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Metal complex catalysis in the chemistry of lower diamondoids

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The review presents the first survey of published data on the use of compounds, complexes and nanoparticles of transition metals (Fe, Co, Ni, Mn, V, Mo, Cu, Pd, Pt, Rh, Ru, Os, Au, Re and Th) in the catalytic transformations of lower diamondoids — adamantane, diamantane and their derivatives. Catalytic halogenation, oxidation, alkylation and cross-coupling reactions are considered, and the formation pathways of C–N, C–S and C–Se bonds in the series of adamantanoids are discussed. Reaction conditions, appropriate catalytic systems and the structures of products are presented.
The bibliography includes 242 references.

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1. Introduction

Adamantane and its derivatives, including higher adamantanoids (diamondoids), represent a special class of cage compounds — diamond-like hydrocarbons, which are widely used in medicine and technology.

The simple and efficient method for the synthesis of the unique hydrocarbon, adamantane (**1**), from the petrochemical monomer, dicyclopentadiene, developed by Schleyer in 1954, stimulated active studies of the chemical reactivity of adamantane and its derivatives. As a result, efficient pharmaceutical agents such as amantadine, memantine, rimantadine, tromantadine, vildagliptin, *etc*., were developed on the basis of compound **1** and its functional derivatives. Furthermore, adamantanes are active against HIV and Ebola virus. Adamantane (**1**) and its derivatives were also used to prepare diamond-like films and sensors for electronic displays.

Chemical transformations of adamantanoids using classical organic synthesis methods were studied in sufficient detail.[1–7] The specific structural features of adamantane, diamantane and higher adamantanoids possessing numerous reactive sites with similar reactivities bring about several problems. First, reactions of these compounds are non-selective and give mixtures of isomers. Monosubstitution of adamantane often results in mixtures of 1- and 2-substituted derivatives, while in the case of diamantane, 1-, 2- and 4-substituted derivatives are formed. Second, the number of isomers can be even higher, as di-, tri- and polysubstitution processes are possible. The number of isomeric products also increases in the case of functionalization of adamantanoids containing substituents of different nature in the molecule. Third, a challenge of the preparative chemistry of adamantanoids is the necessity to ensure complete conversion, as adamantane, diamantane and all of their derivatives are high-melting crystalline solids that are easily sublimed, and their isolation in a pure state is difficult.

The situation has markedly changed when catalytic methods started to be used for functionalization of ada-

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mantanoids, especially with the application of metal complex (MC) catalysts, which allow selective functionalization of these compounds with both electrophilic and nucleophilic reagents. In this regard, it is appropriate to note that during the last 5–10 years, original conjugate reactions have been developed and efficient reagents have been found for selective functionalization of adamantanoids and for their synthesis using metal complex catalysts.

Here we analyzed and systematized the published data on the use of metal complexes as catalysts in the adamantanoid chemistry scattered in the literature all over the world. The reactions described for adamantane, diamantane and their derivatives include catalytic halogenation, oxidation, alkylation and cross-coupling as well as reactions resulting in the formation of C–N, C–S and C–Se bonds.

The following abbreviations and designations are used in the review:

AAEMA — (acetoacetoxy)ethyl acrylate;
ABNO — 9-azabicyclo[3.3.1]nonane-*N*-oxyl;
acac — acetylacetonate;
Ad — 1-adamantyl;
ASMNP — silica coated magnetic nanoparticles;
Bpy — 2,2′-bipyridine;
BTA — benzene-1,3,5-tricaboxylic acid;
CAN — cerium(IV) ammonium nitrate;
Cat — catalyst;
β-CD — β-cyclodextrin;
Cp — cyclopentadienyl;
m-CPBA — *m*-chloroperbenzoic acid;
cyclam — 1,4,8,11-tetraazacyclotetradecane;
DCBPY — 2,2′-bipyridine-4,4′-dicarboxylic acid;
DCE — 1,2-dichloroethane;
DCP — dicumyl peroxide;
$DFSNH_2$ — 2,6-difluorobenzenesulfonamide;
DME — 1,2-dimethoxyethane;
DOSP — (*N*-dodecylbenzenesulfonyl)prolinate;
dppBz — 1,2-bis(diphenylphosphino)benzene;
ee — enantiomeric excess;
esp — α,α,α′,α′-tetramethylphenyl-1,3-dipropionate;
HSA — 8-hydroxyquinoline-2-sulfonic acid;
ICy — 1,3-di(cyclohexyl)imidazol-2-ylidene;
LED — light-emitting diode;
MC — metal complex catalyst;
mmm — micro-, meso- and macroporous (zeolite);
Ms — methanesulfonyl (mesyl);
MS — molecular sieves;
MSTFA — *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide;
NHC — N-heterocyclic carbene;
NFSI — *N*-fluorobis(benzenesulfonyl)imide;
NHPI — *N*-hydroxyphthalimide;
Nor-AZADO — 9-azanoradamantane-*N*-oxyl;
NP — nanoparticles;
Ns — 4-nitrobenzenesulfonyl (nosyl);
Phen — 1,10-phenanthroline;
PFBA — 2,3,4,5,6-pentafluorobenzoic acid;
PicOH — picolinic acid;
PMO — periodic mesoporous organosilicate;
QOH — 8-hydroxyquinoline;
Salen — *N*,*N*′-bis(salicylidene)ethylenediamine;
SBA — a mesoporous material;
Selectfluor — 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate);
SMNP — starch coated magnetic nanoparticles;
SNP — silica nanoparticles;
TBAB — tetra-n-butylammonium bromide;
TBAF — tetra-n-butylammonium fluoride;
TDCPP — *meso*-tetrakis(2,6-dichlorophenyl)porphyrin;
TEMPO — (2,2,6,6-tetramethylpiperidin-1-yl)oxyl;
TFA — trifluoroacetate;
TfO — trifluoromethanesulfonate (triflate);
THA — thymine-1-acetate;
TMDS — 1,1,3,3-tetramethyldisiloxane;
TMG_3trphen — tris[(tetramethylguanidino)phenyl]-amine;
tmp — *meso*-tetra(mesityl)porphyrin;
TMPhen — 3,4,7,8-tetramethyl-1,10-phenanthroline;
TON — turnover number of a catalyst;
TPFPP — *meso*-tetrakis(pentafluorophenyl)porphyrin;
TPP — *meso*-tetraphenylporphyrin;
TPPh2 — hydrotris(3,5-diphenylpyrazol-1-yl)borate;
TPT — 1,3,5-tris(4-pyridyl)triazine;
Troc — 2,2,2-trichloroethoxycarbonyl;
Ts — *p*-toluenesulfonyl (tosyl);
TsCN — *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide.

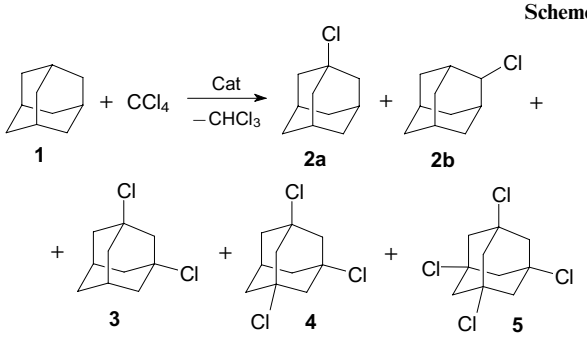
2. Halogenation of adamantanes

Halogen derivatives of the first two representatives of the diamondoid homologous series — adamantane and diamantane — are the key precursors for the synthesis of most of their functional derivatives.

The classical synthetic route to chloro- and bromoadamantanes, that is, chlorination and bromination on treatment with gaseous chlorine or liquid bromine with radical initiation, is very complicated when used for preparative purposes, since the reactions are accompanied by evolution of HCl or HBr in equimolar amounts and afford mixtures of isomers. The use of metal complexes as catalysts in the adamantanoid chemistry resulted in preparatively convenient and selective routes to halogen derivatives in which the source of the halogen atom can be represented by CCl_4, $CHCl_3$, CH_2Cl_2, 1,2-dichloroethane (DCE), Me_3SiCl, chloroisocyanuric acid, CH_2Br_2, CBr_4, Me_3SiBr, Bu^tOCl, NaOCl, *etc*.

In some studies, carbon tetrachloride was used as the source of chlorine. In the presence of compounds of iron,[8–11] titanium,[8] manganese,[12–15] molybdenum,[16] vanadium,[16] palladium,[17] platinum[17,18] and silver,[19] CCl_4 chlorinates compound **1** into the bridgehead position; this gives mono- (**2a**,**b**), di- (**3**), tri- (**4**) and tetrachloro (**5**) derivatives (Scheme 1, Table 1).

Scheme 1



Cat is catalyst

Table 1. Chlorination of adamantane with CCl_4 catalyzed by metal complexes (see Scheme 1).

No.	Catalyst	T/°C	Time /h	Yield (%)					Ref.
				2a	**2b**	**3**	**4**	**5**	
1	$FeCl_3 \cdot 6H_2O$/K-10 montmorillonite	40	2	59	–	–	–	–	8
2	$FeCl_3 \cdot 6H_2O$/K-10 montmorillonite	40	5	–	–	98	–	–	8
3	$TiCl_4$	135	15	–	100	–	–	–	8
4	$Fe(acac)_3$ – MeOH	160	6	–	–	98	–	–	9, 10
5	$Fe(acac)_3$ – EtOH	170	6	93	–	–	–	–	11
6	$Mn(acac)_3$ – MeCN	200	1	92	–	–	–	–	12–15
7	$Mn(acac)_3$ – MeCN	200	3	–	–	86	10	–	12–15
8	$Mn(acac)_3$ – MeCN	200	5	–	–	10	20	70	12–15
9	$Mo(CO)_6 - H_2O$	170	8	48	–	–	–	–	16
10	$VO(acac)_2$	150	1	90	–	–	–	–	16
11	$PtCl_2(PPh_3)_2$	120	6	59	9	–	–	–	17
12	$PdBr_2(PPh_3)_2$ – MeCN	120	8	46	2	–	–	–	17
13	$Pt/Eu_2O_3/TiO_2/SiO_2$	40	0.17	59	30	–	–	–	18
14	AgOAc – AgBr	77	24	54	9	22	–	–	19

Note. acac is acetylacetonate; the dash means that the product was not isolated.

The formation of 2-chloroadamantane (**2b**) was noted only in the presence of two catalysts: $TiCl_4$ (Ref. 8) and $Pt/Eu_2O_3/TiO_2/SiO_2$.[18] The following catalytic systems proved to be the best for selective chlorination of adamantane to 1-chloroadamantane (**2a**) with CCl_4: $FeCl_3$ supported on montmorillonite;[8] $Mn(acac)_3$ activated with nitriles;[12–15] and $Fe(acac)_3$, $Mo(CO)_6$ or $VO(acac)_2$ promoted with alcohols (MeOH, EtOH) or water.[12–16] According to several publications,[12–16] the role of alcohols or water is to ensure the *in situ* formation of alkyl hypochlorites and hypochlorous acid *via* the reaction with CCl_4 in the presence of catalysts. It is known that ROCl and HOCl readily degrade to generate the RO$^\bullet$, HO$^\bullet$ and Cl$^\bullet$ radicals, which can initiate chlorination of adamantane (Scheme 2).

Scheme 2

$$CCl_4 + ROH \xrightarrow[-CHCl_3]{Cat} ROCl \longrightarrow RO^\bullet + Cl^\bullet$$

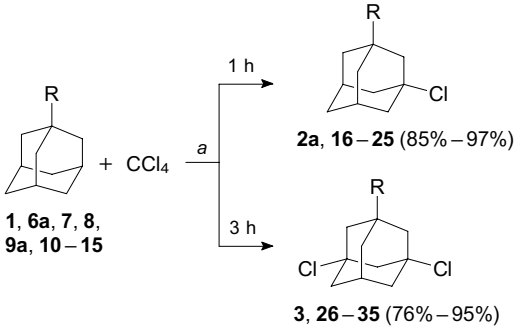
$$CCl_4 + H_2O \xrightarrow[-CHCl_3]{Cat} HOCl \longrightarrow HO^\bullet + Cl^\bullet$$

For most catalysts, except for the $FeCl_3$–monmorillonite system, chlorination of compound **1** with CCl_4 proceeds under drastic conditions (120–200 °C). Conversely, monmorillonite-supported $FeCl_3$ exhibits high activity at 40 °C, which makes it possible to selectively obtain 1-chloroadamantane (**2a**) as soon as in 2 h; longer heating (5 h) furnishes 1,3-dichloroadamantane (**3**) in high yield (98%).[8] Manganese compounds are efficient and versatile catalysts for chlorination of adamantane and its derivatives with CCl_4.

A significant benefit of the $Mn(acac)_3$–MeCN catalytic system is low sensitivity to the presence and to the nature of the substituent in the adamantane molecule; therefore, it can be successfully utilized for chlorination of adamantane derivatives **6a**, **7**, **8**, **9a**, **10**–**15** with various polar substituents (Scheme 3).[12] This gave monochlorides **16**–**25** and dichlorides **26**–**35**.

Adamantane derivative **36** containing a side-chain hydroxyl group shows an interesting behaviour towards

Scheme 3



1, **6a**, **7**, **8**, **9a**, **10**–**15**

2a, **16**–**25** (85%–97%)

3, **26**–**35** (76%–95%)

(*a*) $Mn(acac)_3$–MeCN, 200 °C; R = H (**1**, **2a**, **3**), Br (**6a**, **16**, **26**), OMe (**7**, **17**, **27**), Ac (**8**, **18**, **28**), CO_2H (**9a**, **19**, **29**), C(O)Cl (**10**, **20**, **30**), CO_2Me (**11**, **21**, **31**), CO_2Et (**12**, **22**, **32**), CN (**13**, **23**, **33**), NHCHO (**14**, **24**, **34**), NHAc (**15**, **25**, **35**)

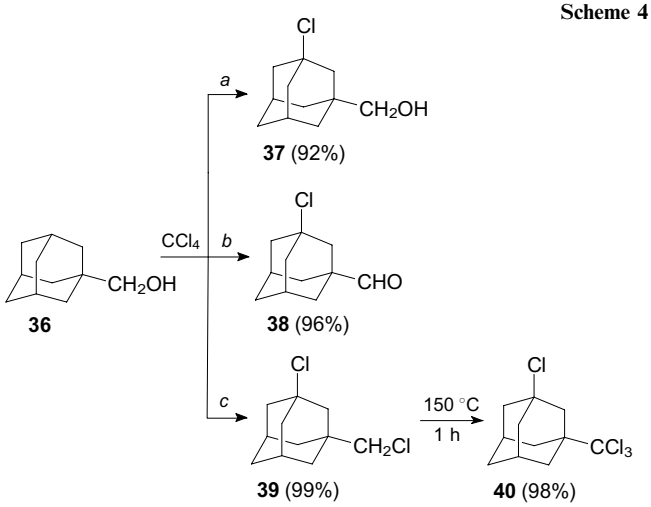
CCl_4 (Scheme 4).[12–16] Whereas in the presence of the $Mn(acac)_3$–MeCN catalytic system, chlorination into the cage takes place, with the hydroxyl group remaining intact (product **37**), in the presence of $VO(acac)_2$, chlorination into the cage and oxidation of the side chain take place simultaneously to give aldehyde **38**. The $Mo(CO)_6$ catalyst leads to chlorination products of the adamantane side chain and the bridgehead carbon atom — polychlorinated compounds **39** and **40**.

The chlorination of homologous alcohol **41** in the presence of $VO(acac)_2$ gives, first, ketone **8**, while longer heating results in the formation of chloride **18** (Scheme 5).

The use of CH_2Cl_2,[20,21] $CHCl_3$,[22] dichloroethane,[22–43] *N*-chloroisocyanuric acid[25] or NaOCl[26] as chlorinating agents is inappropriate because of low yields of 1-chloroadamantane (**2a**) (Table 2).

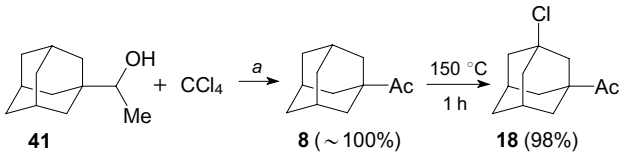
Adamantane chlorination with sodium hypochlorite occurs under very mild conditions. The reaction is catalyzed by the nickel bis(salicylidene)ethylenediamine complex [Ni(Salen)]; the yield of a mixture of products **2a** and **2b** amounts to 34%, the isomer ratio is 8.5 : 1 (Scheme 6).[26]

Scheme 4



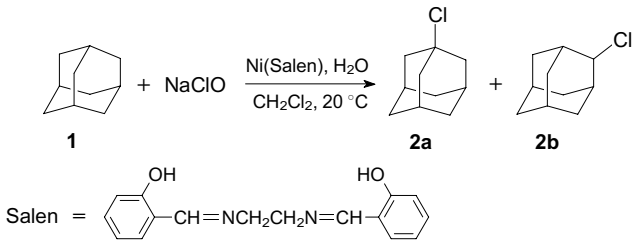
(*a*) $Mn(acac)_3$ – MeCN, 200 °C; (*b*) $VO(acac)_2$, 150 °C; 1 h; (*c*) $Mo(CO)_6$, 150 °C, 1 h

Scheme 5



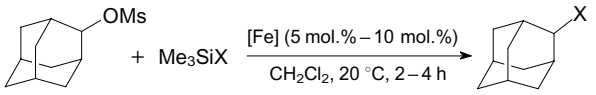
(*a*) $VO(acac)_2$, 150 °C; 1 h

Scheme 6



Ortega *et al.*[27] proposed the use of trimethylsilyl halides Me_3SiX (X = Cl, Br, I) in 1.2 equiv. amount as halogenating agents for halogenation by substitution of 2-adamantyl methanesulfonate (**43**; Ms = SO_2Me). This reaction, which proceeds under mild conditions in CH_2Cl_2 or $CHCl_3$, is catalyzed by iron(III) compounds; the yields of products **2b**, **6b** and **44b** are 87% – 97% (Scheme 7).

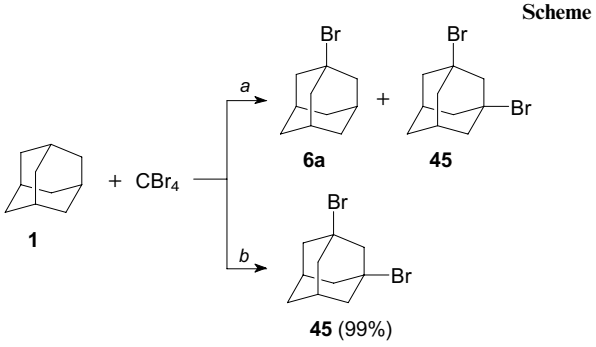
Scheme 7



[Fe] = $FeCl_3$, $Fe(acac)_3$; X = Cl (**2b**), Br (**6b**), I (**44b**)

It was found[28,29] that bromination of adamantane (**1**) can be accomplished using tetrabromomethane (1 equiv.) as the brominating agent in the presence of iron catalysts — $Fe(acac)_2$, $Fe(acac)_3$, $Fe(OAc)_2 \cdot H_2O$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ and $FeCl_3 \cdot 6H_2O$. The reaction proceeds for 2 h at 80 °C and affords a mixture of 1-bromo- (**6a**) and 1,3-dibromoadamantanes (**45**) in 6 : 1 ratio in a total yield from 30% to 66%. At higher temperature and on long-term heating with the $Fe_3(CO)_{12}$ catalyst, dibromoadamantane **45** is formed as the only product in a high yield (Scheme 8).

Scheme 8



(*a*) [Fe] (3 mol.% – 5 mol.%), hexane, 80 °C, 2 – 4 h; (*b*) $Fe_3(CO)_{12}$ (1 mol.% – 3 mol.%), 160 °C, 10 h; [Fe] = $Fe(acac)_2$, $Fe(acac)_3$, $Fe(OAc)_2 \cdot H_2O$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $FeCl_3 \cdot 6H_2O$

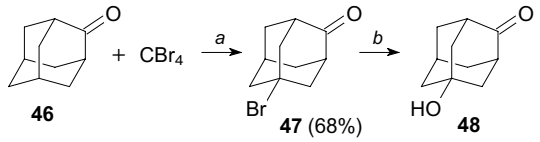
The pathway of the reaction between adamantane and CBr_4 in the presence of iron-containing catalysts depends on the substituent and solvent nature. In particular, the $Fe(acac)_3$-catalyzed bromination of adamantan-2-one (**46**) on treatment with CBr_4 in CH_2Br_2 gives 1-bromoadamantan-4-one (**47**), which can be hydrolyzed to afford 1-hydroxyadamantan-4-one (**48**) — the active substance of

Table 2. Chlorination of adamantane (**1**) catalyzed by metal complexes.

No.	Catalyst	Halogenating agent	*T*/°C	Time/h	Conversion of **1** (%)	Yield (%)		Ref.
						2a	**2b**	
1	$Rh(PPh_3)_3Cl$	CH_2Cl_2	180	30	80	80	–	20
2	$FeBr_3$	$CHCl_3$	200	6	77	77	–	21
3	$Fe_4Ac_2W_{18}-O_2$	DCE	75	300	54	36	18	22
4[a]	$Ru(DMSO)PW_{11}O_{39}-KHSO_5$	DCE	50	24	60	30	20	23
5	$Ru(PhH)MoO_{18}$	DCE	80	3	20	20	–	24
6	$Cu(OAc)_2 \cdot H_2O$ – NHPI	*N*-Chloroisocyanuric acid	30	4	23	13	10	25
7	Ni(Salen)	NaClO	20	1.3	34	29	5	26

Note. NHPI is *N*-hydroxyphthalimide, Salen is *N*,*N*′-bis(salicylidene)ethylenediamine.
[a] 10% of 1-adamantanol (**42a**) is formed.

Scheme 9

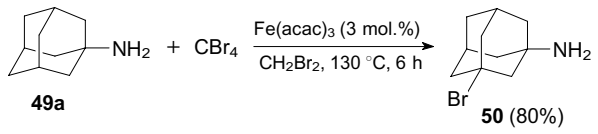


(*a*) $Fe(acac)_3$ (3 mol.%), CH_2Br_2, 170 °C, 5 h; (*b*) NaOH, Δ, 6 h

kemantan known as an immune stimulating drug (Scheme 9).[28,29]

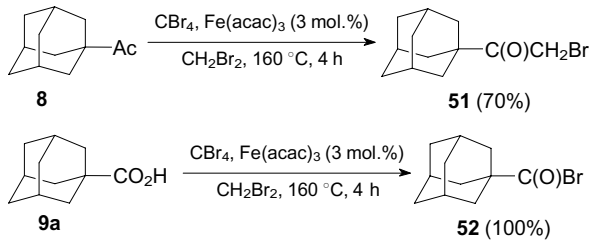
1-Aminoadamantane (**49a**) is highly reactive towards CBr_4; within 6 h at 130 °C, it is converted to 1-amino-3-bromoadamantane in high yield (**50**) (Scheme 10).

Scheme 10



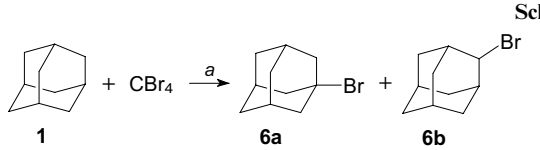
The bromination of 1-acetyladamantane (**8**) and adamantane-1-carboxylic acid (**9a**) with the same reagent in the presence of $Fe(acac)_3$ affords adamantyl bromomethyl ketone **51** and adamantane-1-carboxylic acid bromide **52**, respectively (Scheme 11).

Scheme 11



The reaction between adamantane (**1**), taken in 4 equiv. amount, and CBr_4 is also catalyzed by the complex $\{[PhSiO]_6CuO]\}_n$ (metal concentration is 0.3%). The reaction proceeds at 150 °C for 1.5 h and results in a mixture of 1-bromo- (**6a**) and 2-bromoadamantanes (**6b**) (9.5 : 1 ratio) in a total yield of 95% (Scheme 12).[30]

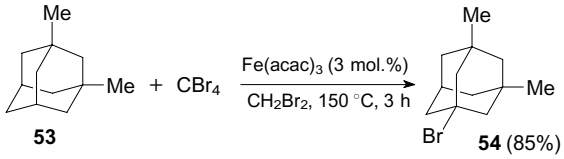
Scheme 12



(*a*) $\{[PhSiO]_6CuO]\}_n$ (10 mass %), 150 °C, 1.5 h

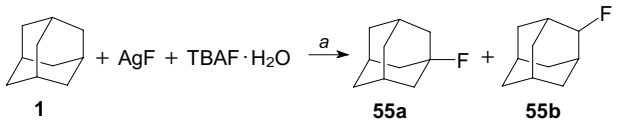
On heating to 150 °C for 3 h, 1,3-dimethyladamantane (**53**) is brominated with tetrabromomethane in the presence of $Fe(acac)_3$ only into the cage to give bromide **54** (Scheme 13).

Scheme 13



The porphyrin complex of manganese catalyzes the fluorination of adamantane (**1**) with silver fluoride (2 equiv.) under mild conditions in the obligatory presence of tetra-n-butylammonium fluoride and iodosobenzene as the oxidant. As a result, a mixture of 1-fluoro- (**55a**) and 2-fluoroadamantanes (**55b**) is formed in 5 : 1 ratio and 53% total yield (Scheme 14).[31,32] In the absence of the catalyst, the reaction does not take place.

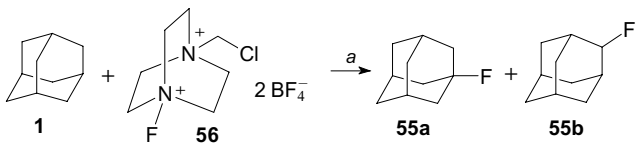
Scheme 14



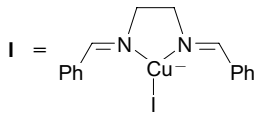
(*a*) [Mn(tmp)]Cl (6 mol.%), PhIO, $MeCN-CH_2Cl_2$ (5 : 1), 70 °C, 6 – 8 h; TBAF is tetra-n-butylammonium fluoride, tmp is *meso*-tetra-(mesityl)porphyrin

The fluorination of adamantane with 2.2 equiv. of Selectfluor [1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), **56**], which shows fluorinating and oxidative behaviour, is catalyzed by copper compounds (CuI, CuBr, CuCl, $CuClO_4$), with CuI being the most active among them. The addition of $KB(C_6F_5)_4$ as the co-catalyst substantially increases the reaction rate and the yield of 1-fluoroadamantane (**55a**). In the presence of the CuI – *N*,*N*′-bis(phenylmethylidene)ethane-1,2-diamine system (10 mol.%) (complex **I** acts as the catalyst), the yield of products **55** is 75% and the 1- and 2-isomer ratio is 8.4 : 1 (Scheme 15).[33]

Scheme 15



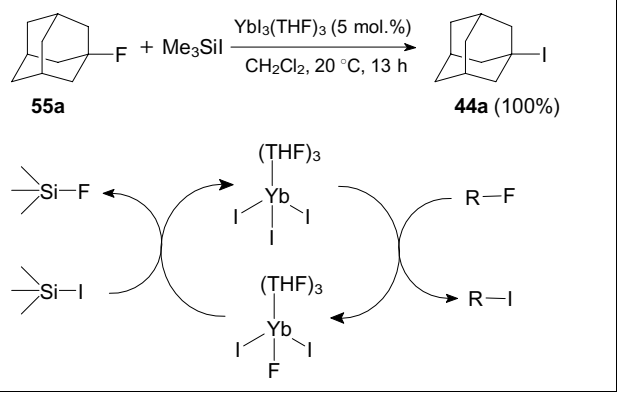
(*a*) **I** (10 mol.%), $KB(C_6F_5)_4$ (10 mol.%), 25 °C, 3 h;



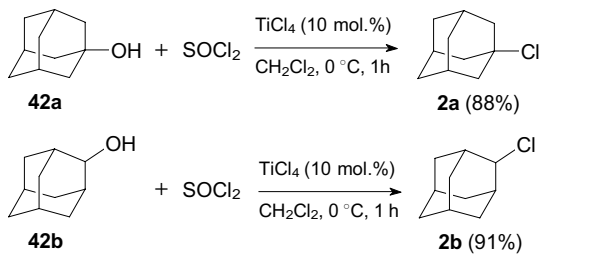
Janjetovic *et al.*[34] accomplished the substitutive iodination of 1-fluorodamantane (**55a**) with iodotrimethylsilane in the presence of a catalytic amount of $YbI_3(THF)_3$ (Scheme 16). The authors proposed a probable mechanism of the transformation giving iodide **44a**.

Titanium tetrachloride catalyzes the substitutive chlorination of adamantan-1- (**42a**) and adamantan-2-ols (**42b**) on treatment with thionyl chloride (Scheme 17).[35] Presumably, the reaction starts with the *in situ* formation of the corresponding chlorosulfite (*e.g.*, compound **57** in the case of

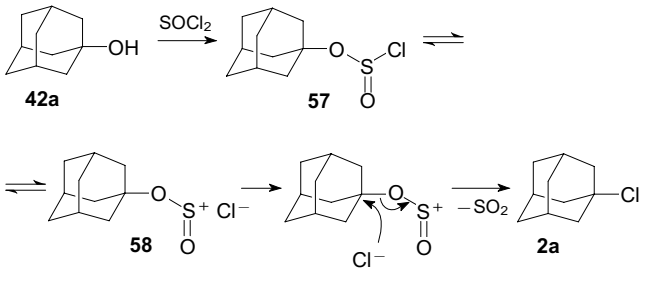
Scheme 16



Scheme 17



Scheme 18

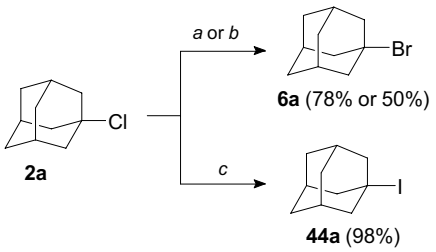


1-isomer), which decomposes in the presence of the catalyst *via* salt **58** to give off SO_2, being thus converted to adamantyl chloride **2a** in a high yield (Schemes 17 and 18).

It is known that 1-bromo-, 2-bromo- and 2-iodoadamantanes are more reactive towards substitution reactions than the corresponding chloro derivatives; therefore, it is of interest to develop efficient ways for converting less expensive and readily accessible adamantyl chlorides to bromides and iodides using HBr, HI or I_2. These reactions are conducted in CH_2Cl_2 or CCl_4 in the presence of iron-containing catalysts. In particular, $FeBr_2$ proved to be an active catalyst for transhalogenation of 1-chloroadamantane (**2a**; 1.52 mmol) *via* the reaction with HBr. The replacement of chlorine by iodine on treatment with I_2 to give iodide **44a** is best catalyzed by $Fe(CO)_5$. During the reaction, the carbonyl is converted *in situ* to FeI_3, which catalyzes the transiodination. This reaction can be conducted for both 1-chloro- (**2a**) and 2-chloroadamantanes (**2b**) (Scheme 19).[36, 37]

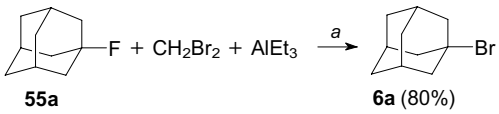
Mizukami *et al.*[38] reported a different method for transhalogenation of 1-haloadamantane with the participation of halomethanes. Treatment of 1-fluoroadamantane (**55a**) with dibromomethane (2 equiv.) in the presence of a catalytic amount of Cp_2TiBr_2 (Cp is cyclopentadienyl) and $AlEt_3$

Scheme 19



(*a*) $FeBr_2$ (0.3 mmol), HBr (5 equiv.), CH_2Cl_2, 25 °C, 0.3 h (78% yield); (*b*) $FeBr_2$ (0.32 mmol), Br_2 (1.5 equiv.), CH_2Cl_2, 25 °C, 15 h (50% yield); (*c*) $Fe(CO)_5$ (0.33 mmol), I_2 (1 equiv.), CH_2Cl_2, 25 °C, 0.5 h

Scheme 20

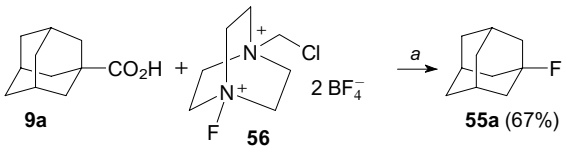


(*a*) Cp_2TiBr_2 (3 mol.%), hexane, from −40 to 25 °C, 24 h

(2 equiv.) affords 1-bromoadamantane (**6a**). The replacement of CH_2Br_2 by CH_2Cl_2 ($CHCl_3$, CCl_4) or CH_2I_2 resulted in the synthesis of 1-chloro- and 1-iodoadamantanes in high yields (Scheme 20).

The substitutive fluorination of adamantanecarboxylic acid **9a** (0.4 mmol) was accomplished by 0.8 mmol of Selectfluor (**56**) or *N*-fluorobis(benzenesulfonyl)imide (NFSI) in water in the presence of the $AgNO_3$ catalyst under mild conditions (Scheme 21).[39]

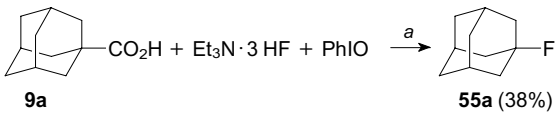
Scheme 21



(*a*) $AgNO_3$ (10 mol.%), H_2O (2 ml), 55 °C, 3 h

According to Huang *et al.*,[40] substitutive fluorination of adamantane-1-carboxylic acid (**9a**) on treatment with the complex $Et_3N \cdot 3\,HF$ (1.2 equiv.) is catalyzed by the manganese porphyrin complex [Mn(tmp)]Cl. The reaction is conducted in the presence of the PhIO oxidant (3.3 equiv.) in 1,2-dichloroethane (Scheme 22).

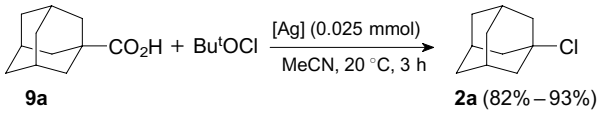
Scheme 22



(*a*) [Mn(tmp)]Cl (2.5 mol.%), DCE, 45 °C, 1.5 h

A higher product yield is obtained in the substitutive chlorination of adamantanecarboxylic acid **9a** (0.5 mmol) with *tert*-butyl hypochlorite (0.75 mmol) catalyzed by silver complexes: $Ag(Phen)_2OTf$, $Ag(Bpy)_2OTf$ and $Ag(TMPhen)_2OTf$ [Phen is 1,10-phenanthroline, Bpy is 2,2′-bipyridine, TMPhen is 3,4,7,8-tetramethyl-1,10-phe-

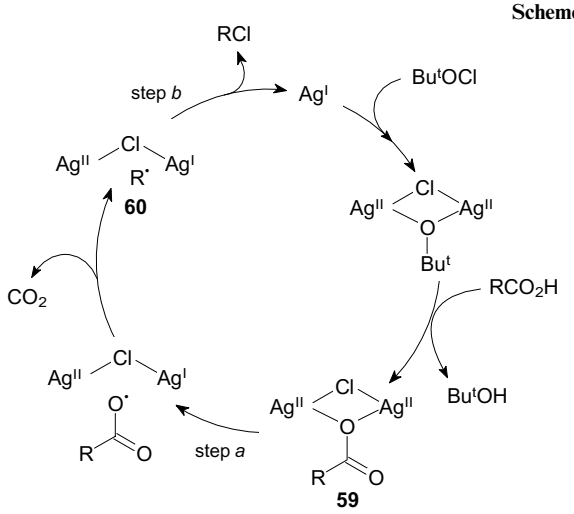
Scheme 23



nanthroline, OTf is trifluoromethanesulfonate (triflate)] (Scheme 23).[41]

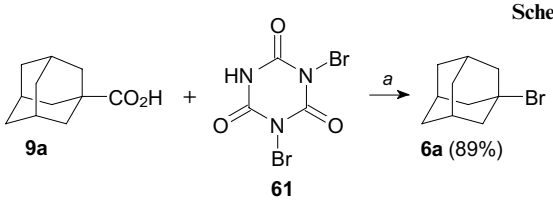
The authors assumed that the key step of the reaction is the single-electron transfer from complex **59** (step *a*), which is followed by chlorine atom transfer from the silver ion in intermediate **60** to the alkyl group (step *b*) (Scheme 24).

Scheme 24



Adamantanecarboxylic acid **9a** reacts with dibromoisocyanuric acid (**61**) (1 : 0.8 ratio) in the presence of $Ag(Phen)_2OTf$ to give 1-bromoadamantane (**6a**), *i.e.*, the reaction is accompanied by decarboxylation (Scheme 25).[42]

Scheme 25



(*a*) $Ag(Phen)_2OTf$ (2.5 mol.%), DCE, 20 °C, 1 h

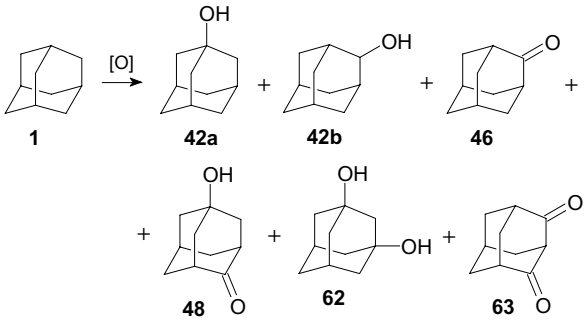
3. Oxidation of adamantanes

Among the reactions of diamondoids induced by metal complex catalysts, a prominent place is occupied by oxidation reactions.

It is known that the primary oxidation products of adamantane include adamantan-1-ol (**42a**), adamantan-2-ol (**42b**) and adamantan-2-one (**46**). In some cases, more extensive oxidation of compound **1** takes place to give 1-hydroxyadamantan-4-one (**48**), adamantane-1,3-diol (**62**) and adamantane-2,4-dione (**63**) (Scheme 26).[6]

Quite a few oxidants were tested for the oxidative functionalization of adamantanoids, in particular, O_2, H_2O_2, Bu^{t}OOH, *m*-chloroperoxybenzoic acid (*m*-CPBA),

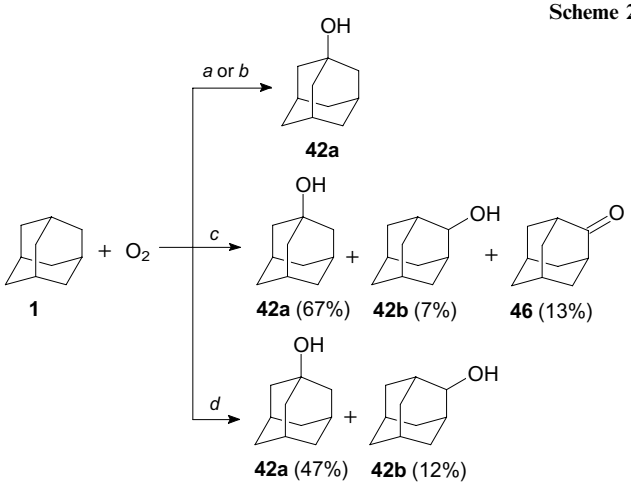
Scheme 26



PhIO, $KHSO_5$, $Bu^n_4NSO_5$, $NaIO_4$ and NaOCl, which are used in combination with Fe-, Co-, Ni-, Cu-, Mn-, Ce-, Ru- and Rh-based catalysts. However, complete substrate conversion in adamantane (**1**) oxidation and high selectivity to products **42a**,**b**, **46**, **48** and **62** are not always observed with the indicated oxidants.

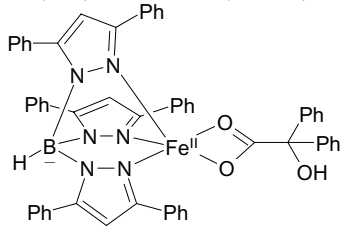
In particular, in the oxidation of compound **1** with oxygen in the presence of isovaleraldehyde, a satisfactory selectivity (98%) to alcohol **42a** was attained by using the iron-based catalyst $Fe(AAEMA)_3$ [AAEMA is the deprotonated form of 2-(acetoacetoxy)ethyl acrylate[43]] and $(NH_4)_2Ce(NO_3)_6$ (CAN).[44] The cobalt-based catalyst CoL_2@SMNP (SMNP are starch-coated magnetic nanoparticles) exhibits a rather high activity (87% conversion) and moderate selectivity (67%) to alcohol **42a** in the presence of a radical initiator — *N*-hydroxyphthalimide.[45]

Scheme 27



(*a*) Bu^{i}CHO, $Fe(AAEMA)_3$ (0.02 mmol), 25 °C, 60 h (60% conversion, 98% selectivity); (*b*) Bu^{i}CHO, CAN, *hν*, MeCN, 25 °C (95% conversion, 90% selectivity); (*c*) CoL_2@SMNP (0.5 mol.%), NHPI (15 mol.%), MeCN, 70 °C, 9 h (87% conversion); (*d*) $(TPPh2)Fe^{II}[Ph_2C(OH)CO_2]$ (**II**);
L = $HO(CH_2)_2N{=}CHCH_2C(OSiMe_3)_3$;

II =

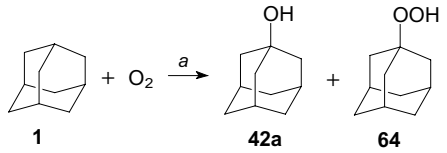


The catalyst can be recovered from the reaction mixture with a magnet and reused.

Low selectivity in the oxidation of adamantane with oxygen was found for iron-based catalyst **II** containing a sophisticated hydrotris(3,5-diphenylpyrazol-1-yl)borate (TPPh2) molecule as a ligand (Scheme 27).[46,47]

The oxidation of adamantane (**1**) with oxygen in the presence of a palladium complex containing 1,3,5-tris(4-pyridyl)triazine (TPT) ligands under photoirradiation followed an unusual pathway. The total yield of the oxidation products was 24% (the ratio was not indicated), and adamantyl 1-hydroperoxide (**64**) was isolated as one of the products (Scheme 28).[48]

Scheme 28

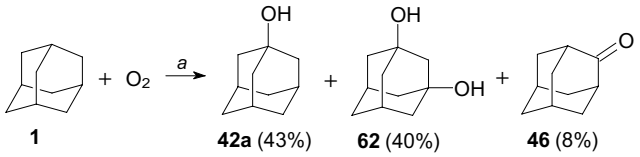


(*a*) *hν*, Hg lamp (300 nm), (Bpy)Pd$(NO_3)_2$–TPT, H_2O, 18 min

The oxidation of adamantane with oxygen (at 1 atm pressure) in the presence of *N*-hydroxyphthalimide (10 mol.%) catalyzed by $Co(acac)_2$ provides a relatively high yield of adamantane-1,3-diol (**62**) (Scheme 29).[49]

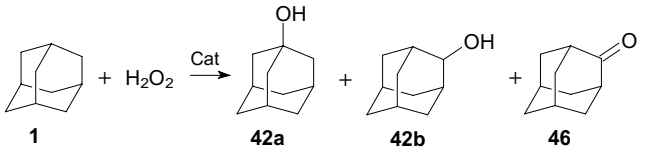
In some studies, hydrogen peroxide was used for the oxidation of compound **1** (Scheme 30)[6] carried out in the presence of iron complexes **III**–**IX**, titanium oxide or copper dichromate.[50–67] Table 3 presents some results of these experiments.

Scheme 29



(*a*) $Co(acac)_2$ (0.5 mol.%), NHPI, AcOH, 75 °C, 6 h (93% conversion)

Scheme 30



Iron compounds[50–67] are active catalysts of oxidation of compound **1** with hydrogen peroxide; however, in the presence of most Fe-based catalysts, this reaction has low selectivity. High selectivity to adamantan-1-ol (**42a**) was observed only in two cases, namely, in the presence of iron ferrocene complex **III** (78% yield)[50] and complex **IV** with a pyridine ligand (89%).[51] When the Fe(sal-L-His)(Bpy)Cl complex (**V**) was used as the catalyst, adamantane oxidation with H_2O_2 gave predominantly adamantan-2-one (**46**) (70% yield) (see Table 3).[52]

It was assumed[52] that oxidation of compound **1** with hydrogen peroxide induced by iron complexes proceeds by a radical mechanism [reactions (1)–(8) in Scheme 31]. In the beginning of the process, hydrogen peroxide forms HO$^\bullet$ and HOO$^\bullet$ radicals under the action of LFe^{III} and $LFe^{IV}{=}O$ complexes. Then the HO$^\bullet$ radical attacks the adamantane molecule (AdH) to give the adamantyl radical, which reacts with oxygen. This gives rise to the peroxide radical, AdOO$^\bullet$, which reacts with one more adamantane molecule to afford the Ad$^\bullet$ radical and adamantyl hydroperoxide AdCOOH (**64**). The latter can degrade along two pathways, one being accompanied by the evolution of oxygen and yielding adamantan-1-ol (**42a**) and the other leading to adamantan-2-one (**46**). In addition, products **42a** and **46** are formed upon recombination of the Ad$^\bullet$ and AdOO$^\bullet$ radicals *via* the formation of the corresponding peroxide (see Scheme 31).

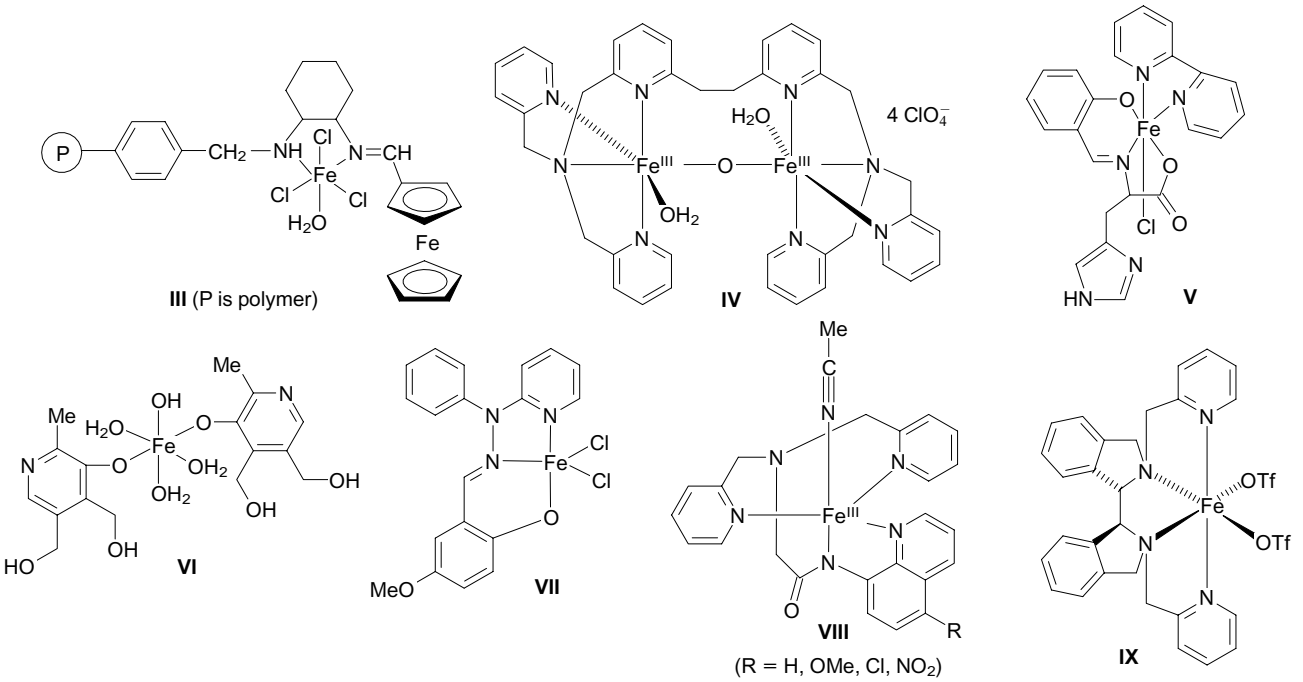
The oxidation of adamantane (**1**) with a H_2O_2–CF_3CO_2H mixture (which generates *in situ* trifluoroperacetic acid) in the presence of rhodium complexes has been studied. In the reaction involving 5 mmol of the substrate, the complex $[Rh_3O(OAc)_6(H_2O)_3]OAc$ showed the highest

Table 3. Oxidation of adamantane (**1**) with hydrogen peroxide catalyzed by metal complexes (see Scheme 30).

No.	Catalyst	*T*/°C	Time /h	Conditions	Conversion (%)	Yield (selectivity) (%)			Ref.
						42a	**42b**	**46**	
1	PS-Fe^{III}-Fc (**III**)	60	10	10 h	80	78	–	–	50
2	$[Fe_2(\mu\text{-}O)(H_2O)_2(6\text{-hpa})(ClO_4)_4]$ (**IV**)	40	4	$PhNO_2$, 4 h	99	(89)	(7)	(3)	51
3	Fe(sal-L-His)(Bpy)Cl (**V**)	80	24	MeCN, 24 h	98	(30)	–	(70)	52
4	$[Fe(pyridoxinato)_2\text{-}OH\cdot(H_2O)_3]$ (**VI**)	80	6	–	90	(64)	–	(36)	53
5	$FeCl_3$–THA	60	10	–	59	53	–	6	54
6	$Fe(L)Cl_2$ (**VII**)	40	8	–	49	28	13	8	55
7[a]	$Fe(dpaq)(MeCN)]^{2+}$ (**VIII**)	25	0.5	–	See[b]	45	5	2	56
8	Fe^{II}-DCBPY	20	20	UV irradiation	See[c]	(49)	(3)	(48)	57
9	(*S*,*S*)-[Fe(BPPI)$(OTf)_2$] (**IX**)	0	0.27	–	53	45	2	6	58–61
10	TiO_2	25	10	UV irradiation (Hg lamp, 150 W)	64	–	–	89	62
11	$CuCr_2O_4$	50	10	–	64	36	–	24	66, 67

Note. PS are polymer particles, Fc is ferrocenyl, hpa is 1,2-bis{2-[bis(2-pyridylmethyl)aminomethyl]-6-pyridyl}ethane, sal-L-His is *N*-salicylidene-L-histidine, THA is thymine-1-acetate, L is 4-methoxy-2-{[2-phenyl-2-(2-pyridyl)hydrazonato]methyl}phenol, dpaq is 2-[bis(2-pyridylmethyl)]-amino-*N*-quinolin-8-ylacetamido, DCBPY is 2,2′-bipyridine-4,4′-dicarboxylate, BPPI is *N*,*N*′-bis(2-picolyl)-2,2′-bis(isoindoline).
[a] 10% of adamantane-1,3-diol (**62**) is formed; [b] TON = 70 (TON is the turnover number of the catalyst); [c] TON = 4.8.

Structures III – IX



Scheme 31

$2\,H_2O_2 \longrightarrow O_2 + 2\,H_2O$ (1)

$H_2O_2 + LFe^{III} \longrightarrow HO^{\bullet} + H + LFe^{IV}{=}O$ (2a)

$H_2O_2 + LFe^{IV}{=}O \longrightarrow HOO^{\bullet} + HO^{\bullet} + LFe^{III}$ (2b)

$HO^{\bullet} + AdH \longrightarrow H_2O + Ad^{\bullet}$ (3)

$Ad^{\bullet} + O_2 \longrightarrow AdOO^{\bullet}$ (4)

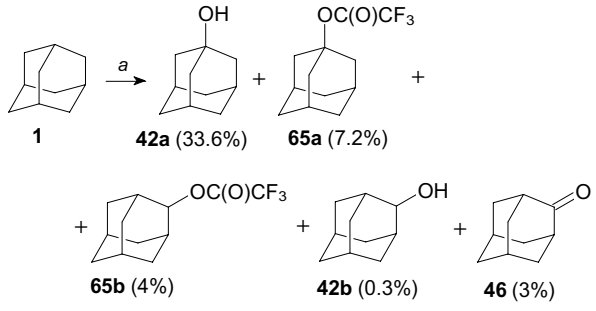
$AdH + AdOO^{\bullet} \longrightarrow Ad^{\bullet} + AdOOH$ (5)
64

$AdOOH \longrightarrow AdOH + 1/2\,O_2$ (6)
64 **42a**

$AdOOH \longrightarrow$ **46** $+ H_2O$ (7)
64

$Ad^{\bullet} + AdOO^{\bullet} \longrightarrow AdOOAd \longrightarrow AdOH +$ **46** (8)
42a

Scheme 32

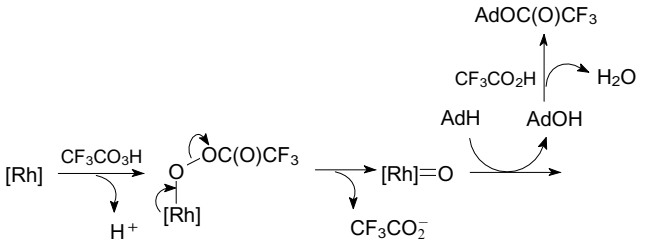


(*a*) 30% H_2O_2 (3 equiv.), CF_3CO_2H (10 ml), [Rh] (0.017 mmol), AcOH (20 ml), 25 °C, 2 days;
[Rh] = $[Rh_3O(OAc)_6(H_2O)_3]OAc$, $Rh_2(OAc)_4$, $Rh(acac)_3$, $[RhCl(CO)_2]_2$, $RhCl(PPh_3)_3$

activity (TON = 144). The reaction gave adamantan-1-ol (**42a**) as the major product; trifluoroacetates **65a**,**b** were also detected in the reaction mixture (Scheme 32).[65]

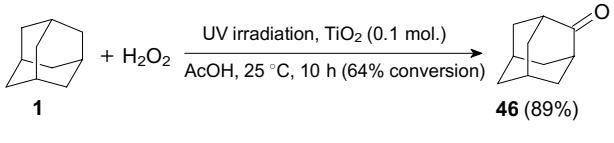
It was assumed[65] that the role of CF_3CO_3H is to generate the rhodium oxo complex [Rh]=O, which is responsible for adamantane oxidation (Scheme 33).

Scheme 33



The reaction of compound **1** with 30% hydrogen peroxide in the presence of titanium dioxide powder under UV irradiation (150 W, Hg lamp) can also be directed towards the formation of adamantan-2-one (Scheme 34).[62]

Scheme 34



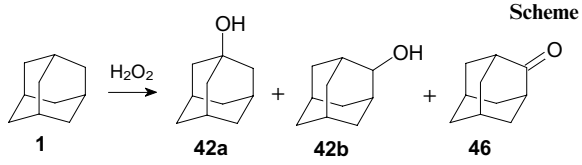
The oxidation of adamantane on treatment with H_2O_2 in the presence of a macrocyclic polyamine cluster containing copper and vanadium proceeds with high conversion but low selectivity.[63] The oxidation selectivity increases, with

Table 4. Oxidation of adamantane (**1**) with 30% hydrogen peroxide in the presence of bimetallic complexes (see Scheme 34).

No.	Catalyst (mol.%)	Conditions	Amount of H_2O_2	Conversion (%)	Yield (%)			Ref.
					42a	**42b**	**46**	
1	[Cu(cyclam)][{Cu(cyclam)}$_2$($V_{10}O_{28}$)] · 10 H_2O (4) [a]	MeCN, 75 °C, 6 h	3 ml	99	36	20	20	63
2	[Bu^n_4N]Os(N)Cl_4 (1) – $FeCl_3$ (10) [b]	CH_2Cl_2 – AcOH (5 : 2), 23 °C, 5 min	0.1 equiv.	93	77	6	3	64

Note. cyclam is 1,4,8,11-tetraazacyclotetradecane. [a] Other products (13%) were isolated; [b] TON = 74.

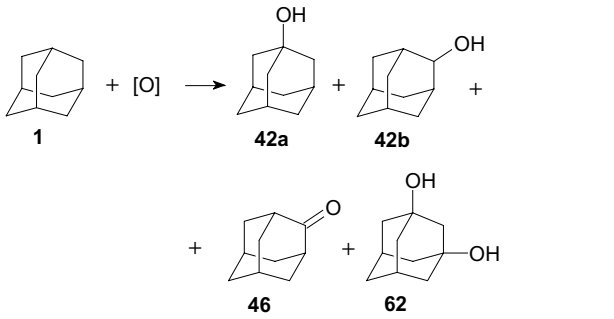
Scheme 35



high conversion being retained, if an Os/Fe bimetallic catalytic system is used (Scheme 35, Table 4).[64]

Classical oxidants such as $Bu^n_4NHSO_5$, Bu^tOOH, *m*-CPBA, 2,6-dichloropyridine *N*-oxide, $NaIO_4$, PhIO, $PyHClO_4$, NaClO and $K_2S_2O_8$ are virtually inert towards adamantane without catalysts. For their activation, Fe-, Co-, Ni-, Mn-, Mo-, Cu-, Ru- and Pd-based metal complex catalysts are required (Scheme 36, Table 5).[68 – 92] However, despite the presence of metal complexes, complete conversion of adamantane (**1**) and high selectivity of oxidation, with hydroxylation being the major pathway, is observed quite rarely.

Scheme 36



The selective oxidation of adamantane to alcohol **42a** was attained by using tetra-n-butylammonium oxone as the

Table 5. Results of oxidation of adamantane (**1**) with conventional oxidants in the presence of metal complex catalysts (see Scheme 36).

No.	Oxidant	Catalyst	*T*/°C	Time /h	Conversion (%)	Yield (%)				Ref.
						42a	**42b**	**46**	**62**	
1	$Bu^n_4NHSO_5$	Mn(Salen)@-ASMNP	80	6	100	94	–	–	–	68
2[a]	$Bu^n_4NHSO_5$	Fe^{III}(TPFPP)	25	0.17	71	49	17	–	–	69
3	Bu^tOOH	Fe · SBA-15	27	144	100	98	–	2	–	70
4	Bu^tOOH	[Fe/Co] [b]	82	6	37	28	–	9	–	71
5	Bu^tOOH	[Co] [c]	82	24	80	60	–	19	14	72
6	Bu^tOOH	[Cu] [d]	60	24	29	23	–	3	3	73
7	*m*-CPBA	[Fe(l)bTAML]$^{2-}$(**X**)	20	1	60	59	0.5	0.5	–	74
8	*m*-CPBA	[Fe(bpmen)(μ-O)-$FeCl_3$	20	1	30	25	3	2	–	75
9	*m*-CPBA	[Ni(L)MeCN] [BPh_4]$_2$ (see [e])	20	2	68	54	12	2	–	76 – 78
10	2,6-Dichloropyridine *N*-oxide	Ru(TPP)(CO)	65	8	100	66	–	–	27	79
11[f]	2,6-Dichloropyridine *N*-oxide	[{Ru(C_6Me_6)}$_3$$Mo_5O_{18}$]	80	3	95	54	–	–	–	80
12	$NaIO_4$	[Mn(TNH_2PP)Cl]	20	22	100	81	–	–	–	81, 82
13	PhIO	Fe(PCl_8)Cl	25	2	100	54	12	–	–	83 – 88
14	PhIO	[$Mn^{III}Br_{12}$T4(OMe)-PPCl]	25	1.5	53	37	16	–	–	83 – 87
15	$PyNHClO_4$	(TPPh_2)Fe^{III}[Ph_2C(OH)CO_2] (**II**)	25	2	45	27	18	–	–	89
16	NaClO	[$RuCl_2$(Bpy)$(CO)_2$]	50	12	77	45	1	2.4	12	90
17	CAN	*cis*-[(pdp)$Ru^{III}$$(OTf)_2$]OTf (**XI**)	20	1.5	74	47	1	2	32	91
18	$K_2S_2O_8$	Pd$(OAc)_2$ – Cu$(OAc)_2$	72	6	96	85	11	–	–	92

Note. ASMNP is silica coated magnetic nanoparticles; TPFPP is *meso*-tetrakis(pentafluorophenyl)porphyrin; SBA is a mesoporous material; bTAML is biuret-modified tetraamido macrocyclic ligand; bpmen is *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)-1,2-diaminoethane; TPP is *meso*-tetraphenylporphyrin; TNH_2PP is *meso*-tetrakis(*p*-aminophenyl)porphyrin; [$Mn^{III}Br_{12}$T4(OMe)PPCl] is manganese chloro-5,10,15,20-tetrakis(3-bromo-4-methoxyphenyl)-2,3,7,8,12,13,17,18-octabromoporphyrin; pdp is 1,1′-bis(2-pyridylmethyl)-2,2′-pyrrolidine; Ts is *p*-toluenesulfonyl (tosyl).

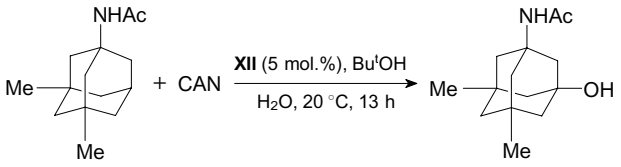
[a] 10% of 1-hydroxyadamantan-4-one (**48**) is formed; [b] catalyst: Fe_3O_4@SiO_2-2@APTMS@[Co_3(PDMT)Cl_6] [APTMS is (3-aminopropyl)trimethoxysilane, PDMT is *N*,*N*′,*N*″-tris(pyrimidin-2-yl)dimethylenetriamine); [c] [Co] = Co_3(BTA)$(HCO_2)_4$(DMF) (BTA is benzene-1,3,5-tricarboxylic acid); [d] [Cu] = [Cu^I4L_4]X_4 [L = 1,3,5-tris(1-benzylbenzimidazol-2-yl)benzene; X = NO_3, OTs, OTf, ClO_4]; [e] L is *N*-methyl-*N*,*N*′,*N*″-tris(2-pyridylmethyl)ethylideneamine; [f] 20% of 1-chloroadamantane (**2a**) is formed.

oxidant (see Table 5, No. 1).[68] The reaction is catalyzed by the manganese complex Mn(Salen)@ASMNP. Hydroxylation of compound **1** with *tert*-butyl hydroperoxide and *m*-CPBA in the presence of Fe catalysts Fe·SBA-15[70] and complex **X** proceeds in a similar way.[75]

A strong oxidant such as cerium(IV) ammonium nitrate proved to be unable by itself to oxidize adamantane (**1**). It showed a noticeable activity only when taken in a threefold excess with respect to the substrate together with 2 mol.% of the ruthenium-based catalyst *cis*-[(pdp)$Ru^{III}(OTf)_2$]OTf (**XI**); the reaction was performed in aqueous n-butanol at 25 °C for 1.5 h (see Scheme 36 and Table 5).[91]

A fairly selective oxidation of 1-acetamido-3,5-dimethyladamantane (**66**) (0.2 mmol) to alcohol **67** takes place on treatment with CAN (1.2 mmol) with the catalysis by *cis*-[(mcp)$Ru^{VI}(O_2)(ClO_4)_2$] [**XII**; mcp is *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)cyclohexane-1,2-diamine] (Scheme 37).

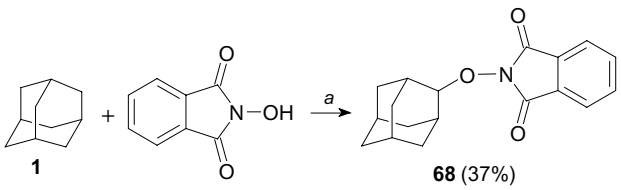
Scheme 37



66 CAN = $(NH_4)_2Ce(NO_3)_6$ **67** (78%)

A convenient method has been developed for the synthesis of 2-adamantyloxyphthalimide (**68**) by the reaction of an equimolar mixture of *N*-hydroxyphthalimide with adamantane in the presence of $Cu(OAc)_2 \cdot H_2O$ and with Selectfluor as the oxidant (Scheme 38).[93]

Scheme 38

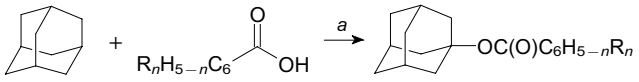


1 **68** (37%)

(*a*) Selectfluor (**56**, 2.5 equiv.), $Cu(OAc)_2 \cdot H_2O$ (5 mol.%), MeCN, 25 °C, 1 h

The oxidant Selectfluor (**56**) was also used to synthesize 1-adamantyl esters of aromatic carboxylic acids **69a–m** from adamantane in the presence of a copper catalyst. Among the tested copper salts [CuBr, $Cu(OTf)_2$, CuCl, CuI, $CuBr_2$], the highest activity in this reaction was found for $CuBr_2$ (Scheme 39).[94]

Scheme 39

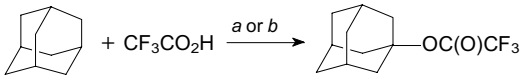


1 **69a–m** (40%–78%)

(*a*) $CuBr_2$ (30 mol.%), Selectfluor (**56**), Bu^nCN (50 mol.%), N_2, 60 °C, 4 h;
R_n = 4-NO_2 (**a**, 72%), 2-NO_2 (**b**, 70%), 4-F (**c**, 78%), 4-Cl (**d**, 73%), 3-Cl (**e**, 65%), 2-Cl (**f**, 75%), 2,4-Cl_2 (**g**, 72%), 4-Br (**h**, 57%), 4-I (**i**, 40%), 4-Me (**j**, 40%), 4-Bu^t (**k**, 65%), 4-OMe (**l**, trace), 4-CHO (**m**, 68%)

At reflux in trifluoroacetic acid in the presence of $Pd(OAc)_2$, adamantane (0.8 mmol) is converted to 1-adamantyl trifluoroacetate (**65a**) in a quantitative yield (Scheme 40, conditions *a*).[95] The same product is formed in 80% yield upon long-term heating of compound **1** (2 mmol) with a stoichiometric amount of $Co(OAc)_3$ in CF_3CO_2H (conditions *b*).[96]

Scheme 40

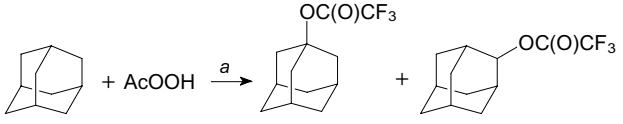


1 **65a**

(*a*) CF_3CO_2H (10 ml), $Pd(OAc)_2$ (0.8 mmol), Δ, 3 h; (*b*) CF_3CO_2H, $Co(OAc)_3$ (2 mmol), CH_2Cl_2, 75 °C, 84 h

The ruthenium salt $RuCl_3 \cdot n\,H_2O$ catalyzes the oxidation of adamantane (2.5 mmol) with peracetic acid (1.25 mmol). The reaction proceeds in a AcOH–CH_2Cl_2–CF_3CO_2H (1 : 2 : 1) mixture at 20 °C for 4 h and affords a mixture of 1- (**65a**) and 2-adamantyl trifluoroacetates (**65b**) in 9 : 1 ratio and in an overall yield of 70% (Scheme 41).[97]

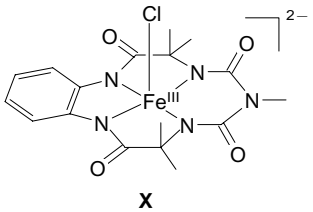
Scheme 41



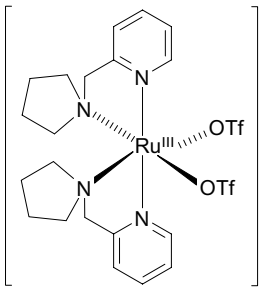
1 **65a** **65b**

(*a*) $RuCl_3 \cdot n\,H_2O$ (0.025 mmol), AcOH–CH_2Cl_2–CF_3CO_2H (1 : 2 : 1), 20 °C, 4 h (70% conversion)

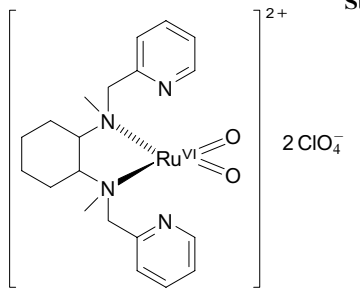
Structures X–XII



X



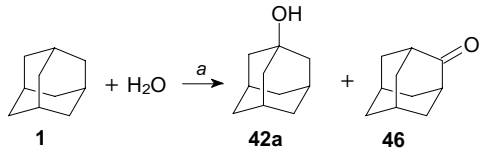
XI



XII

Selective photocatalytic oxidation of adamantane (**1**) (3 mmol) with water as a source of oxygen was accomplished. The catalytic system consisted of three components: $[(Et_4N)(bTAML)Fe^{III}(OH_2)]$ (**A**), $[Ru^{II}(Bpy)_3]Cl_2$ (**B**) and $[Co^{III}(NH_3)_5Cl]Cl_2$ (**C**). In this system, ruthenium and cobalt complexes promote photodegradation of water with oxygen evolution (Scheme 42).[98]

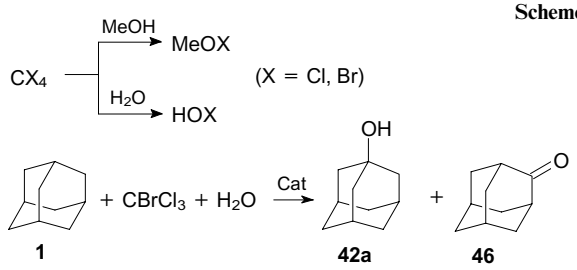
Scheme 42



(*a*) *hν*, LED (3 W, 440 nm), **A** (0.001 mmol) — **B** (0.002 mmol) — **C** (0.001 mmol), argon, MeCN – aqueous phosphate buffer (3 : 2), pH 10, 27 °C, 40 min (76% conversion; **42a** : **46** = 100 : 1); LED is light-emitting diode

A general method was developed for hydroxylation of adamantane and its derivatives with the MeOH $(H_2O)-CX_4$ system (X = Cl, Br) in the presence of W, Mo, Mn, Fe, Ni, Co, Pd, Ni and Ru complexes. The oxidants are MeOX and hypochlorous (HOCl) or hypobromous (HOBr) acids, which are generated from water and halomethanes under the reaction conditions (Scheme 43).[99–104] The molar ratio of the catalyst, substrate, CX_4 and H_2O is 3 : 100 : 100 : 1000. Adamantan-2-one (**46**) is formed only in the presence of Pd- and Mo-containing catalysts: for example, the use of $PdCl_2(PPh_3)_2$ (3 mol.%) at 160 °C for 9 h resulted in the formation of an equimolar ratio of products **42a** and **46** in a yield of 89%.[101, 102]

Scheme 43



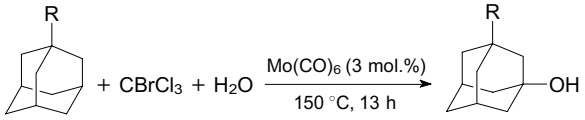
Cat = $PdCl_2(PPh_3)_2$ (89%), $Ru(OH)Cl_3$ (89%), $NiCl_2(PPh_3)_2$ (55%), $NiCl_2(PBu^n_3)_2$ (59%), $CoCl_2[(Ph_2PCH_2)_2]_2$ (66%), $Mo(CO)_3$ (83%), $W(CO)_6$ (78%), $Cr(CO)_6$ (89%), $Fe_3(CO)_{12}$ (64%)

If this reaction is carried out in the presence of $Mo(CO)_6$ and an equimolar amount of tetra-n-butylammonium bromide (TBAB) as a phase transfer catalyst, ketone is formed as the major product after 13 h at 140 °C (the yield of the mixture is 99%; **42a** : **46** = 1 : 2).

1-Substituted adamantanes **2a**, **6a**, **8**, **9a**, **10**, **42a**, **49a** and **70** were converted to adamantanols **62** and **71**–**77** containing various substituents in the bridgehead position in moderate to high yields (Scheme 44); 2-substituted derivatives **6b** and **49b** were converted to alcohols **78**, **79** with substituents in the methylene group; and ketone **46** was transformed to keto alcohol **48** (Scheme 45).

Avdeev *et al.*[105] investigated the oxidation of 1,3-dimethyladamantane (**53**) with potassium persulfate in the presence of manganese and iron tetrapyridylporphyrin complexes. The reaction is non-selective, giving a mixture of three isomers: 1-hydroxy-3,5-dimethyladamantane (**80**), 1,3-dihydroxy-5,7-dimethyladamantane (**81**) and 1,3-dimethyladamantan-2-one (**82**) in 1 : 1 : 1 ratio in a total yield of 60% (Scheme 46).

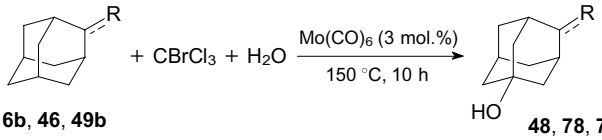
Scheme 44



2a, **6a**, **8**, **9a**, **10**, **42a**, **49a**, **70** → **62**, **71**–**77**

R = Cl (**2a**; **71**, 80%), Br (**6a**; **72**, 92%), Ac (**8**; **73**, 98%), CO_2H (**9a**; **74**, 58%), C(O)Cl (**10**; **75**, 91%), OH (**42a**; **62**, 86%), NH_2 (**49a**; **76**, 80%), $CHMeNH_2$ (**70**; **77**, 99%)

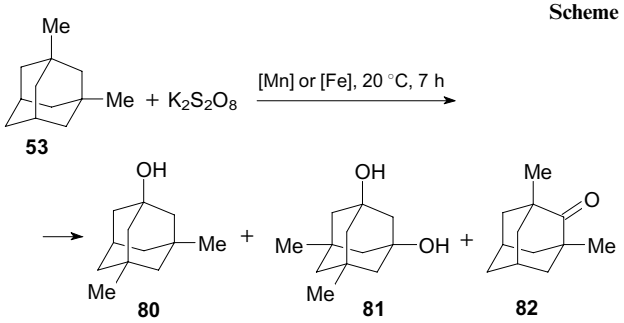
Scheme 45



6b, **46**, **49b** → **48**, **78**, **79**

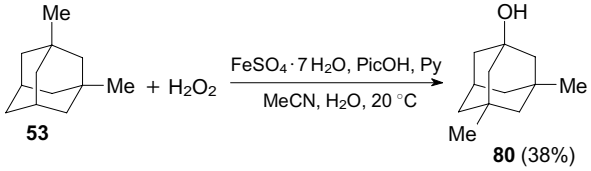
R = Br (**6b**; **78**, 80%), NH_2 (**49b**; **79**, 88%), =O (**46**; **48**, 85%)

Scheme 46



Unlike $K_2S_2O_8$, hydrogen peroxide selectively oxidizes 1,3-dimethyladamantane in the presence of $FeSO_4 \cdot 7H_2O$ and complexing agents — pyridine and picolinic acid (PicOH) — to give 1-hydroxy-3,5-dimethyladamantane (**80**) (Scheme 47).[106, 107]

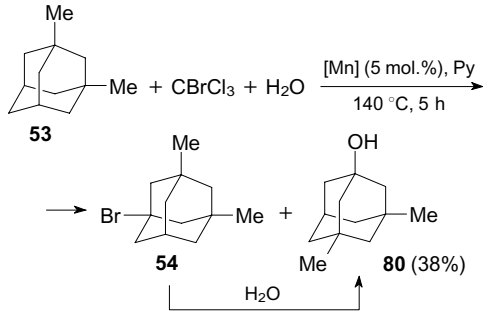
Scheme 47



The oxidation of compound **53** with a $CBrCl_3-H_2O-$[Mn] system [the [Mn] : **53** : $CBrCl_3$: H_2O : Py molar ratio is 5 : 100 : 125 : 6000 : 200] results in a mixture of bromide **54** and alcohol **80** in a total yield of 79% (Scheme 48).[103, 104]

An unusual pathway was observed for the reaction of 1-adamantylmethanol (**36**) with CCl_4 in the presence of

Scheme 48

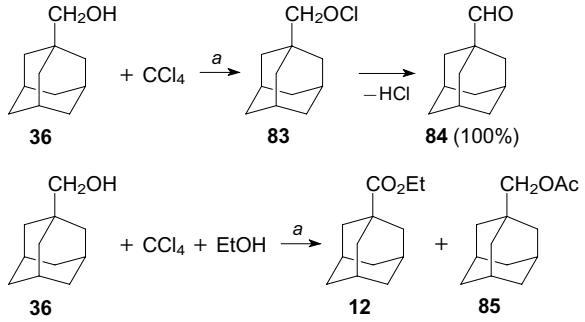


[Mn] = $Mn(acac)_3$, $Mn_2(CO)_{10}$, $Mn(OAc)_2 \cdot 4H_2O$

$VO(acac)_2$ (the [V] : **36** : CCl_4 molar ratio is 1 : 500 : 1500). It was shown that the $VO(acac)_2$-catalyzed reaction of the alcohol with CCl_4 leads to *in situ* generation of 1-adamantylmethyl hypochlorite **83**, which is then converted to aldehyde **84**. In the presence of ethanol (4 equiv.), adamantylmethanol **36** is converted to ethyl adamantanecarboxylate **12** and 1-adamantylmethyl acetate **85** in 2 : 3 ratio, as some of ethanol is oxidized with carbon tetrachloride under the reaction conditions to give acetic acid (Scheme 49).[10]

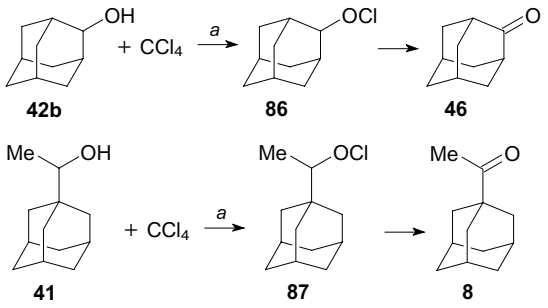
The oxidation of secondary alcohols, adamantan-2-ol (**42b**) and 1-adamantylethanol (**41**), under the action of CCl_4 in the presence of $Mn(acac)_3$ in acetonitrile was described.[108] During the reaction, alkyl hypochlorites **86** and **87** are formed and then decompose with evolution of HCl to give ketones **46** and **8**, respectively. The reaction is carried out at the reactant ratio [Mn] : MeCN : alcohol : CCl_4 = 1 : (2 – 4) : (100 – 200) : (200 – 500), while the yields of chlorination products are 90% (Scheme 50).

Scheme 49



(*a*) $VO(acac)_2$, 200 °C, 1 h

Scheme 50



(*a*) $Mn(acac)_3$, MeCN, 200 °C, 3 h

Adamantan-2-one (**46**) is known to be an important oxygen-containing derivative, serving as the key precursor for the synthesis of 2-substituted adamantanes. The classical method for the synthesis of adamantanone **46** is based on the oxidation of adamantane with an excess of concentrated sulfuric acid.[109, 110] This method found wide use only in laboratory practice, as scaling up of the process results in a sharp decrease in the yield of ketone **46** due to resinification. The simplest synthetic route to adamantan-2-one is oxidation of adamantan-2-ol (**42b**) by treatment with various oxidants such as O_2, H_2O_2, Bu^tOOH, *m*-CPBA, PhIO, $KHSO_5$, $(NH_4)_4Ce(NO_3)_6$ using metal complexes as catalysts. In particular, the oxidation of this substrate with oxygen is catalyzed by copper,[111 – 114] palladium,[115 – 118] platinum,[119, 120] ruthenium[121] and gold[122] complexes (Scheme 51, Table 6).

Scheme 51

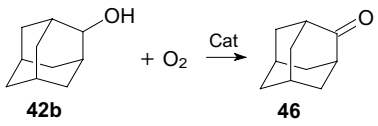


Table 6. Oxidation of adamantanol **42b** with oxygen catalyzed by metal complexes (see Scheme 51).

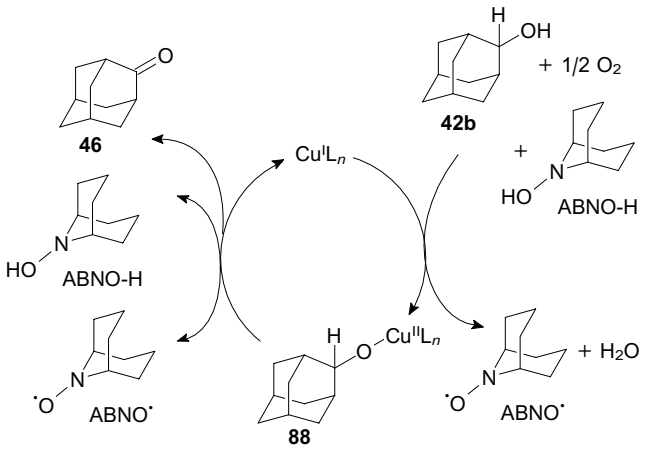
No.	Catalyst	Pressure of O_2 /atm	*T*/°C	Time /h	Initiator	Yield of **46** (%)	Ref.
1	$CuOTf \cdot 0.5\,PhH$	1	25	13	Nor-AZADO	99	111
2	CuI	1	60	2	ABNO	89	112, 113
3	CuBr	1	20	9	TEMPO	91	114
4	PdO@SNP	1	90	24	–	99	115
5	$Pd(OAc)_2 - Bu^n{}_3P{=}O$	1 (air)	80	40	–	90	116
6	$Pd(OAc)_2 - H_3PMo_{12}O_{40}$	30 (air)	100	1	–	100	117
7	$Pd(OAc)_2$ – HSA	30 (air)	100	4	–	89	118
8	Pt(NP)@PMO-IL-2	1 (air)	90	26	–	99	119
9	Pt(ARP)	50	100	See [a]	–	99	120
10	$Ru/Ni(OH)_2$	1	90	1	–	100	121
11	Au(PIONS)	1	60	24	–	See [b]	122

Note. Nor-AZADO is 9-azanoradamantane-*N*-oxyl; ABNO is 9-azabicyclo[3.3.1]nonane-*N*-oxyl; TEMPO is (2,2,6,6-tetramethylpiperidin-1-yl)oxyl; SNP are silica nanoparticles; HSA is 8-hydroxyquinoline-2-sulfonic acid; NP are nanoparticles; PMO-IL-2 is periodic mesoporous organosilicate modified by imidazolium; ARP is amphiphilic polystyrene-poly(ethylene glycol); PIONS are nanoporous ionic organic networks stabilizing gold nanoparticles.

[a] The reaction time is 55 s; [b] TON = 868.

Copper compounds, CuOTf·0.5 PhH, CuI and CuBr, are the best catalysts for oxidation of adamantan-2-ol (**42b**) to ketone **46**.[111–113] The catalyzed reaction can be conducted under mild conditions (20 – 60 °C) at atmospheric pressure with a quantitative yield of the product. However, it is noteworthy that these copper compounds are active only in combination with radical initiators (Nor-AZADO, ABNO and TEMPO). Scheme 52 depicts the mechanism of this transformation in relation to 9-azabicyclo[3.3.1]nonane-*N*-oxyl; the formation of complex **88** is the key step of the reaction.

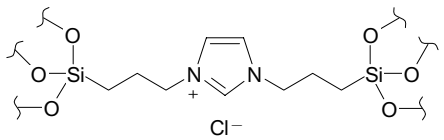
Scheme 52



When palladium compounds are used as catalysts, high pressure of oxygen (30 atm) is required in some cases to attain a high yield of ketone **46** (see Table 6, Nos 6 and 7).[117, 118]

At atmospheric pressure, compound **42b** is oxidized with atmospheric oxygen in the presence of 5 mol.% of the platinum catalyst, Pt(NP)@PMO-IL-2 (see Table 6, No. 8).[119] The process is carried out with long-term heating (90 °C, 26 h) in water in the presence of 1 equiv. of a base (K_2CO_3) and 5 mol.% of the catalyst; the yield of ketone **46** is 99%. The catalyst is composed of ultrasmall platinum nanoparticles ($\leqslant$1.5 nm) deposited on the walls of periodic mesoporous organosilicate, PMO-IL-2, cross-linked by an imidazolium spacer.

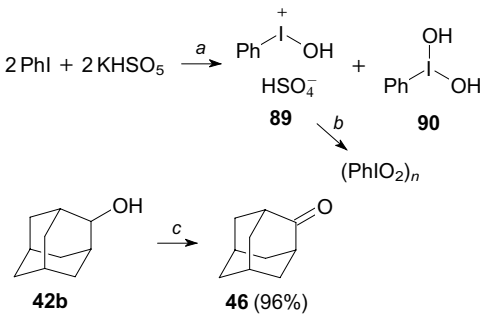
Structure of PMO-IL-2



The bimetallic catalyst $Ru/Ni(OH)_2$ also exhibited high activity in the oxidation of compound **42b** with oxygen (1 atm pressure) (see Table 6, No. 10).[121] The reaction proceeds at 90 °C for 1 h and gives adamantan-2-one in a quantitative yield.

The reaction of adamantan-2-ol (**42b**) with oxone ($KHSO_5$) in the presence of iodobenzene follows an unusual pathway. The reaction starts with the oxidation of iodobenzene to give the protonated (**89**) and hydrated (**90**) forms of iodosobenzene. Then monomeric salt **89** selectively

Scheme 53



(*a*) MeCN, H_2O, 25 °C; (*b*) $KHSO_5$, $RuCl_3$;
(*c*) $KHSO_5$ (1 equiv.), $RuCl_3$ (0.16 mol.%), PhI (5 mol.%), MeCN – H_2O (1 : 1), 25 °C, 0.8 h

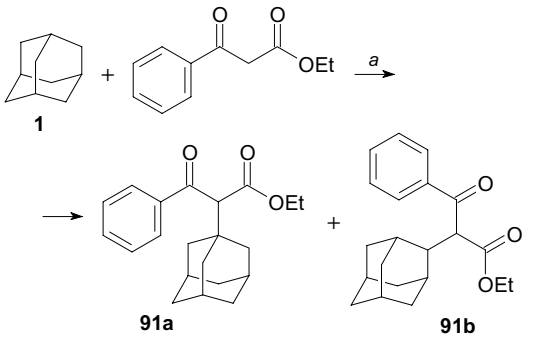
oxidizes adamantanol to ketone **46** in a quantitative yield (Scheme 53).[123]

According to Khusnutdinov *et al.*,[124] adamantan-2-one (**46**) can undergo destructive oxidation on treatment with pentafluoroperbenzoic acid (PFPBA) in the presence of the molybdenum oxo peroxo complex $MoO(O_2)\cdot QOH$ (QOH is 8-hydroxyquinoline) to give lactone — 4-oxaadamantan-5-one (98% yield).

4. Adamantane and its derivatives in alkylation reactions

On treatment with acids, adamantane (**1**) can be converted to a tertiary carbocation, which is relatively stable owing to the electron-donating effect of three neighbouring CH_2 groups.[6] The ease of formation of this carbocation makes it suitable for the alkylation of methylene-active compounds. In particular, the reaction of compound **1** (2.5 mmol) with ethyl benzoylacetate (0.5 mmol) proceeds under the action of *tert*-butyl peroxide as an oxidant in the presence of catalytic amounts of $FeCl_3\cdot 4H_2O$. This gives 1- and 2-substituted adamantanes **91a**,**b** in 4 : 1 ratio and a total yield of 85% (Scheme 54).[125]

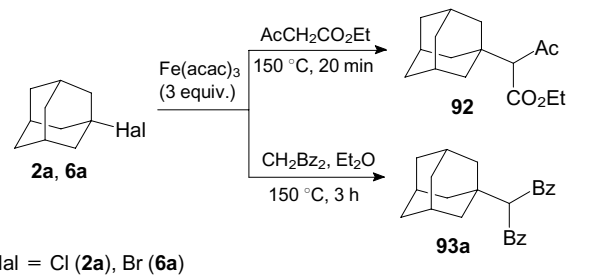
Scheme 54



(*a*) Bu^tOOBu^t (1 mmol), $FeCl_3\cdot 4H_2O$ (0.1 mmol), N_2, PhH (1 ml), 100 °C, 12 h

Compounds with an active hydrogen atom are more readily alkylated by halo-substituted adamantanes. Indeed, adamantyl-substituted dicarbonyl compounds can be obtained by the reaction of 1-haloadamantanes with ethyl acetoacetate, diphenylpropane-1,3-dione and dimethyl malonate in the presence of iron and manganese metal complex catalysts. The reaction of halides **2a** and **6a** catalyzed by iron complexes proceeds with 90% conversion of the sub-

Scheme 55

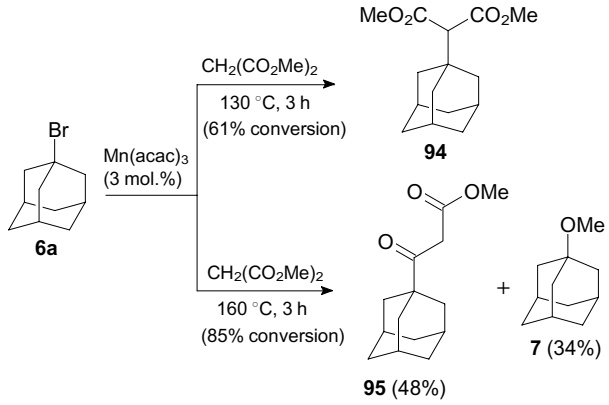


Hal = Cl (**2a**), Br (**6a**)

strate at 150 °C and ends in the formation of products **92** and **93a** (Scheme 55).[126]

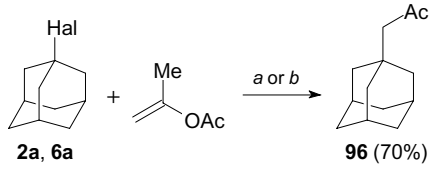
The reaction of 1-bromoadamantane (**6a**) with dimethyl malonate is catalyzed by $Mn(acac)_3$, and the reaction pathway depends on temperature. Indeed, at 130 °C, ester **94** is formed in 3 h, while after temperature rise to 160 °C, 1-adamantyl methyl ether **7** is formed, apart from methyl 3-(1-adamantyl)-3-oxopropanoate (**95**) (Scheme 56).

Scheme 56



Khusnutdinov *et al.*[127] reported the synthesis of 1-adamantylacetone **96** (the active ingredient of the veterinary product used to treat the bird plague) in 70% yield by the reaction of 1-chloro- (**2a**) or 1-bromoadamantane (**6a**) with isopropylidene acetate in the presence of $Fe(acac)_3$ or $Mn(acac)_3$ (Scheme 57, conditions *a*).

Scheme 57

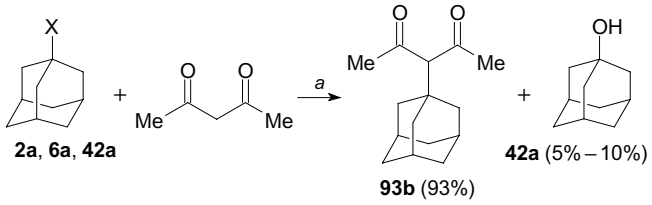


(*a*) $Fe(acac)_3$ or $Mn(acac)_3$ (3 mol.% – 5 mol.%), 110 – 140 °C, 4 – 6 h; (*b*) $MnCl_2 \cdot 4H_2O/SiO_2$ (10 mass % – 20 mass %), 130 – 150 °C, 2 – 3 h

This reaction is highly selective when conducted in the presence of a heterogeneous catalyst, $MnCl_2 \cdot 4H_2O/SiO_2$ (10 mass % – 20 mass %), which does not lose activity over five cycles (see Scheme 57, conditions *b*).

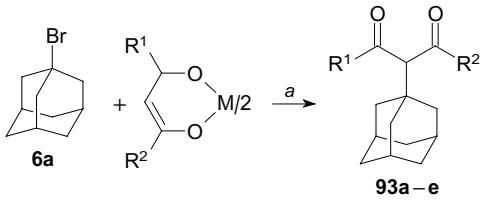
3-(1-Adamantyl)pentane-2,4-dione (**93b**) was obtained [128, 129] in a high yield by the reaction of 1-substituted adamantanes **2a**, **6a** and **42a** with acetylacetone in the presence of catalytic amounts of $Mn(acac)_3$ or $Fe(acac)_3$ (Scheme 58). A known stoichiometric method for the synthesis of α-(1-adamantyl)-β-dicarbonyl compounds **93a – e** is based on the reaction of cobalt(II), copper(II) and palladium β-dicarbonyl complexes with 2 equiv. of bromoadamantane **6a** (Scheme 59).[130 – 132]

Scheme 58



(*a*) $Fe(acac)_3$ or $Mn(acac)_3$ (3 mol.%), 110 – 140 °C, 1 – 6 h (89% – 100% conversion); X = Cl (**2a**), Br (**6a**) OH (**42a**)

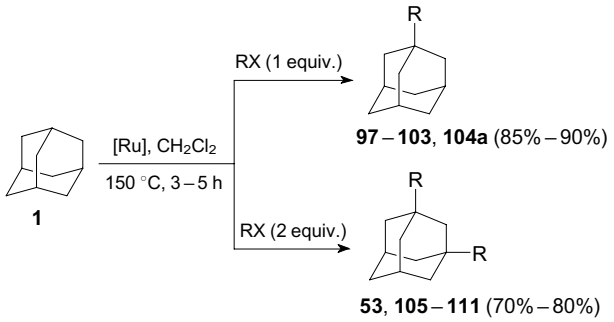
Scheme 59



(*a*) PhCl, Δ, 24 h; M = Co, Cu, Pd; **93**: $R^1 = R^2$ = Ph (**a**, 80%), Me (**b**, 81%), Bu^t (**c**, 31%); R^2 = Me: R^1 = Ph (**d**, 89%), OEt (**e**, 38%)

1-Alkyl(aryl)- (**97 – 103**, **104a**) and 1,3-dialkyl(aryl) adamantane derivatives (**53**, **105 – 111**) were prepared [133] by the reaction of adamantane with chloro-, bromo- and iodoalkanes in the presence of ruthenium compounds ([Ru] : **1** : RX molar ratio is 1 : 100 : 100) in dichloromethane. The process is distinguished by high regioselectivity: the alkylation involves only the bridgehead carbon atom. The product yields depend on the concentration of haloalkane and reaction time and decrease with increasing degree of branching of the alkyl group (Scheme 60).

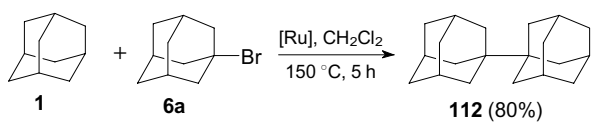
Scheme 60



[Ru] = $RuCl_3$, $Ru(OH)Cl_3$, $Ru(PPh_3)_3Cl_2$; X = Cl, Br, I; R = Me (**53**, **97**), Et (**98**, **105**), Pr^n (**99**, **106**), Pr^i (**100**, **107**), Bu^n (**101**, **108**), Bu^i (**102**, **109**), Bu^t (**103**, **110**), Ph (**104a**, **111**)

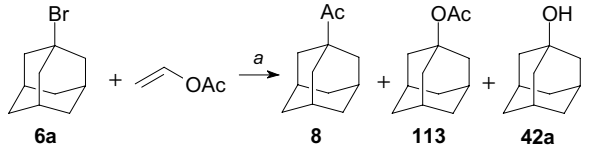
The alkylation of adamantane with 1-chloroadamantane (**2a**) proceeds with difficulty and gives low yields of 1,1′-diadamantyl (**112**) (30% after 3 h). The product yield was increased to 80% by replacing the 1-chloro derivative by 1-bromoadamantane (**6a**) with the reaction being conducted at 150 °C for 5 h (Scheme 61).

Scheme 61



Khusnutdinov *et al.*[134] reported the synthesis of 1-acetyladamantane (**8**) by the reaction of 1-bromoadamantane (**6a**) with vinyl acetate in the presence of manganese complexes (Scheme 62). Apart from the major product, acetoxy derivative **113** and alcohol **42a** were isolated from the reaction mixture (the total yield was 48% – 85%; **8** : **113** : **42a** = 7 : 1 : 2).

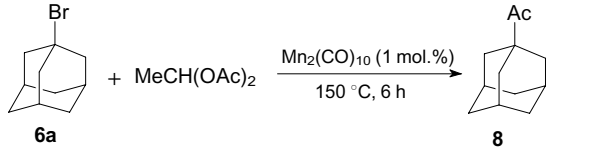
Scheme 62



(*a*) [Mn] (1 mol.% – 2 mol.%), 155 °C, 6 h; [Mn] = $MnCl_2$, $MnBr_2$, $Mn(O_2CC_{17}H_{35})_2$, $Mn(O_2CC_7H_{15})_2$, $Mn(OAc)_2$, $Mn(acac)_2$, $Mn(acac)_3$, $Mn_2(CO)_{10}$; $O_2CC_{17}H_{35}$ is stearate, $O_2CC_7H_{15}$ is 2-ethylhexanoate

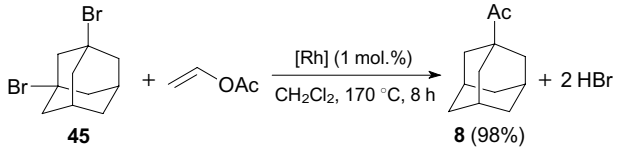
Ethylidene diacetate proved to be a more efficient acylating agent than vinyl acetate; in this case, in the presence of $Mn_2(CO)_{10}$, the yield of compound **8** reached 90% and no by-products were present (Scheme 63).[134]

Scheme 63



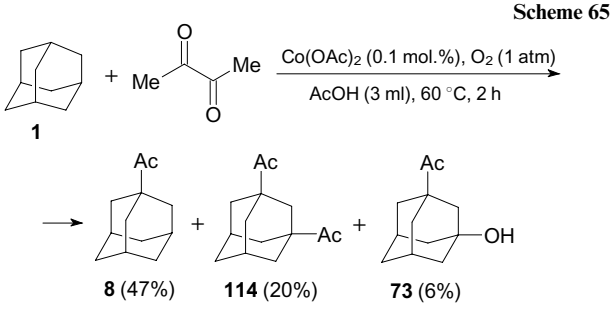
The reaction of vinyl acetate with 1,3-dibromoadamantane (**45**) catalyzed by rhodium complexes, $Rh(PPh_3)_3Cl$ or $[Rh(CO)_2Cl]_2$, affords 1-acetyladamantane (**8**) in a quantitative yield. The reaction is accompanied by the release of free hydrogen bromide (Scheme 64).[135]

Scheme 64



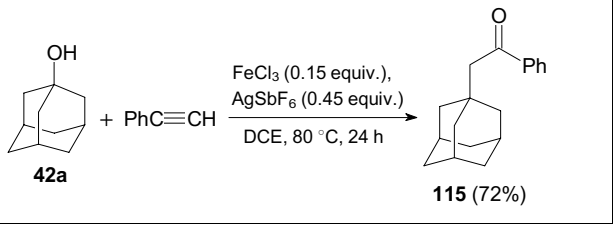
Kishi *et al.*[136] described the acetylation of adamantane with diacetyl under the action of atmospheric oxygen as an oxidant in an acid medium using the $Co(OAc)_2$ catalyst (Scheme 65). The reaction of the substrate (3 mmol) with an excess of diacetyl (6 equiv.) furnished a mixture of products **8**, **114** and **73**, with the substrate conversion being 94%.

Scheme 65



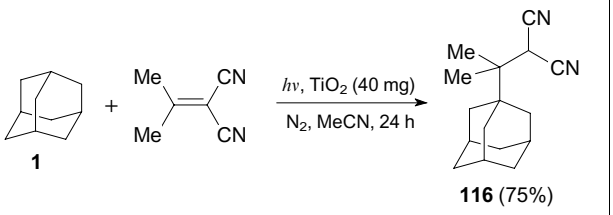
The reaction of phenylacetylene with adamantanol **42a** catalyzed by the $FeCl_3 – AgSbF_6$ system afforded (1-adamantyl)acetophenone **115** (Scheme 66).[137]

Scheme 66



Irradiation of a 0.02 M solution of a mixture of adamantane and isopropylidenemalononitrile in acetonitrile with suspended TiO_2 under an inert atmosphere produces 2-[1-(1-adamantyl)-1-methyl]ethylpropanedicarbonitrile (**116**) (Scheme 67).[138]

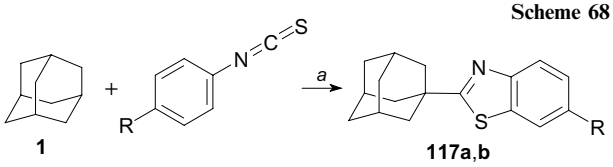
Scheme 67



The $Cu(OAc)_2$-catalyzed one-pot synthesis of 2-(1-adamantyl)benzothiazole (**117a**) and analogous 6-nitro derivative **117b** was accomplished by reactions of the corresponding aryl isothiocyanates with adamantane (**1**) in the presence of di-*tert*-butyl peroxide, which acted as a radical initiator.[139] The authors suggested that the reaction includes the successive formation of the C – C and C – S bonds and, finally, aromatization (Scheme 68).

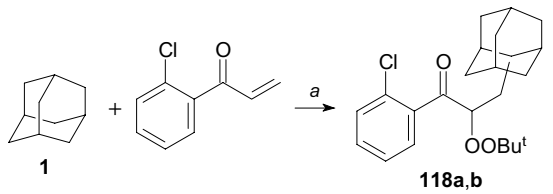
The reaction of *o*-chlorophenyl vinyl ketone with adamantane (10 equiv.) and di-*tert*-butyl peroxide (4 equiv.) carried out in acetonitrile in the presence of CuOAc gives a

Scheme 68



(*a*) $Cu(OAc)_2$ (10 mol.%), Bu^tOOBu^t (4 equiv.), MeCN, 120 °C, 8 h; R = H (**a**, 65%), NO_2 (**b**, 48%)

Scheme 69

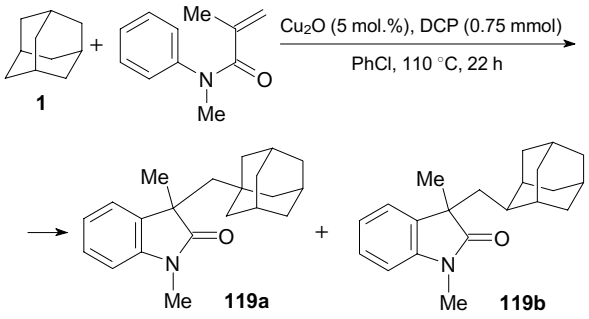


(*a*) CuOAc (5 mol.%), Bu^{t}OOBu^t (4 equiv.), MeCN, 120 °C, 30 min; isomers: 1 (**a**), 2 (**b**)

mixture of 1- and 2-adamantyl peroxy ketones (**118a**,**b**) in 91 : 9 ratio and 60% total yield (Scheme 69).[140]

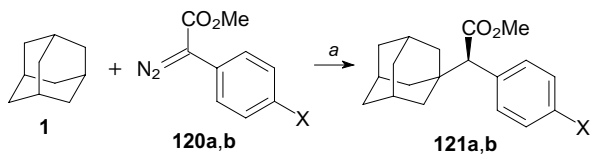
When adamantane (**1**) reacts with *N*-methyl-*N*-phenylacrylamide (0.25 mmol) in chlorobenzene with Cu_2O as the catalyst and dicumyl peroxide (DCP) as a radical initiator, (1- and 2-adamantylmethyl)oxindoles **119a**,**b** are formed in 6 : 1 ratio and in a total yield of 68% (Scheme 70).[141]

Scheme 70

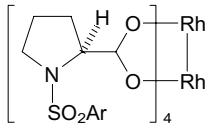


In some studies, functionalization of adamantane **1** with C–C bond formation was accomplished by insertion of carbenes into the CH bond under the action of rhodium complexes. For example, dirhodium tetrakis[(*S*)-(*N*-dodecylbenzenesulfonyl)prolinate], Rh_2((*S*)-DOSP)$_4$ (**XIII**), catalyzes decomposition of methyl aryldiazoacetates **120a**–**c** with generation of carbenes and subsequent carbene insertion into the tertiary CH bond of adamantane, thus giving products **121a**,**b** and **122** with a high enantiomeric excess (*ee*) (Schemes 71, 72).[142–144]

Scheme 71

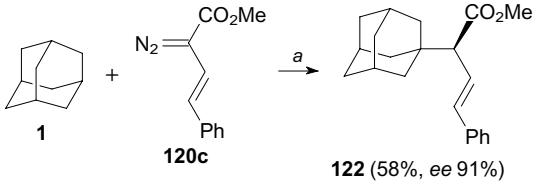


(*a*) Rh_2((*S*)-DOSP)$_4$ (**XIII**, 1 mol.%), hexane, 24 °C;
X = H (**a**, 67%, 90% *ee*), Br (**b**, 70%, 96% *ee*);

XIII =  (Ar = 4-n-$C_{12}H_{25}C_6H_4$)

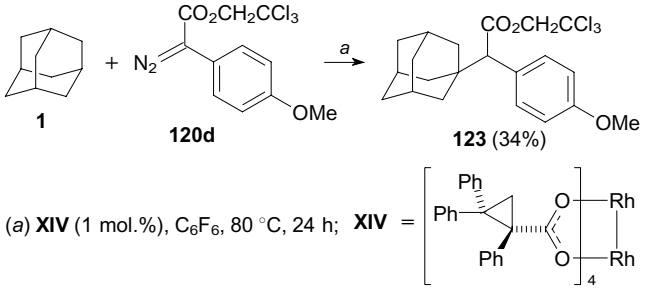
The reaction of 2,2,2-trichloroethyl (4-methoxyphenyl)-diazoacetate (**120d**) with adamantane in hexafluorobenzene in the presence of Rh catalyst **XIV** proceeds in a similar way, giving rise to derivative **123** in a moderate yield (Scheme 73).[145]

Scheme 72



(*a*) Rh_2((*S*)-DOSP)$_4$ (**XIII**, 1 mol.%), hexane, Δ

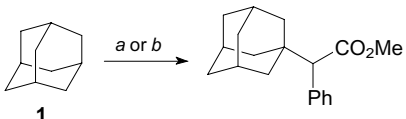
Scheme 73



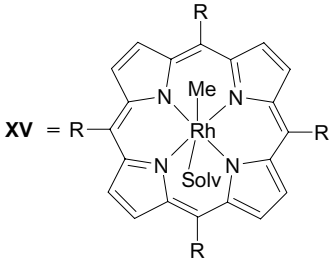
(*a*) **XIV** (1 mol.%), C_6F_6, 80 °C, 24 h; **XIV** =

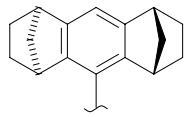
The reaction of phenyldiazoacetate **120a** with compound **1** (2 equiv.) in the presence of the chiral catalyst [Rh(D$_4$-por*)(Me)-(MeOH)] {**XV**, H_2(D$_4$-por*) is *meso*-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl]porphyrin} for 4 h at 60 °C involves the asymmetric induction and affords the product of insertion into the tertiary C–H bond of adamantane, that is, compound **121a**, in a rather high optical yield (88% *ee*) and in a chemical yield of 78% (Scheme 74, conditions *a*).[146]

Scheme 74

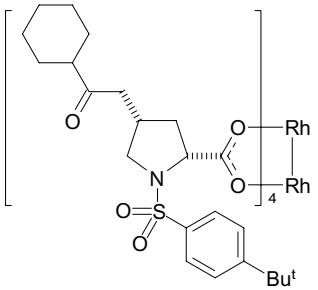


(*a*) N_2C(Ph)CO_2Me (**120a**), **XV** (0.1 mol.%), DCE, 60 °C, 4 h;
(*b*) N_2C(Ph)CO_2Me (**120a**), **XVI** (1 mol.%), hexane, 20 °C, 1 h;

XV = 

R = 

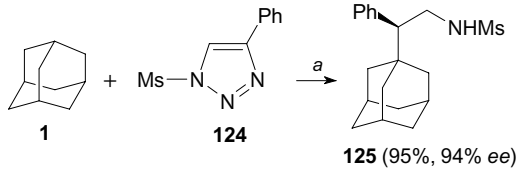
Solv = MeOH

XVI = 

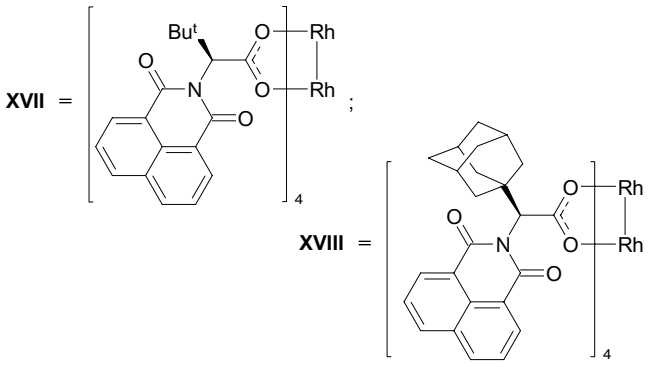
Chiral rhodium complex **XVI**, containing a proline derivative as a ligand in the coordination sphere, showed a higher enantioselectivity (93% *ee*) in a similar carbene insertion reaction; the carbene was generated *in situ* from aryldiazoacetate **120a** (see Scheme 74, conditions *b*).[147]

A unique method for generation of azavinyl carbene was reported.[148] The azavinyl carbene was generated from 1-methanesulfonyl-4-phenyltriazole (**124**), which reacted with adamantane in the presence of chiral rhodium complex **XVII** or **XVIII** to give, after reduction, adamantane derivative **125** (Scheme 75). According to the authors' assumption, first, triazole **124** decomposed under the action of the Rh catalyst to give off a nitrogen molecule, thus yielding rhodium carbene complex **126**, which attacked the adamantane molecule at the C(1)–H bond to give chiral *N*-sulfonylimine **127**. After reduction, product **125** was formed in a quantitative chemical yield with high enantioselectivity (Scheme 76).

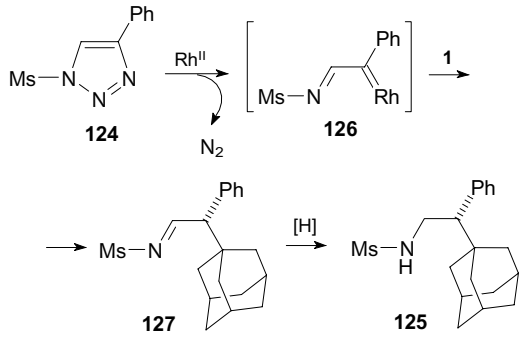
Scheme 75



(*a*) 1) **XVII** or **XVIII** (0.5 mol.%), $CHCl_3$, 25 °C;
2) $LiAlH_4$ (1.2 экв.), 0 °C;

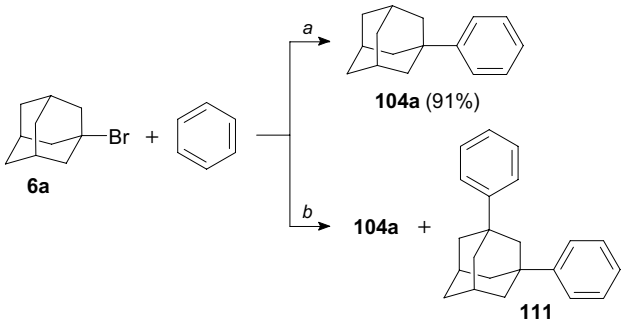


Scheme 76



An efficient catalyst for benzene alkylation with 1-bromoadamantane (**6a**) is $Mo(CO)_6$. The reaction conducted at 140 °C for 1 h gave only one product, 1-phenyladamantane (**104a**). When the reaction duration was increased to 2 h, complete conversion of 1-bromoadamantane resulted in the formation of 1,3-diphenyladamantane (**111**), apart from 1-phenyl derivative **104a**, the ratio being 1 : 9 (Scheme 77).[149]

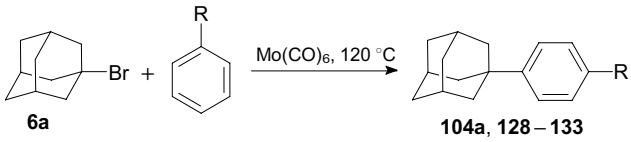
Scheme 77



(*a*) $Mo(CO)_6$ (3 mol.%), 140 °C, 1 h; (*b*) $Mo(CO)_6$ (3 mol.%), 140 °C, 2 h

The reaction of 1-bromoadamantane (**6a**) with monosubstituted arenes in the presence of $Mo(CO)_6$ is directed only to the *para*-position and the substituent nature does not have a significant effect on the yield of products **104a** and **128**–**133** (Scheme 78).[149]

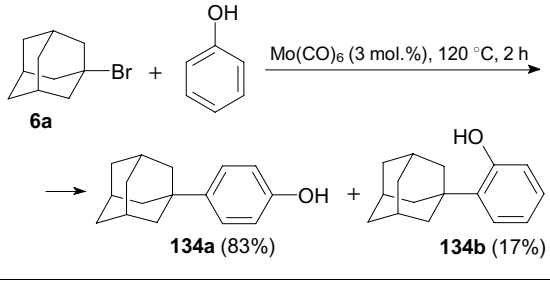
Scheme 78



R = H (**104a**), Me (**128**), Et (**129**), Pr^i (**130**), CH_2OH (**131**), OMe (**132**), CN (**133**)

An exception is phenol, the reaction of which affords a mixture of two isomers, 4-(1-adamantyl)phenol (**134a**) and 2-(1-adamantyl)phenol (**134b**), with 99% conversion of the substrate (Scheme 79).

Scheme 79

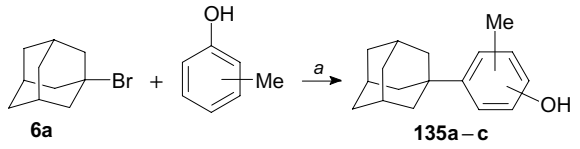


1-Bromoadamantane (**6a**) reacts with *o*-cresol in the presence of $Mo(CO)_6$ at 120 °C for 30 min to give only one product — 4-(1-adamantyl)-2-methylphenol (**135a**) in a quantitative yield (Scheme 80; the substituent positions are indicated with respect to Ad).[149] The reactions with *meta*- and *para*-cresols require a longer time, 3 and 2 h, and the yields of products **135b**,**c** are 84% and 90%, respectively.

2,6-Xylenol does not react with bromide **6a** even on long-term heating (12–14 h). The alkylation of 3,4- and 3,5-xylenols with 1-bromoadamantane gives selectively one of the possible isomers, 2-(1-adamantyl)-4,5-dimethyl- (**136a**) or 2-(1-adamantyl)-3,5-dimethylphenol (**136b**), respectively (Scheme 81).[149]

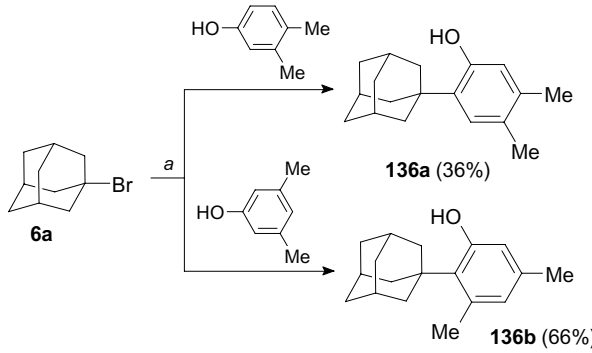
1-(1-Adamantyl)-2,3,5,6-tetramethylbenzene (**137**) is formed from 1-bromoadamantane and durene under similar conditions (Scheme 82).[149]

Scheme 80



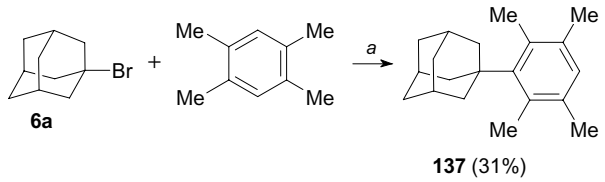
(*a*) $Mo(CO)_6$ (3 mol.%), 120 °C, 3 h;
isomers of **135**: 3-Me, 4-OH (**a**); 2-OH, 4-Me (**b**); 2-OH, 5-Me (**c**)

Scheme 81



(*a*) $Mo(CO)_6$ (3 mol.%), 120 °C, 3 h

Scheme 82

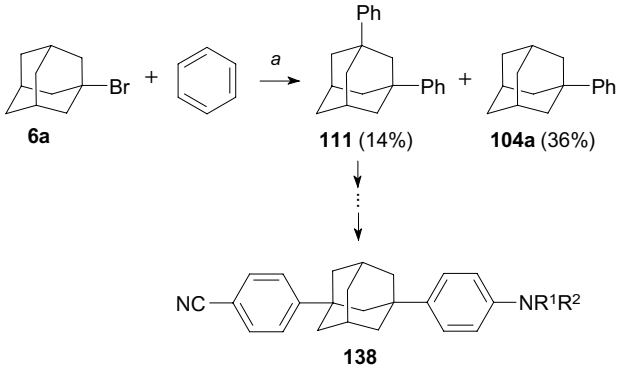


(*a*) $Mo(CO)_6$ (3 mol.%), 120 °C, 3 h

Refluxing compound **6a** (4.64 mmol) in 20 ml of benzene in the presence of a catalytic amount of $FeCl_3$ for 2 h produces a mixture of 1-phenyl- (**104a**) and 1,3-diphenyladamantanes (**111**). The latter is significant for practical purposes: further functionalization of its aromatic rings with introduction of CN and NR^1R^2 groups (R^1, R^2 is alkyl) gives rise to compounds **138**, which find use as nonsteroidal progesterone receptor antagonists (Scheme 83).[150]

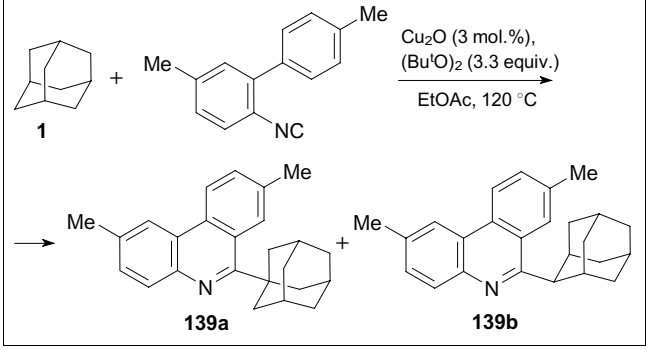
Zhu *et al.*[151] described an unusual reaction of adamantane (10 equiv.) with 4′,5-dimethylbiphenyl-2-isonitrile (0.2 mmol) induced by di-*tert*-butyl peroxide (3.5 equiv.) as an oxidant, which results in the formation of 6-(1-

Scheme 83



(*a*) $FeCl_3$ (1.4 mmol), Δ, 2 h

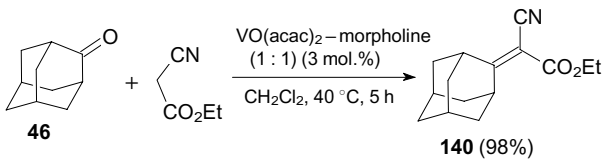
Scheme 84



adamantyl)- and 6-(2-adamantyl)phenanthridines **139a**,**b** (51% total yield, 2 : 1 ratio), formed *via* cyclization and alkylation steps (Scheme 84).

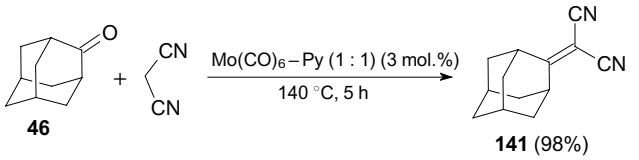
The $VO(acac)_2$–morpholine system catalyzes the condensation of adamantan-2-one (**46**) with ethyl cyanoacetate to give ethyl 2-adamantylidenecyanoacetate **140** in a quantitative yield (Scheme 85).[152]

Scheme 85



A similar reaction with malononitrile is induced by the $Mo(CO)_6$–Py catalytic system under more drastic conditions and gives product **141** (Scheme 86).[153]

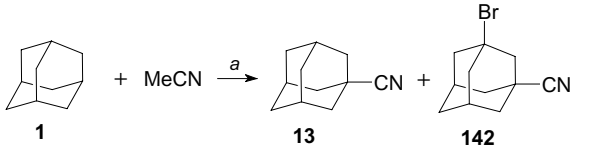
Scheme 86



5. Synthesis of nitriles

Direct cyanation of adamantane with acetonitrile was accomplished[154] in the presence of molybdenum hexacarbonyl and tetrabromomethane. The reaction proceeds quantitatively at a temperature of 140–160 °C for 5–6 h (Scheme 87). Nitrile **13** is formed as the major product and bromo derivative **142** is a minor product (3.7 : 1 ratio).

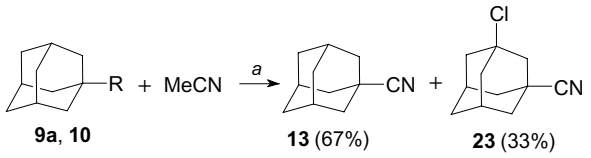
Scheme 87



(*a*) $Mo(CO)_6$ (3 mol.%), CBr_4, 140 °C, 6 h

Adamantane-1-carboxylic acid (**9a**) and its chloride **10** react with acetonitrile in the presence of $VO(acac)_2$ in CCl_4 by an unusual pathway. This reaction gives adamantane-1-

Scheme 88

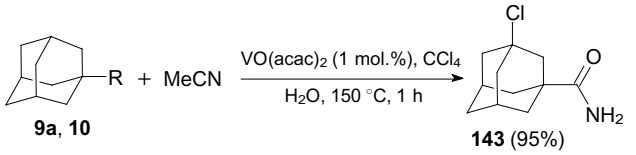


(*a*) $VO(acac)_2$ (1 mol.%), CCl_4, 150 °C, 1 – 3 h; R = CO_2H (**9a**), C(O)Cl (**10**)

carbonitrile (**13**) and 1-chloro-3-cyanoadamantane (**23**); that is, the CO_2H and C(O)Cl groups in compounds **9a** and **10** are replaced by the CN group with simultaneous chlorination of the bridgehead carbon atom (Scheme 88).[155]

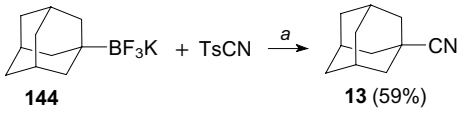
When this reaction is carried out in the presence of water, 3-chloroadamantane-1-carboxamide **143** is formed as the only product (Scheme 89).

Scheme 89



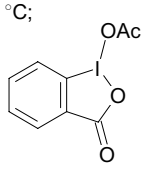
Under visible light irradiation ($\lambda_{max} = 425 \pm 15$ nm; blue LED as a light source), the ruthenium complex $[Ru(Bpy)_3](PF_6)_2$ catalyzes substitutive cyanation of potassium 1-adamantyl trifluoroborate (**144**) with TsCN. The reaction proceeds smoothly with the use of a mild oxidant, 1-acetoxy-1,2- benziodoxol-3(1*H*)-one (BI-OAc, **145**). In the authors' opinion, the role of the oxidant is to prevent the competitive quenching of the excited ruthenium catalyst with 1-adamantyltrifluoroborate **144**. An increase in the oxidant amount promotes an increase in the yield of the target nitrile **13** (Scheme 90).[156]

Scheme 90



(*a*) $[Ru(Bpy)_3](PF_6)_2$ (2 mol.%), BI-OAc (**145**), blue LEDs, CH_2Cl_2, H_2O, 25 °C;

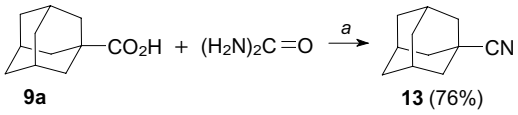
145 =



Furuya *et al.*[157] described a one-pot synthesis of compound **13** by the reaction of adamantane-1-carboxylic acid (1 mmol) with urea (3 equiv.) in the presence of a catalytic amount of perrhenic acid [$(HO)ReO_3$] and 3,5-bis(trifluoromethyl)phenylboronic acid under long-term azeotropic reflux in mesitylene (1,3,5-trimethylbenzene) (Scheme 91).

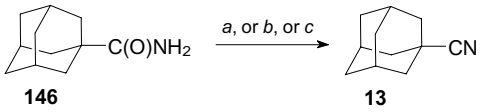
There are several examples of adamantane-1-carbonitrile **13** synthesis from the corresponding amide catalyzed by metal complexes.[158] In particular, the iron carbonyl complexes $Fe_2(CO)_9$ and $[Et_3NH][HFe_3(CO)_{11}]$ catalyze dehydration of adamantane-1-carboxamide (**146**) on treatment with $(EtO)_2MeSiH$ to give nitrile **13** in a quantitative yield (Scheme 92, conditions *a*).

Scheme 91



(*a*) $(HO)ReO_3$ (10 mol.%), 3,5-$(F_3C)_2C_6H_3B(OH)_2$ (10 mol.%), mesytilene (8 ml), Δ, 20 h

Scheme 92



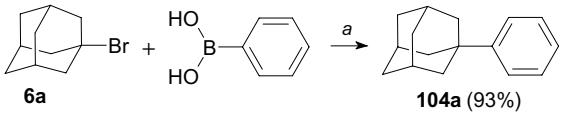
(*a*) $(EtO)_2MeSiH$ (3 equiv.), $Fe_2(CO)_9$ or $[Et_3NH][HFe_3(CO)_{11}]$ (4 mol.%), PhMe, 100 °C, 3 h (99% yield); (*b*) $(HO)ReO_3$ (0.9 mol.% – 1 mol.%), mesitylene, 165 – 170 °C, 1 day (84% yield); (*c*) MSTFA (2 equiv.), CuCl (2.5 mol.%), PhMe, 100 °C, 24 h (92% yield)

Nevertheless, one more example is the heating of amide **146** under azeotropic reflux in mesitylene (165 – 170 °C) for 24 h in the presence of [$(HO)ReO_3$] (conditions *b*),[159] while dehydration of this amide induced by CuCl requires the presence of a dehydrating agent — *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (MSTFA) (conditions *c*).[160 – 163]

6. Halogen derivatives of adamantanes in the cross-coupling reactions

The Suzuki cross-coupling of 1-bromoadamantane (**6a**) with phenylboronic acid giving 1-phenyladamantane (**104a**) is catalyzed by $Pd(OAc)_2$ in the presence of water-soluble pyridine-modified β-dextrins (Py-β-CD). A base is required for the reaction to successfully proceed. When Cs_2CO_3 or K_2CO_3 base is used, the yield of product **104a** is moderate, while in the case of K_3PO_4 the yield is substantially higher (Scheme 93).[164]

Scheme 93

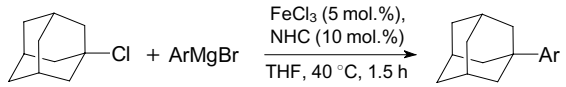


(*a*) $Pd(OAc)_2$ (0.5 mol.%), Py-β-CD (1 mol.%), K_3PO_4 (2 equiv.), H_2O, 80 °C, 0.5 h

Iron(III) chloride activated by N-heterocyclic carbene (NHC) ligands is an efficient catalyst for the cross-coupling of 1-chloro- (**2a**) and 1,3-dichloroadamantanes (**3**) with 2 equiv. of the Grignard reagent based on the corresponding arenes. As a result, aryl- (**104a**, **132**, **147**) and diaryladamantanes (**111**, **148**, **149**) are obtained (Schemes 94 and 95).[165]

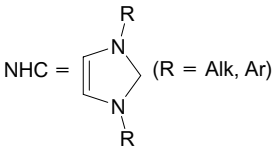
A complex of $FeCl_2$ with the *o*-phenylenebis(phosphine) ligand (**XIX**) showed a high activity in the cross-coupling of bromide **6a** with PhMgBr taken in an equimolar ratio under relatively mild conditions (Scheme 96).[166]

Scheme 94

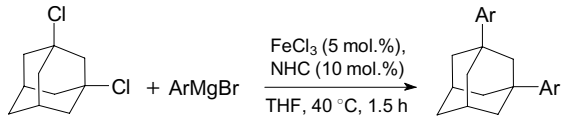


2a **104a**, **132**, **147** (87% – 90%)

Ar = Ph (**104a**), 4-$MeOC_6H_4$ (**132**), 4-FC_6H_4 (**147**);



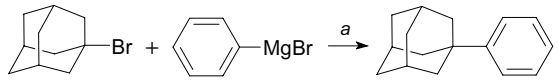
Scheme 95



3 **111**, **148**, **149** (60% – 68%)

Ar = Ph (**111**), 4-$MeOC_6H_4$ (**148**), 4-FC_6H_4 (**149**)

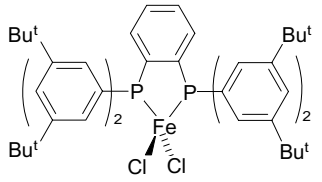
Scheme 96



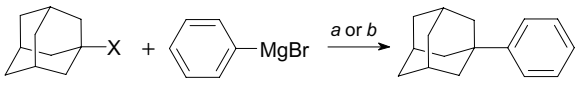
6a **104a** (81%)

(*a*) **XIX** (0.5 mol.%), THF, 40 °C, 3 h;

XIX =



Scheme 97



2a,**6a** **104a** (69% – 78%)

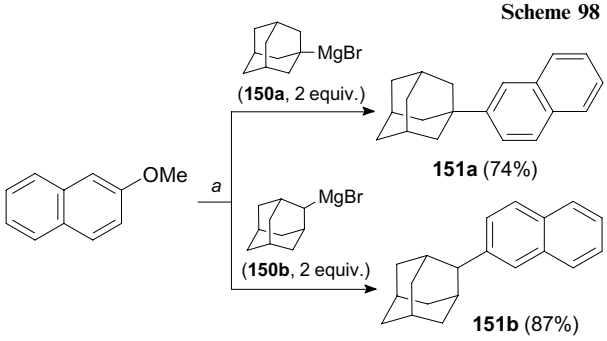
(*a*) CuI (10 mol.%), PhMe, 80 °C, 18 h; (*b*) AgBr/KF (10 mol.%), – 10 °C, 15 h

The reactions of 1-chloro(bromo)adamantanes with PhMgBr (1 : 1 ratio) are also catalyzed by copper(I) and silver salts (Scheme 97).[167, 168]

The cross-coupling of 1-adamantyl- (**150a**) and 2-adamantylmagnesium bromides (**150b**) with 2-methoxynaphthalene was accomplished using the $Ni(OAc)_2$ catalyst with the NHC ligand (R = cyclo-C_6H_{11}). This resulted in the synthesis of naphthyl-substituted adamantanes **151a**,**b** (Scheme 98).[169]

An unusual type of cross-coupling of the phthalimide ester of adamantane-1-carboxylic acid **152a** with phenylzinc chloride (3 equiv.), accompanied by elimination of CO_2 and formation of 2-phenyladamantane (**104b**), is catalyzed by a nickel complex with ethylene glycol dimethyl ether (1,2-

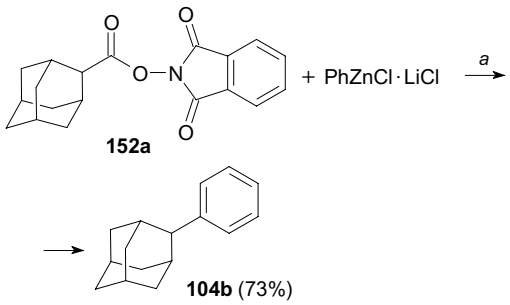
Scheme 98



151a (74%) **151b** (87%)

(*a*) $Ni(OAc)_2$ (5 mol.%), ICy · HCl (10 mol.%), PhMe, 100 °C, 18 h; ICy is 1,3-di(cyclohexyl)imidazol-2-ylidene

Scheme 99



152a

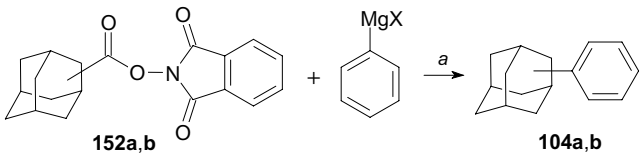
104b (73%)

(*a*) $NiCl_2$ · DME (20 mol.%), Bu^t_2Bpy, THF – DMF (3 : 2), 25 °C, 16 h

dimethoxyethane, DME) in the presence of 4,4′-di-*tert*-butylbipyridine (Bu^t_2Bpy) (Scheme 99).[170]

A similar reaction of isomeric phthalimide esters of adamantanecarboxylic acids **152a**,**b** with the Grignard reagents and organozinc compounds occurs in the presence of $Fe(acac)_3$ activated by a bis-phosphine ligand — 1,2-bis(diphenylphosphino)benzene (dppBz). The yields of cross-coupling products **104a**,**b** are 59% – 67% (Scheme 100).[171]

Scheme 100



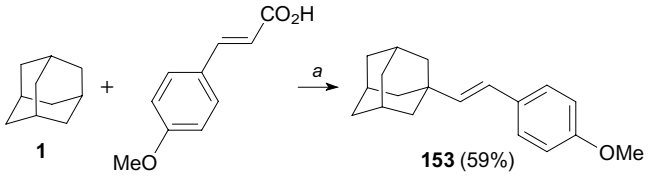
152a,**b** **104a**,**b**

(*a*) $Fe(acac)_3$ (10 mol.%), dppBz (12 mol.%), THF, DMF, 0 °C, 1 h; X = Cl, Br

The reaction of adamantane (**1**) with 4-methoxycinnamic acid catalyzed by copper salt and *tert*-butyl hydroperoxide is also accompanied by decarboxylation and subsequent alkenylation of adamantane, producing (*E*)-β-adamantylstyrene **153** (Scheme 101).[172]

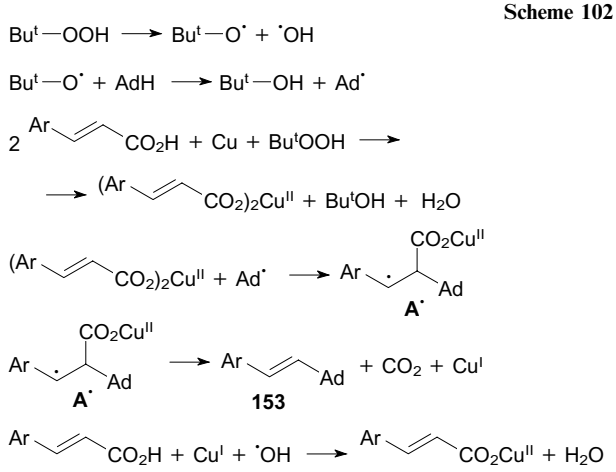
The authors proposed a possible reaction mechanism according to which the initial step is decomposition of *tert*-butyl hydroperoxide giving the $Bu^tO^•$ and $HO^•$ radicals. Then the $Bu^tO^•$ radical reacts with adamantane, which is thus converted to the $Ad^•$ radical. The latter attacks the copper cinnamate, yielding radical $\mathbf{A}^•$, which decomposes with the release of CO_2, thus giving the final product (Scheme 102).

Scheme 101



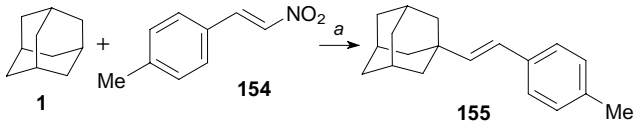
(*a*) Bu^{t}OOH (1.2 equiv.), $Cu(OAc)_2 \cdot H_2O$ (2 mol.%), 110 °C, 12 h

Scheme 102



The cross-coupling of adamantane with nitrostyrene **154** (3 equiv.) follows a similar pathway with simultaneous elimination of NO_2. The reaction proceeds in the presence of copper powder and di-*tert*-butyl peroxide. Compound **155** was isolated in a good yield (84%) (Scheme 103).[173]

Scheme 103



(*a*) Cu (1 mol.%), Bu^{t}OOBu^t (2 equiv.), DCE, 110 °C, 8 h

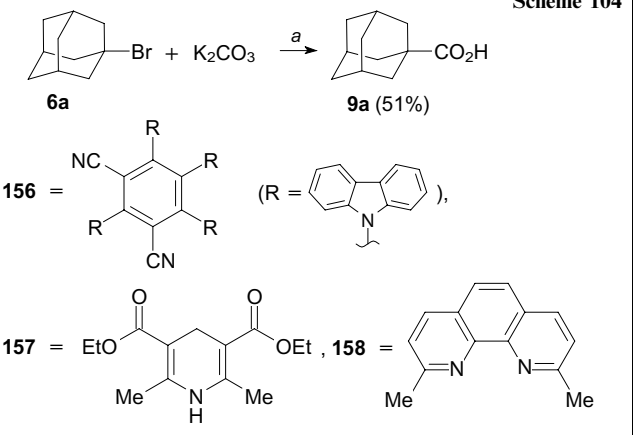
7. Carbonylation and carboxylation of adamantane and its derivatives

Adamantane carbonylation and carboxylation can be induced by superacids: $HF-SbF_5$, SbF_5-TfOH and $B(OTf)-TfOH$ systems and CF_3CO_3H.[6] However, when the reactions are conducted in the presence of metal complex catalysts, no superacids are required.

On exposure to visible light, the $NiBr_2 \cdot DME$ complex catalyzes carboxylation of 1-bromoadamantane (**6a**) with CO_2 generated *in situ* from K_2CO_3 (1 equiv.). The reaction proceeds under mild conditions and yields acid **9a**. 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (**156**) was used as the photosensitizer; Hantzsch ester **157** and neocuproine (**158**) were also added to the reaction mixture (Scheme 104).[174]

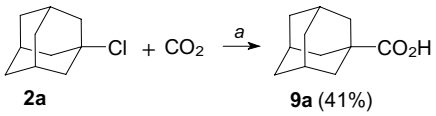
1-Chloroadamantane (**2a**) undergoes a similar reaction with CO_2 (1 atm) catalyzed by the $NiBr_2 \cdot DME-2,9$-di-n-butyl-4,7-dimethyl-1,10-phenanthroline (**159**) system. Zinc metal serves as the chlorine acceptor in this case (Scheme 105).[175]

Scheme 104

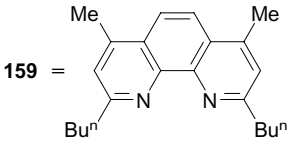


(*a*) **156** (1 mol.%), $NiBr_2 \cdot DME$ (10 mol.%), **157** (2 equiv.), **158** (0.04 mol.%), 4 Å zeolite, CO_2, DMF, blue LEDs, 20 °C, 24 h

Scheme 105

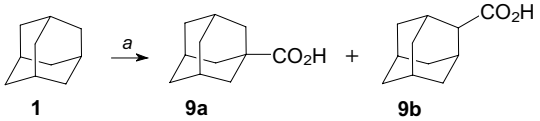


(*a*) $NiBr_2 \cdot DME$ (10 mol.%), **159** (24 mol.%), TBAB, Zn (3 equiv.), DMF, 80 °C, 20 h;



There are several reported examples of the synthesis of adamantanecarboxylic acid **9a** by oxidative carbonylation of adamantane on treatment with CO and the $K_2S_2O_8$ oxidant in the presence of metal complex catalysts. One such reaction proceeds in an autoclave, is catalyzed by a water-soluble copper complex with a triethanolamine ligand and affords a mixture of 1- and 2-adamantanecarboxylic acids **9a**,**b** (1 : 14 ratio) in a total yield of 73% (Scheme 106).[176]

Scheme 106

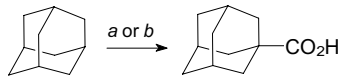


(*a*) CO (20 atm), $K_2S_2O_8$ (1.5 equiv.), $[OCu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4] \cdot (BF_4)_2$ (4 mmol.%), $H_2O-MeCN$ (1 : 2), 50 °C, 6 h

A similar reaction of adamantane (5 ml) with CO (20 atm) proceeding in the presence of $K_2S_2O_8$ and $Pd(OAc)_2$ under mild conditions selectively gives adamantane-1-carboxylic acid (**9a**) in 938% yield based on Pd (Scheme 107, conditions *a*).[177]

The oxidative carboxylation of compound **1** (10 mmol) by treatment with CO and oxygen in acetic acid is catalyzed by the $Co(acac)_2-1$-hydroxy-6-trifluoromethylbenzotriazole system; the yield of acid **9a** is 26% (see Scheme 107, conditions *b*).[178]

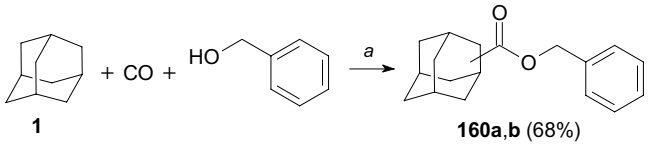
Scheme 107



(*a*) CO (20 atm), $K_2S_2O_8$ (9 mmol), $Pd(OAc)_2$ (0.2 mmol), CF_3CO_2H (3.3 ml), 20 °C, 20 h;
(*b*) CO (1 litre), O_2 (0.5 litre), $Co(acac)_2$ (0.005 mmol), 1-hydroxy-6-trifluoromethylbenzotriazole (1 mmol), AcOH (25 ml), 60 °C, 6 h

Lu *et al.*[179] performed the $PdCl_2-PPh_3$-catalyzed oxidative benzyloxycarbonylation of adamantane (1 mmol) at a carbon monoxide pressure of 5 atm in the presence of *tert*-butyl peroxide. The reaction afforded a mixture of isomeric benzyl adamantanecarboxylates **160a**,**b** in 3 : 1 ratio in a total yield of 68% (Scheme 108).

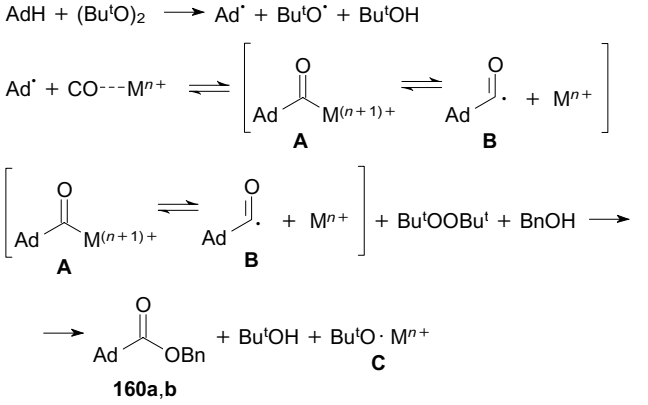
Scheme 108



(*a*) $PdCl_2$ (10 mol.%), PPh_3 (22 mol.%), Bu^tOOBu^t (4 equiv.), $PhCF_3$ (0.5 ml), DCE (0.5 ml), 110 °C, 24 h; isomers: 1 (**a**), 2 (**b**)

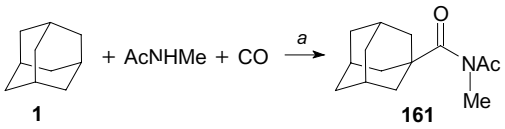
According to the mechanism proposed by the authors, the process starts with elimination of a hydrogen atom from adamantane under the action of *tert*-butyl peroxide to generate the Ad$^\bullet$ radical. In the next step, the Ad$^\bullet$ radical attacks a metal-coordinated CO molecule to give metal acyl intermediate **A**. In the final step, acyl radical **B** reacts with benzyl alcohol and *tert*-butyl peroxide to give target product **160** and complex **C** (Scheme 109).

Scheme 109



Carbonylation of compound **1** (0.5 mmol) with carbon monoxide (20 bar) induced by *N*-methylacetamide in the presence of the copper catalyst $CuBr(Me_2S)-(MeO)Phen$ [(MeO)Phen is 4-methoxy-1,10-phenanthroline] follows an unusual pathway. The reaction involves only the $C(sp^3)-H$ bond and gives adamantylmethylimide **161** in 31% yield (Scheme 110).[6, 180]

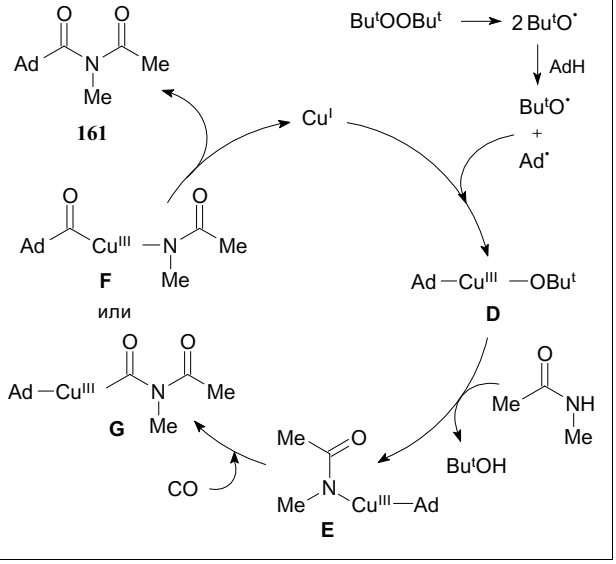
Scheme 110



(*a*) $CuBr(Me_2S)$ (5 mol.%), (MeO)Phen (22 mol.%), Bu^tOOBu^t (0.75 mmol), 120 °C, 24 h

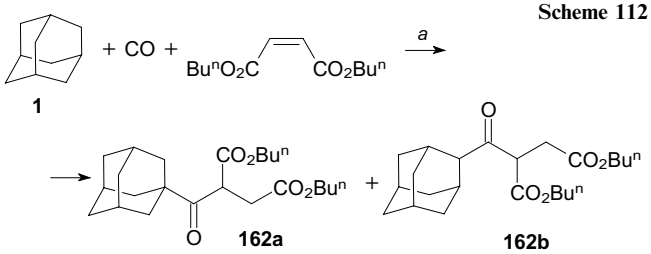
The authors proposed a reaction mechanism that includes, first, degradation of *tert*-butyl peroxide to give two $Bu^tO^\bullet$ radicals. The radical attacks adamantane, which is thus converted to the Ad$^\bullet$ radical. In the next step, copper(III) complex **D** is formed, which then reacts with *N*-methylacetamide to give intermediate **E**. This is followed by the insertion of CO into the Cu–N bond with the formation of intermediate complexes **F** or **G**. The latter undergo reductive elimination to give target product **161** and the active form of the Cu^I catalyst, which continues the catalytic cycle (Scheme 111).

Scheme 111



The photocatalytic carbonylation (CO pressure of 80 atm) of adamantane (**1**) at the tertiary and secondary carbon atoms with the simultaneous addition of di-n-butyl maleate proceeds on irradiation of an acetonitrile solution of the reactants with a xenon lamp for 20 h in the presence of tetra(n-butyl)ammonium decatungstate. The total yield of products **162a**,**b** is 35% and their ratio is 1 : 1.3 (Scheme 112).[181]

Scheme 112

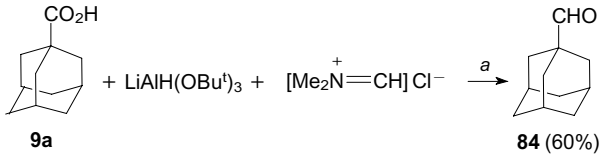


(*a*) *hν* (Xe lamp, 500 W), $(Bu^n_4N)_4W_{10}O_{12}$ (4 mol.%), MeCN, 20 h

8. Synthesis of aldehydes, ethers and esters based on adamantane

Metal complex catalysts are utilized in the synthesis of adamantane-1-carbaldehyde (**84**) by the reduction of adamantanecarboxylic acid **9a** using various procedures. Fujisawa *et al.*[182] accomplished the CuI-catalyzed selective reduction of adamantane-1-carboxylic acid to aldehyde **84** on treatment with $LiAlH(OBu^t)_3$ (2 equiv.) and chloroiminium salt (Scheme 113).

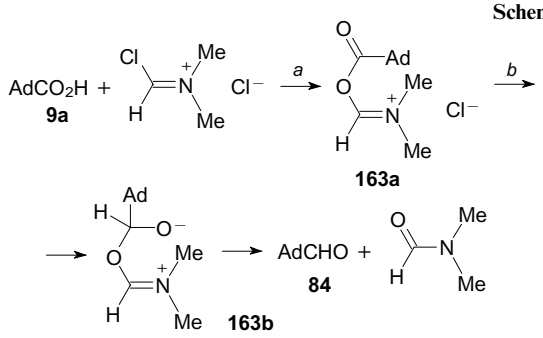
Scheme 113



(*a*) CuI (10 mol.%), Py, −30 → −78 °C

The authors assumed that the conversion of adamantane-1-carboxylic acid to aldehyde **84** proceeds *via* the *in situ* formation of iminium salt **163a**. Then salt **163a** is reduced by $LiAlH(OBu^t)_3$ under the action of CuI to give a stable intermediate, betaine **163b**, which is converted to aldehyde **84** after DMF elimination (Scheme 114).

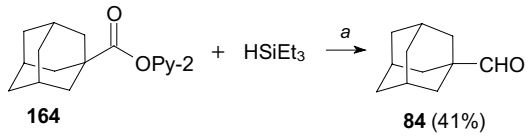
Scheme 114



(*a*) Py, −30 °C; (*b*) $LiAlH(OBu^t)_3$, CuI, −78 °C

Adamantane-1-carbaldehyde can be prepared by reduction of 2-pyridyl adamantane-1-carboxylate (**164**, 1 mmol) with triethylsilane (2 mmol) catalyzed by the $Pd(OAc)_2 - PPh_3$ system (Scheme 115).[183]

Scheme 115

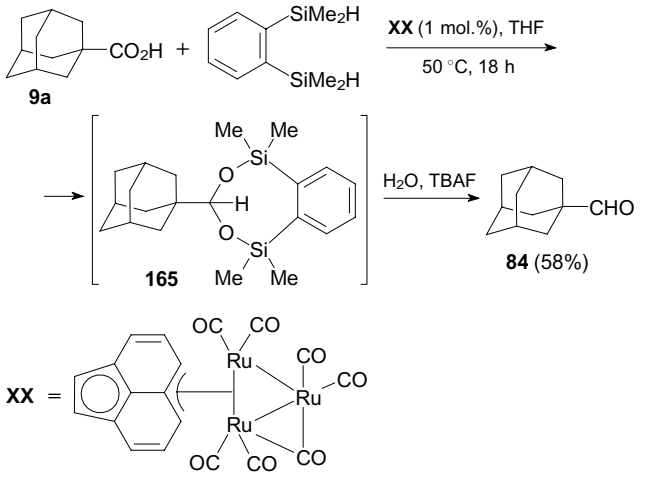


(*a*) $Pd(OAc)_2$ (0.03 mmol), Ph_3P (0.09 mmol), DMF (2 ml), 60 °C, 12 h

Adamantanecarboxylic acid **9a** was also reduced to aldehyde **84** with 1,2-bis(dimethylsilyl)benzene in the presence of Ru catalyst **XX**. Intermediate **165** was hydrolyzed with an aqueous solution of tetra-n-butylammonium fluoride (Scheme 116).[184]

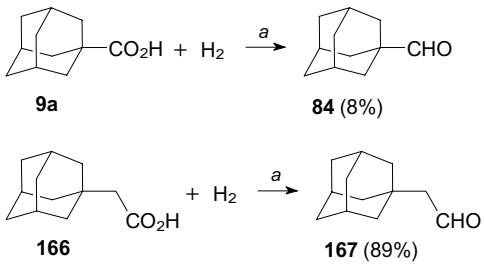
Adamantane-1-carbaldehyde was prepared in a moderate yield (8%) by hydrogenation of acid **9a** (2 mmol) with hydrogen under a 3 MPa pressure in the presence of 2,2-

Scheme 116



dimethylpropionic anhydride and palladium-based catalytic systems, $Pd(OAc)_2 - Ph_3P$ and $Pd(OAc)_2 - (4\text{-}MeC_6H_4)_3P$. Under analogous conditions, 1-adamantylacetic acid (**166**) is converted to 1-adamantylacetaldehyde **167** in a high yield (Scheme 117).[185]

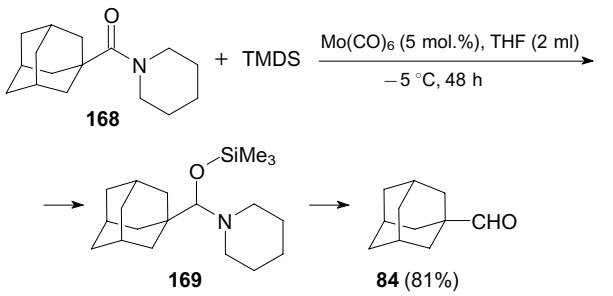
Scheme 117



(*a*) $[Pd(PPh_3)_4]$ (0.02 mmol), $(Bu^tC(O))_2O$ (6 mmol), THF (5 ml), 50 °C, 18 h

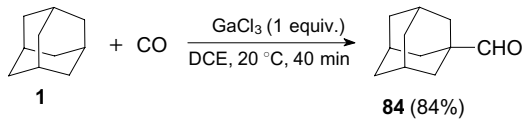
The $Mo(CO)_6$-catalyzed chemoselective reduction of 1-(piperidinocarbonyl)adamantane (**168**, 1 mmol) to aldehyde **84** proceeds on treatment with 1,1,3,3-tetramethyldisiloxane (TMDS, 4 equiv.) as a source of hydrogen under very mild conditions (Scheme 118).[186] Trimethylsilyl ether **169** is formed intermediately.

Scheme 118



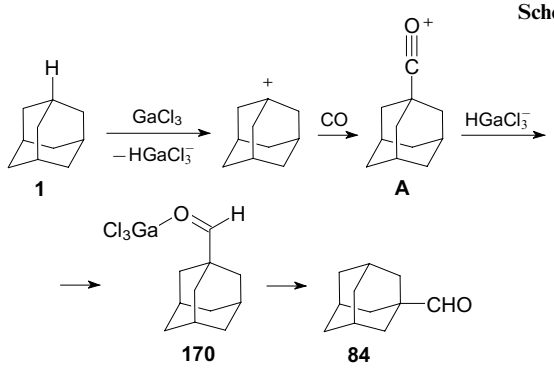
Oshita and Chatani[187] described a nontrivial synthesis of adamantane-1-carbaldehyde (**84**) by carbonylation of adamantane with carbon monoxide (1 atm) in the presence of gallium trichloride in dichloroethane at room temperature (Scheme 119).

Scheme 119



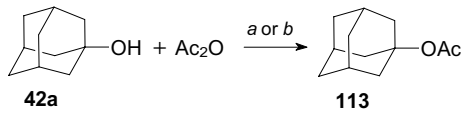
The authors suggested that initially $GaCl_3$ abstracts a hydrogen atom from adamantane. This yields the adamantyl cation, which reacts with CO to give acylium cation **A**. Gallium hydride rather than adamantane serves as the source of hydrogen at the final step; therefore, 1 equiv. of $GaCl_3$ is needed for the formation of intermediate **170** (Scheme 120).

Scheme 120



Examples of using metal complexes as catalysts for the synthesis of ethers and esters of adamantanol **42a** and adamantanecarboxylic acid **9a** are known from the literature. It was shown [188, 189] that heteropolyacid salts — aluminium dodecatungstophosphate and cobalt potassium dodecatungstate trihydrate — catalyze acetylation of adamantan-1-ol (**42a**) with acetic anhydride. The reactions proceed at room temperature and give 1-acetoxyadamantane (**113**) in a high yield (Scheme 121).

Scheme 121

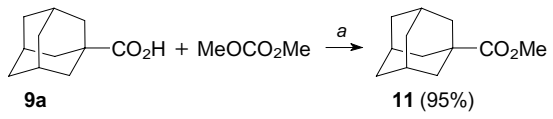


(*a*) $AlPW_{12}O_{40}$ (5 mol.%), 20 °C, 100 min (92% yield);
(*b*) $K_5CoW_{12}O_{40} \cdot 3H_2O$ (10 mol.%), MeCN, 20 °C, 240 min (70% yield)

Methyl adamantanecarboxylate **11** was obtained by methylation of acid **9a** with dimethyl carbonate catalyzed by the manganese carbonyl complex $Mn_2(CO)_{10}$ (Scheme 122).[190]

Adamantyl alkyl ethers were synthesized by alcoholysis of 1-chloroadamantane (**2a**) with alcohols catalyzed by

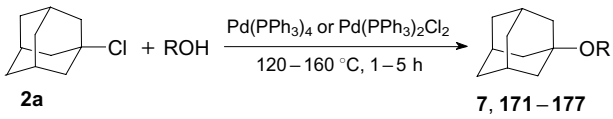
Scheme 122



(*a*) $Mn_2(CO)_{10}$ (1 mol.%), 180 °C, 1 h (elimination of MeOH, CO_2)

palladium complexes. The yields of 1-adamantyl alkyl ethers **7** and **171** – **176** depend substantially on the catalyst concentration and temperature and are maximized (98%) at a temperature of 160 °C and a **2a** : [Pd] molar ratio from 1 : 0.005 to 0.01 : 0.005. Among the tested palladium salts and complexes, the highest catalytic activity was exhibited by $Pd(PPh_3)_4$ and $Pd(PPh_3)_2Cl_2$ preactivated by heating at 200 °C for 2 – 3 h in CH_2Cl_2 in a sealed autoclave. The reaction of 1-chloroadamantane (**2a**) with adamantanol **42a** catalyzed by $Pd(PPh_3)_4$ at 160 °C gave diadamantyl ether **177** in a high yield over a period of 3 h (Scheme 123).[191]

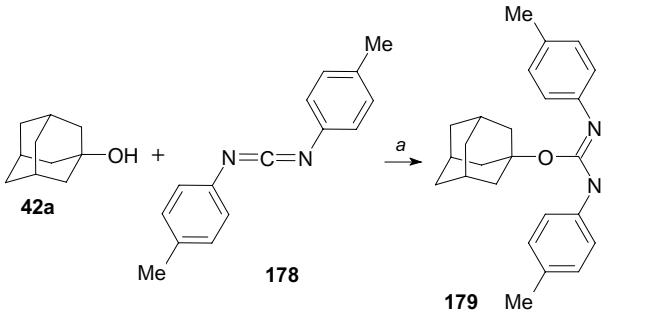
Scheme 123



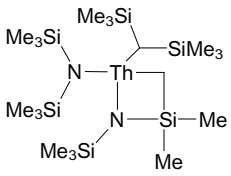
R = Me (**7**, 98%), Et (**171**, 98%), Pr^n (**172**, 85%), Pr^i (**173**, 80%), Bu^n (**174**, 80%), Bu^i (**175**, 71%), Bu^t (**176**, 50%), 1-Ad (**177**, 80%)

With thorium complex **XXI** as a catalyst, adamantanol **42a** reacts with 1,3-di(*p*-tolyl)carbodiimide (**178**) to furnish adamantyl-containing isourea **179** (78% yield) (Scheme 124).[192]

Scheme 124



(*a*) **XXI** (0.4 mol.%), PhH, 75 °C, 2 h;



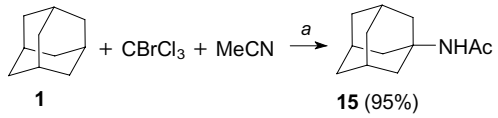
9. Formation of the C – N bond in the series of diamondoids

It was ascertained [193, 194] that direct amidation of adamantane with acetonitrile and water is catalyzed by molybdenum hexacarbonyl in bromotrichloromethane. The reaction takes place on heating and results in *N*-adamantylacetamide **15** in a high yield with complete conversion of the substrate. 1-Bromoadamantane (**6a**) is formed as a minor product in 5% yield (Scheme 125).

In the presence of $Mo(CO)_6$, 1,3-dimethyladamantane (**53**) also actively reacts with acetonitrile and water (Scheme 126).[195]

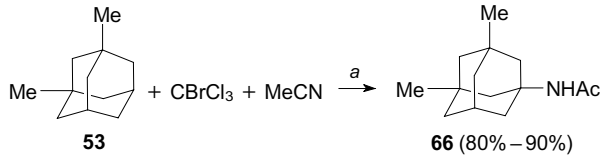
1-Adamantylamides can be prepared by reacting 1-haloadamantanes with organic nitriles and water under the action of manganese complexes.[196, 197] The amidation of 1-bromoadamantane (**6a**) with acetonitrile and other nitriles

Scheme 125



(*a*) $Mo(CO)_6$ (1 mol.% – 3 mol.%), H_2O, 130 – 140 °C, 2 – 3 h

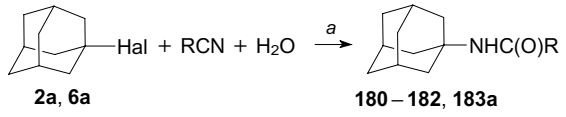
Scheme 126



(*a*) $Mo(CO)_6$ (1 mol.% – 3 mol.%), H_2O, 140 – 160 °C, 5 – 6 h

is catalyzed by $MnCl_2$, $MnBr_2$, $Mn(OAc)_2$, $Mn(acac)_2$, $Mn(acac)_3$ and $Mn_2(CO)_{10}$; the catalysts of choice are $Mn_2(CO)_{10}$ and $Mn(acac)_3$. The reaction proceeds in water at the component molar ratio **6a** : MeCN : H_2O : [Mn] = 100 : (300 – 500) : 100 : (1 – 3). The yields of products **180** – **182** and **183a** vary from 75% to 100%. Under the optimal conditions (100 °C, 3 h or 130 °C, 1 h), bromoadamantane **6a** is completely converted, with *N*-(1-adamantyl)-acetamide **15** being the only product of the reaction with acetonitrile (Scheme 127).

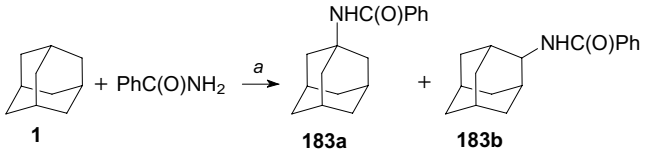
Scheme 127



(*a*) [Mn] (3 mol.%), 130 °C, 2 – 3 h; R = Et (**180**), CH=CH_2 (**181**), CH_2CN (**182**), Ph (**183a**)

The possibility of direct amidation of adamantane (**1**) with benzamide in the presence of a copper catalyst was established. The reaction involves an oxidant (Bu^tOOBu^t, 2 equiv.) and both a secondary and tertiary C – H bonds and gives *N*-(1-adamantyl)- (**183a**) and *N*-(2-adamantyl)-benzamides (**183b**) in 1.6 : 1 ratio in a total yield of 38%. When the oxidant is replaced by Bu^tOOH, Bu^tOOAc or H_2O_2, the yields of amides **183a**,**b** decrease by 5% (Scheme 128).[198]

Scheme 128

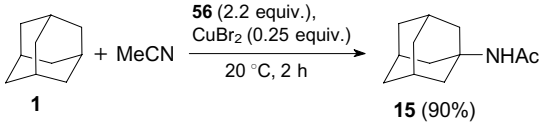


(*a*) CuI (2.5 mol.%), (MeO)Phen (2.5 mol.%), Bu^tOOBu^t (2 equiv.), PhCl, 100 °C, 36 h

Meanwhile, when Selectfluor (**56**), which is a potent oxidant, is used instead of Bu^tOOBu^t, adamantane amidation proceeds under milder conditions (Scheme 129).[199]

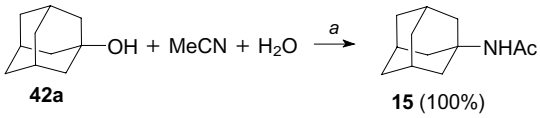
Adamantanol **42a** is less reactive towards amidation catalyzed by manganese compounds. The involvement of this substrate into this reaction was made possible *via*

Scheme 129



activation of manganese catalysts [$Mn(acac)_2$, $Mn(acac)_3$, $Mn(OAc)_2$, $Mn_2(CO)_{10}$] by hydrobromic acid. The [Mn] – HBr (1 : 1) catalytic system affects the reaction of adamantan-1-ol (**42a**) with acetonitrile and water (1 : 8 : 1 molar ratio) at 100 – 120 °C over a period of 3 – 5 h.[200] Under these conditions, the yield of *N*-(1-adamantyl)acetamide **15** reaches 100% (Scheme 130).

Scheme 130

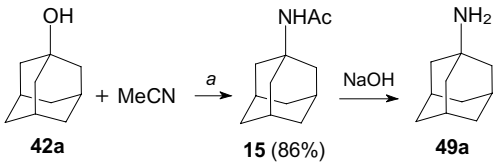


(*a*) H_2O, [Mn] – HBr (1 : 1) (1 mol.% – 3 mol.%), 100 – 120 °C, 5 – 6 h

High reactivity towards adamantanol **42a** in the presence of the $Mn_2(CO)_{10}$ – HBr system was also found for other nitriles — propionitrile, benzonitrile, malononitrile and acrylonitrile.[200]

The $FeCl_3$ – $AgSbF_6$ bimetallic system is also an active catalyst for amidation of adamantan-1-ol with acetonitrile (3 equiv.). Upon removal of the acyl goup in compound **15** in alkaline medium, amine **49a** was isolated (Scheme 131).[201]

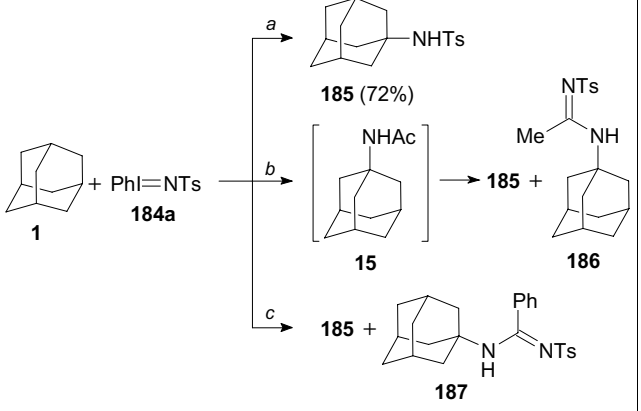
Scheme 131



(*a*) $FeCl_3$ (0.15 equiv.), $AgSbF_6$ (0.45 equiv), DCE, 100 °C, 24 h

In some studies, tosyliminophenyl-λ^3-iodane PhI=NTs (**184a**) and {[4-nitrophenyl)sulfonyl]imino}phenyl-λ^3-iodane PhI=NNs [**184b**, where Ns is 4-nitrophenylsulfonyl (nosyl)] were employed as amidating reagents. The amidation of adamantane (**1**) and its derivatives with PhI=NTs (2 equiv.) and PhI=NNs is catalyzed by copper, iron, ruthenium, manganese and rhodium complexes. Bagchi *et al.*[202] reported the amidation of adamantane catalyzed by [Cu^I(TMG$_3$trphen)][PF_6] (TMG$_3$-trphen is tris[(tetramethylguanidino)phenyl]amine) in various solvents for 12 h at room temperature. The reaction conducted in the acetonitrile – chlorobenzene system (1 : 10) gives *N*-adamantyltosylamine **185** in 72% yield as the only product. In acetonitrile, this reaction affords the expected *N*-adamantyltosylamine **185** (31% yield) and *N*-adamantyltosylamide **186** (30% yield). Presumably, product **186** is formed step by step *via* the initial amidation of compound **1** with acetonitrile and the subsequent condensation of amide **15** with PhI=NTs. The reaction of adamantane with benzonitrile follows a similar pathway, with amide **187** being isolated in 20% yield, apart from *N*-adamantyltosylamine **185** (38% yield) (Scheme 132).

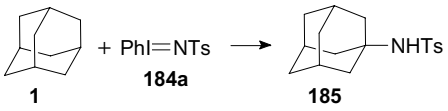
Scheme 132



(*a*) [Cu^{I}(TMG$_3$trphen)][PF$_6$] (0.1 equiv.), MeCN, PhCl, 20 °C, 12 h;
(*b*) [Cu^{I}(TMG$_3$trphen)][PF$_6$] (0.1 equiv.), MeCN, 20 °C, 12 h;
(*c*) [Cu^{I}(TMG$_3$trphen)][PF$_6$] (0.1 equiv.), PhCN, 20 °C, 12 h

Ruthenium(II) and manganese *meso*-tetrakis(pentafluorophenyl)porphyrin complexes (molar ratio Cat : **1** : **184a** = 1 : 75 : 150) are also efficient catalysts for amidation of adamantane with compound **184a**. The Mn complex is distinguished by the highest turnover number (TON), which reaches 2600. In the presence of the Ru complex, the reaction proceeds over 4 h and ends in the formation of the target amine **185** in a yield of 80% with 98% conversion of the substrate (Scheme 133, Table 7, No. 1).[203, 204]

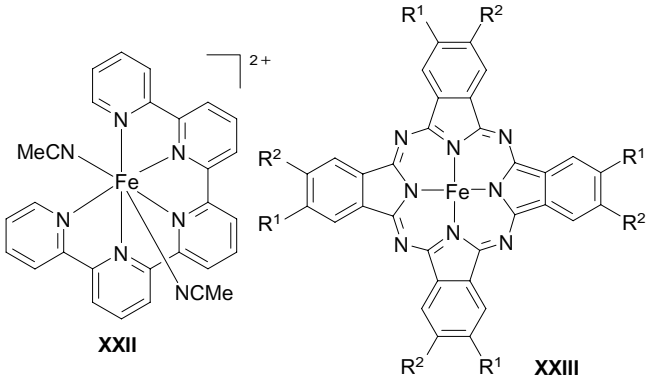
Scheme 133



A low activity in this reaction was observed for the ruthenium complex *cis*-[Ru^{III}(6,6′-Cl$_2$Bpy)$_2$Cl$_2$] (6,6′-Cl$_2$Bpy is 6,6′-dichloro-2,2′-bipyridine). The conversion of adamantane **1**, taken in a 10% excess, catalyzed by this complex was 52% (see Table 7, No. 2).[205] The amidation of adamantane with **184a** catalyzed by iron compound **XXII** with the quinquepyridine ligand has been described [206] (see Table 7, No. 3). Iron phthalocyanine complexes **XXIII** (Ref. 207) and manganese chloroporphyrin complex [Mn(TDCPP)(OTf)] exhibited a fairly high activity in the amidation of adamantane (see Table 7, Nos 4, 5).[208]

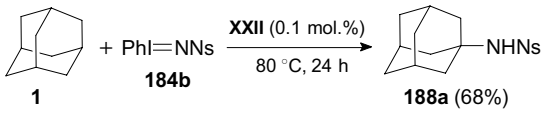
Iron catalyst **XXII** containing the quinquepyridine ligand was also used for the amidation of adamantane with phenyl-λ^3-iodane **184b**; this gave the corresponding *N*-adamantylamine derivative **188a** (Scheme 134).[206]

Structures XXII, XXIII



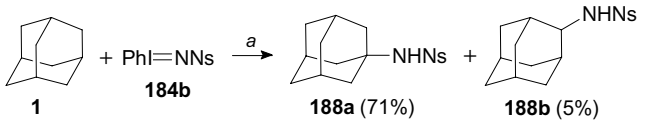
(R^1, R^2 = H or 3-F$_3$CC$_6$H$_4$O)

Scheme 134



The rhodium-catalyzed reaction of adamantane (**1**) with **184b** is less selective (gives a mixture of 1- and 2-isomers **188a**,**b**) (Scheme 135).[209]

Scheme 135



(*a*) Rh$_2$(OAc)$_4$, CH$_2$Cl$_2$, 20 °C

In the presence of rhodium-based catalyst **XVII**, adamantane (5 equiv.) reacts with 2,2,2-trichloroethyl-*N*-tosylcarbamate **189** to give 1-TrocNH- and 2-TrocNH-substituted (Troc is 2,2,2-trichloroethoxycarbonyl) adamantanes **190a**,**b** in 12 : 1 ratio in an overall yield of 58% (Scheme 136).[210, 211]

The reaction of 1,3-dimethyladamantane (**53**) with 2,6-fluorobenzenesulfonamide (1.2 equiv.) catalyzed by [Rh$_2$(esp)$_2$] (esp is α,α,α′,α′-tetramethylphenyl-1,3-dipropionate) proceeds in a similar way. The 2,6-difluorobenzenesulfo group in product **191** is readily removed under reflux in aqueous acetonitrile; the amine was isolated as trifluoroacetate **192** (Scheme 137).[212]

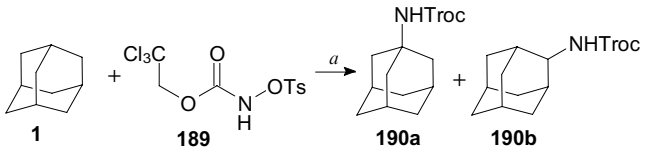
The reaction of adamantane (**1**) with (*S*)-*N*-(*p*-toluenesulfonyl)iminoamide (1.2 equiv.) catalyzed by the chiral rhodium complex [Rh$_2$((*S*)-nta)$_4$] [nta is *N*-(1,8-naphthyl)-

Table 7. Amidation of adamantane with tosyliminophenyl-λ^3-iodane (**184a**) catalyzed by metal complexes (see Scheme 133).

No.	Catalyst (mol.%)	Solvent	*T* /°C	Time /h	Yield of **185** (%)	Ref.
1	[Ru^{II}(TPFPP)(CO)] or [Mn(TPFPP)Cl]	CH_2Cl_2	40	1	74 – 80	203, 204
2	*cis*-[Ru^{III}(6,6′-Cl$_2$Bpy)$_2$Cl$_2$] (2)	MeCN	25	3	87	205
3	**XXII** (0.1)	MeCN	80	2	86	206
4	**XXIII** (1)	MeCN	25	3	71	207, 208
5	[Mn(TDCPP)(OTf)] (1)	CH_2Cl_2	20	0.5	56	207, 208

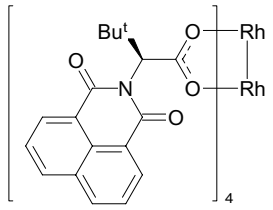
Note. TDCPP is *meso*-tetrakis(2,6-dichlorophenyl)porphyrin.

Scheme 136

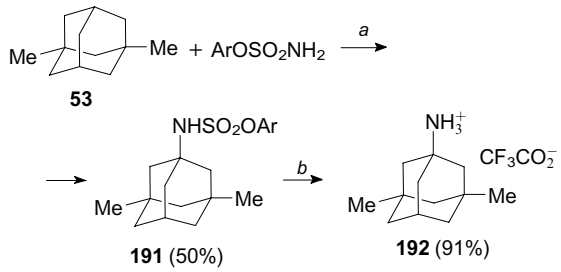


(*a*) **XVII** (5 mol.%), K_2CO_3 (3 equiv.), CH_2Cl_2 (0.5 M), 25 °C, 16 h;

XVII =



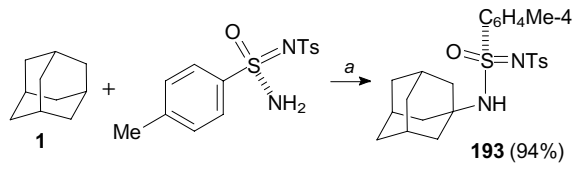
Scheme 137



(*a*) $[Rh_2(esp)_2]$ (1 mol.%), $PhI(OAc)_2$ (2 equiv.), $PhMe_2CCO_2H$ (0.5 equiv.), MgO (2 equiv.), MS 5Å, Pr^iOAc; (*b*) 1) H_2O, MeCN, 80 °C; 2) CF_3CO_2H; MS are molecular sieves; Ar = 2,6-$F_2C_6H_3$

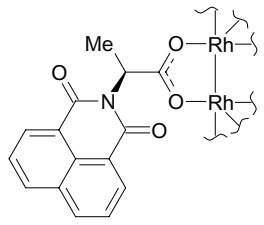
alanine], a fragment of which is shown as structure **XXIV**, in the presence of the $PhI(O_2CBu^t)_2$ oxidant yields compound **193**, resulting from amidation at the bridgehead carbon atom (Scheme 138).[213–215]

Scheme 138



(*a*) **XXIV** (3 mol.%), $PhI(O_2CBu^t)_2$ (1.4 equiv.), DCE – MeOH (3 : 1);

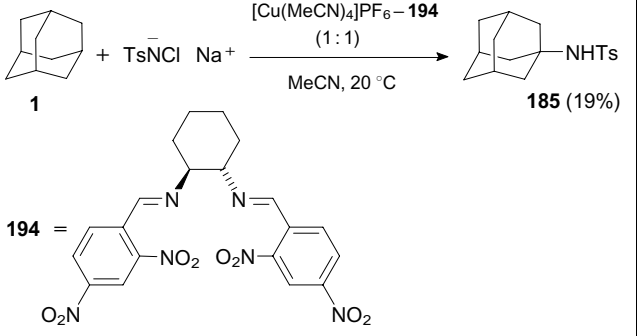
XXIV =



Compound **1** was amidated with chloramine-T catalyzed by the $[Cu(MeCN)_4]PF_6$ – L system, where L is the nitro-substituted diimine ligand **194**. The yield of amide **185** at 20 °C was 19% and did not increse as the temperature was raised to 70 °C (Scheme 139).[216]

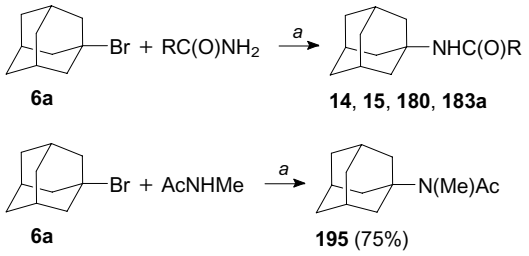
An alternative method proposed[217–219] for the synthesis of adamantylamides is based on the reaction of 1-haloadamantanes with amides in the presence of manganese catalysts. In particular, the reaction of 1-bromoadamantane

Scheme 139



(**6a**) with formamide is catalyzed by the following manganese compounds: $MnCl_2$, $MnBr_2$, $Mn(OAc)_2$, $Mn(acac)_3$ and $Mn_2(CO)_{10}$. Under the optimal conditions (120 – 130 °C, 2 – 3 h) and at complete conversion of 1-bromoadamantane, 1-adamantylformamide **14** is formed as the only product. Other organic amides such as acetamide, propionamide, benzamide and *N*-methylformamide actively participate in this reaction to give the corresponding *N*-(1-adamantyl)amides **15**, **180**, **183a** and **195** in 78% – 100% yields (Scheme 140).

Scheme 140



(*a*) [Mn] (3 mol.%), 120 – 130 °C, 2 – 3 h; R = H (**14**, 97%), Me (**15**, 96%), Et (**180**, 92%), Ph (**183a**, 99%)

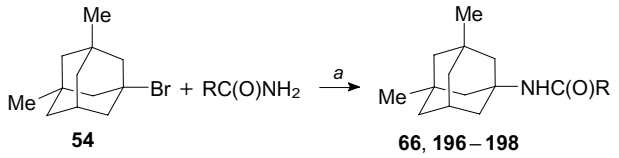
Malonamide also takes part in a similar reaction with bromoadamantane **6a**, involving one $C(O)NH_2$ group, but the product is formed in a low yield (10%). The reactivity of 1-chloroadamantane (**2a**) in this reaction is almost not inferior to that of bromide **6a**; compound **2a** is converted to target *N*-(1-adamantyl)amides in 45% – 90% yields.

1-Bromo-3,5-dimethyladamantane (**54**) also reacts with acetamide, formamide, propionamide and benzamide in the presence of manganese compounds [$Mn_2(CO)_{10}$, $MnCl_2$, $MnBr_2$, $Mn(OAc)_2$, $Mn(acac)_3$] giving rise to *N*-(3,5-dimethyladamantan-1-yl)amides **66** and **196** – **198** in high yields (Scheme 141).[220,221]

The amidation of adamantane (**1**) with benzenesulfonamide in 3 : 1 ratio is catalyzed by $Cu(OTf)_2$ in the presence of *tert*-butyl peracetate (1.5 equiv.) as an oxidant. The reaction results in the formation of 1-adamantylsulfonamide (**199**) in a moderate yield (Scheme 142).[222]

Huang *et al.*[223] accomplished the azidation of adamantane with sodium azide catalyzed by manganese complexes in the presence of PhIO. This resulted in the synthesis of isomeric 1-adamantyl and 2-adamantyl azides **200a**,**b**. The isomer ratio depends on the nature of the ligand in the Mn complex catalyst. For example, the use of the manganese porphyrin complex Mn(tmp)Cl results in a **200a** : **200b** ratio of 1.5 : 1, while in the presence of Mn(Salen)Cl, this ratio is 4 : 1. When the adamantane molecule contains substituents

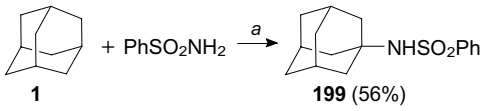
Scheme 141



54 **66**, **196**–**198**

(*a*) [Mn] (3 mol.%), 120–130 °C, 2–3 h; R = H (**196**, 78%), Me (**66**, 99%), Et (**197**, 98%), Ph (**198**, 97%)

Scheme 142

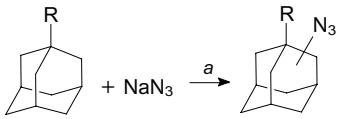


1 **199** (56%)

(*a*) $Cu(OTf)_2$ (5 mol.%), phen (5 mol.%), Bu^tOOAc (1.5 equiv.), DCE, 80 °C, 6 h

(OH, Me), the reaction involves the bridgehead position of adamantane, irrespective of the catalyst and gives 3-substituted azides **201** and **202** (Scheme 143).

Scheme 143



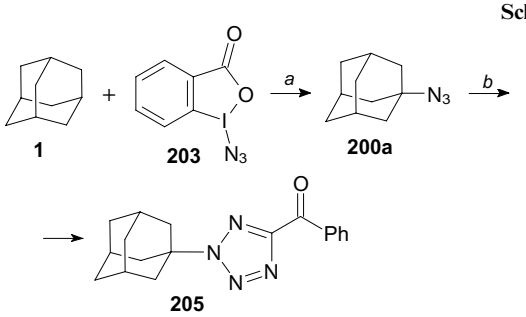
1, **42a**, **97** **200a**,**b**; **201**, **202**

(*a*) Mn(tmp)Cl or Mn(Salen)Cl (1.5 mol.%), PhIO (3–6 equiv.), EtOAc, 23 °C, 3–12 h; R = H (**1**; **200a**,**b**, 60%), OH (**42a**; **201**, 50%), Me (**97**; **202**, 67%)

It was reported[224,225] that 1-adamantyl azide **200a** can be prepared by the reaction of adamantane with hypervalent iodine compound **203** containing an azide substituent with the $Fe(OAc)_2$–ligand **204** system as the catalyst. In turn, 1-adamantyl azide **200a** reacts with nitriles to give tetrazoles, for example, compound **205** in good yield (Scheme 144).

The reaction of adamantane (**1**) with *p*-nitrophenyl azide (5 : 1 ratio) catalyzed by iron porphyrinolactone complex

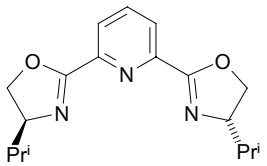
Scheme 144



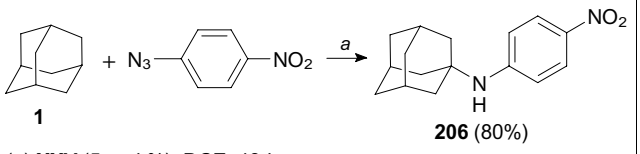
1 **203** **200a** **205**

(*a*) $Fe(OAc)_2$ (10 mol.%), **204** (11 mol.%), MeCN, 23 °C; (*b*) BzCN, 130 °C, 48 h;

204 =

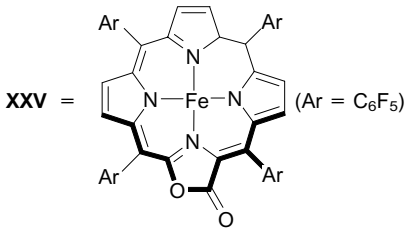


Scheme 145



1 **206** (80%)

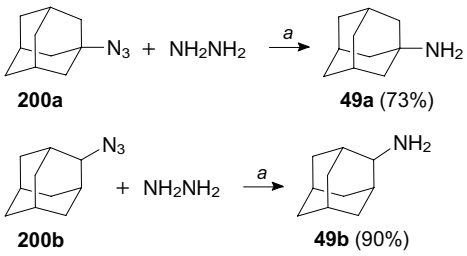
(*a*) **XXV** (5 mol.%), DCE, 48 h;



XXV follows a different route, resulting in the formation of *N*-adamantyl-*p*-nitrophenylamine **206** in a high yield (Scheme 145).[226,227]

Adamantyl azides exhibit high activity in catalytic reactions. In particular, 1-adamantyl and 2-adamantyl azides **200a**,**b** are readily converted to practically valuable amines **49a**,**b** on treatment with excess hydrazine in refluxing methanol in the presence of carbon-supported palladium hydroxide (Scheme 146).[228]

Scheme 146



200a **49a** (73%)

200b **49b** (90%)

(*a*) $Pd(OH)_2/C$ (20%), MeOH, Δ, 2–4.5 h

In the presence of the copper ketimine complex $[\{(Cl_2NNCu\}_2(\mu\text{-PhH})]$ $[Cl_2NN$ = (2,6-$Cl_2C_6H_3NCH(Me)CH_2CH(Me)NC_6H_3Cl_2$-2,6], 1-adamantyl azide **200a** undergoes an unusual reaction with hydrocarbons such as alkyl-substituted arenes (toluene, ethylbenzene, cumene and indane), acetophenone and cyclohexane. The reaction proceeds on heating for 1–48 h and gives adamantylarylamines **207**–**212** in high yields (Scheme 147, Table 8). Badiei *et al.*[229] presented a probable reaction mechanism, which includes the successive formation of dicopper nitrene $[\{(Cl_2NNCu\}_2(\mu\text{-NAd})]$ (**A**) and the complex $[(Cl_2NN)Cu{=}NAd]$ (**B**). The latter reacts with the hydrocarbon, thus yielding the complex [Cu]NH(Ad)R (**C**). At the final step, decomposition of complex **C** furnishes AdNHR. Simultaneously, the initial copper complex capable of initiating a new catalytic cycle is regenerated (Scheme 147).

Huang *et al.*[230] reported the synthesis of 1-adamantyl and 2-adamantyl isocyanates **213a**,**b** by the reaction of adamantane with trimethylsilyl isocyanate (2–4 equiv.) in the presence of an oxidant and a manganese porphyrin complex. The reaction proceeds under mild conditions and affords an 1 : 1.2 mixture of isomers in a total yield of 60% (Scheme 148).

Scheme 147

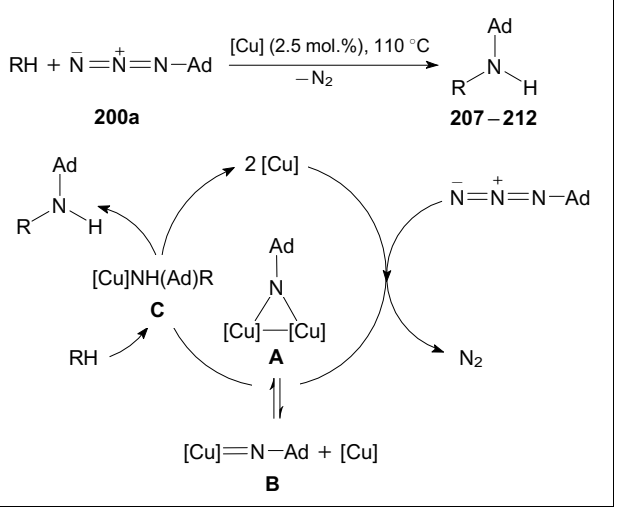
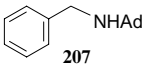
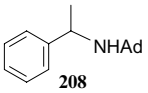
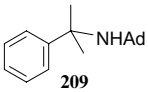
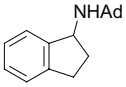
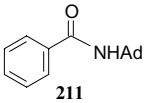
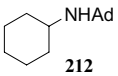
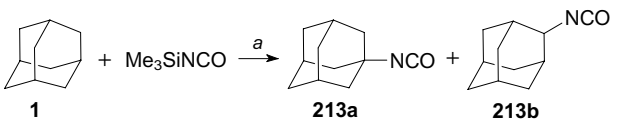


Table 8. Reactions of 1-azidoadamantane (**200a**) with hydrocarbons and acetophenone in the presence of the copper ketimine complex (see Scheme 147).[229]

No.	Substrate	Product	Time /h	Yield (%)
1		 **207**	4	92
2		 **208**	5	90
3		 **209**	24	80
4		 **210**	1	93
5		 **211**	16	91
6		 **212**	48	90

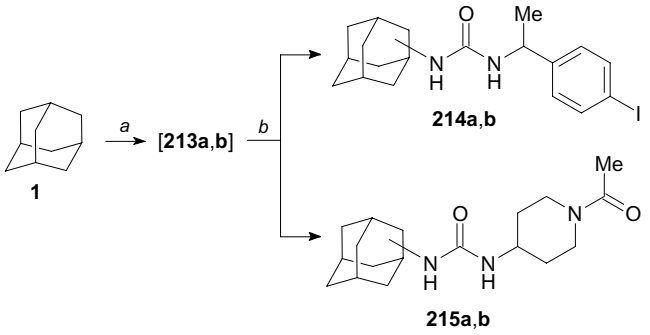
Scheme 148



(*a*) Mn(tmp)F (8 mol.%), AgF (0.25 equiv.), PhIO (3 – 6 equiv.), EtOAc, 20 °C

On treatment with secondary amines, isocyanates **213a**,**b** are converted to substituted ureas. This approach was used, for example, to prepare mixtures of isomeric adamantyl-containing ureas **214a**,**b** (80% yield; 30% content of 2-isomer) and **215a**,**b** (27% yield, 0.9 : 1 ratio) without the isolation of intermediate isocyanates (Scheme 149).

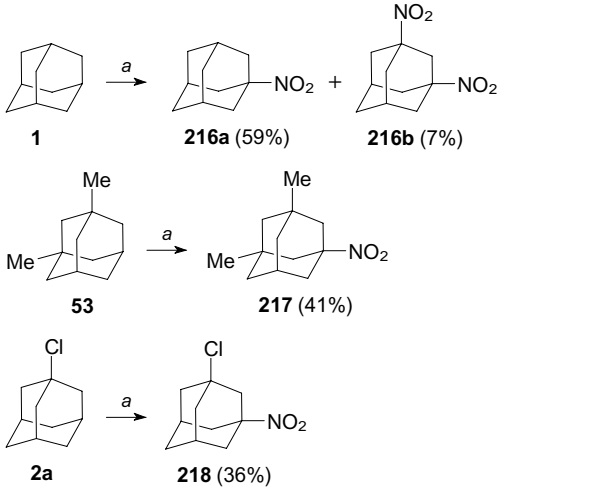
Scheme 149



(*a*) Me_3SiNCO, Mn(tmp)F, AgF, PhIO, EtOAc, 20 °C;
(*b*) RNH_2 (5 equiv.), PhMe, N_2, 60 °C; R = 4-$IC_6H_4CH(Me)$ (for **214**), $Ac[N(CH_2CH_2)_2CH]$-cyclo (for **215**)

Nitration of adamantane (**1**) with an $HNO_3 - H_2SO_4$ or $HNO_3 - N_2O_2$ mixture has low selectivity. The problem of selective nitration of adamantanes was solved by Shinachi *et al.* [231] by using Keggin-type vanadium-substituted phosphomolybdates, $[H_4PVMo_{11}O_{40}]$, $[H_5PV_2Mo_{10}O_{40}]$ and $[H_6PV_3Mo_9O_{40}]$, as catalysts (Scheme 150). The first-mentioned compound was employed to convert adamantane and dimethyl- (**53**) and chloroadamananes (**2a**) to nitroadamantanes **216** – **218**.

Scheme 150

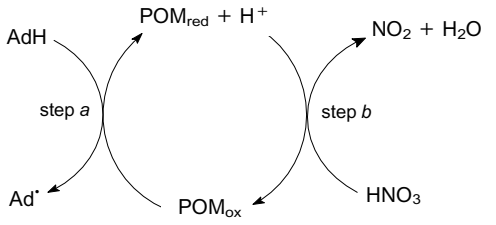


(*a*) HNO_3, $[H_4PVMo_{11}O_{40}]$ (0.5 mol.%), $PhCF_3$, 356 K, 24 h

According to NMR and IR spectroscopy data, including the external reflection spectroscopy (ERS) technique, polyoxometallates, *e.g.*, $[H_4PVMo_{11}O_{40}]$, decompose during this reaction to give free vanadium cations and Keggin-type anions ($[PMo_{12}O_{40}]^{3-}$). Polyoxometallates eliminate a hydrogen atom from adamantane, thus generating the adamantyl radical and reduced polyoxometallates (step *a*), which then react with nitric acid to give the oxidized forms and nitrogen dioxide. This step is promoted by phosphomolybdates $[PMo_{12}O_{40}]^{n-}$ and vanadium cations. In turn, the adamantyl radical is captured by nitrogen dioxide (step *b*), thus giving nitroadamantanes (Scheme 151).

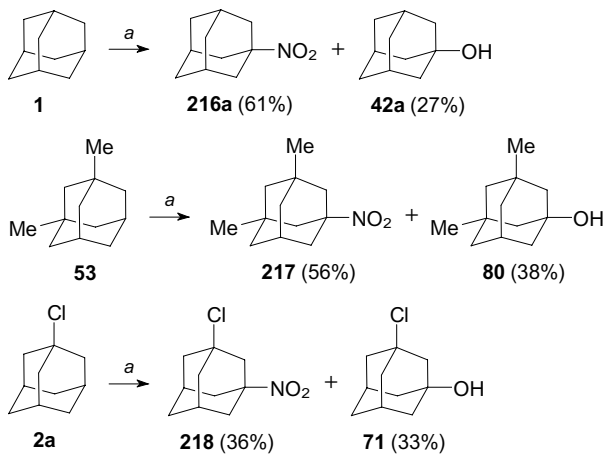
When this reaction is catalyzed by $[VO(H_2O)_5]H[PMo_{12}O_{40}]$, its selectivity decreases due to the formation of adamantanols **42a**, **71** and **80** as side products (Scheme 152).[232]

Scheme 151



POM_{ox} = V^{5+} + $[PMo_{12}O_{40}]^{3-}$; POM_{red} = V^{4+} + $[PMo_{12}O_{40}]^{3-}$ or V^{5+} + $[PMo_{12}O_{40}]^{4-}$

Scheme 152

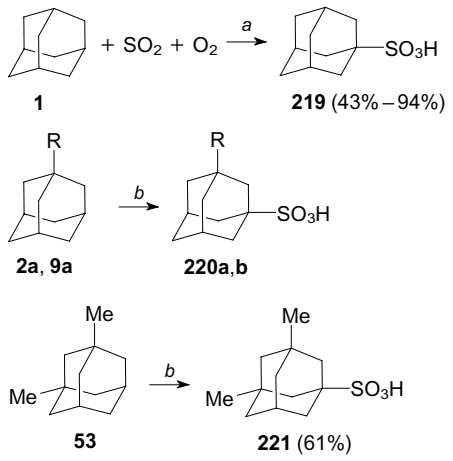


(*a*) HNO_3 (2 equiv.), $[VO(H_2O)_5]H[PMo_{12}O_{40}]$ (0.5 mol.%), AcOH, 356 K, 12 h

10. Formation of C–S and C–Se bonds involving adamantane

Ishii *et al.*[233] found that sulfoxidation of adamantane to adamantane-1-sulfonic acid (**219**) on treatment with a mixture of SO_2 and O_2 (1 atm pressure) is catalyzed by vanadium compounds, the most efficient of which is $VO(acac)_2$. The $VO(acac)_2$-catalyzed sulfoxidation of adamantane derivatives **2a**, **9a** and **53** also proceeds rather smoothly, giving rise to sulfonic acid derivatives **220a**,**b** and **221** (Scheme 153).

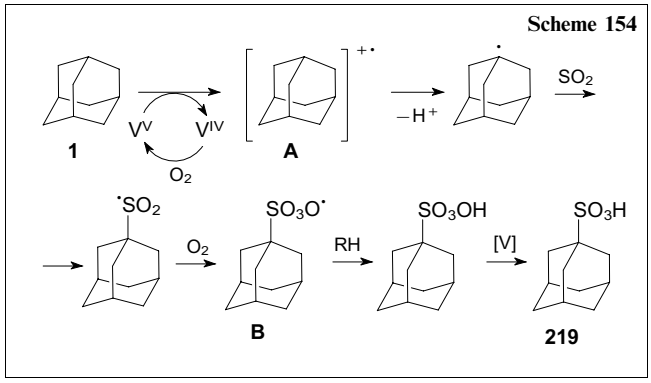
Scheme 153



(*a*) [V] (0.5 mol.%), AcOH, 40 °C, 2 h; [V] = $VO(acac)_2$, $VOCl_3$, $VO(O_2CC_{17}H_{35})_2$, $VOSO_4$;
(*b*) SO_2 + O_2 (1 atm), $VO(acac)_2$ (0.5 mol.%), AcOH, 40 °C, 5 h;
R = Cl (**2a**; **220a**, 56%), CO_2H (**9a**; **220b**, 70%)

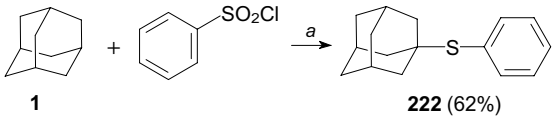
The authors suggested[233] that the process includes the generation of adamantane radical cation **A** *via* electron transfer from the substrate to V^V. In turn, the latter is formed upon oxidation of $VO(acac)_2$ with oxygen. Radical cation **A** eliminates a proton to give the Ad• radical, which first captures SO_2 and then O_2, being thus converted to adamantylsulfonylperoxy radical **B**. At the final stage, **B** reacts with adamantane to give product **219** (Scheme 154).

Scheme 154



Guo *et al.*[234] proposed an unusual method for thiylation of adamantane with phenylsulfonyl chloride (3 : 1 ratio) in the presence of an oxidant and the $Ru_3(CO)_{12}$ catalyst. The reaction gives 1-adamantyl phenyl sulfide **222** (Scheme 155).

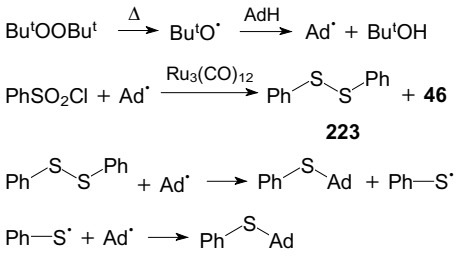
Scheme 155



(*a*) $Ru_3(CO)_{12}$ (2 mol.%), Bu^tOOBu^t (2 equiv.), 100 °C, 12 h

The authors proposed a general mechanism for this reaction of arylsulfonyl chlorides, which implies an initial decomposition of Bu^tOOBu^t to give the *tert*-butoxyl radical. At the next step, Bu^tO• attacks adamantane, being converted to alcohol and generating the adamantyl radical. Then Ad• reacts with arylsulfonyl chloride under the action of $Ru_3(CO)_{12}$ to give disulfide **223** and adamantan-2-one (**46**) as a side product. An attack by the Ad• radical on the disulfide affords 1-adamantyl aryl sulfide and the ArS• radical, which is captured by another Ad• radical (Scheme 156, for Ar = Ph).

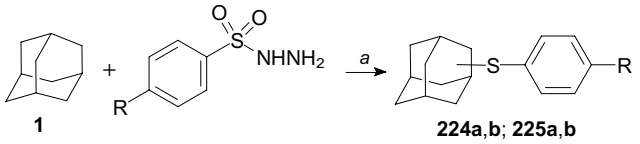
Scheme 156



Yet another unusual method for the preparation of adamantyl aryl sulfides is based on the reaction of adamantane (**1**) with the appropriate arylsulfonyl hydrazides in the

presence of di-*tert*-butyl peroxide and $Pd(OAc)_2$. This reaction affords adamantyl aryl sulfides **224a**,**b** (R = Me, 79% yield and 92 : 8 ratio of 1- and 2-isomers) and **225a**,**b** (R = CF_3, 71%, 85 : 15) (Scheme 157).[235]

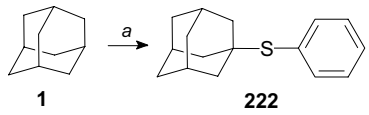
Scheme 157



(*a*) $Pd(OAc)_2$ (2 mol.%), Bu^tOOBu^t (0.9 equiv.), 120 °C, 4 – 8 h; R = Me (**224**), CF_3 (**225**); isomers: 1 (**a**), 2 (**b**)

Adamantane was thiylated with diphenyl disulfide **223** or with benzenethiol in the presence of the $Cu(OAc)_2 \cdot H_2O$ catalyst and the di-*tert*-butyl peroxide oxidant; 1-adamantyl phenyl sulfide (**222**) was formed in 52% or 62% yield, respectively (Scheme 158).[236]

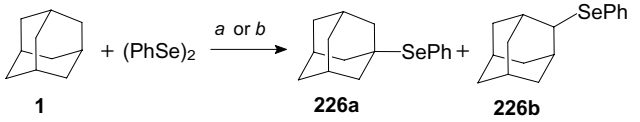
Scheme 158



(*a*) PhSSPh (**223**, 1.5 equiv.) or PhSH (3 equiv.), $Cu(OAc)_2 \cdot H_2O$ (2 mol.%), Bu^tOOBu^t (0.9 equiv.), 120 °C, 18 h

Compound **1** reacts with diphenyl diselenide (1.5 equiv.) in the presence of Barton's Gif system (with air oxygen as the oxidant) to afford adamantyl phenyl selenides **226a**,**b** in 4% and 12% yields, respectively (Scheme 159, conditions *a*).[237]

Scheme 159



(*a*) Zn (10 equiv.), O_2 (air), $[Fe_3O(OAc)_6Py_{3.5}]$, Py, H_2O, AcOH, 20 °C, 9 h; (*b*) Fe^0 (20 equiv.), Py, H_2O, AcOH, 20 – 30 °C, 11 h

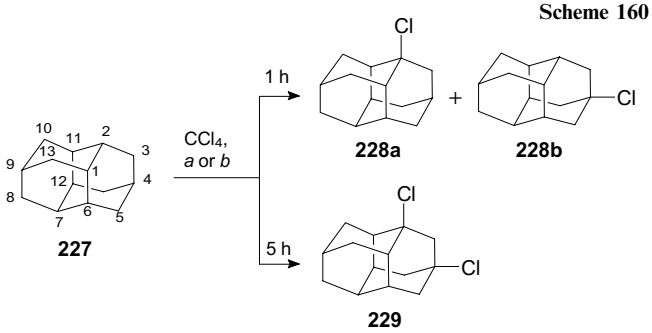
When iron metal powder is used in this reaction as a catalyst and reducing agent with an equimolar ratio of the reactants, the yields of adamantyl phenyl selenides **226a**,**b** are 15% and 17%. In the absence of atmospheric oxygen, the reaction does not proceed (see Scheme 159, conditions *b*).[237]

11. Catalytic reactions of diamantane

The data available from the literature on the chemical transformations of the second representative of the adamantanoid homologous series — diamantane (**227**) — in the presence of metal complex catalysts are scarce. Meanwhile, the problem of selective functionalization is even more challenging for diamantane than for adamantane, because its molecule has three rather than two types of carbon atoms: two types of tertiary carbons (medial atoms in positions 1, 2, 6, 7 and 12; apical atoms in positions 4, 9) and secondary carbons (in positions 3, 5, 8, 10, 13 and 14). Owing to the different environments, the apical and medial carbon atoms differ in the reactivity, which is manifested in the syntheses of monosubstituted diamantanes by classical organic chemistry methods, usually resulting in 1- and 4-isomers. As regards the catalytic reactions of diamantane, in some cases, high selectivity is possible.

Khusnutdinov *et al.*[12] investigated the chlorination of diamantane (**227**) with carbon tetrachloride catalyzed by the $Mn(acac)_3$ – MeCN system. The reaction is nonselective; depending on the duration of the experiment, a mixture of 1-chloro- and 4-chlorodiamantanes **228a**,**b** (93% total yield) or 1,4-dichlorodiamantane **229** (87% yield) is formed (Scheme 160, conditions *a*).

Scheme 160

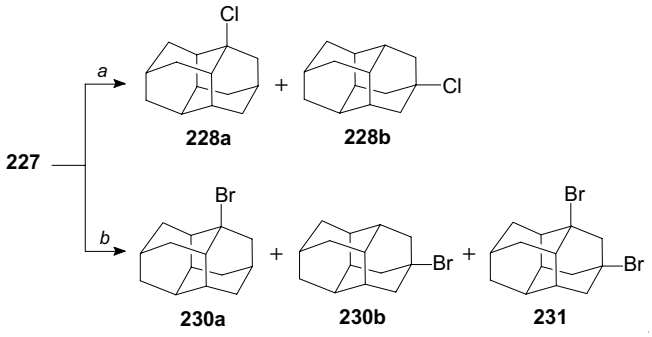


(*a*) $Mn(acac)_3$, MeCN, 200 °C; (*b*) $VO(acac)_2$ (1 mol.%), MeOH, 150 °C

The chlorination of diamantane catalyzed by the $VO(acac)_2$ – MeOH system is also nonselective (see Scheme 160, conditions *b*).[12] On short-term heating, a mixture of isomers **228a**,**b** is formed in 90% yield, while increasing the reaction time to 5 h gives dichloro derivative **229** (80% yield).

The rhodium complexes $Rh(PPh_3)_3Cl$ and $[Rh(CO)_2Cl]_2$ catalyze the chlorination and bromination of diamantane with CH_2Cl_2 and CH_2Br_2, respectively (Scheme 161).[20] The product ratio **228a** : **228b** is 3 : 2, while in the case of bromo derivatives, **230a** : **230b** : **231** = 2 : 4 : 3.

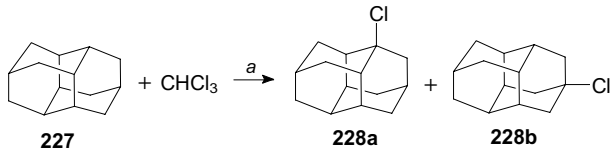
Scheme 161



(*a*) CH_2Cl_2, $Rh(PPh_3)_3Cl$ or $[Rh(CO)_2Cl]_2$ (1 mol.%), 180 °C, 30 h (76% yield); (*b*) CH_2Br_2, $Rh(PPh_3)_3Cl$ or $[Rh(CO)_2Cl]_2$ (1 mol.%), 200 °C, 40 h (100% yield)

Chloroform was used as a source of chlorine for the chlorination of diamantane.[21] The reaction can be catalyzed by iron, chromium, cobalt and nickel compounds [$FeBr_2$, $Fe(acac)_3$, $CrCl_3$, $Cr(acac)_3$, $CoBr_2$, $CoCl_2$, $Co(acac)_2$, $NiCl_2$, $NiBr_2$, $Ni(acac)_2$]. The salts were preactivated by being kept in a $CHCl_3$ solution under an inert atmosphere in a sealed autoclave at 200 °C for 3 h (Scheme 162).

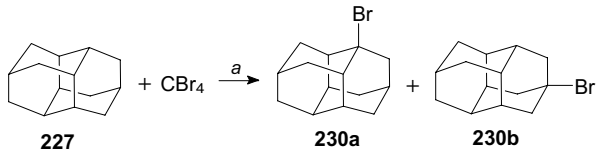
Scheme 162



(*a*) Cat, 200 °C, 6 h (75% yield; **228a** : **228b** = 1 : 1.2)

The $Fe(acac)_3$-catalyzed bromination of diamantane (**227**) with tetrabromomethane gave a mixture of isomeric bromodiamantanes **230a**,**b** in 2 : 1 ratio (Scheme 163).[28]

Scheme 163

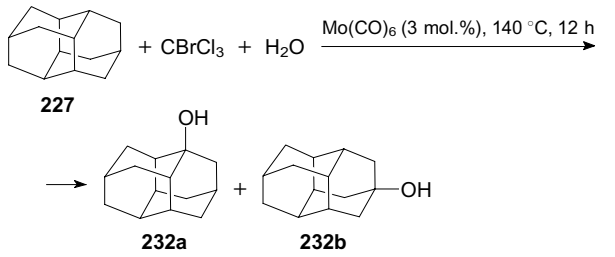


(*a*) $Fe(acac)_3$, CH_2Cl_2, 110 °C, 5 h (75% yield)

The selective halogenation of diamantane with CCl_4 and CBr_4 became possible by using the iron-based HFeYmmm catalyst, which was prepared by impregnation of micro-, macro- and mesoporous HYmmmo zeolite with iron(III) salts followed by heat treatment.[238] In this case, the reaction took place at 150 °C for 5 h; the yield of chlorodiamantanes **228a**,**b** was 85% (10 : 1 ratio) and the yield of bromo derivatives **230a**,**b** was 81% (6 : 1). One more benefit of the HFeYmmm catalyst is the absence of polyhalogenated diamantane derivatives among the reaction products, which can be attributed to the molecular sieve effect of the HYmmm zeolite.

Khusnutdinov *et al.*[101] utilized the $Mo(CO)_6$–$CBrCl_3$–H_2O system for hydroxylation of diamantane. The reaction involved the bridgehead carbon atoms and gave a mixture of 1- and 4-diamantanols **232a**,**b** in 2 : 1 ratio in a total yield of 75% (Scheme 164).

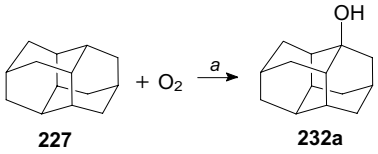
Scheme 164



A rare example of a highly selective transformation of diamantane (**227**) was reported by Neuman *et al.*[239] The oxidation of diamantane with oxygen (1 atm) in the presence of ruthenium-containing polyoxometalate $Na_{11}WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2 \cdot 42\,H_2O$ affords diamantanol **232a** as the only product in high yield (Scheme 165).

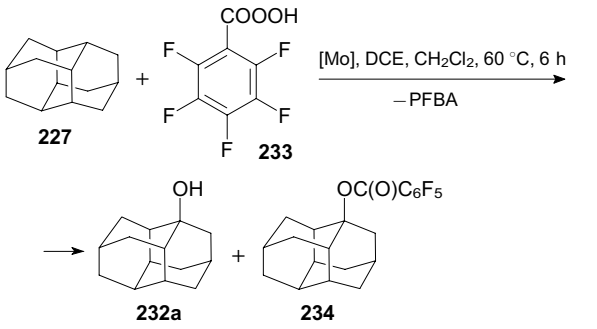
The oxidation of diamantane at the bridgehead position under the action of 2,3,4,5,6-pentafluoroperbenzoic acid (**233**) (6% of active oxygen) catalyzed by molybdenum complexes $MoO(O_2) \cdot 2\,QOH$ (52% yield) or $MoO(O_2)(H_2O)_2$ (40%) is also selective and furnishes diamantan-1-ol (**232a**) and its 2,3,4,5,6-pentafluorobenzoate **234** in 1.9 : 1 ratio.[240] According to authors' assumption, the incomplete conversion of compound **227** is caused by destruction of the molybdenum complexes by 2,3,4,5,6-pentafluorobenzoic acid (PFBA), which is a strong acid and is generated as a by-product in this reaction. For decreasing the deactivating effect of the acid, it was proposed to carry out the oxidation of compound **227** in the presence of bases ($NaHCO_3$, K_2CO_3 or NaOAc), which considerably increased the yield of alcohol **232a** (up to 68%) with a simultaneous increase in the reaction selectivity to 100% (Scheme 166).

Scheme 165



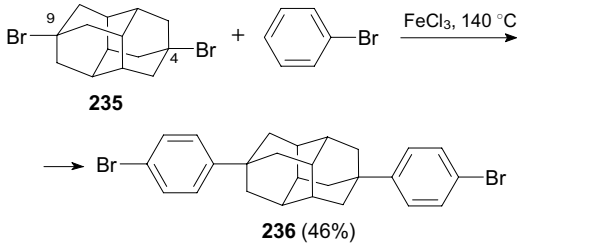
(*a*) $Na_{11}WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2 \cdot 42\,H_2O$ (0.1 mol.%), DCE, 80 °C, 24 h

Scheme 166



Zhu *et al.*[241] performed double Friedel–Crafts alkylation of bromobenzene with 4,9-dibromodiamantane (**235**) catalyzed by $FeCl_3$. The reaction gave 4,9-bis(4-bromophenyl)diamantane (**236**), which is used in the synthesis of oligo(phenylenevinylene)polychromophores (Scheme 167).

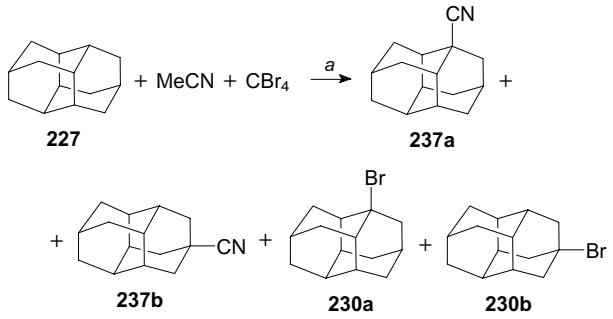
Scheme 167



Molybdenum hexacarbonyl catalyzes the direct cyanation of diamantane with acetonitrile in the presence of CBr_4. The reaction has low selectivity: together with nitriles **237a**,**b**, bromo diamantane derivatives **230a**,**b** are formed as side products in 6.5 : 5 : 1.5 : 1 ratio (Scheme 168).[153]

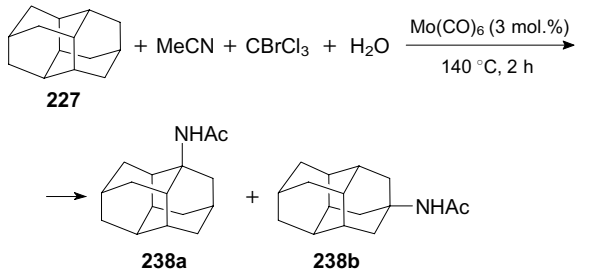
If the reaction of diamantane (**227**) with acetonitrile is carried out with addition in water and with CBr_4 being replaced by $CBrCl_3$, the reaction pathway changes towards the formation of amides **238a**,**b** in 2 : 1 ratio in a quantitative yield (Scheme 169).[197]

Scheme 168



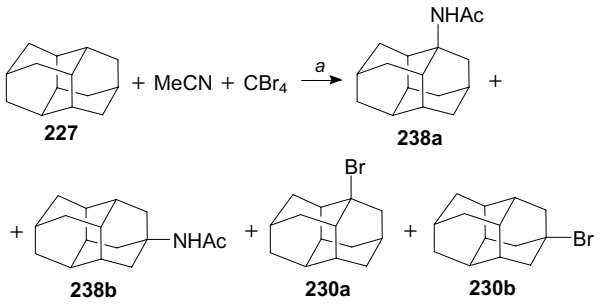
(*a*) $Mo(CO)_6$ (3 mol.%), 140 – 160 °C, 6 h (68% yield)

Scheme 169



The Fe-containing FeHYmmm zeolite proved to be the catalyst of choice for the amidation of diamantane. The presence of the zeolite support with hierarchical micro-, macro- and mesoporous structure promotes the predominant formation of 1-substituted isomer **238a** (**238a** : **238b** = 11 : 1) (Scheme 170).[242] Bromides **230a**,**b** were isolated as minor products in 2% – 3% yields.

Scheme 170



(*a*) FeHY-mmm (5 mass %), H_2O, 150 °C, 5 h (85% yield)

12. Conclusion

As can be seen from the data summarized in the review, the application of metal complex catalysts in the chemistry of adamantane, diamantane and their derivatives proved to be fairly fruitful. These catalysts enabled selective functionalization of adamantanoids under mild conditions with high conversion on treatment with conventional and nontrivial reagents. The use of catalysts made it possible to reduce the number of steps of the syntheses of practically valuable acyl-, cyano- and amidodiamandoids and provided selective halogenation and oxidation of diamantane giving 1-halogen and 1-hydroxy derivatives.

This promising line of research will be further developed, possibly, towards increasing activity and selectivity of metal complex catalysts, first of all, *via* the design and application of new bulky and conformationally rigid ligands. The catalytically active complexes with such ligands should not decompose under the action of functional adamantanoid derivatives, which are formed in the reactions. The selectivity of metal complex catalysts can be increased by using immobilized complexes. The hierarchically structured micro-, macro- and mesoporous zeolites are expected to become the best supports for these catalysts; their molecular sieve effect would also boost the selectivity of the reaction.

In the future, metal complex catalysts should find use in the selective functionalization of higher diamondoids where the problem of preparation of a single product has not yet been solved in some cases.

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