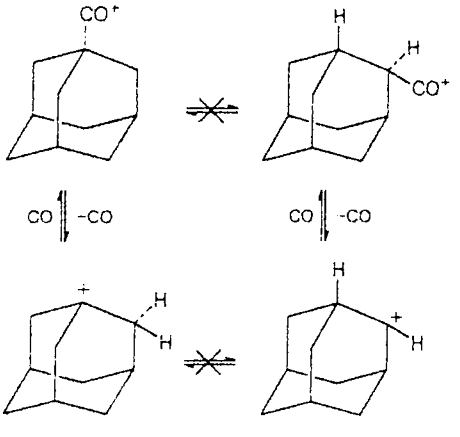
[a] In those cases where $AdCH(OEt)_2$ was formed along with AdCHO, the yield based on AdCHO is given. [b] 2-AdCOOEt; in the rest of cases, 1-Ad derivatives were formed. [c] The yield after 2 h. [d] 24% $AdCH_2OH$ (**5**) was also obtained.

The results indicate that an excess of AdH has a substantial effect on the selectivity of the formation of aldehyde **1**. At 0 °C, the ratio of compounds **1**, **2**, and **3** markedly changes, and if excess of adamantane is present (Table 1, entries 5, 7, and 8), aldehyde **1** is the main reaction product and the proportions of compounds **2** and **3** in the reaction mixture are very low. It is noteworthy that the highest yield of aldehyde **1** based on the catalyst can reach 180% (Table 1, entry 5). At 0 °C and an equimolar AdH : $CBr_4 \cdot 2AlBr_3$ ratio, the yield of product **1** is as low as 8% (Table 1, entry 4), although adamantane is consumed completely. The reaction is even less selective: after treatment of the reaction mixture with ethanol, in addition to compounds **2** and **3** (overall yield 63%), noticeable amounts of some other products were detected. Judging from mass spectra, these products can be identified as disubstituted adamantyl derivatives (probably, brominated derivatives) containing COOEt (m/z 207, 134, 44) and $CH(OEt)_2$ (m/z 237, 163, 103) groups.

At 20 °C, the yield of aldehyde **1** in the presence of $CBr_4 \cdot 2AlBr_3$ is almost 4 times higher than that at 0 °C (Table 1, entries 4 and 6). It is of interest that under these conditions, together with ester **2**, a considerable amount of its isomer, 2-AdCOOEt, is formed; the 1-AdCOOEt : 2-AdCOOEt ratio is 2 : 1. According to a previous study,[18] the 1,2-shift in the tertiary $AdCO^+$ and Ad^+ is forbidden for orbital symmetry reasons (Scheme 1).

Therefore, it can be assumed that the secondary $AdCO^+$ cation results from the addition of a CO molecule to the secondary adamantyl cation (see Scheme 1). Unlike $1\text{-}AdCO^+$, which is stable with respect to decarbonylation,[18] the $2\text{-}AdCO^+$ cation easily loses CO. For example, the reaction of $2\text{-}AdCO^+$ with $i\text{-}Pr^+$ in the SbF_5—SO_2ClF system at 0 °C yields $i\text{-}PrCO^+$.[18] In view of the fact that $2\text{-}AdCO^+$ is susceptible to decarbonylation, it seems surprising that at 20 °C, it is accumulated in significant quantities (Table 1, entry 6).

Scheme 1

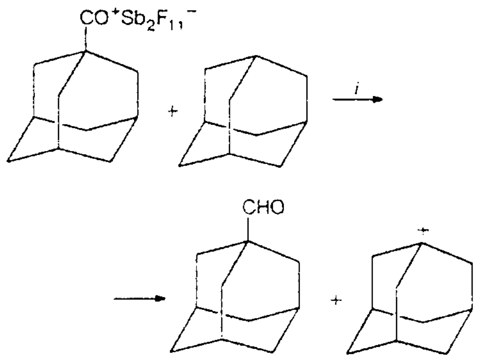


The $CH_2Br_2 \cdot 2AlBr_3$ complex proved to be fairly active in the formylation of 20 °C. The yield of aldehyde **1** was 57% and compounds **2** and **3** were totally absent (Table 1, entry 9). It should be noted that small amounts of products of more extensive reduction of $AdCO^+$, *viz.*, alcohol **5** or bromide **6**, were also formed at 20 °C.

$$\mathrm{AdCHO} \xrightarrow{+\mathrm{H}^-} \mathrm{AdCH_2O^-} \xrightarrow{+\mathrm{H}^+} \underset{\mathbf{5}}{\mathrm{AdCH_2OH}} \xrightarrow{\mathrm{HBr}} \underset{\mathbf{6}}{\mathrm{AdCH_2Br}}. \qquad (5)$$

When the $CH_2Br_2 \cdot 2AlCl_3$ complex was used as the catalyst, compounds **1** and **5** were formed in comparable amounts over a period of 2 h (Table 1, entry 10). Note that at 20 °C, the overall yield of products **1**—**6** after 1 h was 90% in the experiment with $CBr_4 \cdot 2AlBr_3$ and 60% in the experiment with $CH_2Br_2 \cdot 2AlCl_3$ (Table 1, entries 6 and 10, respectively).

Let us compare the results obtained with published data concerning the reaction of $1\text{-}AdCO^+$ (prepared from 1-AdCOCl and SbF_5) with adamantane acting as a source of a hydride ion.[7] At 0 °C, the yield of compound **1** was 0.2—1.1% based on the starting acylium salt:



1 (6)

i. 0 °C, Freon-113, 4—6 h.

It is obvious that when polyhalomethanes combined with aluminum halides are used as initiators, reaction (2) occurs more efficiently, and aldehyde **1** can be obtained in a yield of up to 45% based on adamantane (Table 1, entry 5). It should be noted that in order to carry out formylation (as well as other functionalization reactions) of adamantane,[19] which is readily converted into the corresponding cation, there is no need to use superacids. This reaction can be accomplished with high selectivity using weaker electrophiles such as $CH_2Br_2 \cdot nAlX_3$.[15] In the presence of $CBr_4 \cdot nAlBr_3$ superacids, adamantane is removed too quickly from the reaction area. At the same time, softer electrophiles ($CH_2Br_2 \cdot nAlX_3$) that ensure relatively slow generation of Ad^+ from AdH create more favorable conditions for the reaction of $AdCO^+$ with AdH.

The formation of products **1**—**3** can be described by Scheme 2. According to this Scheme, an electrophile generates the cation from adamantane and is thus transformed into the reduced state. The adamantyl cation, which is nonplanar and less stable than tertiary aliphatic carbenium ions, is fairly reactive; it adds the X^- anion (this process occurs most easily) to give halide **3**, and this step is reversible. By adding CO, the Ad^+ cation is irreversibly converted into $AdCO^+$. The subsequent reaction of $AdCO^+$ with AdH affords aldehyde and an Ad^+ cation. In terms of this Scheme, the maximum yield of aldehyde **1** is 50% based on the initial AdH (even when no bromoadamantane **3** is formed).

Scheme 2

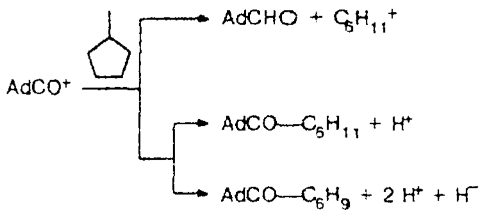
$$\begin{aligned}
\mathrm{AdH} + \mathrm{E}^+ &\xrightarrow{\mathrm{AlX_3}} \mathrm{Ad}^+ + \mathrm{EH} \\
\mathrm{Ad}^+ &\xrightarrow{\mathrm{CO}} \mathrm{AdCO}^+ \\
\mathrm{AdH} + \mathrm{AdCO}^+ &\longrightarrow \mathrm{AdCHO} + \mathrm{Ad}^+ \\
\hline
2\mathrm{AdH} + \mathrm{E}^+ + \mathrm{CO} &\longrightarrow \mathrm{AdCHO} + \mathrm{Ad}^+ + \mathrm{EH}
\end{aligned}$$

Since the Ad^+ cation can again add CO and the $AdCO^+$ cation can add a hydride ion, chain formylation according to reaction (2) initiated by the superacid is, in principle, possible. However, the data obtained indicate that this process virtually does not occur. Apparently, this is due to the fact that at [AdH] = [E], the formation of $AdCO^+$ is a fast reaction, while the abstraction of a hydride ion from AdH through the action of $AdCO^+$ occurs slowly, *i.e.*, the system is deficient in hydride ions. On the other hand, at [AdH] > [E], the fact that the accumulation of compound **1** capable of being coordinated to the superacid "decelerates" the reaction becomes more significant.

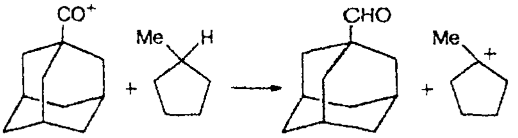
We showed that in the presence of methylcyclopentane (acting as the alternative donor of the hydride ion), adamantane can be converted almost quantitatively into aldehyde **1** (Table 2). In the presence of the

$CBr_4 \cdot 2AlBr_3$ system (Table 2, entry 2), aldehyde **1** is formed in 70% yield and with a selectivity of 81% over a period of 1 h even at 0 °C. When the reaction is carried out in the presence of the same system at 20 °C, the yield of compound **1** amounts to 95% after 0.5 h (Table 2, entry 4). In this case, adamantane is converted completely. In the reaction with $CH_2Br_2 \cdot 2AlBr_3$ under the same conditions, 60% of the adamantane remains unreacted, the yield of compound **1** is 16%, and the overall yield of products **5** and **6** resulting from the further reduction of the aldehyde is 21% (Table 2, entry 8). At 20 °C and in the presence of the $CH_2Br_2 \cdot 2AlBr_3$ system, aldehyde **1** can be obtained in a nearly quantitative yield over a period of 1 h (Table 2, entry 9). It is noteworthy that the use $CH_2Br_2 \cdot 2AlCl_3$ under the same conditions makes it possible to synthesize product **1** in 87% yield (Table 2, entry 10). When the duration of the reaction is increased to 2 h, this compound is formed in a quantitative yield (Table 2, entry 11). When the quantity of the catalyst with respect to adamantane is halved, the yield of product **1** decreases (Table 2, entries 12 and 13): the maximum yield of aldehyde **1** based on the catalyst does not exceed 160%. Other superacid systems ($Br_2 \cdot 2AlBr_3$ and $SOCl_2 \cdot 2AlBr_3$) showed no advantages over aluminum halides. However, it should be noted that, as in the case of the initiation of cracking of alkanes,[16] the $Br_2 \cdot 2AlBr_3$ superacid system behaves as an initiator of formylation rather than as a brominating system: no bromides are obtained in the reaction. It is of interest that in this case, together with the usual products, substantial amounts of the isomers $AdCOC_6H_9$ and $AdCOC_6H_{11}$ are produced. These compounds have also been formed in low yields in the other reactions of adamantane with CO in the presence of methylcyclopentane. Apparently, these ketones result from an alternative pathway of the reaction of $AdCO^+$ with cycloalkane:

Scheme 3



Thus, methylcyclopentane changes dramatically the route of the reaction of adamantane with CO, *viz.*, a nonselective and relatively ineffective reaction is transformed into quantitative and regioselective monoformylation of adamantane. It can be assumed that in the presence of methylcyclopentane, an alternative process involving methylcyclopentane occurs in parallel with the reaction shown in Scheme 2:



(7)

It should be noted that esters of cyclohexanecarboxylic and methylcyclopentanecarboxylic acid as well as other products derived from methylcyclopentane, *viz.*, isomeric dimethyldecalines, are formed in only minor amounts. Thus, the methylcyclopentyl cation, unlike

Table 2. Formylation of adamantane by CO in the presence of methylcyclopentane in CH_2Br_2[a]

Entry	Catalyst (Cat)	[AdH] : [Cat] : [MeC_5H_9]	τ/h	Yield of products (mol.%) (based on AdH) AdCHO (**1**)	AdCOOEt (**2**)	AdBr (**3**)	$AdCH_2OH$ (**5**)
1	$CBr_4 \cdot 2AlBr_3$	1 : 1 : 2	0.5	58	16	17	0
2	$CBr_4 \cdot 2AlBr_3$	1 : 1 : 4	1	70	3	16	0
3	$CBr_4 \cdot 2AlBr_3$	1 : 1 : 4	0.5	53	6	3	0
4	$CBr_4 \cdot 2AlBr_3$	1 : 1 : 2	0.5	95	0	0	0
5	$CBr_4 \cdot AlBr_3$	1 : 1 : 2	1	62	0	0	14 (5)[b]
6	$Br_2 \cdot 2AlBr_3$	1 : 1 : 2	1	52	0	0	0
7	$SOCl_2 \cdot 2AlBr_3$	1 : 1 : 2	1	36	0	0	0
8	$CH_2Br_2 \cdot 2AlBr_3$	1 : 1 : 2	0.5	16	0	3	9 (12)[b]
9	$CH_2Br_2 \cdot 2AlBr_3$	1 : 1 : 2	1	97	0	0	11
10	$CH_2Br_2 \cdot 2AlCl_3$	1 : 1 : 2	1	87	0	0	7
11	$CH_2Br_2 \cdot 2AlCl_3$	1 : 1 : 2	2	100	0	0	5
12	$CH_2Br_2 \cdot 2AlCl_3$	2 : 1 : 4	3	81	0	0	4
13	$CH_2Br_2 \cdot AlCl_3$	2 : 1 : 4	5	49	0	0	3

[a] In entries 1—9, $[AlBr_3]$ = 4 mmol mL^{-1} of CH_2Br_2; in entries 10—13, $[AlCl_3]$ = 2 mmol mL^{-1} of CH_2Br_2. *T*/°C: 0 (entries 1 and 2) and 20 (entries 3—13). [b] The yields of $AdCH_2Br$ (**6**) are given in parentheses.

Ad$^+$, does not form any stable products with CO under the reaction conditions.

The enthalpies of the reactions (in kcal mol^{-1}) given below, which we have calculated using the data reported previously[20] (the AM1 method), imply that the overall reaction of formylation of adamantane is exothermal.

$$\underset{-43.2}{\mathrm{AdH}} + \underset{-5.7}{\mathrm{CO}} \longrightarrow \underset{-69.6}{\mathrm{AdCHO}} \qquad (\Delta H_f = -20.7 \text{ kcal mol}^{-1})$$

The transfer of a hydride ion from the saturated hydrocarbon to AdCO$^+$ is accompanied by the absorption of heat.

$$\mathrm{AdCO^+ + RH \longrightarrow AdCHO + R^+}$$

R	Ad	*cyclo*-C_6H_{11}	*i*-C_4H_9	*cyclo*-C_5H_8Me
ΔH_f	15.7	17.0	8.2	5.5

It can be seen from the enthalpies presented that the transfer of a hydride ion to AdCO$^+$ from methylcyclopentane is 10.2 kcal mol^{-1} more favorable than that from adamantane and that methylcyclopentane is the best hydride-ion donor among the above-mentioned compounds.

Thus, the inefficient reaction of adamantane with CO initiated by systems based on polyhalomethanes and aluminum halides changes dramatically its route in the presence of a hydride ion donor and yields 1-adamantanecarbaldehyde in a virtually quantitative yield.

Experimental

The reaction mixtures were analyzed by GLC on a Finnigan 9001 chromatograph with a flame ionization detector (using a 30 m×0.3 mm quartz capillary column filled with DB-5.625 and helium as the carrier gas) under conditions of linear temperature programming: 100→280 °C (8 °C min^{-1}).

Mass spectra were recorded on a AEI MS 1073 GC/MS spectrometer at an ionization energy of 70 eV using a similar capillary chromatographic column.

General procedure for the formylation of adamantane. a. A catalyst and the solvent (CH_2Br_2, 0.25 mL per mmol of AlX_3) were placed in a round-bottom flask and stirred with a magnetic stirrer for 5—10 min. The flask with the homogeneous reaction mixture was cooled with liquid nitrogen, then the calculated quantity of adamantane was added in one portion. The flask was again cooled, evacuated, and connected to a CO line under atmospheric pressure. The mixture was stirred at a specified temperature. After a certain time, the supply of CO was discontinued, and the reaction mixture was treated with ethanol (and water) with cooling and stirring. The standard was added, and the mixture was poured into ice water and extracted with ether. The organic layer was washed with a solution of $NaHCO_3$ and water and dried with Na_2SO_4. The results of the experiments are presented in Table 1.

b. The experiments were carried out by a procedure similar to that described in **a** except that methylcyclopentane was added together with adamantane. The results are listed in Table 2.

MS, *m/z* (I_{rel} (%)): AdCHO (**1**), 164 [M$^+$] (25), 137 (100), 107 (24), 91 (33), 79 (45), 67 (39), 65 (21); 1-AdCOOEt (**2**), 208 (M$^+$, 28), 180 (13), 163 (3), 136 (44), 135 (100), 107 (18), 93 (45), 91 (17), 79 (54), 67 (24); 2-AdCOOEt (**2´**), 208 [M$^+$] (40), 180 (4), 162 (57), 134 (100), 119 (10), 92 (34), 79 (47), 67 (37), 52 (12); AdCH(OEt)$_2$ (**4**), 193 (11), 165 (5), 135 (43), 103 (100), 93 (15), 79 (23), 75 (62), 54 (10), 47 (64); AdCH$_2$OH (**5**), 166 [M$^+$] (3), 135 (100), 107 (5), 93 (16), 79 (22), 67 (10); AdCH$_2$Br (**6**), 228 [M$^+$] (1), 149 (3), 135 (100), 107 (4), 93 (13), 79 (15), 67 (5).

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