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Unsaturated Adamantane Derivatives

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The literature data on the methods of synthesis and the physical and chemical properties of adamantane derivatives containing C = C double bonds are described systematically and surveyed. Dehydroadamantanes, unsaturated adamantane derivatives with an exocyclic double bond and a double bond remote from the nucleus, as well as their functional derivatives are considered. Much attention is devoted to the reactivity of unsaturated adamantane derivatives.
The bibliography includes 165 references.

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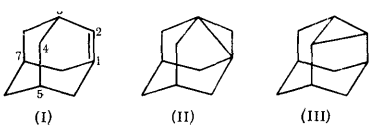
I. INTRODUCTION

The chemistry of organic polyhedranes and in the first place adamantane has developed vigorously in recent years†. Owing to their unusual properties, compounds of this class play an important role in both theoretical and experimental organic chemistry. The biological activity of organic polyhedranes has assumed considerable importance. Many medicinal drugs (rimantadine, amantidine) are at present manufactured on their basis. The high thermal stability of adamantane derivatives and their pronounced hydrophobic properties are used in the manufacture of technical products (polymeric materials, lubricating oils) with improved operational properties.

A series of reviews[1-7] and a monograph[8] have been published in recent years on the chemistry of adamantane and other polyhedranes. However, they devote little space to the chemistry of unsaturated adamantane derivatives. At the same time these compounds are of special interest primarily in view of their high reactivity; they can be used as the starting materials for the synthesis of various functional derivatives of adamantane and also as monomers. The aim of the present review is to give a systematic account and to survey the available data on the methods of synthesis and the chemical properties of adamantane derivatives containing C=C double bonds. The review includes the literature data up to 1980 inclusive and some data published in 1981–1982.

II. DEHYDROADAMANTANES

Three isomers of dehydroadamantane $C_{10}H_{14}$ are possible: 1,2-dehydroadamantane (I), 1,3-dehydroadamantane (II), and 2,4-dehydroadamantane (III):

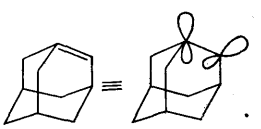


(I) (II) (III)

1,2-Dehydroadamantane belongs to the class of the so-called anti-Bredt olefins[9]. The isomers (II) and (III) can be classified as unsaturated derivatives only as a matter of convention. However, it is useful to consider them in view of the fact that, in terms of their chemical properties (primarily their high reactivity), they are extremely close to adamantane derivatives containing a multiple bond.

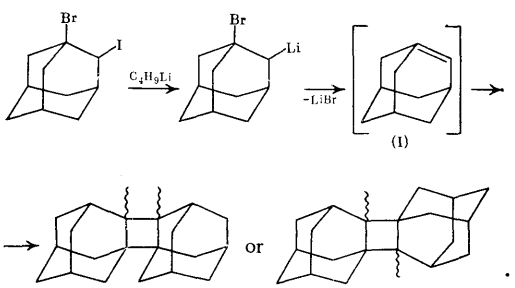
1,3-Dehydroadamantane is a strained system with two inverted carbon atoms. The 2,4-dehydroadamantane molecule is less strained and in terms of its properties is close to other alicyclic hydrocarbons containing a three-membered ring.

The possibility of the existence of 1,2-dehydroadamantane, or tricyclo[3.3.1.$1^{3,7}$]dec-1-ene, or adamantene constitutes an interesting problem in the chemistry of adamantane. Calculations have shown that adamantene is a highly strained olefin, since the overlap of the p orbitals of the C(1) and C(2) atoms, located in different planes, is difficult (a major deformation of the rigid skeleton is required). Under the usual conditions, this compound is unstable. At the same time there is much indirect evidence for its existence, 1,2-dehydroadamantane being formed as an intermediate in many reactions usually employed for the synthesis of strained olefins:



(I)

Thus bisdehalogenation of 1-bromo-2-iodoadamantane with n-butyl- or s-butyl-lithium yielded a hydrocarbon $C_{20}H_{28}$:[10]

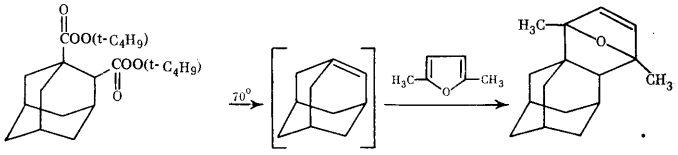


Analogous dimers have been obtained in 98% yield on treatment of 1,2-di-iodoadamantane with n-butyl-lithium in pentane at 0 °C;[11] at -80 °C in pentane in the presence of a large excess of butadiene a butadiene–adamantane adduct was isolated in addition to the dimer (85%).[12,13] When a

† During this year, 50 years have elapsed since the discovery of adamantane; it was first detected by Landa and Macháček in the petroleum of the Hodonin deposit (Czechoslovakia).

mixture of 1,2-di-iodoadamantane and lithium diphenyl phosphate is heated in tetrahydrofuran (VHF) and then oxidised with hydrogen peroxide, an adamantane dimer is also formed[14].

Adamantene is likewise produced as an intermediate in the decomposition of the di-t-butyl ester of the adamantane-1,2-dicarboxylic peracid in 2,5-dimethylfuran[15]. An adamantane–dimethylfuran adduct was then obtained by the Diels–Alder reaction:



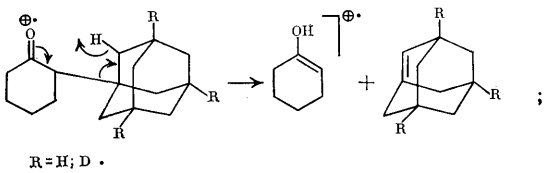
Debromination of 1,2-dibromoadamantane by treatment with $(CH_3Si)_2Hg$ in boiling benzene also leads to the formation of adamantene as an intermediate, which dimerises in the absence of acceptors and, when the reaction is carried out in the presence of 2,5-dimethylfuran, gives rise to the corresponding Diels–Alder adduct[16].

The formation of adamantene has been confirmed by spectroscopic methods. According to infrared and EPR spectroscopic data, the main product of the interaction of 1,2-dibromo- and 1,2-di-iodo-adamantane with sodium and potassium vapours stabilised in an argon matrix at 10 K is adamantene; the 1-adamantyl radical is also formed in small amounts[17]. After heating the matrix to approximately 20 °C, [2 + 2] dimers and small amounts of 1,1'-biadamantyl were detected in the reaction mixture by gas chromatography–mass spectrometry. Judging from the infrared spectroscopic data, the character of the C=C bond in adamantene is closer to that of an unstrained C=C bond than to a biradical. However, this double bond has a partial radical character, which is evident from the formation of a dimer, of which ordinary olefins are incapable[17].

The attempt to obtain adamantene by the photoelimination reaction from 1-adamantylacetone was unsuccessful[18]. At the same time the formation of adamantene from adamantyl esters (1- and 2-adamantyl phenylacetates) via the photoelimination reaction in methanol has been observed; in both cases the subsequent ionic addition of the residue of the solvent molecule to adamantene leads to the same product; 1-methoxyadamantane[19].

The formation of the adamantene ion (*m/e* 134) from 2-adamantyl trifluoroacetate has been demonstrated by the kinetic field ionisation method[20].

The ionisation of 2-(1-adamantyl)cyclohexanone on electron impact in a high vacuum (10^{-6} mmHg) leads to the formation of the 1-hydroxycyclohexenylium radical-cation and the neutral compound (I):[21]



R=H; D.

The closest cyclic homologue of adamantene is 3-homoadamantene (IV), whose strain energy is much lower in view of the greater size of the ring containing the C=C double bond (Table 1)[22]. The theoretical existence of 3-homoadamantene was predicted in a number of studies[23–25]. It was obtained in a pure form (condensed on a NaCl plate at −196 °C) by the pyrolysis of 1-adamantyldiazomethane *in vacuo* (10^{-3} mmHg, 375 °C). When compound (IV) is heated to room temperature, the 3-homoadamantene dimer is formed according to infrared spectroscopic data[26]; it has also been described in other communications[27,28]. Its pyrolysis at 500° to 520 °C leads to 3-vinylnoradamantane (V), 4-methylene-protoadamantane (VI), and 4-homoadamantane (VII):[27]

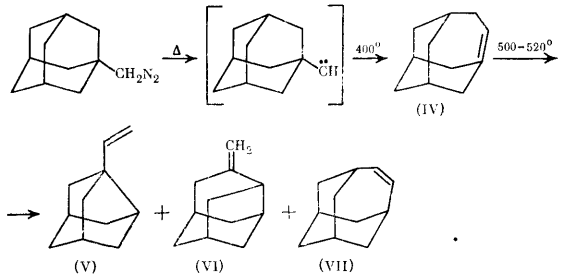


Table 1. The stability of certain olefins with a C=C bond at the base of the bridge[22].

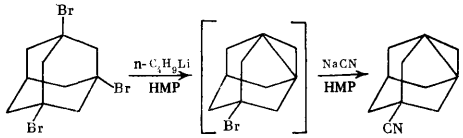
Olefin	$\Delta H°$, kcal mol^{-1}	$E°$, kcal mol^{-1}	$\Delta E°$, kcal mol^{-1}
Bicyclo[2,2,2]oct-1-ene	+42.72	50.6	40.4
Adamantene	+32.26	43.0	39.5
3-Homoadamantene	+18.92	35.3	20.2
Bicyclo[3,3,2]dec-1-ene	+6.18	25.2	4.7
Bicyclo[4,4,1]undec-1-ene	−8.95	15.7	−1.5

Note. $\Delta H°$ is the heat of formation, $E°$ the strain energy, and $\Delta E°$ the difference between the strain energies of the alkene and the corresponding alkane.

1,3- and 2,4-Dehydroadamantanes, which are entirely stable compounds, are obtained by the reactions usually employed for the synthesis of cyclopropane hydrocarbons (1,3-elimination, insertion of a carbene, etc.).

1,3-Dehydroadamantane was first synthesised by treating 1,3-dibromoadamantane with the Na–K alloy in boiling heptane; its structure was confirmed by chemical reactions involving the opening of the three-membered rings[29] A 9 : 1 mixture of 1,3-dehydroadamantane and adamantane has been obtained analogously in 77% yield from 1,3-dibromoadamantane in ether containing traces of t-butyl alcohol and (or) hexamethylphosphoramide (HMP).[30] Under these conditions, 1,3-dibromo-5,7-dimethyladamantane gives rise to a 1 : 1 mixture of 1,3-dehydro-5,7-dimethyladamantane and 1,3-dimethyladamantane in 78% yield[30].

When lithium is used, the cyclisation of 1,3-dibromoadamantane takes place in THF at room temperature. However, the presence of a catalyst, namely alkylarylchlorosilane, is required in this instance; the yield of compound (II) is 80%.[31] Treatment of 1,3,5-tribromoadamantane with n-butyl-lithium at −35 °C in ether containing HMP (in proportions of 25 : 1) leads to 5-bromo-1,3-dehydroadamantane, which is converted into the stable 5-cyano-1,3-dehydroadamantane following the addition of NaCN:[32]



The formation of compound (II) is also observed in the polarographic reduction of 1,3-dibromoadamantane[33].

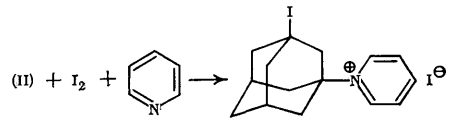
Like other alicyclic hydrocarbons containing a strained three-membered ring, 1,3-dehydroadamantane and its derivatives are very reactive. The C(1)–C(3) bond in compound (II) is greatly weakened; its length is 1.64 Å while the lengths of other C–C bonds in adamantane are 1.53 Å [Majerski et al.[5] (p.37)]. Because of this, the reactions of 1,3-dehydroadamantane proceed selectively with the opening of the three-membered ring and the formation of 1-mono- or 1,3-di-substituted derivatives of adamantane; the fragmentation of the adamantane ring also takes place sometimes.

The oxidation of compound (II) with air at 20 °C in heptane leads to a peroxide, which decomposes explosively at 160 °C.[29] In air and in solution in pentane at room temperature, compound (II) is converted into a mixture of copolymers with oxygen, whose main component is the explosive polyperoxyadamantane $(OC_{10}H_{14}O)_n$.[29,30]

On heating (130–160 °C) in a sealed tube, compound (II) is converted into a white polymer (1,3-polyadamantane) having the composition $(C_{10}H_{14})_n$, which is insoluble in organic solvents and is stable in an atmosphere of nitrogen at 400 °C. An analogous polydimethyladamantane is formed from 1,3-dehydro-5,7-dimethyladamantane at 90–145 °C. In the absence of oxygen, compound (II) is thermally stable, its half-life at 195 °C in solution in n-octane amounting to approximately 4 h.[29,30]

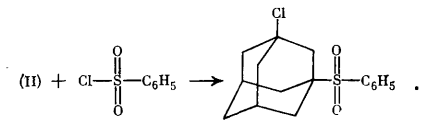
Catalytic hydrogenation of compound (II) leads to adamantane in 82% yield and the interaction of compound (II) with bromine or iodine gives rise to 1,3-dibromo- and 1,3-di-iodo-adamantane respectively[29].

Treatment of compound (II) with iodine in the presence of pyridine produces *N*-(3-iodo-1-adamantyl)pyridinium iodide[34]:

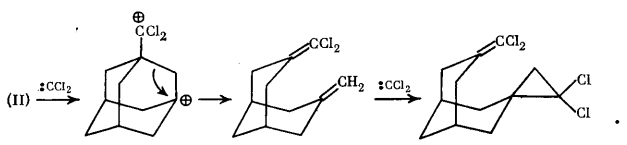


This reaction is one of the first examples of coupled intermolecular halogenoamination.

1,3-Dehydroadamantane combines with benzenesulphonyl halides even in the absence of a catalyst[35]:

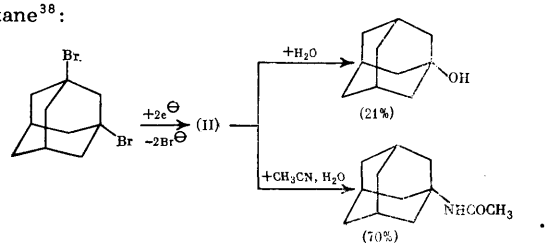


Under the conditions of the catalytic generation of dichlorocarbene, 1,3-dehydroadamantane combines with two equivalents of the carbene to form 7-dichloromethylenebicyclo[3.3.1]nonane-3-spiro-1-(2',2'-dichloro)cyclopropane[36]:



The reaction of compound (II) with aryliodosocarboxylates having the general formula $ArI(OCOR)_2$, where R = alkyl or aryl, has been investigated[37]. The main products of this reaction in inert solvents at room temperature are iodobenzene and 1,3-diacyloxyadamantenes.

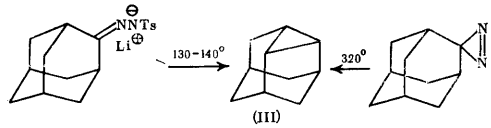
1,3-Dehydroadamantane is formed in the electrochemical reduction of 1,3-dibromoadamantane in acetonitrile at a mercury electrode. It reacts with acetonitrile and the water contained in it to form 1-adamantanol and 1-acetamidoadamantane[38]:



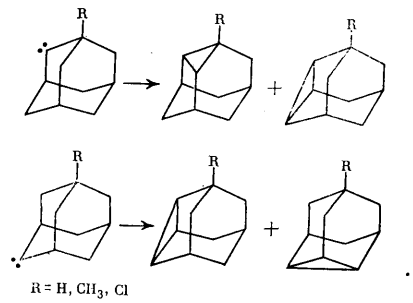
The addition of acetic acid to compound (II) leads to 1-adamantyl acetate[39].

The reaction of compound (II) with maleic anhydride, acrylonitrile, and dimethyl acetylenedicarboxylate results in the formation of oligomeric products[40]. The reactions are carried out at room temperature and in the absence of polymerisation initiators; the homopolymerisation of each monomer takes place under more severe conditions.

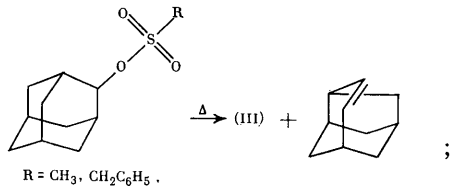
2,4-Dehydroadamantane or tetracyclo[4.3.1.$0^{2,4}$.$0^{3,8}$]decane is an extremely stable compound (m.p. 202.5–203.5 °C). In a pure form, compound (III) has been obtained by the pyrolysis of the dry lithium salt of 2-adamantanone *p*-tosylhydrazone at 130–140 °C (yield 65%)[41] and adamantane-2-spiro-3'-diazirine at 320 °C (yield 96%):[42]



Derivatives of 2,4-dehydroadamantane containing bridgehead substituents have been obtained recently by the hydrolysis of the corresponding alkali metal salts of tosylhydrazones#. It was established that the proportions of the products of the intramolecular insertion of the intermediate carbenes in the C–H bond depend on the substituent and its position relative to the carbene centre:



The pyrolysis of adamantane-2-sulphonate at 520 °C leads to compound (III) and protoadamantene (in 57 and 38% yields respectively):[43]



S.Hiršl-Starčevič and Z.Majerski, J.Org.Chem., 1982, **47**, 2520.

Irradiation of solutions of 2-iodo- and 2-bromo-adamantanes with ultraviolet light leads to a mixture of adamantane, compound (III), protoadamantene and respectively (depending on the solvent employed) 2-ethoxy- or 2-methoxy-adamantane[44]. The last two compounds are obtained as a result of the nucleophilic attack by solvent molecules on the intermediate 2-adamantyl cation; the deprotonation of the cation leads to a mixture of compound (III) and protoadamantene:

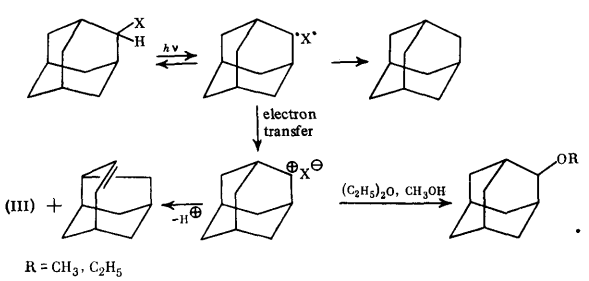
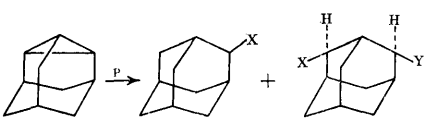


Table 2. 2-Substituted adamantanes formed on interaction of 2,4-dihydroadamantane with electrophiles[45].

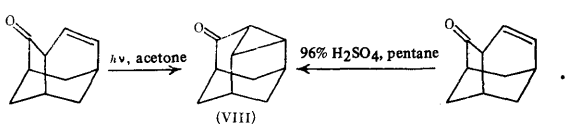
Reagents P	Substituent X	Yield, %
HI	I	24
CH_3COOH, H_2SO_4	$OCOCH_3$	94
CH_3OH, BF_3	OCH_3	80
C_6H_6, $AlCl_3$, BF_3	C_6H_5	70
$C_6H_5CH_3$, $AlCl_3$, BF_3	$C_6H_4CH_3$	50
$C_6H_5OCH_3$, $AlCl_3$, BF_3	$C_6H_4OCH_3$	86

The availability of 2,4-dehydroadamantane provides a unique possibility for the synthesis from it of 2-mono- and 2,4-di-substituted adamantane derivatives, which are otherwise difficult to obtain, as a result of the opening of the three-membered ring by electrophiles (Tables 2 and 3).[45,46] The reactions of compound (III) with such reagents (P) proceed in accordance with the following general mechanism:



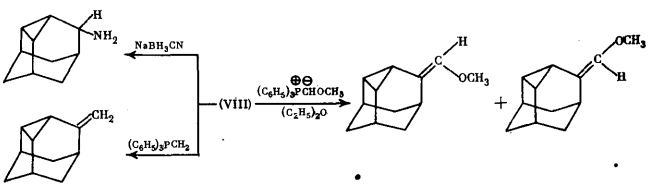
The oligomerisation of compound (III) under the influence of $AlCl_3$ leads to a dimer and a trimer; higher oligomers have not been detected in the reaction products[47]. It has been suggested that the oligomerisation proceeds via an ionic chain mechanism with the intermediate formation of the 1-adamantyl cation.

The 2,4-dehydroadamantane derivative (VIII) has been obtained by the photoisomerisation[48,49] of 2-protoadamantenone or its isomerisation in the presence of an acid catalyst[50]:



Compound (VIII) has been synthesised in several stages from norbornadiene with an overall yield of 2%.[51] It is readily converted into compound (III) by the Wolff–Kishner reaction in 75% yield[52].

The presence of the active carbonyl group permits the synthesis of other 2-substituted 8,9-dehydroadamantanes from compound (VIII):[48]



2,4-Methano-2,4-dehydroadamantane, which is the closest cyclic homologue of 2,4-dehydroadamantane, has been obtained by the pyrolysis of the dry sodium salt of 4-methylene-2-adamantanone tosylhydrazone[53], is relatively stable at room temperature, and reacts rapidly with oxygen, methanol, and bromine to form a complex mixture of products. The structure of this propellane has been demonstrated by ^{13}C NMR.[54]

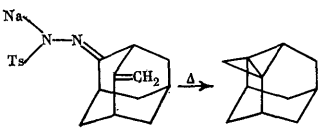
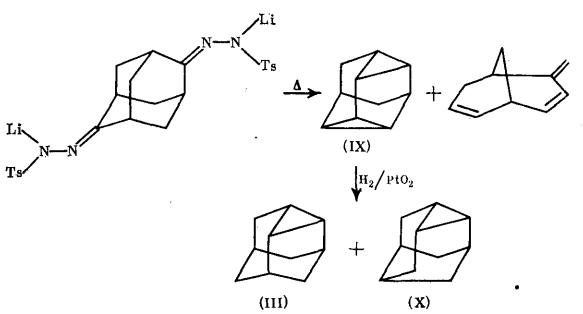


Table 3. 2,4-Disubstituted adamantanes formed on interaction of 2,4-dehydroadamantane with electrophiles[45].

Reagents P	Substituents		Yield, %
	X	Y	
Cl_2, CCl_4	Cl	Cl	77
Br_2, CCl_4	Br	Br	86
I_2, CCl_4	I	I	100
Cl_2, CH_3CN, H_2O	Cl	$HNCOCH_3$	76
Br_2, CH_3CN H_2O, $AgClO_4$	Br	$HNCOCH_3$	78
I_2, CH_3CN, H_2O, $AgClO_4$	I	$HNCOCH_3$	81
Cl_2, H_2O, $(C_2H_4O)_2$	Cl	OH	71
N-Bromosuccinimide, H_2O	Br	OH	83
C_3H_5OH, H_2O, $AgNO_3$	OH	OH	50
CH_3OH, *N*-bromosuccinimide	Br	OCH_3	23
$Hg(CH_3COO)_2$, H_2O	OH	$HgOCOCH_3$	95
NOCl, $CHCl_3$	Cl	NOH	38

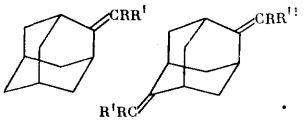
2,4,6,9-Tetradehydroadamantane (IX) or pentacyclo-[4.4.0.$0^{2,10}$.$0^{3,5}$.$0^{4,8}$]decane is of considerable interest. It is a stable compound, melting at 152–154 °C and capable of withstanding heating to 250 °C for 10 min without change of structure. It has been obtained by the thermolysis of the dilithium salt of 2,6-adamantanedione bistosylhydrazone[55,56]:



Catalytic hydrogenation of compound (IX) over a platinum catalyst at room temperature and atmospheric pressure in the presence of THF and acetic acid results in the cleavage of only one cyclopropane ring with formation of a mixture of two $C_{10}H_{14}$ hydrocarbons: 2,4-dehydroadamantane and, mainly, dehydroprotoadamantane (X) or tetracyclo[4.4.0. .$0^{2,10}$.$0^{4,8}$]decane. Compound (IX) does not isomerise under the influence of temperature and a catalyst (80 °C, $AgBF_4$).[56]

III. ADAMANTANE DERIVATIVES CONTAINING AN EXOCYCLIC C=C DOUBLE BOND

By virtue of the characteristic features of the adamantane structure, an exocyclic π-bond is possible only in a bridging position in the nucleus:

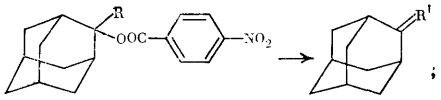


(XI) (XII)

Compounds of type (XI) are as a rule obtained by the traditional method—the dehydration of the corresponding tertiary alcohols produced by the condensation of adamantanone and lithium alkyls or Grignard reagents. In particular, 2-methyleneadamantane[57,58], 2-ethylideneadamantane[60,61], 2-propylideneadamantane[60], 2-isobutylideneadamantane[60], and 2-butylideneadamantane[60,62] have been obtained in this way.

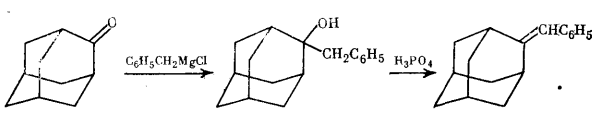
Certain derivatives of unsaturated compounds of type (XI) such as 2-hydroxy-6-methyleneadamantane[65], 6-ethylidene-2-methyladamantane or 6-propylideneadamantane[68], and 8-methylene- and 8-isopropylidene-2,6-dioxa-adamantanes[69] are also obtained by the dehydration of the corresponding alcohols. Iodine is the best dehydrating agent[63], since acid catalysts can lead to the formation of side products, as happens, in particular, on heating 2-methyl-2-adamantanol with phosphoric acid[58,64]. When 2-methyl- and 2-isopropyl-2-adamantanols are treated with acetic anhydride, methyleneadamantane and a mixture of isopropylideneadamantane with isopropenyladamantane are obtained respectively[65]. Refluxing of 2-isopropyl-2-adamantanol and 2-isopentyl-2-adamantanol in xylene in the presence of I_2 resulted in the formation of isopropylideneadamantane and isopentylideneadamantane respectively[63].

Another way of obtaining these olefins involves the solvolysis of 2-alkyl-2-adamantyl *p*-nitrobenzoates[59]:

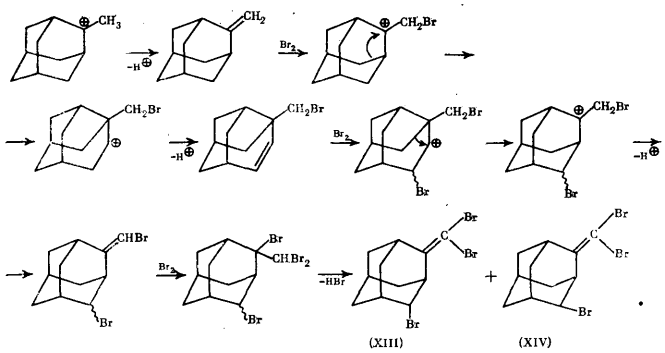


R = CH_3, C_2H_5, $CH_2C(CH_3)_3$, iso-C_3H_7;
R' = CH_2, $CHCH_3$, $CHC(CH_3)_3C(CH_3)_2$.

There are data concerning the synthesis of di-t-butylmethyleneadamantane by the thermolysis of the corresponding adamantane-2-spiro-thiadiazoline[66]. Benzylideneadamantane has been obtained in 90% yield by the dehydration of 2-benzyl-2-adamantanol in the presence of a tenfold excess of 85% orthophosphoric acid at 120 °C:[67]



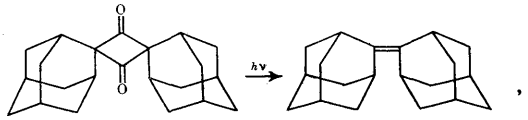
Bromo-derivatives of 2-methyleneadamantane (XIII) and (XIV) have been obtained as a result of the unusual course of the bromination of 2-methyladamantane[70]:



(XIII) (XIV)

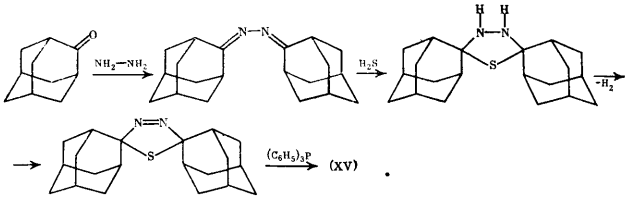
ω-Bromomethyleneadamantane has been synthesised by brominating methyleneadamantane with *N*-bromosuccinimide in the presence of Br_2O_2 or by the Wittig reaction from 2-adamantanone and $(C_6H_5)_3P{=}CHBr$.[71]

Adamantylideneadamantane (XV) is of significant interest; it is formed by the photochemical decarbonylation of the 2-adamantylketen dimer[72],

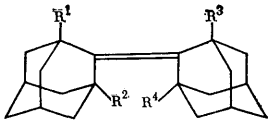


(XV)

and the debromination of *gem*-2-dibromoadamantane with the aid of the zinc–copper couple[73]. Compound (XV) has also been synthesised in accordance with the following scheme[74]:



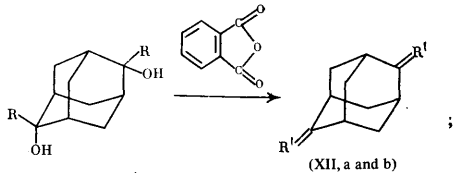
Many methyl derivatives of adamantylideneadamantane (XV, a–e) have been synthesised too[75,76]:



(XVa-e)

(a) R^1, R^2, R^3, R^4 = H;
(b) R^1, R^4 = H, R^2, R^3 = CH_3;
(c) R^1, R^3 = H, R^2, R^4 = CH_3;
(d) R^1, R^2 = H, R^3, R^4 = CH_3;
(e) R^1, R^2, R^3, R^4 = CH_3.

The bisunsaturated derivatives of adamantane of type (XII) have been obtained by the dehydration of the corresponding diols[77]:

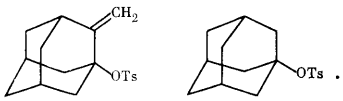


(XII, a and b)

(a) R = CH_3, R' = CH_2 (45%);
(b) R = C_2H_5, R' = C_2H_4 (90%).

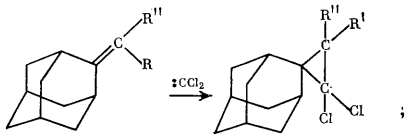
In terms of their chemical properties, unsaturated derivatives of adamantane of types (XI) and (XII) are close to other alicyclic hydrocarbons containing an isolated exocyclic C=C double bond. The catalytic hydrogenation of hydrocarbons of types (XI) and (XII) leads to 2-alkyl- and 2,6-dialkyl-adamantanes[77]: on reaction with methylene iodide in the presence of the zinc-copper couple or with diazomethane in the presence of copper bromide, methylene- and ethylidene-adamantanes give rise to the corresponding cyclopropane derivatives[78]: methyleneadamantane combines with dichloro- and dibromo-carbenes to form 2,2-dichloro- and 2,2-dibromo-(2-adamantyl)spiro-1'-cyclopropanes[79].

At the same time the presence of the bulky adamantyl group gives rise to major steric hindrance, which reduces the reactivity of the C=C bond and the rigidity of the structure prevents the appearance of the possible conjugation effects. Thus, as a consequence of the hindrance to the conjugation between the cationic centre and the adjoining double bond in 2-methylene-1-adamantanyl tosylate, the rate of solvolysis of the tosylate (XVI) is lower than that of the unsubstituted tosylate (XVII) by a factor of 10^4, although the opposite relation might have been expected[80]:



(XVI) (XVII)

The reactivity of the double bonds of the olefins (XI) in the reactions with dichlorocarbene depends significantly on the size and character of the substituent[81]:

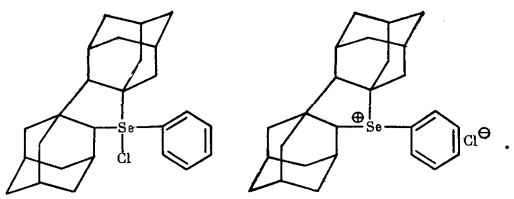


(XI)

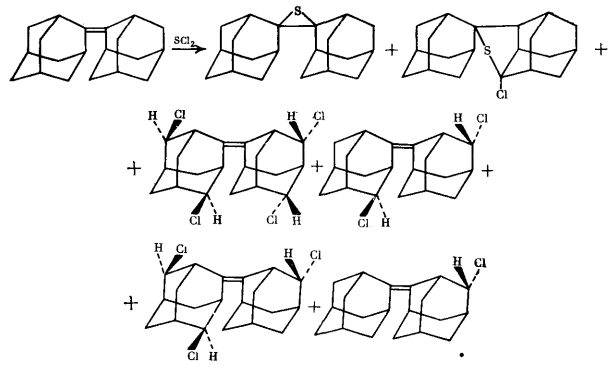
R′ = R″ = H; R′ = CH_3, R″ = H; R′ = C_2H_5, R″ = H; R′ = $(CH_3)_2CH$, R″ = H; R′ = $(CH_3)_2CHCH_2$, R″ = H; R′ = C_6H_5, R″ = H; R′ = R″ = CH_3; R′ = R″ = C_6H_5. The groups R′ and R″ increase (primary alkyl groups) or decrease (isopropyl and phenyl groups) the reactivity of the double bond in conformity with the manifestation of the inductive and steric effects by the latter. The hydrocarbon (XI, R′ = R″ = C_6H_5) does not react with dichlorocarbene.

Steric effects are shown particularly strikingly for adamantylideneadamantane. When compound (XV) was halogenated, its stable complexes with chlorine and bromine were isolated[82,83]. On the basis of ^{13}C NMR investigations, the structure of two-electron three-centre π-complexes was attributed to them[84].

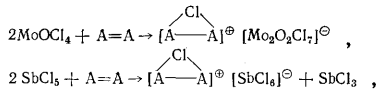
The unique behaviour of the double bond of compound (XV) permits the synthesis of thermally stable complexes[85]:



The reaction of SCl_2 with the highly hindered double bond in compound (XV) proceeds in an unusual manner and, depending on the reaction conditions, results in the formation of compounds containing S-heterocycles and also chloro-substituted adamantylideneadamantanes[86,87]:



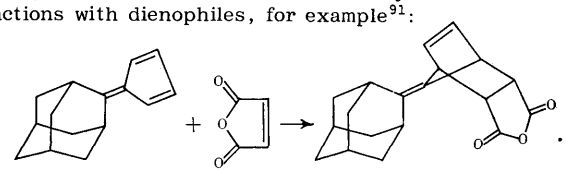
The reaction of compound (XV) with $MoOCl_4$ or $SbCl_5$ in the presence of Lewis acids leads respectively to adamantylideneadamantanechloronium heptachlorodioxodimolybdate and hexachloroantimonate[88]:



where A = 2-adamantylidene.

As a result of the considerable hindrance of the double bond, the addition of dichlorocarbene to compound (XV) takes place twenty times more slowly than to the hydrocarbon (XI, R′ = R″ = H).

2-Cyclopentadienylideneadamantane (XVIII), which can be readily obtained from 2-adamantanone and cyclopentadiene, has interesting synthetic possibilities[89]. Its hydrogenation leads to 2-cyclopentenyl- and 2-cyclopentyl-adamantanes[89,90]. The hydrocarbon (XVIII) enters actively into condensation reactions with dienophiles, for example[91]:



(XVIII)

IV. ADAMANTANE DERIVATIVES WITH A C=C DOUBLE BOND IN A SIDE CHAIN

The adamantane derivatives belonging to this group include compounds containing an unsaturated substituent at both bridgehead and bridging positions, as well as compounds having two (identical or different) substituents in the 1- and 3-positions. Traditional methods are usually employed successfully for their synthesis, although some exceptions are known. Thus, despite the wide-scale variation of the reaction conditions in the dehydration of 1-(1-hydroxyethyl)-adamantane, 1-vinyladamantane (XIX) could not be obtained[92]. The attempt to synthesise compound (XIX) by the pyrolysis of a quaternary ammonium base, namely 2-(1-adamantyl)-ethyltrimethylammonium hydroxide, was also unsuccessful[93].

1-Vinyladamantane was first synthesised by the dehydration of 1-ethyladamantane in the presence of a catalyst containing aluminium and chromium, molybdenum, and tungsten hydroxides[94]. A patent was later published[95] in which several methods for the dehydration of 1-(1-hydroxyethyl)-adamantane are described. Compound (XIX) has been obtained in the highest yields (85–95%) by the pyrolysis of the borate and acetate derived from the initial alcohol. The yield of compound (XIX) in the dehydration of the unsubstituted alcohol over alumina at 350–400 °C did not exceed 30%.

The thermal cleavage of 2-(1-adamantyl)ethyl *S*-methyl xanthate leads to compound (XIX) in 77% yield[93] §:

$$AdCH_2CH_2OC(=S)SCH_3 \xrightarrow{270^\circ} AdCH{=}CH_2 + S{=}C(OH)SCH_3$$
(XIX)

Compound (XIX) has been synthesised in 80% yield by the dehydration of the borate of 1-(2-hydroxyethyl)adamantane at 300 °C.[96] 1-(Vinyl)adamantane is the product of the debromination (with Zn in dimethylformamide) of 1-adamantyl-1,2-dibromoethane[97,98].

The interaction of adamantane with acetylene under the influence of ^{60}Co γ-radiation also leads to compound (XIX) in 8% yield[99]. This method cannot evidently have any preparative value, although it is of interest as the first example of the formation of 1-vinyladamantane via a radical chain mechanism.

A procedure has been proposed recently for the synthesis of 1-vinyladamantane homologues by the reaction of 1-propenyladamantanes with ethylene in the presence of an alumina–rhenium heptoxide catalyst (10–20% Re_2O_7 and 80 to 90% Al_2O_3) at 20 °C and atmospheric pressure[100].

Propenyladamantanes are formed when adamantane and its homologues react with propene over industrial alumina and zeolite-containing catalysts[101]. If the starting material is 1-adamantanol, trifluoroacetic acid can also be used as the catalyst[102,103].

Regardless of the method of preparation of 1-propenyladamantane (XX), its formation is accompanied by that of its isomer—1-allyladamantane (XXI). In the dehydrohalogenation of 1-(2-bromopropyl)adamantane, the contents of compounds (XX) and (XXI) in the reaction mixture are 80 and 7.4 respectively[104]:

$$AdCH_2CHBrCH_3 \rightarrow \underset{(XX)}{AdCH{=}CHCH_3} + \underset{(XXI)}{AdCH_2CH{=}CH_2}$$

The products of the pyrolysis of 1-(1-adamantyl)-2-propyl acetate contain 70% of compound (XX) and 30% of compound (XXI).[105] Compound (XX) is probably thermodynamically more stable.

1-Allyladamantane has been synthesised by the debromination of 3-(1-adamantyl)-1,2-dibromopropane with zinc in boiling ethanol in 89% yield[104], and also by the reaction of 1-chloroadamantane with $CH_2{=}CHCH_2SI(CH_3)_3$ with participation of Lewis acids ($TiCl_4$).[106,107]

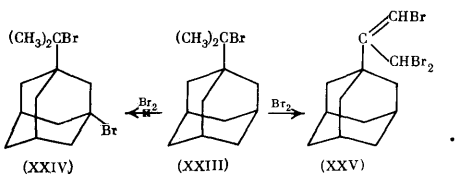
1-Isopropenyladamantane (XXII) has been synthesised by the dehydration of a tertiary alcohol—2-(1-adamantyl-2-propanol—by acetic anhydride[108] or iodine[109]:

$$AdC(CH_3)_2OH \rightarrow \underset{(XXII)}{AdC(CH_3){=}CH_2}$$

When an attempt was made to synthesise t-butyladamantane from 2-(1-adamantyl)-2-propanol, the main product was also compound (XXII):[110]

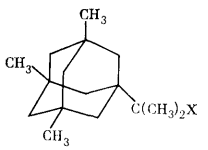
$$AdC(CH_3)_2OH \xrightarrow{SOBr_2} AdC(CH_3)_2Br \xrightarrow{CH_3MgI} AdC(CH_3)_3$$
$$\rightarrow \underset{(XXII)}{AdC(CH_3){=}CH_2} \leftarrow$$

Unsaturated derivatives of the type considered are likewise formed in halogenation reactions. Thus, instead of the expected bromo-derivative (XXIV), the unsaturated tribromo-derivative (XXV) is obtained on bromination of 2-(1-adamantyl)-2-bromopropane (XXIII):[111]



(XXIV) (XXIII) (XXV)

Bromination of compounds (XXVI) and (XXVII) proceeds analogously, i.e. with formation of unsaturated products[111]:



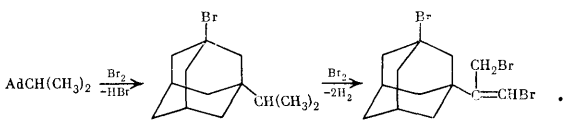
(a) X = Br (XXVI)
(b) X = H (XXVII)

In conformity with the proposed reaction mechanism, the C=C bond is formed on deprotonation of the intermediate carbonium ions[111], as in the bromination of 2-methyladamantane considered above[70]:

$$AdC(CH_3)_2Br \xrightarrow[-Br_3^\ominus]{+Br_2} AdC^\oplus(CH_3)_2 \xrightarrow{-H^\oplus} AdC(CH_3){=}CH_2 \xrightarrow{+Br_2}$$
$$\rightarrow AdC(CH_3)BrCH_2Br \xrightarrow[-2H^\oplus,\,-Br_3^\ominus]{+Br_2} \underset{CHBr_2}{AdC^\oplus CH_2Br} \xrightarrow{-H^\oplus} \underset{CHBr_2}{AdC{=}CHBr}$$

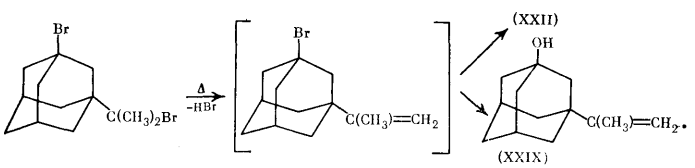
An analogous mechanism operates in all probability in the alkenylation of adamantane by propene[101].

1-Isopropyladamantane is usually brominated exclusively in the nucleus, forming 1-bromo-3-isopropyladamantane. However, on increasing the reaction time under the conditions adopted [95–100 °C, $AdCH(CH_3)_2 : Br_2 = 1 : 22$], further bromination takes place with formation of compound (XXVIII):[112]



(XXVIII)

Thermal dehydrobromination of 2-bromo-2-(3-bromo-1-adamantyl)propane results in the formation of a monobromide, which is converted into the olefin (XXII) and the unsaturated alcohol (XXIX)[113] (p.75):



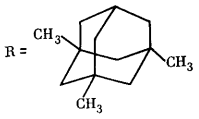
(XXIX)

Fluoro-substituted alkenyladamantanes, which are of great practical interest, are obtained by the dehydrofluorination reaction. Thus dehydrofluorination of 1-hexafluoropropyladamantane in the presence of $C_2H_5OH/NaOH$ leads to 1-pentafluoropropenyladamantane in 75% yield[114]. Spectroscopic data demonstrate the presence of a double bond in the vinyl position.

§ Here and henceforth Ad = 1-adamantyl.

1-Isopropenyl-3,5,7-trimethyladamantane (XXX) has been synthesised[113] by the dehydration of the corresponding alcohol, which was obtained from methyl 3,5,7-trimethyladamantane-1-carboxylate (XXXI):

$$\underset{\text{(XXXI)}}{RC(O)OCH_3} \xrightarrow{CH_3MgI} RC(CH_3)_2OH \xrightarrow{-H_2O} \underset{\text{(XXX)}}{RC(CH_3)=CH_2};$$



1-Isopropenyl-2-methyladamantane is a product of the dehydration of 2-(2-methyl-1-adamantyl)-2-propanol by acetic anhydride[115].

1-(1-Adamantyl)-2-methyl-2-propanol has been used to synthesise the butenyladamantanes (XXXIII) and (XXXIV).[116] The dehydration takes place both on heating the alcohol with acetic anhydride[115] or anhydrous oxalic acid[105] and on treatment of the alcohol with hydrogen bromide in glacial acetic acid[105,116]. Evidently, the conversion of the alcohol takes place in two stages—via the intermediate formation of the tertiary carbonium ion (XXXII), which is stabilised as a result of the electron-donating effect of the adamantane nucleus:

$$AdCH_2C(CH_3)_2OH \xrightarrow{HBr,CH_3COOH} \underset{\text{(XXXII)}}{AdCH_2\overset{\oplus}{C}(CH_3)_2} \begin{cases} \xrightarrow{-H^{\oplus}} \underset{\text{(XXXIII)}}{AdCH_2C(CH_3)=CH_2} + \underset{\text{(XXXIV)}}{AdCH=C(CH_3)_2} \\ \longrightarrow \overset{\oplus}{Ad} + CH_2=C(CH_3)_2 \end{cases}.$$

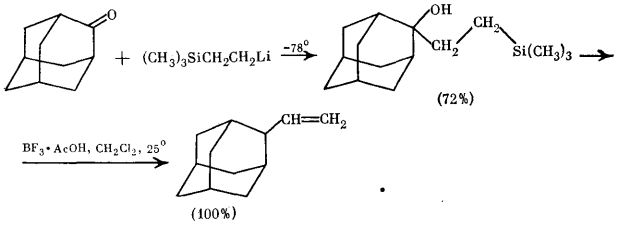
Further reactions of the ion (XXXII) take place with formation of the more stable 1-adamantyl cation as an electrophilic fragment or with elimination of the proton and the formation of unsaturated compounds.

1-(1-Adamantyl)-2-chloro-2-phenylethylene (XXXV) has been synthesised from 1-chloroadamantane[106,107]:

$$AdCl + C_6H_5C{\equiv}CSi(CH_3)_3 \xrightarrow{TiCl_4} \underset{\text{(XXXV)}}{AdCH=CClC_6H_5}.$$

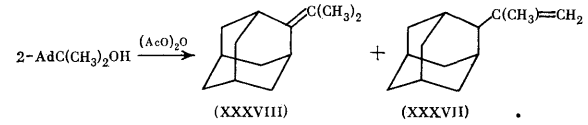
To confirm the structure of compound (XXXV), $C_6H_5CH=$CHAd (XXXVI) was synthesised by the Wittig reaction from adamantane-1-carboxyaldehyde and $C_6H_5CH=P(C_6H_5)_3$. The reduction of compound (XXXV) by zinc in boiling alcohol leads to *cis*-(XXXVI).

Adamantanes with an unsaturated side chain in the 2-position have been hardly investigated. 2-Vinyladamantane can be obtained in a high yield by the direct conversion of adamantanone under the influence of β-[(trimethylsilyl)ethyl]-lithium¶:

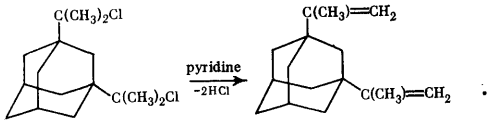


¶ S.R.Wilson and A.Shedrinsky, J.Org.Chem., 1982, **47**, 1983.

The formation of 2-isopropenyladamantane (XXXVII) in a 1 : 4 mixture with 2-isopropylideneadamantane (XXXVIII) on dehydration of 2-(2-adamantyl)-2-propanol has been noted[65]:



Adamantanes containing two unsaturated substituents in the molecule have been obtained by analogous methods. Thus 1,3-di-isopropenyladamantane has been synthesised by the dehydrochlorination of a dichloro-derivative[117]:



1-Allyl-3-vinyladamantane and 1,3-diallyladamantane have been obtained by the dehydrobromination of the corresponding bromo-derivatives[104].

Unsaturated hydrocarbons of the adamantane series, containing the double bond in the α-position in the side chain, are as a rule liquids with boiling points above 200 °C, which are fairly stable on heating. A study of the mass spectra of these compounds has shown that their molecular ions (M^+) are much more stable than the M^+ derived from the corresponding alkyladamantanes (the M^+ intensities for 1-ethyl- and 1-vinyl-adamantanes are 4 and 92% respectively)[118,119]. The intensity of the ions with *m/e* 135 (or their homologues), corresponding to the elimination of alkenyl groups, is low. These data indicate the greater stability of the C_{ad}–C_{alk} bond in alkenyl adamantanes than in alkyladamantanes. This may be the result of the interaction of the C=C bond with the excess electron density within the adamantane nucleus (1,3-conjugation); such conjugation can arise as a result of the overlap within the skeleton of the rear portions of the orbitals of the four bridgehead carbon atoms (a cage effect is postulated—see, for example, Fort[8] (p.161). However, such interaction, if it does in fact occur, is energetically insignificant, since its appreciable influence on the chemical properties of the compounds has not been observed. Thus 1-vinyladamantane and 1-allyladamantane have the same reactivities in relation to iodine[120]. The hydrogenation of these olefins gave high yields (80–95%) of the corresponding alkyladamantanes[93,105,116]. 1-Vinyladamantane usually combines with HBr according to the Markovnikov rule[93]. However, under certain conditions the main product of the addition of HBr to 1-vinyladamantane is 1-(1-adamantyl)-2-bromoethane and not 1-(1-adamantyl)-1-bromoethane (XXXIX):[121]

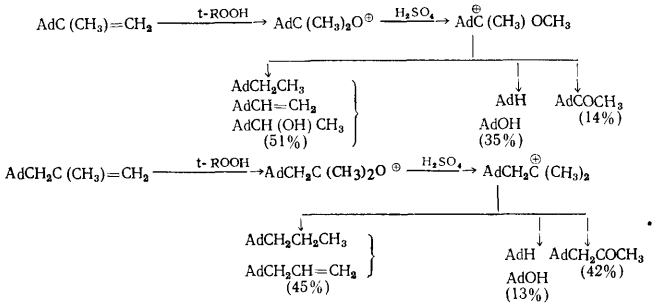
$$\overset{\delta\ominus}{AdCH}=\overset{\delta\oplus}{CH_2} \xrightarrow{H^{\oplus}(HBr)} AdCH_2\overset{\oplus}{C}H_2 \rightarrow Ad\overset{\oplus}{C}HCH_3 \xrightarrow{Br^{\ominus}} \underset{\text{(XXXIX) (27\%)}}{AdCHBr_2CH_3}$$
$$\xrightarrow{Br^{\ominus}} \underset{\text{(73\%)}}{AdCH_2CH_2Br}.$$

The addition of bromine to 1-vinyladamantane yields 1-(1-adamantyl)-1,2-dibromoethane, the dehydrobromination of which leads to a mixture of unsaturated compounds[121]:

$$AdCH=CH_2 + Br_2 \rightarrow AdCHBrCH_2Br \xrightarrow[5h,\ reflux]{C_2H_5OH+KOH}$$
$$\rightarrow \underset{(59\%)}{AdCBr=CH_2} + \underset{(34\%)}{\textit{trans}\text{-}AdCH=CHBr} + \underset{(7\%)}{AdC{\equiv}CH}.$$

The epoxidation of 1-vinyladamantane has been achieved with the aid of t-butyl hydroperoxide in the presence of $Mo(CO)_6$; 1-epoxyadamantane has been polymerised with the opening of the epoxide ring[122].

The introduction of the adamantane nucleus into tertiary hydroperoxides should influence significantly their rearrangement in an acid medium, because a high tendency towards the formation of a cation is a distinctive feature of adamantane derivatives. Thus the hydroperoxides obtained from 1-isopropenyl- and 1-isobutenyl-adamantanes in 70% H_2SO_4 in the presence of cyclohexane give rise to a complex mixture of products[123]:



The interaction of 1-isopropenyl- and 2-isopropenyl-adamantanes[124] or 3-bromo-1-isopropenyladamantane[125] with methylene iodide in the presence of the zinc–copper couple or with diazomethane in the presence of copper bromide results in the formation of the corresponding cyclopropane derivatives, whose hydrogenolysis leads to alkyladamantanes.

Unsaturated adamantane derivatives are active in the 1,3-dipolar cycloaddition of nitrile *N*-oxides[120]. The reactivities of the unsaturated compounds investigated vary in the sequence

$$AdCH{=}CH_2 \cong AdCH_2CH{=}CH_2 > AdC(CH_3){=}CH_2 > AdC{\equiv}CH\ .$$

The decrease of reactivity in this sequence can be accounted for partly by the influence of steric factors.

Unsaturated hydrocarbons of the adamantane series can be polymerised. Thus the polymer of 1-allyladamantane has been obtained in 12.5% yield in the presence of a Ziegler–Natta catalyst. The copolymerisation of 1-allyladamantane with vinylcyclohexane led to a copolymer in 10% yield[104]. The kinetics of the copolymerisation of 3,5-dimethyl-1-vinyladamantane with vinyl acetate have been investigated[126].

The cationic polymerisation of 1-vinyladamantane takes place in anhydrous solvents under the influence of AlX_3 (X = Cl or Br);[127,128] the temperature of the onset of the decomposition of poly-1-vinyladamantane is 300 °C.[96] The use of other catalysts of the type of Lewis acids (boron trifluoride etherate, triethyloxonium fluoroborate) does not lead to the formation of a polymer.

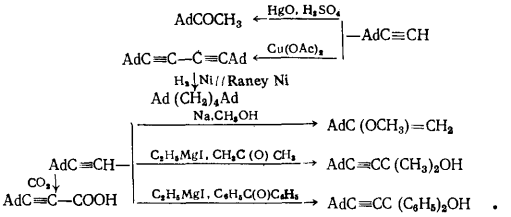
$$AdCH{=}CH_2 \xrightarrow{AlCl_3} AdCH_2CH_2{-}[{-}CH(Ad)CH_2{-}]_n{-}CH(Ad)CH_2Cl\ .$$

It has been established for the unsaturated adamantane derivatives

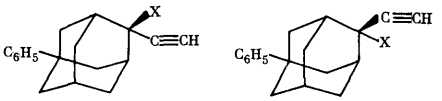
$$CH_2{=}C(CH_3)C(O)O(R)AdX;\quad CH_2{=}CH{-}O(O)C(R)AdX;$$
$$X{=}H,\ Br,\ C(O)OCH_3;\qquad R{=}(CH_2)_n,\ n = 0-2\ ,$$

that the introduction of the adamantyl group into monomers not only does not inhibit their polymerisation but in some cases leads to an increase of their capacity for polymerisation. In the series of methacrylic derivatives of adamantanes and the vinyl esters of adamantanecarboxylic acid, the type of variation of the polymerisation constants shows that, with increase of the distance between the adamantane nucleus and the double bond, the capacity of the monomers for polymerisation diminishes[129–131]. Thermal stability, resistance to hydrolysis, and enhanced surface hardness are distinctive properties of the polymers based on these adamantane derivatives.

1-Ethynyladamantane has been synthesised by the reaction of AdBr with vinyl bromide in the presence of $AlBr_3$ and subsequent dehydrohalogenation of the 1-(1-adamantyl)-1,2-dibromoethane formed by KOH in diethylene glycol[132]. 1-Ethynyladamantane undergoes many reactions characteristic of acetylenic hydrocarbons[132]:

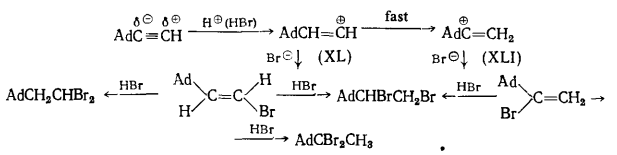


Derivatives of 2-ethynyladamantane have also been synthesised[133]:



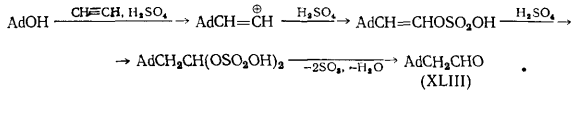
X = Cl; X = OH.

It has been suggested that the reactions of AdBr and AdOH with acetylene in concentrated sulphuric acid[135–138] and of 1-ethynyladamantane with 90% sulphuric acid[139] and with HBr in glacial acetic acid[134] proceed via the intermediate formation of adamantylvinyl cations (XL), which readily isomerise to the more stable cations (XLI). The reaction pathways of the cations (XL) and (XLI), which depends on the source from which (XL) is obtained (AdX + HC≡CH or AdC≡CH), the nature of the leaving group X (Br or OH) in AdX, and the degree of substitution in the adamantane nucleus, determine the composition of the reaction products. Thus 1-ethynyladamantane combines with HBr in glacial acetic acid to form a mixture of all the possible products[134]:



In concentrated sulphuric acid the reaction of acetylene with AdBr leads to 1-adamantyl methyl ketone (XLII) (yield 75%),[135] while the reaction with AdOH results in the formation of a mixture of three products: 1-adamantylacetaldehyde (XLIII) (yield 72%), compound (XLII), and 3-methyl-4-homoadamantanone (XLIV).[136,137] In 90% sulphuric acid 1-ethynyladamantane gives rise to a mixture of the ketones (XLII) and (XLIV).[139]

The study of the reaction of AdOH with acetylene in sulphuric and deuterosulphuric acids showed that compound (XLIII) is formed via the mechanism[138]

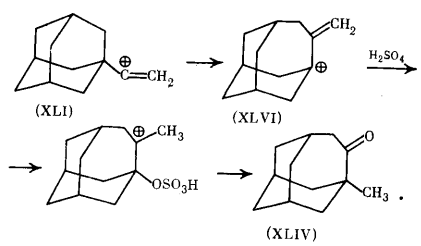


The mechanism of the formation of the ketones (XLII) and (XLIV) has still not been rigorously demonstrated. 1-Adamantyl methyl ketone is probably formed by reaction (1),[137]

while 3-methyl-4-homoadamantanone results from the rearrangement of the adamantanylvinyl cation to the more stable cation (XLVI) [reaction (2)]:[136]

$$AdBr \xrightarrow{H^{\oplus},\ CH\equiv CH} AdCH=\overset{\oplus}{C}H \xrightarrow{Br^{\ominus}} AdC\equiv CH \xrightarrow{H^{\oplus}} Ad\overset{\oplus}{C}=CH_2 \xrightarrow{H_2O} AdC(O)CH_3; \quad (1)$$

(XL) (XLV) (XLI) (XLII)



(XLI) (XLVI) (XLIV) (2)

When 1-bromoadamantane was allowed to react with acetylene in solution in methylene chloride in the presence of $AlBr_3$, 1-(1-adamantyl)-2-bromo(chloro)ethylene was formed, which has also been attributed to the intermediate formation of the cation (XLI). It may be that there is also a radical interaction in this instance. 1-Adamantanol does not enter into this reaction[140].

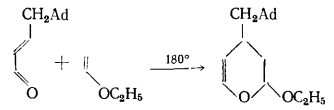
Together with the unsaturated adamantane derivatives discussed above, adamantane-containing unsaturated aldehydes, ketones, acids, and esters have now been also invstigated fairly completely[120].

β-(1-Adamantyl)acrolein (XLVII) and γ-(1-adamantyl)-crotonaldehyde (XLVIII) have been obtained from the corresponding diethyl acetals in yields of 84 and 87% respectively[141,142]:

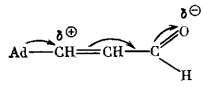
$$AdCH(OC_2H_5)_2 \xrightarrow[BF_3\cdot(C_2H_5)_2O]{CH_2=CHOC_2H_5} AdCH(OC_2H_5)CH_2CH(OC_2H_5)_2 \xrightarrow{H^{\oplus}} AdCH=CHCHO; \quad (XLVII)$$

$$AdCH_2CH(OC_2H_5)_2 \xrightarrow[BF_3\cdot(C_2H_5)_2O]{CH_2=CHOC_2H_5} AdCH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2 \xrightarrow{H^{\oplus}} AdCH_2CH=CHCHO \quad (XLVIII)$$

γ-(1-Adamantyl)crotonaldehyde undergoes the Diels–Alder reaction with ethyl vinyl ether to form a substituted 3,4-dihydro-1,2-pyran (XLIX) in 75% yield. On the other hand, the corresponding pyran could not be obtained from compound (XLVII).[141,143]

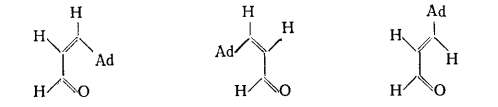


The different behaviour of the aldehydes (XLVII) and (XLVIII) in the reactions with ethyl vinyl ether is probably a consequence of the different degrees of influence of the Ad and $AdCH_2$ residues on the charge separation in the reaction centre of the aldehyde molecule[141]. In compound (XLVII) the electron-donating effect of the adamantyl residue diminishes the positive charge on the α-carbon atom of the aldehyde, as a result of which the molecule is insufficiently polarised for interaction with ethyl vinyl ether:



The methylene group in compound (XLVIII), which is located between the adamantyl group and the β-carbon atom, weakens the effect of the adamantyl residue and the molecule is polarised to a much greater extent.

Another factor which has a significant influence on the ability of the unsaturated aldehydes to undergo the Diels–Alder reaction with vinyl ethers is the configuration of the heterodiene. Heterodienes with the cisoid *trans*-conformation (C) are capable of undergoing this reaction:



cisoid *cis*-conformation (A) transoid *cis*-conformation (B) cisoid *trans*-conformation (C)

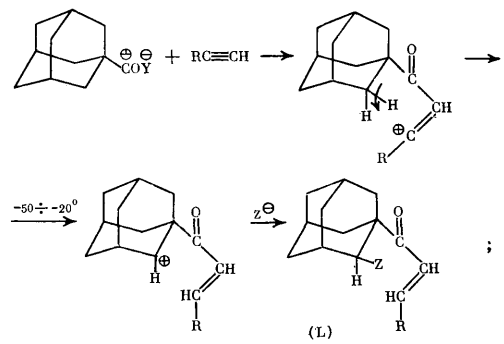
It has been established by infrared spectroscopy[141] that compound (XLVII) exists predominantly in the *cis*-conformation (A), while its homologue (XLVIII) has mainly the conformation (B). The (A) → (B) transition is apparently impossible for compound (XLVII) because of steric hindrance, while the (B) → (C) transition is entirely feasible for compound (XLVIII).[120,141]

The behaviour of 1-adamantyl vinyl ketone[144] in this reaction has also been investigated[141,143].

Under the influence of acid catalysts (formic acid, toluene-*p*-sulphonic acid, hydrochloric acid, and phosphorus pentoxide), 2-ethynyl-2-hydroxyladamantane is smoothly converted into adamantylideneacetaldehyde[145], which readily undergoes various reactions characteristic of aldehydes (the Knoevenagel and Wittig reactions), forming adamantane derivatives which are otherwise difficult to obtain.

Many adamantane derivatives containing a double bond and a functional group in the side chain have been obtained from the products of the interaction of 1-adamantyl methyl ketone with bromoacetic ester in THF; their reactions have been investigated in two studies[144,146].

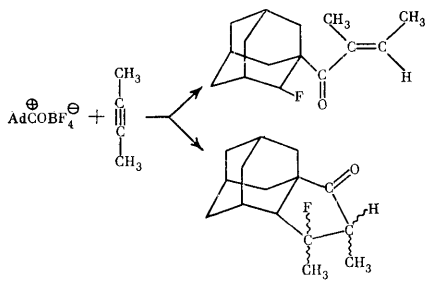
The acylation of terminal acetylenes RC≡CH by 1-adamantanoyl tetrafluoroborate or hexafluoroantimonate leads to α,β-unsaturated ketones (L):[147]



Z = F, Cl; Y = BF_4, SbF_6;
R = CH_3, *n*-C_3H_7, $CH_2C(CH_3)_3$, *m*-C_4H_9, C_6H_5.

The reaction of $CH_3C\equiv CH$ and 1-adamantanoyl hexafluoroantimonate in a CH_2Cl_2–$C_2H_4Cl_2$ mixture results in the formation mainly of 2-Cl-(*trans*-$CH_3CH=CHCO$)Ad.[147,148] 2-Phenyl-1-adamantyl 1-propenyl ketone or 1′-propenyl 2-tolyl-1-adamantyl ketone (L, Z = C_6H_5 or $CH_3C_6H_4$, R = CH_3) and 1-adamantyl 2-phenylpropenyl ketone or 1-adamantyl 2-tolylpropenyl ketone are formed under these conditions in benzene and toluene. The interaction of 1-adamantanoyl tetrafluoroborate and $CH_3C\equiv CCH_3$ leads to a mixture of

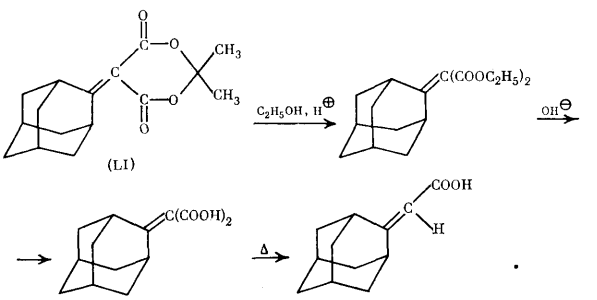
2-fluoro-1-(*cis*-$CH_3CH{=}CHCH_3CO$)Ad and 5-fluoro-5,6-dimethyltetracyclo[6.3.1.1^{3,10}.0^{4,8}]-7-tridecanone:



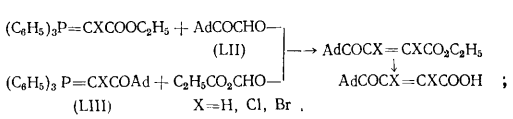
Among unsaturated acids of the adamantane series, adamantylideneacetic[149,150], adamantylidenemalonic[151–153], adamantylidenecyanoacetic[151], β-(1-adamantyl)acrylic[154,155], and α-(2-adamantylacrylic acids[155] are known.

The condensation of 2-adamantanone with malonic acid derivatives (cyanoacetic acid and its methyl ester) makes it possible to obtain derivatives of adamantylidenemalonic acid[151].

The adamantylidene derivative of Meldrum's acid (LI) has been obtained by the reaction of 2-adamantanone with Meldrum's acid in pyridine; 2-adamantylidenemalonic ester has been obtained by the transesterification of compound (LI) in the presence of acid[152]. Hydrolysis of the ester yields adamantylidenemalonic acid, which is converted into adamantylideneacetic acid on decarboxylation:

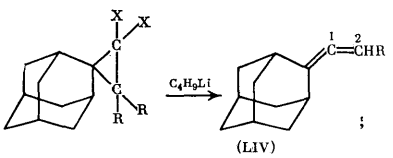


β-(1-Adamantanoyl)acrylic acid and its halogeno-derivatives have been investigated; their esters have been synthesised by the Wittig reaction from 1-adamantylglyoxal (LII) and ethoxycarbonylmethylenetriphenylphosphorane or from ethyl glyoxalate and 1-adamantanoylmethylenetriphenylphosphorane (LIII):[156–159]



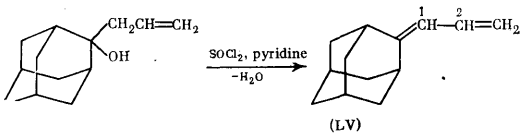
The bromination of β-(1-adamantyl)-β-hydroxybutyric and a series of its derivatives with liquid bromine results in the formation of 2-(1-adamantyl)-1-bromo-2-bromomethylpropiolactone[160].

Functional derivatives of adamantane can be used for the synthesis of compounds containing several double bonds in the side chain. Vinylideneadamantane (LIVa) has been obtained by treating 2,2-dibromo- or 2,2-dichloro-(2-adamantyl)-spiro-1-cyclopropane with butyl-lithium:

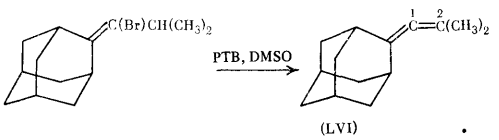


(a) R = H, (b) R = CH_3, (c) R = C_6H_5; X = Cl, Br .

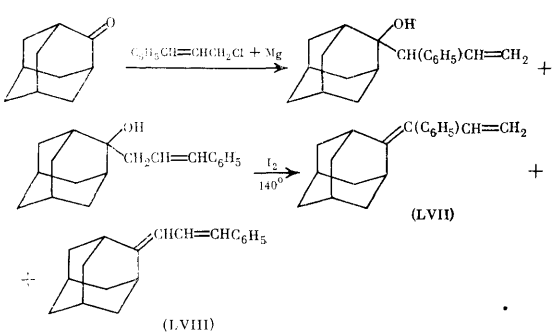
1-Propenylideneadamantane (LIVb) and 2-phenylethynylideneadamantane (LIVc) have been synthesised analogously[63]: the dehydration of 2-allyl-2-adamantanol leads to allylideneadamantane (LV):[161]



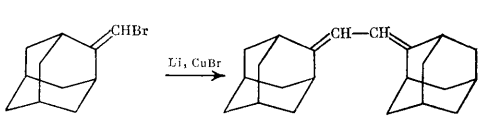
1-(2-Adamantylidene)-2-methyl-1-propene (LVI) has been obtained using potassium t-butoxide (PTB) in dimethyl sulphoxide as the dehydrobrominating agent[63]:



The products of the reaction of 2-adamantanone with 3-chloro-1-phenyl-1-propene and magnesium give rise to a mixture of adamantylidene-2-propenes (LVII) and (LVIII) after dehydration[63]:



1,2-Diadamantylidene-ethane has been obtained by treating bromomethyleneadamantane with lithium in the presence of CuBr:[63]



Certain characteristic features of the variation of the reactivity of the double bond as a function of the size of the substituent, the degree of substitution, and the distance between the double bonds and the nucleus have been discovered in the reaction of dihalogenocarbenes with allenes of the adamantane series[63]. The reactivities of the C(1)=C(2) double bond of vinylideneadamantane (2-Ad=$\overset{1}{C}=\overset{2}{C}H_2$), which is closest to the nucleus, is 12 times lower than in vinylidenecyclohexane and 1.8 times lower than in 1,1-dimethylallene. The cause of this consists in its steric shielding by the adamantane nucleus. The reactivity of the

C(1)=C(2) bond of 1-propenylideneadamantane, which is closest to the nucleus, is smaller almost by a factor of 2 compared with compound (LIVa), while the reactivity of the corresponding bond in methylpropenylideneadamantane (LVI) is zero. Evidently such decrease of reactivity can be accounted for by the steric interaction between the carbene and the methyl group at the C(2) atom in the transition state. In vinylideneadamantane the approach of the carbene to the plane of the C(1)=C(2) bond is equally probable from either side, while in 1-propenylideneadamantane one of the pathways followed in the approach is eclipsed by the methyl group and in compound (LVI) the methyl substituents shield the C(1)=C(2) bond from either side.

The reactivity of the terminal C(2)=C(3) bond in allylideneadamantane (LV) is lower amost by a factor of 6 than in buta-1,3-diene and is higher by a factor of 20 than the reactivity of the double bond in methyleneadamantane (XI, R=R′=H). The reactivity of the 2-Ad=C(1) bond of the diene (LV) is lower by a factor of 36 than the reactivity of the C(2)=C(3) bond. The main cause of the different reactivities of the double bonds in allylideneadamantane is apparently, as in the case of vinylideneadamantane, the steric influence of the adamantane nucleus shielding the 2-Ad=C(1) bond adjoining it. On the other hand, the reduction of the reactivity of the 2-Ad=C(1) bond in allylideneadamantane by a factor of 1.8 compared with methyleneadamantane shows that the steric factor does not operate alone in the case of the diene (LV). As a result of the polarisation of the molecule, the electron-donating effect of the adamantane substituent is transmitted to the terminal double bond and activates it, while the 2-Ad=C(1) bond closest to the nucleus is relatively deactivated. Thus the adamantane nucleus has a strong steric influence on the C=C bond adjoining it, shielding it and hindering the approach of a carbene to it.

1-Adamantyl-substituted allenes, namely 1-(1-adamantyl)-3-chloroallene [162] and 1,3-di(1-adamantylallene [163] have been described:

$$AdCHOHC{\equiv}CH \xrightarrow{SOCl_2} AdCH{=}C{=}CHCl\ ;$$

$$AdC{\equiv}CLi + AdCHO \rightarrow AdC{\equiv}CCHOHAd \xrightarrow{LiAlH_4} AdCH{=}C{=}CHAd\ .$$

The allenes as a rule polymerise on heating, but under certain conditions dimeric products with a cyclobutane structure can be isolated from 1-(1-adamantyl)-3-chloroallene[162]. The attempt to obtain dimers on heating 1,3-di(1-adamantyl)allene was unsuccessful; the reaction mass contained only polymeric products[163].

Allene derivatives of adamantane (LIX) have been obtained by the reaction of alkenynes with AdBr in the presence of metallic lithium[164]:

$$RC{\equiv}CC(R'){=}CH_2 \xrightarrow{Li,\ THF} Li^{\oplus},$$

$$R\overset{\ominus}{C}{=}C{=}C(R')\dot{C}H_2 \xrightarrow{(AdBr)^{\ominus},\ Li} Li^{\oplus},$$

$$R\overset{\ominus}{C}{=}C{=}C(R')CH_2Ad \xrightarrow{H_2O} RCH{=}C{=}C(R')CH_2Ad\ ;$$

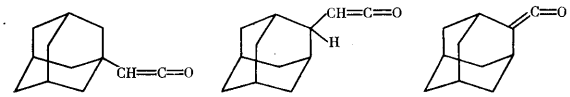
$$R{=}C_2H_5,\ R'{=}H;\ R{=}C(CH_3)_3,\ R'{=}H;\ R{=}R'{=}CH_3\ .$$

1-Adamantylallene has been synthesised by treating 1-chloroadamantane with trimethylpropargylsilane[106,107]:

$$AdCl + CH{=}CCH_2Si(CH_3)_3 \rightarrow AdCH{=}C{=}CH_2\ .$$

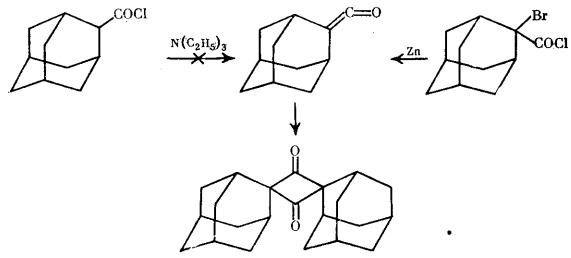
Chloroallene can be obtained with retention of configuration by treating the pure isomer of 2-ethynyl-2,5-dihydroxyadamantane with thionylchloride[133].

Ketens of the adamantane series have also been investigated:

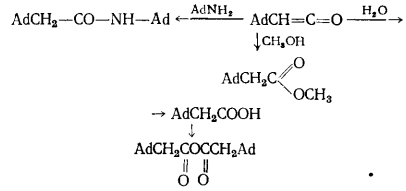


(LX) (LXI) (LXII)

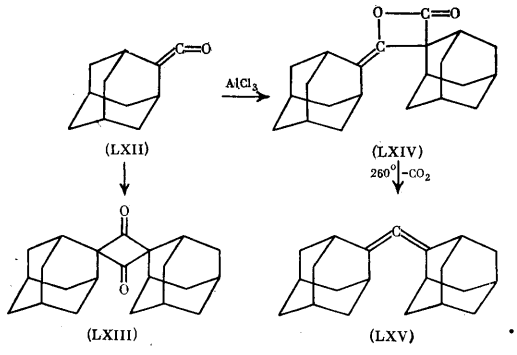
Although the yield of $N(C_2H_5)_3.HCl$ was 90% on treating the chlorides of the corresponding acids with triethylamine, the ketens (LX) and (LXI) could not be obtained in a pure form; only the di-, tri-, and tetrameric products were isolated[72]. The keten (LXII) is formed only when the chloride of 2-bromoadamantane-2-carboxylic acid is treated with zinc in boiling ether, whereupon it is converted immediately into a dimer[72]:



The chemical properties of 1-(1-adamantyl)keten (LX) could be investigated by employing dilute ethereal solutions[72]:



It was shown above that, whereas the keten (LXII) dimerises to the corresponding cyclobutane-1,3-dione under the usual conditions, after the addition of $AlCl_3$ to a boiling dilute ethereal solution of the keten dimerisation to the lactone (LXIV) takes place; on pyrolysis, the compound loses CO_2 and is converted into the allene (LXV):[165]



(LXII) (LXIV) (LXIII) (LXV)

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Thus, apart from the features which it has in common with the chemistry of unsaturated derivatives of other alicyclic hydrocarbons, the chemistry of unsaturated adamantane derivatives is characterised by a series of features determined primarily by the presence of the bulky adamantane

nucleus. As a result of the rigidity of the adamantane structure, dehydroadamantanes are highly strained reactive hydrocarbons, which make it possible to obtain from them a wide variety of mono- and di-substituted adamantane derivatives in one stage.

The reactivity of the compounds containing an exocyclic double bond is appreciably lower as a result of steric shielding; at the same time these compounds are of interest in view of the possibility of obtaining stable complexes. In derivatives with a C=C bond in the α,β-position in a side chain, the bond is subjected to appreciable shielding and an electron-donating influence by the adamantyl group. These compounds are also extremely reactive, undergo homopolymerisation and particularly copolymerisation reactions, and can be used to prepare polymeric materials with valuable properties as well as various functional derivatives of adamantane which are of interest from the standpoint of their biological activity.

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