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Synthesis and Chemical Properties of Ketones from Adamantane Series

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Abstract—The review is summing up the data on the synthesis and chemical transformations of various ketones belonging to adamantane series.

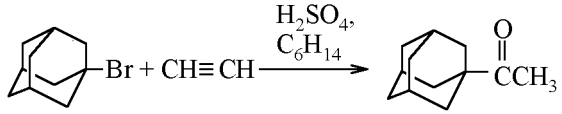
I. INTRODUCTION

The history of discovery, natural occurrence, preparation procedures, physico-chemical characteristics, and biological activity of adamantane and its derivatives are described in detail in two well-known treatises [1, 2]. Some later review focused on special problems of adamantane chemistry. For instance, the synthesis and application was described of adamantane-containing polymers [3], unsaturated compounds of the adamantane series [4], the synthesis of heteryladamantanes [5, 6], the adamantane behavior in the electrophilic media [7], the biological activity of adamantane derivatives [8]. However none of the above articles treats the preparation procedures and investigation of chemical properties of adamantane carbonyl derivatives. Only in [5, 6] were demonstrated some examples of heterocyclic compounds syntheses originating from ketones of adamantane series. Meanwhile we believe that just the carbonyl-containing compounds offer versatile opportunities for the synthesis of derivatives therefrom. Besides although the practical applications of the carbonyl compounds are described in a few papers, it is still known that alkyl adamantyl ketones are used in treatment of animals affected with Newcastle disease [9], and NRR'-1-amino-2-(1-adamantyl)-ethan-2-ones and NRR'-1-amino-3-(1-adamantyl)-propan-3-ones show antibacterial and antiviral activity [10, 11]. Therefore we believed that it would be useful and interesting to sum up the random data on preparation methods and chemical properties of adamantane carbonyl derivatives and to add thereto our own results obtained in this field.

II. SYNTHESIS OF KETONES FROM ADAMANTANE SERIES

Some preparation procedures for adamantane series ketones start with R-substituted adamantanes (R = Hlg, OH, CN, COOH, etc.).

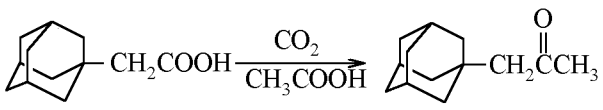
The reaction of 1-bromoadamantane (**1**) with acetylene in the mixture of sulfuric acid and hexane at 5°C results in 1-acetyladamantane (**2**) [12].



1 **2**

In the similar way occurs the reaction of 1-hydroxyadamantane (**3**) with acetylene in sulfuric acid [13, 14]. However here alongside ketone (**2**) arise 3-methylhomoadamantan-4-one (**4**) and (1-adamantyl)-acetaldehyde (**5**).

At passing a mixture of 1-adamantanecarboxylic (6) and acetic acids in a flow of CO_2 through a special catalyst containing MnO_2 ketone (**2**) formed in 50% yield [15]. A similar reaction carried out with (1-adamantyl)acetic acid (**7**) gave (1-adamantyl)-acetone (8) in 48% yield.



7 **8**

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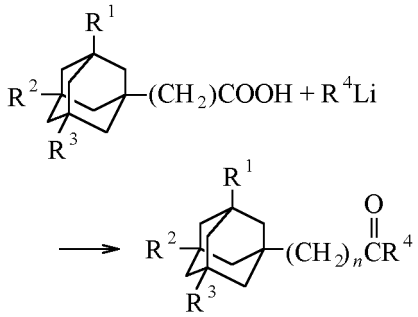
A number of studies is dedicated to preparation of alkyl 1-adamantyl ketones (**9**) from carboxylic acids of the adamantane series and alkyllitium compounds.



n = 0, R^1 = R^2 = R^3 = H, R^4 = Me, Et, Pr, C_6H_{13};
n = 1, R^1 = R^2 = R^3 = R^4 = Me.

$$AdCOOH + RLi \rightarrow AdCOOLi + RH$$

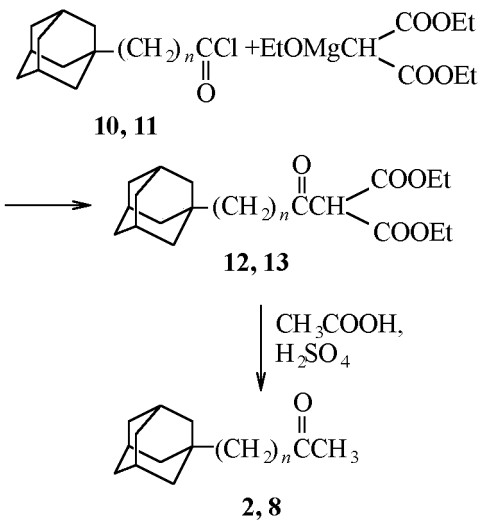
$$COOLi + RLi \rightarrow \left[Ad(OLi)(R)C(OLi) \right] \rightarrow AdC(O)R$$

R = Me, Et.

As show the studies [16] here always forms alongside ketone a minor amount of tertiary alcohols, especially with large excess of alkyllithium.

$$AdC(O)R + RLi \rightarrow AdCR_2OLi \rightarrow AdCR_2OH$$

In the most investigations on the syntheses of adamantane series ketones as initial compounds are used 1-adamantanecarbonyl (**10**) and (1-adamantyl)-acetyl (**11**) chlorides. The simplest alkyl ketones are



obtained in reactions of the above chlorides with ethoxymagnesiummalonic ester.

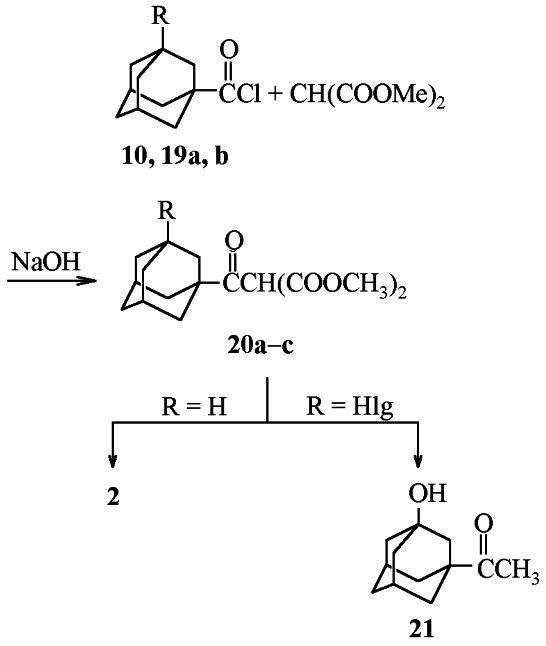
With 1-adamantanecarbonyl chloride (**10**) instead of diethyl ester of diacid (**12**) was isolated its hydrolysis product, ethyl (1-adamantoyl)acetate (**14**) [19].

This method was later modified by replacing sodium for magnesium [20].

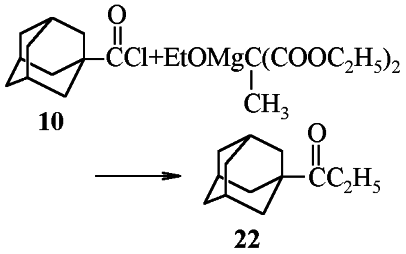
Several studies [21–25] treat the synthesis of (1-adamantyl)acetone (**8**) by reacting (1-adamantyl)-acetyl chloride (**11**) with the ethoxymagnesium-malonate. In contrast to condensation of 1-adamantanecarbonyl chloride (**10**) with ethoxy-magnesiummalonate that is accompanied with the cleavage of one ester group, the reaction of its next homolog, (1-adamantyl)acetyl chloride (**11**), results in (1-adamantylacetyl)malonate (**13**) [25]. On heating compound (**13**) with anhydrous oxalic acid one ester group is eliminated to afford ethyl γ-(1-adamantyl)acetoacetate (15); solvolysis of both keto-esters (**13**) and (**15**) with a mixture of acetic and sulfuric acids yields ketone (**8**).

This procedure for ketones preparation was extended to 3-chloro-1-adamantanecarbonyl chloride (**16**) [26], 3-bromo-1-adamantanecarbonyl chloride (**17**) [27], and bis-1-adamantyl-3,3'-dicarbonyl dichloride (**18**) [28, 29].

Unlike the above reports we carried out condensation of 3-R-1-adamantanecarbonyl chlorides (**10, 19a, b**) with dimethyl malonate in the presence of sodium hydroxide in toluene to obtain dimethyl 3-R-(1-adamantanoyl)malonates (**20a–c**) [30, 31], and proved their structure and composition with ^{1}H NMR and IR spectroscopy and elemental analysis. Since the acyl chlorides are prone to hydrolysis the sodium hydroxide in the ketone synthesis with malonates can find only limited application. The hydrolytic stability of acids may be apparently estimated by the value of the dissociation constant of 1-adamantanecarboxylic acid, 3-chloro- and 3-bromo-1-adamantanecarboxylic acids [32] [$k_d \times 10^7$ 1.55 (1-AdCOOH), 6.46 (3-Br-1-AdCOOH), 7.13 (3-Cl-1-AdCOOH)]. In reaction of 3-chloro-1-adamantanecarbonyl chloride with ethoxy-magnesiummalonate followed by hydrolysis in a mixture AcOH–H_2SO_4–HCl–$H_2$0 (100 : 3 : 40 : 30) without separation of the intermediate reaction products was obtained 3-chloro-1-adamantyl methyl ketone in 65% yield [26]. Unlike that the hydrolysis of ketoesters (**20**) in a mixture AcOH–H_2SO_4–H_2O results in ketone (**2**) at R = H and at R = Cl, Br in 3-hydroxy-1-adamantyl methyl ketone (**21**) in 82% yield.

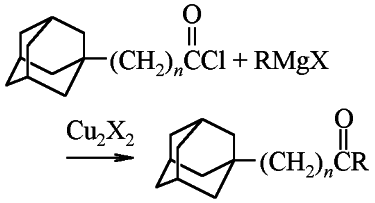


The condensation of 1-adamantanecarbonyl chloride (**10**) with methyl ethoxymagnesiummalonate followed by hydrolysis affords ethyl 1-adamantyl ketone (**22**) [33].



However all the methods cited above provide only lower ketones (methyl and ethyl adamantyl ketones).

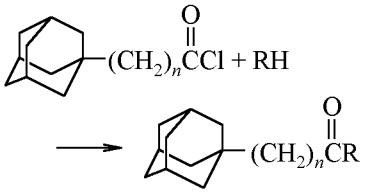
Reactions of acyl chlorides from adamantane series with the Grignard reagents under conventional conditions give rise only to mixtures of various alcohols, whereas the application of CuCl results in ketones with high yields due to formation of an active complex between the acyl chloride and CuCl [34–36].



n = 0, R = Me, Et, Pr, *i*-Pr, Bu, *s*-Bu, *t*-Bu, C_5H_{11}, C_6H_{11}, C_6H_5; *n* = 1, R = Me, Et, Pr, *i*-Pr, Bu, *s*-Bu, C_5H_{11}, C_6H_{11}.

Organomagnesium compounds can be replaced by organocadmium compounds. This procedure furnished ketones (**2**) and (**8**) in nearly 70% yield [37].

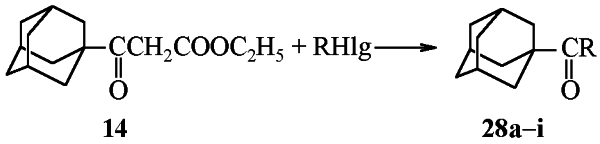
In the last decade Friedel–Krafts reaction found extensive application in the synthesis of aryl and hetaryl ketones of the adamantane series [38–45].



n = 0, 1, R = Ph, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, 2-thienyl, 2,2'bithien-5-yl, 5-methyl-2-thienyl, 3-Bu-4-OH-5-BuC_6H_2.

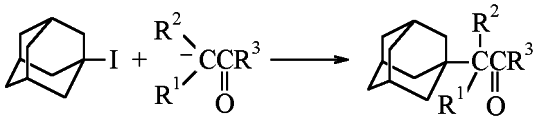
$AlCl_3$ and $SnCl_4$ are used for catalyst. Ketones are formed in ~70% yield. The investigation of the reaction [38] demonstrated that side products arise due to alkylation: 1-phenyladamantane (**23**), 2-phenyladamantane (**24**), 1-p-tolyladamantane (**25**), 1-*m*-tolyladamantane (**26**), 1-o-tolyladamantane (**27**) etc. The reaction was extended to 3-bromo-1-adamantanecarboxylic [42], 3-trifluoromethyl-1-adamantanecarboxylic [42], 1,3-adamantanedicarboxylic, and 1,3-adamantyldiacetic acids etc. [44, 45].

Reaction of ethyl 1-adamantylcarbonylacetate (**14**) with alkyl halides followed by hydrolysis of the arising ester in alkaline medium and decarboxylation of the hydrolysis product with aqueous acid solution provides alkyl adamantyl ketones (**28**) [46, 47].



R = Et (**a**), Pr (**b**), Bu (**c**), heptyl (**d**), pentyl (**e**), isopentyl (**f**), isohexyl (**g**), nonyl (**h**), decyl (**i**).

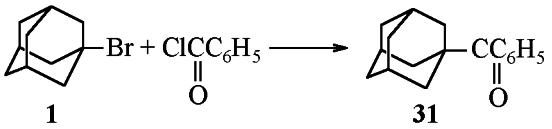
Within the last five years a preparation method for ketones (29) was developed consisting in reaction of 1-iodoadamantane (**30**) with ketone enolates [48–51].



R^1 = R^2 = H, R^3 = CH_3; R^1 = R^2 = CH_3, R^3 = Ph; R^1 = R^2 = H, R^3 = Ph.

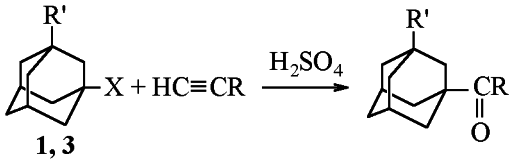
This reaction is photostimulated; the yield of the final product is increased at addition of 18-crown-6 to the reaction mixture [48]. However side products arise in each case reducing the ketone yield. The reaction is presumed [48] to follow $S_{RN}1$ mechanism.

Similar ketones were prepared from 1-bromoadamantane (**1**) [52] (R^1 = R^2 = Me; R^3 = *i*-Pr, R^1 = Me, R^2 = H, R^3 = Et; R^1 = R^2 = H, R^3 = *t*-Bu). In the reaction of 1-bromoadamantane (**1**) with benzoyl chloride in the presence of zinc as catalyst phenyl 1-adamantyl ketone (**31**) was obtained in 72% yield [53].



1 **31**

By passing acetylene or its homologs through a mixture of sulfuric acid with 1-bromoadamantane (**1**) or 1-hydroxyadamantane (**3**) or derivatives thereof alkyl 1-adamantyl ketones were obtained [54–57].



1, 3

X = Br, OH; R = *i*-Pr, hexyl, Ph, Me; R' = H, Me, MeO, AcO, Br.

The reaction is presumed [56] to proceed through a rearrangement of a primary vinyl cation (**32**) arising on addition of adamantyl cation (**33**) to acetylene into a secondary vinyl cation (**34**).

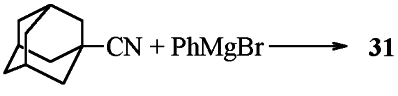
$$Ad^+ + HC{\equiv}CH \rightarrow \underset{\mathbf{33}}{} AdC^+{=}CH_2 \quad \mathbf{32}$$

$$\xrightarrow{H_2O} AdC(OH)CH_2^+ \rightarrow \mathbf{2}$$

34

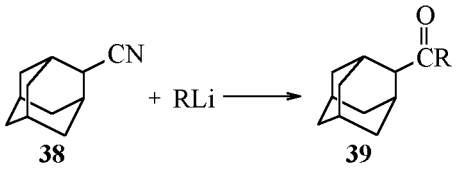
1-Adamantylacetylene (**35**) treated with 90% sulfuric acid affords a mixture of ketone (**20** and homoadamantan-4-one (**36**) [58].

1-Cyanoadamantane (**37**) reacting with phenylmagnesium bromide in ether yields phenyl 1-adamantyl ketone [59].



37

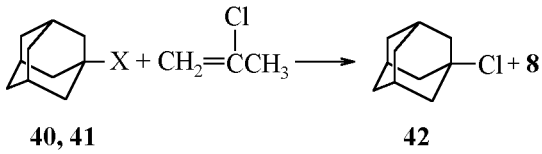
Similarly the reaction of RLi-derivatives with 2-cyanoadamantane (**38**) provides R 2-adamantyl ketones (**39**) [60].



38 **39**

R = Me, Bu, Ph.

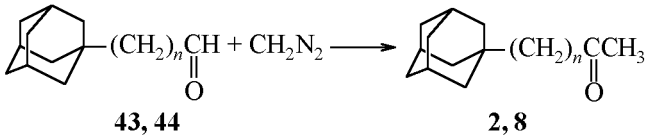
Reaction of 1-adamantanol (**40**) or its nitrate (**41**) with 2-chloropropene in the presence of concn. H_2SO_4 results in a mixture of 1-chloroadamantane (**42**) and ketone (**8**).



40, 41 **42**

X = OH, ONO_2.

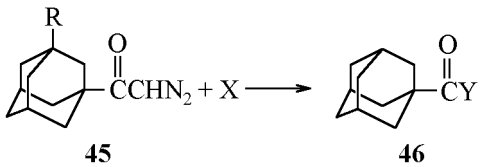
The treatment of 1-adamantanecarbaldehyde (**43**) or 1-adamantylacetaldehyde (**44**) with diazomethane in ether under argon atmosphere gave rise to ketones (**20** and **(8) [62].**



43, 44 **2, 8**

n = 0 (**43**), 1 (**44**).

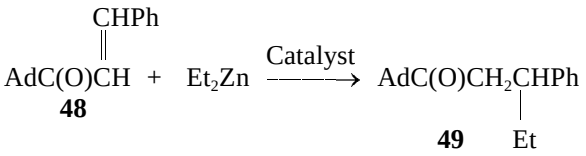
The reaction of (1-adamantanoyl)diazomethane (**45**) and its 3-substituted derivatives with saturated, unsaturated, and aromatic hydrocarbons catalyzed with transition metal complexes afforded new previously unavailable ketones (**46**) [63–65].



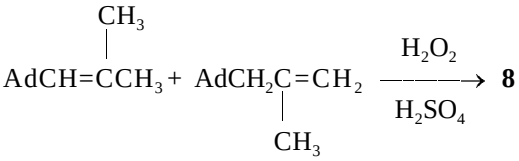
45 **46**

R = H, Br. X = methane, benzene, cyclohexane, 1,2-dimethylcyclopentane. Y = methyl, cycloheptatrienyl, cyclohexyl, 2,3-dimethylcyclopropyl.

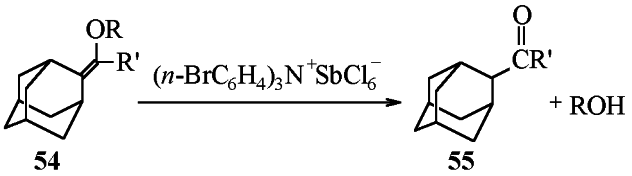
3-Chloro-1-(1-adamantyl)propan-2-one (**47**) in reaction with acetic acid in the presence of zinc provided ketone (**8**) in good yield [66]. The reduction of styryl adamantyl ketone (**48**) with Et_2Zn in the presence of chiral catalysts affords ketone (**49**) [67].



When a mixture of 1-(1-adamantyl)-2-methylpropene (**50**) and 3-(1-adamantyl)-2-methylpropene (**51**) are added to a mixture of hydrogen peroxide and sulfuric acid arises a set of products [initial compounds (**50**) and (**51**), adamantane, methyladamantane (**53**)], among them ketone (**8**) in 17% yield [68].

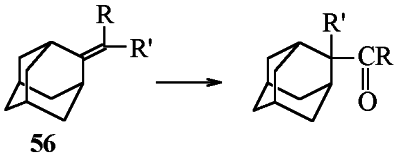


A new catalyst, tris-*p*-bromophenylammonium hexachloroantimonate, was found [69, 70] for preparation of ketones from unsaturated compounds of the adamantane series. For instance, enol ethers (**54**) at 0°C in dichloromethane saturated with argon yield adamantyl aryl ketones (**55**) [69].



R = CH_3, R' = Ph, $CH_2C_6H_5$, 1-$C_{10}H_7$, 2-$C_{10}H_7$.

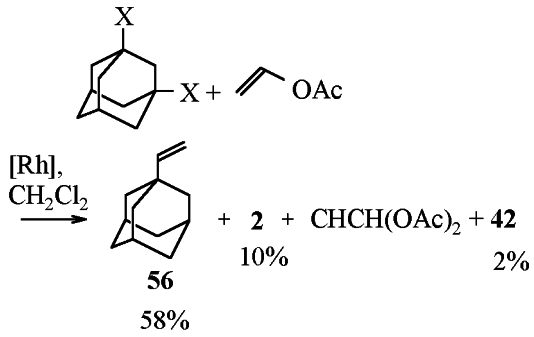
Adamantylidene derivatives (**56**) similarly behave in this reaction [70].



R = R' = Me; R = H, R' = Ph; R = Me, R' = Ph; R = R' = Ph; R = R' = fluorenyl; R = R' = 1-adamantyl.

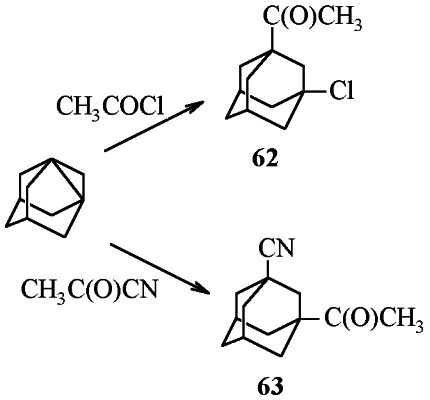
In the similar way reacts spiro(oxirane-2,2'-adamantane) (**57**) yielding di(1-adamantyl) ketone (**58**) [71].

Unexpected results were obtained in reaction of adamantane and its derivatives with vinyl acetate [72]. Conjugate vinylation of adamantane effected by rhodium complexes $Rh(PPh_3)_3Cl$, $[Rh(CO)_2Cl]_2$ under stringent conditions (170°C, 8 h) in CH_2Cl_2 medium resulted in a mixture of products where alongside 1-vinyladamantane (**59**) (58%) and ketone (**2**) appeared ethylenediacetate (30%), and 1-chloroadamantane (**42**) (2%). An attempt to carry out a similar reaction with 1-chloroadamantane (**42**) provided ketone (**2**) in 5% yield and a large amount of unidentified oligomers presumed to originate from vinyladamantane (**59**). Less obvious was the result of reaction between vinyl acetate and 1,3-dibromoadamantane (**60**). Here ketone (**2**) was obtained in quantitative yield.



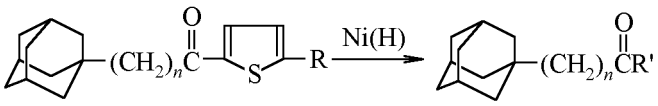
X = H, Br.

Synthesis of ketones containing adamantyl rest may be carried out not only by transforming side chains in adamantane derivatives as was shown above by quite a few examples but also be cycle opening. In [73] was performed the cleavage of a three-membered cycle in tetracyclo[3.3.1.$1^{3,7}0^{1,3}$]decene (**61**) with some acetyl- and cyano-containing reagents to provide 1-acetyl13-chloroadamantane (**62**) in 93% yield and 1-cyano-3-acetyladamantane (**63**) in 33% yield.



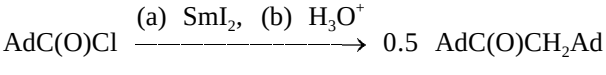
The above mentioned 1-adamantyl 2-thienyl, 1-adamantyl 2,2'-bithien-5-yl, and (1-adamantyl)-methyl 2-thienyl ketones were subjected to de-

sulfurization on Raney nickel W-7 [45] in ethanol at boiling for 5–9 h to result in butyl 1-adamantyl, octyl 1-adamantyl, and butyl (1-adamantyl)methyl ketones [74].



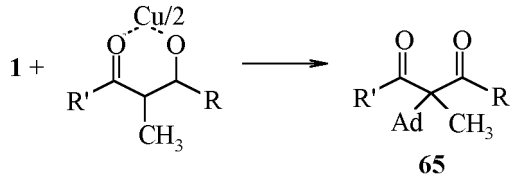
n = 0, R = H, R' = Bu; *n* = 0, R = 2-thienyl, R' = C_8H_{17}; *n* = 1, R = H, R' = Bu.

By the reductive coupling of adamantanecarbonyl chloride (**10**) with excess SmI_2 (4 mol) at room temperature within 1 h was obtained 1-adamantyl (1-adamantyl)methyl ketone (**64**) in 60% yield [75].



10 **64**

Metal β-diketonates of copper or cobalt were applied [76–78] to the synthesis of α-adamantyl-β-dicarbonyl compounds. For instance, the reaction of copper bis(3-methylpentane-2,4-dithionate) with bromoadamantane (**1**) at heating in chloroform or chlorobenzene for 48 h afforded 3-(1-adamantyl)-3-methylpentane-2,4-dione (**65**) [76].



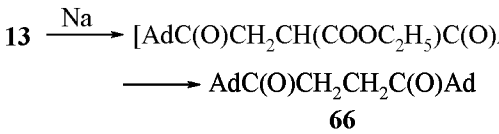
65

R = R' = CH_3 (81%); R = C_6H_5, R' = CH_3 (89%); R = OC_2H_5, R' = CH_3 (38%); R = R' = C_6H_5 (80%); R = R' = *t*-C_4H_9 (31%).

The dipole moments of β-diketones (**65**) are reported in [79]. Basing on the ^1H NMR data the compounds (**65**) were assigned exclusively diketo structure.

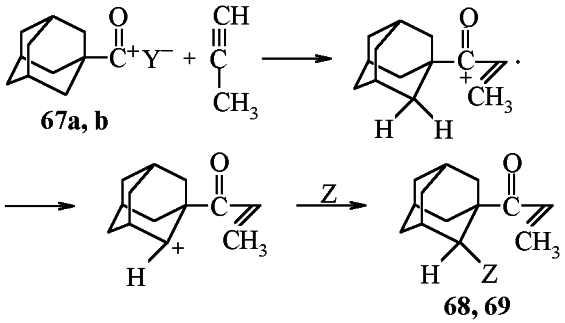
The reaction between 3-R-1-adamantanecarbonyl chlorides (R = H, Br) and 1-morpholinocyclohexene in ether or dioxane in the presence of triethylamine followed by hydrolysis with diluted hydrochloric acid gave rise to a new class of cyclic β-diketones of the adamantane series, 2-(3-R-1-adamantoyl)cyclohexanones [80].

A synthesis of γ-diketones was reported, e.g. of 1,4-di(1-adamantyl)butane-1,4-dione (**66**), by reacting esters (**13**) with sodium [19].



66

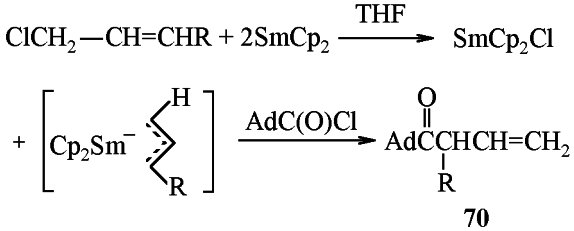
Several studies [81–83] concern acylation of acetylene homologs with the derivatives of 1-adamantanecarboxylic acid: adamantanoyl tetrafluoroborate (**67a**), or adamantanoyl hexafluoroantimonate (**67b**). This process can afford a number of 1,2-disubstituted adamantanes. The character of the products depends on the reagent nature and on the nucleophile present in the medium. The reaction of adamantanoyl tetrafluoroborate (**67a**) in CH_2Cl_2–CH_2Cl_2 at −40°C resulted in fluoroketone (**68**), and methylacetylene with adamantanoyl hexafluoroantimonate (**67b**) yielded chloroketone (**69**). The reactions in the presence of benzene or toluene can afford aromatic derivatives.



67a, b **68, 69**

Y = BF_4, SbF_6; Z = F (**68**), Cl (**69**), C_6H_5, *o*,*p*-$CH_3C_6H_4$.

It was reported [84] that in reaction of allyl chlorides with a suspension of samarium dicyclopentadiene in tetrahydrofuran formed an allylsamarium complex which with 1-adamantanecarbonyl chloride (**10**) yielded α,β-unsaturated ketones (**70**).



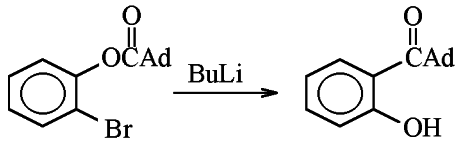
70

R = CH_3, C_6H_5.

The synthesis of vinyl ketones from the adamantane series we describe in the section on the chemical properties of adamantane series ketones.

Another interesting procedure for preparation of aryl ketones in the adamantane series is promoted by

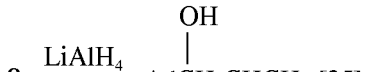
butyllithium Fries rearrangement of aryl esters (**71**) into o-hydroxyketones (**72**) providing 81% yield [85].

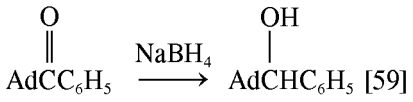


71 **72**

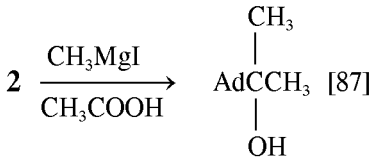
III. CHEMICAL PROPERTIES OF CARBONYL DERIVATIVES OF ADAMANTANE

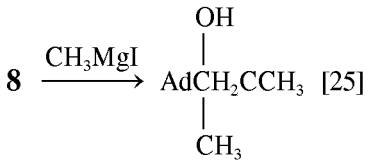
Starting with ketones are prepared alkohols of the adamantane series. The carbonyl compounds are transformed into the corresponding alcohols by reduction with sodium borohydride, lithium aluminum hydride, or by treating with the Grignard reagents.





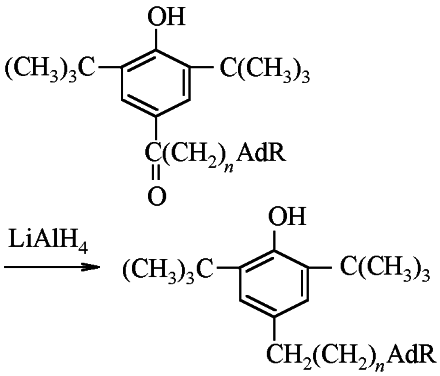
x = 0, 1; R = H, Cl; R' = C_6H_5, 2-thienyl.





The reduction of 1-adamantyl methyl ketone (**2**) was successfully carried out with a new efficient reductant, 2,5-dimethylborolanyl mesylate obtained by treating dihydroborate in pentane with methanesulfonic acid [88].

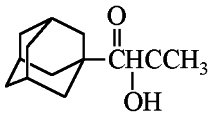
The reduction of adamantyl-substituted aromatic ketones with the lithium aluminum hydride or the sodium borohydride at room temperature or at heating in anhydrous ether or THF results in complete hydrogenetion of the carbonyl group into a methylene group [89].



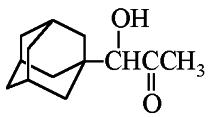
R = H, Br, CF_3; n = 0, 1.

A similar result is obtained in reactions of ketones **20** and **8** with hydrazine hydrate in the triethylene glycol [59].

Hydrolysis of 1-bromoethyl 1-adamantyl ketone in aqueous dioxane in the presence of sodium carbonate results in replacement of the halogen atom by hydroxy group with simultaneous isomerization. The reaction provides a mixture of α-hydroxyketones (**74**) and (**75**) [90, 91].



74



75

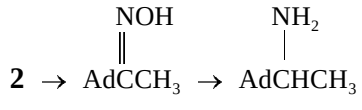
The study of reaction between bromomethyl 1-adamantyl ketone (**76**) with sodium alcoholates in alcohols revealed among the other products hydroxymethyl 1-adamantyl ketone (**77**) [92, 93].

The amine preparation from adamantane series ketones is among the most practically important reactions leading to the medicine nominated "Remantadine." The other amines prepared from adamantane series ketones also were tested for biological activity. However neither among them was more efficient than "Midantane" or "Remantadine."

The reaction of methyl 1-adamantyl ketone (**2**) with urea in formic and sulfuric acid medium affords *N*-methyl(1-adamantylmethyl)amine (**79**) [94].

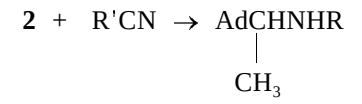
79

The reduction of ketone (**2**) oxime with sodium metal in alcohol afforded 1-adamantyl-1-aminoethane (**80**) [95].



80

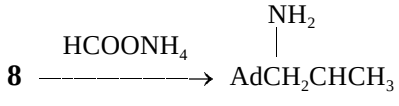
N-substituted 1-adamantyl-1-aminoethanes (**81**) possessing antiviral activity are claimed to form at passing at 250°C and hydrogen pressure 20 atm of a mixture containing ketone (**2**) and R'CN through a layer of catalyst [96].



81

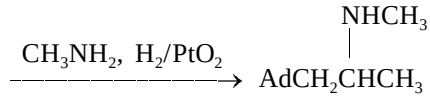
R = CH_3, R' = H; R = C_2H_5, R' = CH_3; R = C_3H_7, R' = C_2H_5.

Similarly (1-adamantyl)acetone (**8**) with ammonium formate affords 1-(1-adamantyl)-2-aminopropane (**82**) [25].



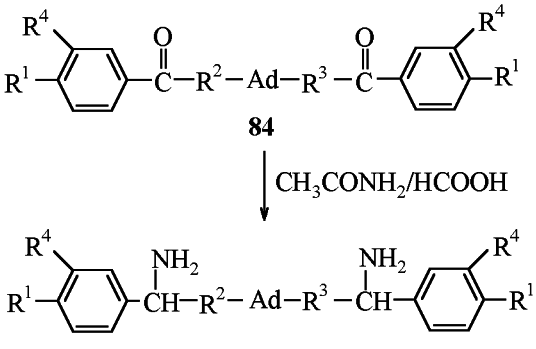
82

The preparation procedure of 1-(1-adamantyl)-2-(*N*-methylamino)propane (**83**) from ketone (**8**) and methylamine in acetic acid with simultaneous hydrogenation catalyzed by PdO_2 was described in patents [21, 24].



83

Adamantane related diketones (**84**) were subjected to reductive amination according to Leicart to obtain diamines with adamantane rest (**85**) [97].

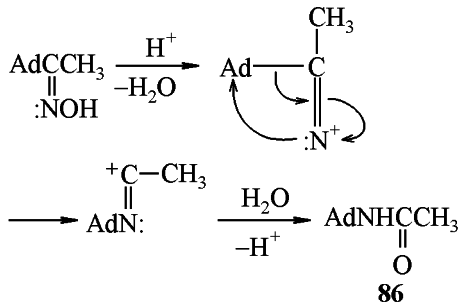


85

R^1, R^4 = H, CH_3; R^2 = 0, CH_2; R^3 = CH_2.

Actually every publication concerning the synthesis of ketones from adamantane series contains data on preparation of derivatives thereof (oximes, 2,4-dinitrophenylhydrazones, thiosemicarbazides etc). A number of papers treats the chemical properties of oximes formed by ketones from adamantane series and the kinetics of the oximation process.

The Beckmann rearrangement of ketones (**2, 8, 31**) oximes was investigated in [98]. Polyphosphoric acid was used as catalyst. All the rearrangement products obtained from the above oximes were acetamides from the adamantane series (86). Thus the migrating groups were respectively 1-adamantyl and 1-adamantylmethyl ones. Only ketone **20** oxime yielded two products, acylaminoadamantane (**86**) and adamantane. The highest yield of compound (**86**) at minimum amount of adamantane was obtained at weight ratio oxime to polyphosphoric acid 1 : 3.4, at 100°C and reaction time 30 min.



86

The reactivity in oximation of the adamantane series ketones (R = CH_3, C_2H_5, C_3H_7, *iso*-C_3H_7, C_4H_9, C_5H_{11}, C_6H_5) in relation to different shielding of the reaction center and variation in the charge on the carbon atom of the carbonyl group was studied in [35, 99]. The study was carried out by iodometric titration of the unreacted hydroxylamine. In all cases the degree of conversion of ketones and hydroxylamine was over 50%. From the data on oximation rate constants (Table 1) Ivanova et al concluded that the ketones under investigation were not significantly sterically hindered.

Another set of ketones investigated [35] was as follows: 1-(1-adamantyl)-2-pentanone, 1-(1-adamantyl)-2-hexanone, 2-(1-adamantyl)-1-cyclohexyl-2-ethanone, 1-(3-isopropyl-1-adamantyl)-1-ethanone, 1-(3-isopropyl-1-adamantyl)-2-propanone, 1-adamantyl cyclohexyl ketone, 1-(1-adamantyl)-1-butanone, and 1-(1-adamantyl) isopropyl ketone. Isopropyl group was chosen as alkyl group attached to adamantane core since among the previously studied alkyls in this ketone series it possessed the highest inductive and steric effects. It was interesting to

Table 1. Oximation rate constants for 1-adamantyl ketones, $k \times 10^{-3}$, l mol^{-1} s^{-1}

Ketone	pH 6.5		pH 5.0, 25°C
	15°C	25°C	
1-AdCOCH$_3$	5.00	6.1	17.01
1-AdCOC$_2$H$_5$	2.40	4.08	8.17
1-AdCOC$_3$H$_7$	1.10	2.09	4.24
1-AdCOC$_3$H$_7$-*iso*	0.57	1.20	2.42
1-AdCoC$_4$H$_9$	0.96	2.30	3.89
1-AdCOC$_5$H$_{11}$	0.71	2.06	3.61
1-AdCOC$_6$H$_5$	0.34	0.67	1.21

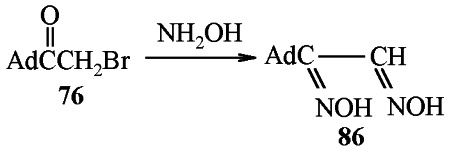
Table 2. Oximation rate constants for adamantyl-containing ketones, $k \times 10^{-3}$, l mol^{-1} s^{-1}

Compound	25°C	15°C
1-(1-Adamantyl)-2-pentanone	1.75	0.80
1-(1-Adamantyl)-2-hexanone	1.55	–
2-(1-Adamantyl)-1-cyclohexyl-2-ethanone	0.43	0.21
1-(3-Isopropyl-1-adamantyl)-1-ethanone	4.10	3.20
1-(3-Isopropyl-1-adamantyl)-2-propanone	2.70	–
1-Adamantyl cyclohexyl ketone	0.67	0.34
Aceton	303	223

compare the influence on the reactivity of carbonyl produced by the same group either neighboring to the reaction center or attached to the adamantane core. The corresponding oximation rate constants measured at pH 6.5 and 25 or 15°C are given in Table 2.

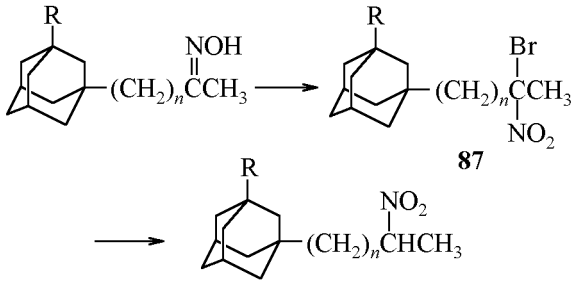
If the reactivity of carbonyl group were affected only by the inductive effect of 1-AdCH$_2$, then the reactivity of ketones possessing the methylene group would have surpassed that of ketones lacking the bridging methylene group. This statement contradicts the experimental data. The methylene group included between the adamantyl and keto groups provides a decrease in the reactivity of ketones due to growing steric hindrance of the reaction center by the substituent.

The extremely interesting studies [100, 101] concern oximation of 1-adamantyl bromomethyl ketone (**76**) whose synthesis we describe further. At molar reagents ration arises a-haloketone oxime. With the 6-fold excess of hydroxylamine free base dioximes (**86**) are obtained with *amphi*-configuration according to ^{1}H NMR spectra.



76 **86**

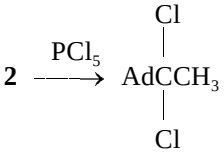
The ketone (**2, 8**) oximes from the adamantane series were used in a two-step synthesis of nitro compounds of this series [102]. In the first stage these ketone oximes reacted with *N*-bromosuccinimide in the presence of $NaHCO_3$ in 50% aqueous dioxane to afford bromonitrocompounds (**87**). The latter were reduced by sodium borohydride in methanol and by subsequent treating with hydroxylamine hydrochloride were transformed into nitroalkyladamantanes (**88**).



87

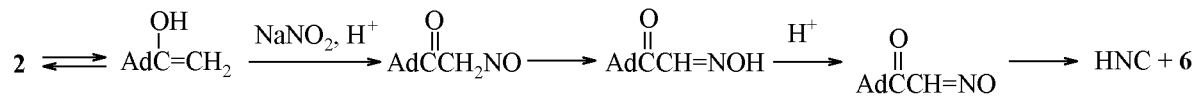
88

In [103] was described a synthesis of 1-*tert*-butyladamantane (**89**) from ketone (**2**) effected by dichlorodimethyltitanium (Me_2TiCl_2) in dichloromethane by raising temperature from –30 to 20°C. The reaction of ketone (**2**) with PCl_5 afforded 1,1-dichloro-1-(1-adamantyl)ethane (**90**) [104].



90

A transformation of ketone (**2**) into acid (**6**) was studied [105] occurring in the presence of sodium nitrite and pyridinium poly(HF) at 20°C within 16 h.



It is presumed that the reaction proceeded through nitrosation of the enol form of ketone (**2**).

A number of studies concerned the synthesis and investigation of the chemical properties of adamantane series vinyl ketones and their analogs. In particular, vinyl ketones (**91**) were prepared by aldol-crotonic condensation of ketone (**2**) with aromatic and heterocyclic aldehydes [106–109].

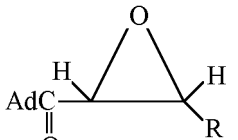
$$\mathbf{2} + RC(O)H \rightarrow AdC(O)CH{=}CHR$$

91

R = Ar.

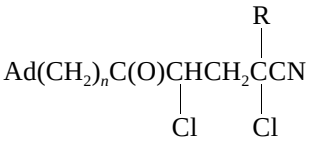
A similar synthesis of chalcones of the adamantane series was performed with ketones (**8, 21**) [110].

The reaction of chalcones (**91**) with hydrogen peroxide in alkaline medium gave rise to *cis*-1-(1-adamantyl)-2,3-epoxy-3-R-propanes (**92**) [111].



92

Oximation of chalcones (**91**) afforded the corresponding oximes [112], and the reaction with polychloronitriles resulted in 1,5-ketonitriles (**93**) [113].



93

n = 0, 1.

A mixture of ketone (**2**) and ethyl formate treated with sodium afforded sodium salt of 3-(1-adamantyl)-1-hydroxy-1-propen-3-one (**94**) that was subsequently transformed into 6-(1-adamantyl)-3-cyanopyridin-2(1H)-ones, -thiones, and -selenones [114–117].

$$\mathbf{2} + HCOOC_2H_5 \xrightarrow{Na} AdC(O)CH{=}CHONa$$

94

Later we extended this reaction to ketones (**8**) and (**21**) [118, 119].

Ketone (**2**) formylation according to Willsmeier gives 3-(1-adamantyl)-3-chloro-2-propenal (**95**) that is widely used in the synthesis of thiophene derivatives [120, 121].

$$\mathbf{2} \xrightarrow[DMF]{POCl_3,} AdC(Cl){=}CHC(O)H$$

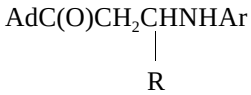
95

Inexorably associated with vinyl ketones synthesis is the preparation of β-aminoketones (**96a**) via Mannich reaction with paraformaldehyde and amine hydrochlorides. By now this reaction is known only for ketone (**2**), and it was carried out with aliphatic, aromatic, and heterocyclic amines [122–125].

$$\mathbf{2} + CH_2O + NRR'{-}HCl \rightarrow AdC(O)CH_2CH_2NRR'{-}HCl$$

96a

From vinyl ketones (**91**) and arylamines were also obtained β-aminoketones (**96b**) [126].



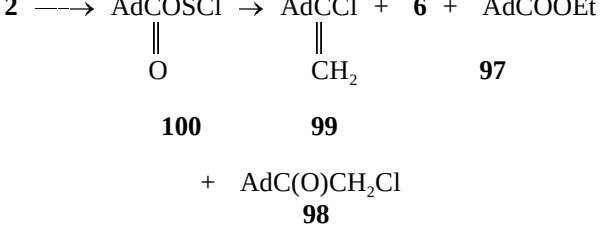
96b

R = Ar.

Transamination of 1-(1-adamantyl)-3-(diethylamino)propan-1-one hydrochloride with aniline afforded 1-(1-adamantyl)-3-(*N*-phenylamino)propan-1-one (**296b**, R = H, Ar = Ph) [127].

Mannich reaction was carried out also with *N*-methyl-*N*-(1-adamantyl)amine hydrochloride and aliphatic (acetone), aromatic (*p*-hydroxyacetophenone), and heterocyclic (2-acetylthiophene) ketones [128].

Among the ketone derivatives applied to the synthesis of heterocycles the most widely used are α-haloketones. The reaction between ketone (**2**) and thionyl chloride was investigated by GLC, IR, ^1H and ^{13}C NMR spectroscopy [129–131]. The reaction products consisted of a mixture: acid (**6**), its ethyl ester (**97**), 1-adamantyl chloromethyl ketone (**98**), 1-adamantyl-1-chloroethene (**99**). It was suggested that first arose compound (**100**) that then decomposed into several compounds.



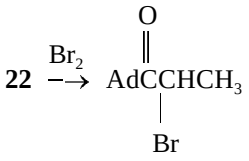
100 **99** **97**

+ $AdC(O)CH_2Cl$

98

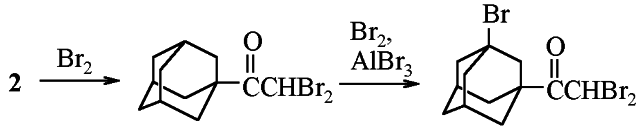
Several studies concerned bromination of adamantane series ketones. By bromination of ketone

(**22**) [33] was obtained 1-adamantyl-2-bromo-1-propanol (**101**).



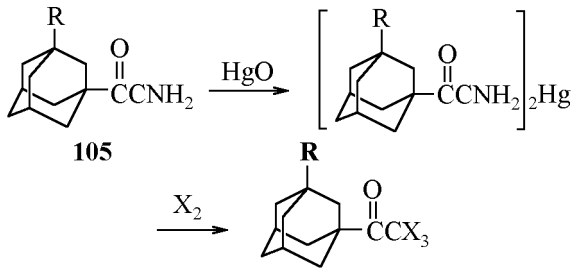
101

The bromination of ketone (**2**) with excess bromine in ether solution results in 1-adamantyl dibromomethyl ketone (**102**), and only at prolonged heating with bromine in the presence of traces of aluminum bromide one more bromine atom enters into position 3 of adamantane to furnish 3-bromo-1-adamantyl dibromomethyl ketone (**103**) [33].



102 **103**

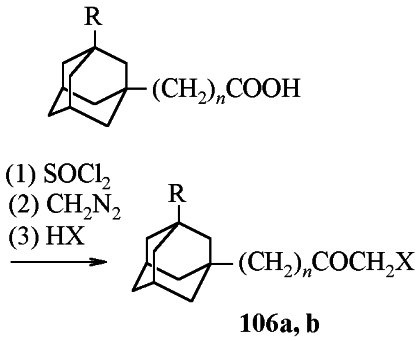
Quite a number of studies [132–135] is dedicated to the synthesis of haloketones from diazoketones. This method provided both trihaloketones and α-haloketones substituted in position 3 of the adamantane core. 1-Adamantyl tribromomethyl ketones (**104**) were synthesized by bromination (chlorination) under mild conditions of the mercury derivatives of adamantanoyldiazomethane. The latter were obtained from diazoketones (**105**) and yellow mercury(II) oxide [132, 134].



105 **R** **104**

X = Cl, Br; R = H, Cl, Br.

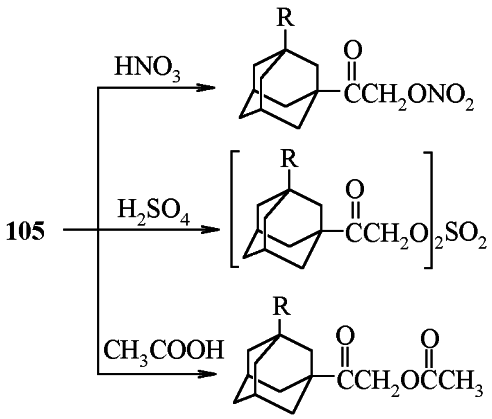
The treatment of the same diazoketones (**105**) with HCl or HBr gives rise to α-haloketones (**106a, b**) [133, 135]. Similar reactions without isolation of the intermediate diazoketones were carried out on 1-adamantanecarboxylic (**6**) and 1-adamantylacetic (**7**) acids [33].



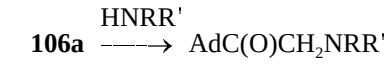
106a, b

n = 0 (**a**), 1 (**b**); R = H, Cl, Br; X = Cl, Br.

The same diazoketones (**105**) with HNO_3, H_2SO_4, CH_3COOH yield the corresponding derivatives of the α-hydroxyketones [135–137].



In attempt to prepare new adamantane derivatives possessing biological activity was synthesized α-aminoketones (**107**) from bromoketone (**106a**) and various amines [138–141].



107

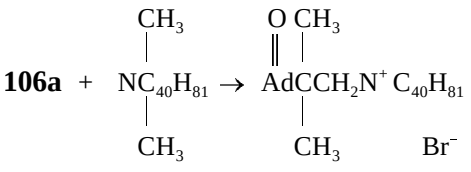
This reaction was also carried out with 1-adamantyl 1-bromoethyl ketone (**101**) [140]. 1-and 2-amino-adamantanes similarly react with bromomethyl ketones to afford compounds (**108**) [142].

$RC(O)CH_2NHAd$-1(2)

108

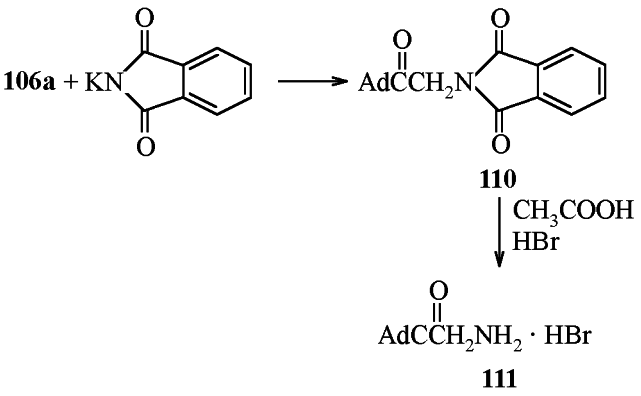
R = Ar, *t*-Bu, Ad.

Ketone (**106a**) with dimethyltetradecylamine give rise to quaternary salts (**109**) showing bactericidal activity [143].



109

A known preparation method for primary α-aminoketones was Gabriel reaction that was successfully carried out with ketone (**106a**) [144]. From ketone (**106a**) and potassium phthalimide was obtained 1-adamantyl *N*-phthalimidomethyl ketone (**110**) that by treatment with HBr in CH_3COOH solution was transformed into 1-adamantanylmethylamine (111). Similarly were performed transformations of ketone (106b) [145].



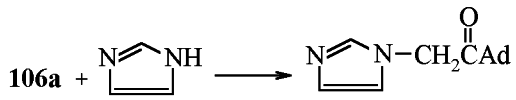
110

111

For a number of aminoketone derivatives of adamantane were prepared oximes, thiosemicarbazides, phenylhydrazones, and also was studied nitrosation thereof [146].

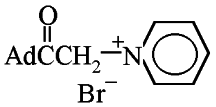
Under unlike conditions ketones (**106a, b**) with amines form different reaction products: the already described α-aminoketones (**108**) or Schiff's bases [145]. The latter are obtained in toluene in the presence of $ZnCl_2$.

The N-alkylation in the series of adamantyl-containing α-haloketones was studied not only by the example of the α-aminoketones synthesis, but also on reaction of bromoketone (**106a**) with nitrogen-containing heterocycles. The reaction between ketone (**106a**) with imidazole affording 1-(1-adamantanoylmethyl)imidazole (**112**) was described in patent [147].



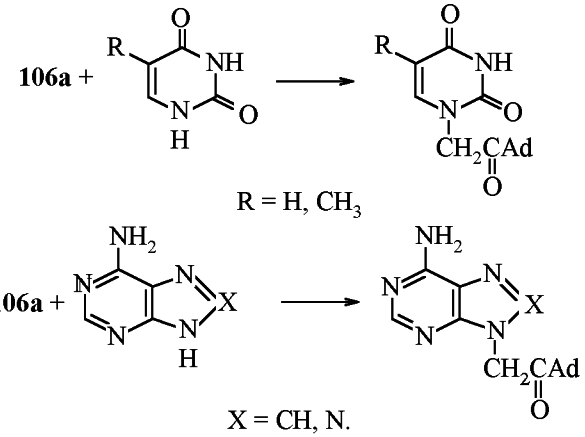
112

Reaction of bromoketone (**106a**) with pyridine yields 1-adamantanoylmethylpyridinium bromide (**113**) which was demonstrated to be very efficient in neutralizing paraoxone [148, 149].

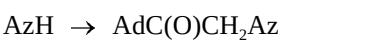


113

Under conditions of phase transfer catalysis ketone (**106a**) regioselectively alkylates uracil and thymine at N^1, adenine and 8-azaadenine at N^9, and theophylline at N^7. Under the same conditions barbital and phenobarbital are alkylated to afford the corresponding N^1,N^3-di(adamantanoylmethyl) derivatives [150].

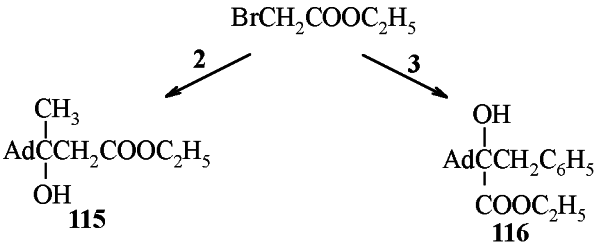


A study was published [151] on reaction between haloketone (**106a**) and a series of azoles: 1,2,4-triazole, benzotriazole, benzimidazole, 5-aminotetrazole, and 3(5)amino-1,2,4-triazole. The reactions carried out in dimethylformamide, tetrahydrofuran, and acetone in the presence of such bases as KOH, K_2CO_3, $NaHCO_3$, and Et_3N yield mixtures of substances hard to separate and to identify. The best results were obtained with sodium hydride as the base and hexametylphosphoramide as the solvent. Under these conditions we obtained 1-(1-adamantanoylmethyl)azoles (**114**).

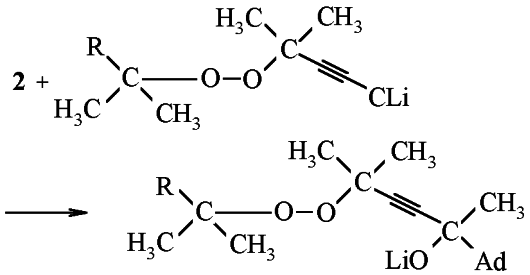


114

Among the other reactions of ketone (**106a**) should be mentioned the preparation of sodium 3-(1-adamantanoyl)propionate from bromoketone (**106a**) and ethoxymagnesiummalonate [124]. It is also worth mentioning the dehalogenation of ketone (**106a**) effected by molybdenum hexacarbonyl on alumina affording ketone (**2**) in 88% yield [152, 153]. A number of α- (**107**) and β-aminoketones (**96**) was reduced by sodium borohydride in methanol into β- and γ-aminoalcohols [154]. Preparation methods for β-aminovinyl ketones AdC(=O)CH=CHNRR' were developed proceeding from sodium salts (**94**) and amines in alcoholic medium [155]. This method was extended to 1-aminoadamantane and ketones from various series [156, 157]. The reaction of ketone (**2**) with dimethylsulfoxonium methylide in the presence of lithium methylsulfinylmethylide was suggested as a new easy way to 2-(1-adamantyl)-1,4-diene [158]. The Reformatsky reaction of ketone (**2**) with ethyl bromoacetate in the tetrahydrofuran results in ethyl β-(1-adamantyl)β-hydroxybutyrate (**115**) [122], and with 1-adamantyl phenyl ketone (**31**) arises ethyl α-(1-adamantyl)-α-hydroxy-β-phenylpropionate (**116**) [159].

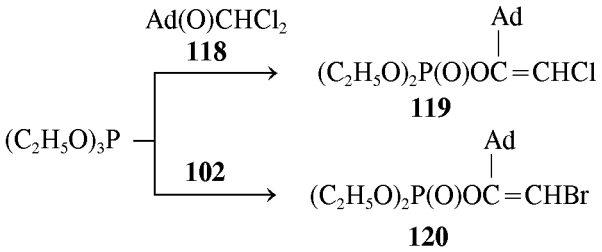


Recently were published reports on the synthesis of adamantyl-containing peroxides (**117**), among them those prepared from ketone (**2**) and lithium peroxyacetylides (molar ratio of the reagents 1:1.25, reaction temperature −40… −20°C [160].



117

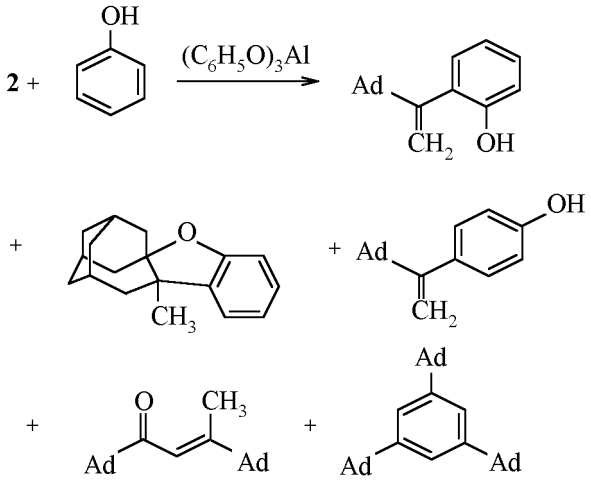
In reaction of 1-adamantyl dichloromethyl ketone (**118**) with triethyl phosphite the formation of the corresponding vinyl phosphate (1190 was detected by NMR spectroscopy only after heating the reagents in the NMR tube at 100°C for over 12 h. The reaction is strongly hindered by shielding of the carbonyl carbon by the 1-adamantyl substituent. Unlike dichloroketones the dibromoketones are phosphorylated according Perkov under nearly similar (and milder) conditions disregarding the structure of the radical. Even 1-adamantyl dibromomethyl ketone (**102**) reacts with triethyl phosphite at room temperature to afford vinyl phosphate (**120**). The structure of the latter was proved by X-ray diffraction study. However it should be mentioned that in concurrent reaction between triethyl phosphite and a mixture of dibromoketone (**102**) and α,α-dibromoacetophenone in CD_2Cl_2 medium at room temperature the α,α-dibromoacetophenone reacted 4 times faster than ketone (**102**) [161].



120

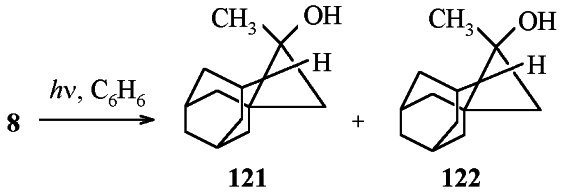
A condensation of phenol with methyl ketone (**2**) in the presence of aluminum phenolate results in 1-(1-adamantyl)-1-(2-hydroxyphenyl)ethene, 1-(1-adamantyl)-1-(4-hydroxyphenyl)ethene, 2,3(3,4-homoadamantano)-3-methyl-2,3-dihydrobenzofuran, 1,3-di(1-adamantyl)-2-buten-1-one, and 1,3,5-tri(1-adamantyl)-benzene [162].

The reaction was studied in the temperature range 180–230°C and time interval 1–10 h, at molar ratio



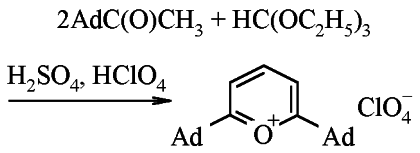
ketone (**2**), phenol, and aluminum phenolate 0.3–0.5 : 1 : 0.25–0.5. In some cases the process was carried out in solution of 1-butyl-2,4-dimethylbenzene, cyclohexylbenzene, or diphenyl ether.

The effect of solvents and ketone (**8**) multiplicity on the stereochemistry and efficiency of its phototransformations was studied [66, 163]. The irradiation of the diluted (0.1–0.2 M) ketone (**2**) solution in degassed and nondegassed benzene provides cyclobutanones in nearly quantitative yield: *exo*-3-hydroxy-*exo*-3-methyltetracyclo[5.3.1.1^{5,9}0^{1,4}]dodecane (**121**) and its stereoisomer (**122**) in 3 : 1 ratio.



121 **122**

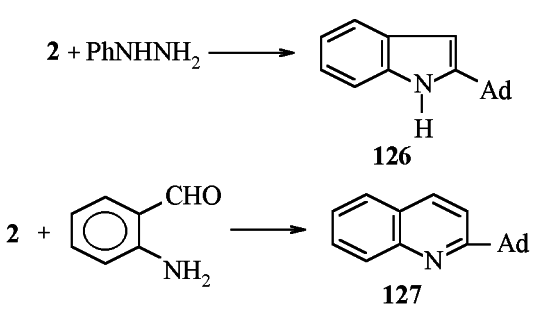
Among the most interesting applications of adamantane carbonyl derivatives should be mentioned the synthesis of heterocyclic compounds. Ketone (**2**) and triethyl orthoformate in the presence of sulfuric acid after subsequent addition of perchloric acid furnish 2,6-di(1-adamantyl)pyrilium perchlorate (**123**) in 22% yield [87].



123

A reaction of isatin with acetyladamantane (**2**) in ethanol in the presence of ammonia results in 3-(1-adamantanoylmethyl)-3-hydroxy-2-oxoindole (**124**) that by boiling in a mixture of acetic and sulfuric acids with water yields 2-(1-adamantyl)-4-carboxyquinoline (**125**) [164].

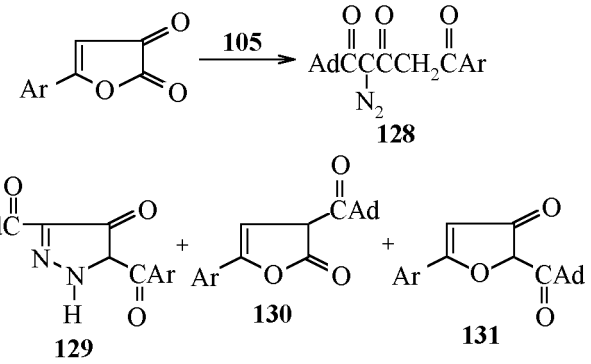
A cyclization of ketone (**2**) with phenylhydrazine in polyphosphoric acid afforded 2-(1-adamantyl)-indole (**126**) in 85% yield [165], and with o-aminobenzaldehyde according to Frindler formed 2-(1-adamantyl)quinoline (**127**) [166].



126

127

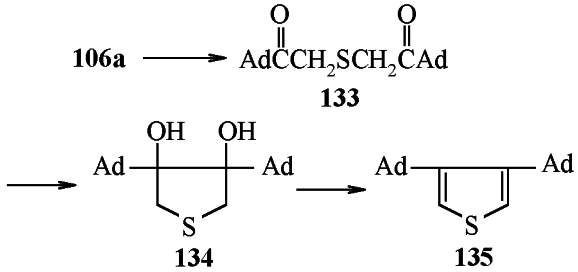
Diazoketones (**105**), the precursors of α-haloketones from adamantane series, also participate in the synthesis of heterocycles. The reaction of 1-adamantylcarbonyldiazomethane (**105**) with 5-aryl-2,3-dihydrofuran-2,3-diones provides 1-adamantyl-5-aryl-2-diazo-1,3,5-pentatrione (**128**) and also the products of its thermal cyclization: 3-(1-adamantylcarbonyl)-5-aroylpyrazolin-4-one (**129**), 3-(1-adamantylcarbonyl)-5-aryl-2,3-dihydrofuran-2-one (**130**), and 2-(1-adamantylcarbonyl)-5-aryl-2,3-dihyrofuran-3-one (**131**) [167].



128

129 **130** **131**

In reaction of diazoketone (**105**) with acrylonitrile were obtained 3-R-(1-adamantanoyl)-5-R-pyrazoles (**132**) [168]. From ketone (**106a**) and Na_2S in aqueous acetone was obtained diketosulfide (**133**) that by intramolecular pinacolin reduction effected by low-valence titanium reagent (prepared from $TiCl_4$ and zinc powder) within 9 h at –18°C in THF afforded diol (**134**). Dehydration of the diol catalyzed with *p*-toluenesulfonic acid gave 3,4-di(1-adamantyl)thiophene (**135**) in 60% yield [169–171].



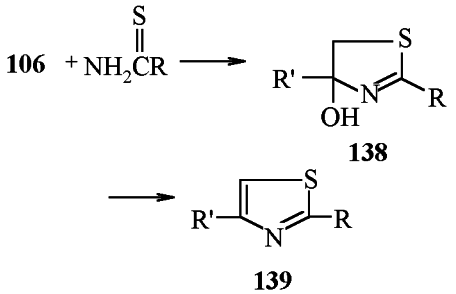
133

134 **135**

A synthesis was described [172, 173] of 4-(1-adamantyl)thiazol-2-one (**136**) effected by treating haloketone (**106a**) with MSCN (M = K, Na, NH_4) with subsequent cyclization in the presence of acid. Compound (**136**) possesses fungicidal and antiviral

activity. The treatment of haloketones (**106a, b**) with potassium thiocyanate provided thiocyanatoketones that under the action of HCl transformed into 2-chlorothiazoles (**137**) with 1-adamantyl or 1-adamantylmethyl substituent in position 4 [174].

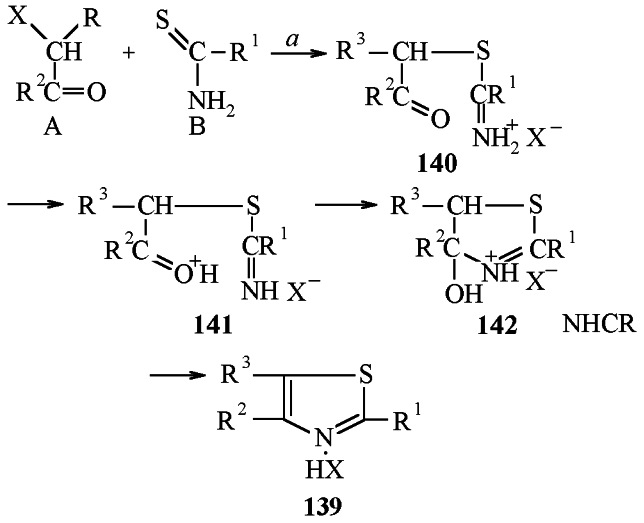
Bromoketones (**106a, b**) with thioformamide in ether solution react in dissimilar fashion [175–176]. Ketone (**106b**) affords an intermediate 4-(1-adamantylmethyl)4-hydroxythiazoline (**138**) that already at storage in air transforms into 4-(1-adamantyl)thiazole hydrobromide (**139**). At the same time bromoketone (**106a**) reacts with direct formation of substituted thiazoles (**139**).



106 **138** **139**

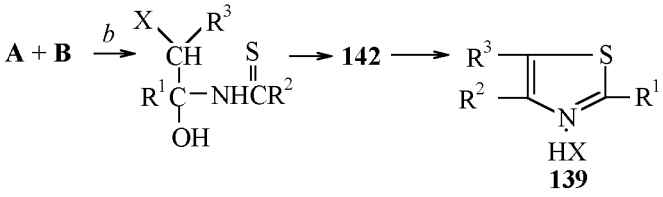
R = H, CH_3, NH_2; R' = Ad, CH_2Ad.

The conventional scheme of thiazole formation from α-haloketones (A) and thioamides (B) assumes as the first stage (*a*) S_N2-substitution with sulfur attack on the carbon atom neighboring to halogen.



A **B** **140** **141** **142** **139**

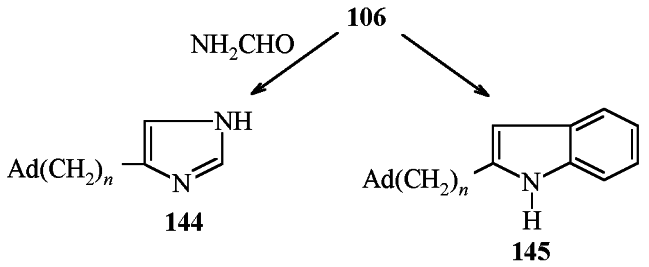
However in the reaction of ketone (**106b**) in ether solution a precipitate was formed consisting of hydroxythiazolium halides (**142**) although according to the above scheme acyclic products should have formed. This fact and also on the grounds that the stage of intermediates (**140, 141**) formation required transition of a proton from nitrogen to the oxygen of the carbonyl group which is 10^6 times less basic demanded the introduction of another scheme (*b*).



A + **B** **142** **139**

The monitoring of reaction after mixing of haloketones and thioamides with the use of IR and UV spectroscopy confirmed formation in the first stage of the reaction of acyclic oxyamine (**142**).

Haloketones (**106a, b**) in reaction with N-substituted ureas in acetonitrile at 20°C give 2-aminothiazoles (**143**) [179, 180], at boiling in formamide turn into imidazole derivatives (**144**), and with aniline according Bischler transform into substituted indoles (**145**) [181], therewith the yield with ketone (**106b**) is lower. The bridging methylene group is presumed to facilitate side reactions that decrease the yield of the target product.

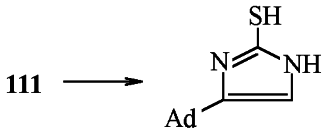


106 **144** **145**

n = 0, 1.

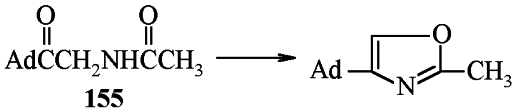
Bromoketone (**106a**) with ammonium formate in concn. H_2SO_4 affords 4-adamantyloxazole (**146**) [179]. 5-Aryl-2,3-dihydrofuran-2,3-diones by a thermal decarbonylation are transformed into aroylketenes, and the latter with ketone (**106a**) in CCl_4 within 2,5 h form 2-adamantyl-2-methyl-6-aryl-1,3-dioxan-4-ones (**147**) and 6-aryl-3-benzoylpyran-2,4-diones (**148**) [182]. The reaction of ketone (**106a**) with 2-amino-1,3-dimethylimidazo[4,5-c]pyridin-2-one results in 8-adamantyl-1,3-dimethylimidazo[4,5-c]imidazo[1,2-a]pyridin-2-one (**149**) [183]. Haloketone (**106a**) with α-picoline, 2-aminopyridine, and 2-aminothiazole affords respectively 2-adamantylindolisine (**150**), 2-adamantylimidazo[1,2-a]pyridine (**151**), and 2-adamantylimidazo[1,2-a]thiazole (**152**) [184]. A synthesis was reported of 4(5)-(1-adamant-

yl)-2-mercaptoimidazole (**153**) from 1-adamantanoylmethylamine (**111**) and ammonium thiocyanate [144].



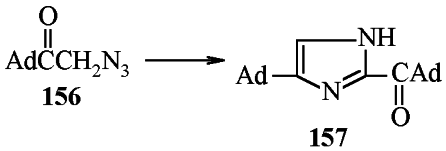
153

This reaction was later extended to the other α-aminoketones from the adamantane series. Adamantyl-substituted oxazoles (**154**) were obtained by cyclization of 1-admantyl N-acetylaminomethyl ketone (**155**) when treated with a mixture of trifluoroacetic anhydride and trifluoroacetic acid [185].



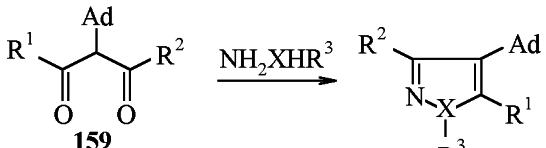
155 **154**

The hydrolysis of 1-adamantyl azidomethyl ketone (**156**) by boiling in xylene affords in good yield 2-(1-adamantanoyl)-4(5)-(1-adamantyl)imidazole (**157**) [186].



156 **157**

From β-aminoketones and phenylhydrazine in alcohol in the presence of sodium hydroxide was obtained 3-(1-adamantyl)-1-phenylpyrazoline (**158**) [125]. β-Diketones (**159**) with phenylhydrazine and hydroxylamine furnish the corresponding five-membered heterocycles: adamantyl-substituted pyrazoles (**160**) and oxazoles (**161**) [76].



159 **160, 161**

R^1 = Me, Ph, OEt, *t*-Bu; R^2 = Me, Ph, *t*-Bu; R^3 = H, Ph; X = N, O.

The addition of trichloroacetonitrile to 1-adamantyl vinyl ketone (**162**) gave adducts (**163**) that treated with HCl in ether afforded 6-(1-adamantyl)-3,3,5-trichloro-3,4-dihydro-2-pyridone (**164**) [187, 188].

The presented published material shows that the synthetic methods for adamantane series ketones are sufficiently developed. However the studies of their chemical properties and on the synthesis therefrom of still unavailable heterocyclic compounds are scarce and nonsystematic.

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