HETEROADAMANTANES AND THEIR DERIVATIVES.

7.* SYNTHESIS AND MASS-SPECTROMETRIC STUDY OF FUNCTIONAL DERIVATIVES OF 5-MONO- AND 5,7-DISUBSTITUTED 1,3-DIAZAADAMANTANES

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UDC 547.853.5'68.07;543.51'422.25

The chemical behavior of the carbonyl group of 5-mono and 5,7-disubstituted 6-oxo-1,3-diazaadamantanes was studied. The structures of the functional derivatives obtained were confirmed by IR and ^1H and ^{13}C NMR spectral data. The behavior of the compounds under the influence of electron impact was studied, and the principal pathways of fragmentation of their molecules were ascertained.

A study of the chemical behavior of the keto group of 6-oxo-1,3-diazaadamantanes in the case of the most accessible representative — 5,7-diphenyl-6-oxo-1,3-diazaadamantane — demonstrated its unusual inertness with respect to some typical carbonyl reagents. This compound does not react with Grignard reagents, diazomethane, and 2,4-dinitrophenylhydrazine [2, 3]; it forms the corresponding hydrazone [2] and undergoes Wolff–Kishner reduction [4] under extremely severe conditions. However, recently, after our report [5], Hickmott and coworkers [6] were able, with difficulty, to obtain 5,7-diphenyl-6-oxo-1,3-diazaadamantane oxime and reduce it to the corresponding amino derivative.

On the basis of a study of the spectral characteristics of 5,7-diphenyl-6-oxo-1,3-diazaadamantane it was assumed that the behavior of the keto group is a consequence of long-range interaction of the π orbitals of the carbonyl group with the free electron pairs of the nitrogen atoms in the β-amino ketone fragment of the molecule with the participation of the σ bonds and is characteristic for compounds of this series [2]. The nature of this phenomenon has not yet been sufficiently clear.

We have studied the chemical transformations with the participation of the carbonyl group of the previously synthesized 5-mono- [7] and 5,7-disubstituted 6-oxo-1,3-diazaadamantanes [1], on the basis of which diverse functional derivatives were obtained. It was found that, despite the assumption of Sasaki and coworkers [2], the keto group in 6-oxo-1,3-diazaadamantanes Ia-c is not inert and undergoes the reactions that are characteristic for it (Scheme 1).

Thus hydrazones IIa,c are readily formed when ketones Ia,c are heated in a large excess of hydrazine hydrate. It is interesting that methyldiazaadamantanone Ib under similar conditions gives almost exclusively azine IIb. 1,3-Diazaadamantanes IIIa,c were obtained by fusing hydrazones IIa,c with potassium hydroxide. Diazaadamantanone oximes IVa-c are readily formed by the action of hydroxylamine in an aqueous alkaline medium on the corresponding ketones Ia-c. The reduction of oximes IVa-c by fusion in an aqueous alkaline medium led to the production of amino derivatives Va-c. By an exchange reaction with acetone cyanohydrin in acetone diazaadamantanone Ia was converted to hydroxy cyano derivative VIa. Sodium borohydride in alcohol readily reduces ketones Ia-c to the corresponding diazaadamantanols VIIa-c [7]. Diazaadamantanol VIIIa was synthesized by the reaction of diazaadamantanone Ia with phenyllithium. The structures of the synthesized compounds were confirmed by data from the IR, PMR, and mass spectra, while the structure of IIb was also confirmed by data from the ^{13}C NMR spectrum (Tables 1-4).

*See [1] for Communication 6.

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0009-3122/89/2505-0541$12.50

TABLE 1. Functional Derivatives of 5-Mono- and 5,7-Disubstituted 1,3-Diazaadamantanes

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1}	Yield, %
IIa	$C_{10}H_{18}N_4$	168...169	3360, 3300, 1615 (NH), 1650 (C=N)	93
IIb	$C_{18}H_{28}N_6$	321...322	1640 (C=N)	88
IIc	$C_{14}H_{18}N_4$	224...225	3340, 3250 (NH), 1640 (C=N), 1600(arom.)	74
IIIa	$C_{10}H_{18}N_2$	109...110	—*	97
IIIc	$C_{14}H_{18}N_2$	159...161	1605 (arom.)	82
IVa	$C_{10}H_{17}N_3O$	240...241	3260...3080 (OH), 1660 (C=N)	89
IVb	$C_9H_{15}N_3O$	211...212	3270...3000 (OH), 1660 (C=N)	87
IVc	$C_{14}H_{17}N_3O$	273...274	3160 (OH), 1640 (C=N), 1600 (arom.)	67
Va	$C_{10}H_{19}N_3$	138...140	3300, 3100, 1600...1580 (NH)	92
Vb	$C_9H_{16}N_3$	94...95	3300, 3100, 1600...1580 (NH)	90
Vc	$C_{14}H_{19}N_3$	237...238	3310, 3220, 1580 (NH), 1600 (arom.)	78
VIa	$C_{11}H_{17}N_3O$	148...149	3240 (OH), 2230 (C=N)	70
VIIIa	$C_{16}H_{22}N_2O$	214...215	3160 (OH), 1605 (arom.)	71

*Absorption bands of functional groups are absent.

TABLE 2. PMR Spectra of Functional Derivatives of 5-Mono- and 5,7-Disubstituted 1,3-Diazaadamantanes

Compound	Chemical shifts, ppm (SSCC, ^2J, HZ)			
	$N-CH_2-N$	$N-CH_2-C$	R, R'	others
IIa	4,00 s	3,30...2,70 m	1,33 s, 0,72 s	—
IIb	4,14 d*, 4,04 d (18,5)	3,50...2,90 m	2,96 s, 0,96 s	—
IIc	4,31 d, 4,17 d (13,0)	3,75 d, 3,58 d (13,0); 3,66 d, 3,38 d (13,0)	7,44...7,19 m, 2,94 m	4,92br.s (NH_2)
IIIa	3,95 s	2,92 d, 2,78 d (12,5)	0,41 s	1,46 s ($C-CH_2-C$)
IIIc	4,28 d, 4,18 d (13,0)	3,53 d, 3,35 d (13,0); 3,45 d, 3,27 d (13,0)	7,39...7,19 m, 1,72 s	2,37 s ($C-CH_2-C$)
IVa	4,07 s	3,21 d, 3,09 d (13,0); 3,08 d, 2,98 d (13,0)	1,37 s, 0,87 s	8,76 br.s (OH)
IVb	4,24 d*, 4,10 d (13,0)	3,21 d, 3,05 d (13,0); 3,50 d, 3,16 d (13,0)	3,37 br.s, 0,90 s	10,12 br.s (OH)
IVc	4,29 d, 4,13 d (13,0)	3,78 d, 3,56 d (13,0); 3,62 d, 3,36 d (13,0)	7,44...7,24m, 3,47s	—
Va	4,03 s	3,26...2,85m	0,52s	2,65 s (H_2N-C-H)
Vb	4,05d, 3,90 d (13,0)	3,35...2,90 m	0,57 s, 2,76 d (13,0) ($\equiv C-H$) †	2,62 d (13,0) (H_2N-C-H) †
Vc	4,20 d, 3,98 d (13,0)	3,60 d, 3,57 d, 3,36 d, 3,19 d, 3,16 d (13,0); 3,39m ‡	7,43...7,15 m, 3,67 s	4,04 s (NH_2-C-H), 1,48 br.s. (NH_2)
VIa	3,96 s	3,28 d, 3,03 d (13,5); 3,19 d, 2,75 d, (13,5)	0,84s	6,93 br.s. (OH)
VIIIa	3,94 s	3,79...3,59 m	0,53 s	7,18...7,50 m (arom), 2,93br.s (OH)

*An AB system.
†A ^3J value that is possibly the opposite of the assignment of the signals presented in parentheses.
‡The signals of the remaining protons are masked by a multiplet signal.

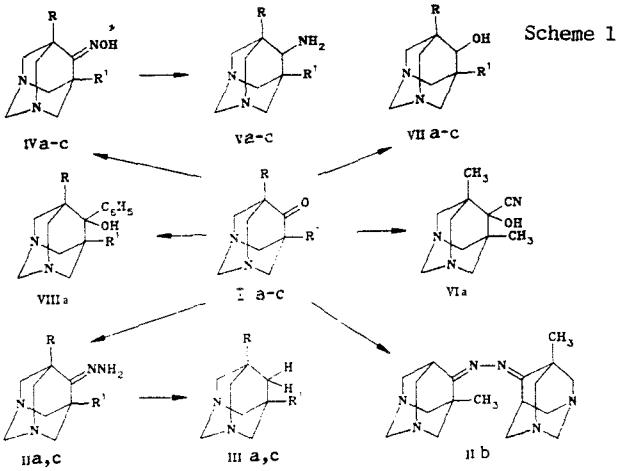
The results obtained constitute evidence that the inertness of the keto group of 5,7-diphenyl-6-oxo-1,3-diazadamantane can hardly be explained only by long-range interaction "through the bond" observed in 6-oxo-1,3-diazaadamantane molecules. Steric factors associated with the shielding effect of the phenyl substituents evidently have a more appreciable effect on the decrease in the reactivity of the carbonyl group. Taking into account the rigidity of the carcass structure of the molecule and the large effective volume of the latter one may expect significant hindrance to axial attack at the carbonyl group.

TABLE 3. Mass Spectra of II-VIII*

Compound	m/z values (I_{rel}, %)
IIa	194 (100), 178 (10), 152 (17), 151 (43), 150 (17), 137 (16), 136 (12), 135 (14), 123 (34), 122 (21), 58 (16)
IIb	328 (55), 164 (19), 149 (12), 121 (25), 108 (17), 68 (18), 58 (36), 55 (14), 43 (30), 42 (100), 41 (49)
IIc	242 (100), 200 (20), 199 (31), 198 (42), 183 (18), 171 (47), 170 (21), 103 (25), 58 (31), 43 (24), 42 (61)
IIIa	166 (84), 124 (30), 123 (30), 122 (45), 108 (22), 82 (25), 71 (20), 58 (100), 55 (32), 42 (50), 41 (27)
IIIc	214 (78), 184 (12), 171 (19), 170 (42), 115 (11), 91 (14), 68 (16), 58 (100), 43 (16), 42 (34), 41 (17)
IVa	195 (73), 179 (25), 152 (37), 137 (33), 136 (28), 135 (52), 82 (29), 58 (25), 55 (29), 42 (100), 41 (50)
IVb	181 (100), 165 (39), 164 (31), 139 (60), 138 (35), 135 (32), 123 (44), 122 (30), 121 (54), 42 (96), 41 (55)
IVc	243 (60), 201 (35), 200 (24), 183 (36), 103 (23), 91 (24), 77 (24), 58 (78), 43 (44), 42 (100), 41 (39)
Va	181 (100), 165 (11), 123 (19), 122 (24), 110 (12), 109 (16), 108 (17), 84 (41), 73 (15), 70 (43), 58 (36)
Vb	167 (92), 108 (59), 96 (30), 94 (32), 84 (33), 70 (100), 68 (28), 58 (51), 56 (48), 42 (62), 41 (36)
Vc	229 (100), 200 (19), 170 (70), 156 (55), 132 (49), 117 (28), 70 (37), 58 (21), 57 (42), 56 (46), 42 (57)
VIa	207 (22), 190 (16), 180 (41), 138 (100), 110 (18), 84 (14), 82 (20), 69 (23), 55 (19), 42 (38), 41 (30)
VIIa	182 (100), 165 (37), 140 (9), 138 (15), 122 (21), 108 (8), 84 (34), 82 (12), 71 (17), 70 (10), 58 (71)
VIIb	168 (100), 151 (25), 124 (25), 108 (36), 84 (22), 70 (44), 68 (26), 58 (55), 55 (24), 42 (24), 41 (34)
VIIc	230 (100), 186 (52), 170 (47), 91 (27), 70 (61), 69 (41), 68 (32), 58 (82), 57 (53), 43 (41), 42 (65)
VIIIa	258 (100), 241 (63), 198 (16), 184 (9), 153 (12), 147 (12), 110 (11), 84 (24), 82 (9), 70 (17), 58 (11)

*The M^+ peaks and the 10 most intense ion peaks are presented.

Scheme 1



Ia--Va, VIIa R=R¹=CH₃; Ib, IVb, Vb, VIIb R=H, R¹=CH₃; Ic-Vc, VIIc R=H, R¹=C₆H₅

We also observed the effect of the effective volume of the substituents attached to the $C_{(5)}$ and $C_{(7)}$ atoms on the reactivity of the carbonyl group in series of alkyl-substituted 6-oxo-1,3-diazaadamantanes. Thus the reaction of methyldiazaadamantanone Ib with hydrazine hydrate leads to the formation of azine IIb, while dimethyldiazaadamantanone Ia gives hydrazone IIa, and 5,7-di-isopropyl-6-oxo-1,3-diazaadamantane under similar conditions does not react with hydrazine as a consequence of the large effective volume of the substituents. Like 5,7-diphenyl-6-oxo-1,3-diazaadamantane it is also inert in reactions with hydroxylamine and sodium borohydride.

Intense (and in some cases maximum) molecular-ion peaks (M^+), the stabilities of which with respect to fragmentation (the W_M values, Table 4) for functional derivatives of 5-methyl-, 5,7-dimethyl-, and 5-phenyl-substituted 1,3-diazaadamantanes, with allowance for the data in [1], decrease in the order —OH > =NNH₂ > =O > —NH₂ > =H₂ ≈ NOH, are observed in the mass spectra of II-VII.

An analysis of the mass-spectra of II-VIII, as well as the 6-oxo-1,3-diazaadamantanes that we previously studied [1], shows that for these compounds one can single out three principal

pathways of the fragmentation of M^+ that are associated with the nature of the functional substituent.

The first pathway, which leads to the formation of F_1–F_7 ions (Scheme 2), is common for all of the investigated compounds and characterizes the fragmentation of the 1,3-diazaadamantane skeleton. However, whereas the fragmentation of the M^+ ions of 6-oxo-1,3-diazaadamantanes via this pathway dominates (the F_2 ion peaks have the maximum intensities in the mass spectra [1]), the probability of this sort of fragmentation is considerably smaller for II-VIII (Table 4).

One of the pathways of the fragmentation of the M^+ ions of V-VIII is splitting out of a substituent (OH or NH_2) in the form of a radical with the formation of an F_8 ion (Scheme 2). In a study of the mass spectra of 2-adamantanols [8-13] and 2-adamantylamines [8, 10, 13] it was shown that the most characteristic process for these compounds is splitting out of the substituent in the form of a neutral HX molecule from the M^+ ion. The detachment of the X substituent from the M^+ ion is a two-step process and gives a substantially less intense peak. The substantial differences are observed in the character of the detachment of the substituent from the M^+ ions of V-VIII and 2-adamantanols, as well as 2-adamantylamines. The subsequent fragmentation of the F_8 ion proceeds with the detachment of neutral C_2H_5N and C_3H_7N molecules and leads to F_9 and F_{10} ions, respectively.

The fragmentation of the M^+ ion with the formation of the [M=HCN] ion (6.3% of the total ion current), which probably has the 6-oxo-1,3-diazaadamantane structure, is also possible for VIa. The presence in the spectrum of VIa of a maximum (in intensity) peak of an $[M - HCN, -C_2H_4N]^+$ ion (15.5% of the total ion current) constitutes evidence in favor of this assumption.

Scheme 2

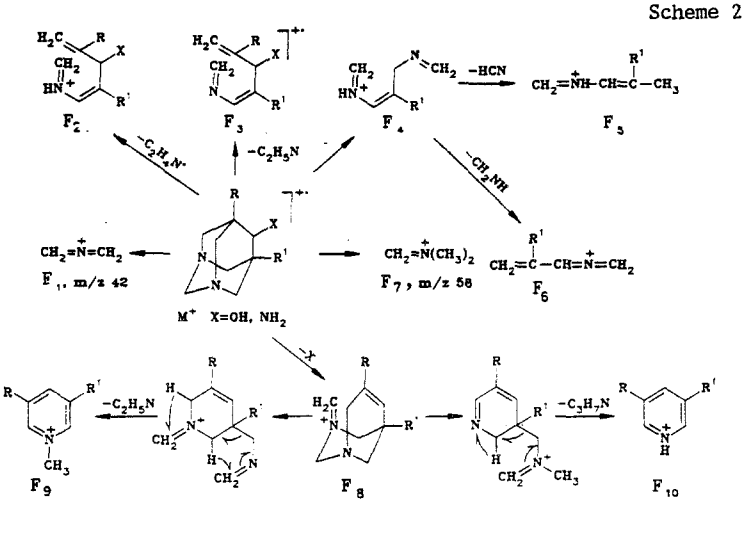


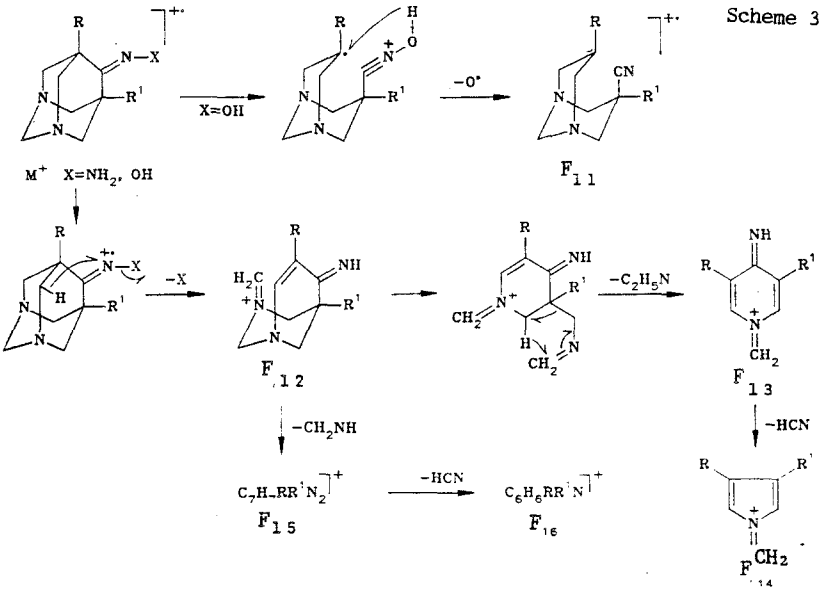
TABLE 4. Intensities of the Peaks of the Characteristic

Compound	W_M	Intensity						
		F_1	F_2	F_3	F_4	F_5	F_6	F_7
IIa	18,9	1,1	0,3	7,1	0,4	1,0	1,2	2,6
IIb	7,9	11,6	1,1	1,1	0,5*	2,4*	3,1*	4,2
IIIa	11,5	6,1	3,6	3,6	0,7	1,3	3,0	12,1
IVa	9,0	10,9	2,3	4,1	0,4	1,4	3,2	2,8
IVb	9,1	7,8	4,9	2,8	2,2*	2,4*	3,8*	1,8
IVc	6,3	8,9	3,1	2,2	0,7*	1,4*	2,7*	7,0
Va	15,5	0,4	0,5	1,0	1,4	7,6	1,9	6,6
Vb	10,3	5,8	0,7	1,3	1,9*	12,5*	4,8*	4,8
Vc	9,5	4,6	0,2	0,9	1,1*	4,1*	3,0*	1,7
VIa	3,9	5,9	1,0	0,5	1,4	2,2	3,1	1,5
VIIa	22,1	1,0	1,8	1,6	1,2	6,8	2,4	13,9
VIIb	15,7	7,3	1,8	1,1	2,6*	9,2*	5,8*	7,7
VIIc	9,2	5,2	0,6	1,0	1,1*	10,0*	3,5*	6,5
VIIIa	17,4	0,7	0,9	0,8	0,8	4,1	1,6	1,9

*The overall intensity of the peaks of ions with R and R^1

The third pathway of fragmentation of the M^+ ions is determined by the presence of an oximino (IV) or hydrazono (II) grouping (Scheme 3) and is typical for these classes of compounds [13-17]. Splitting out of an oxygen atom and the loss of a hydroxy group (the F_{11} and F_{12} ions) are characteristic for alicyclic and aromatic ketoximes [13-16]. The peaks of the F_2 and F_3 ions, which contain an oximino group, are less intense in the spectra of IV than the peaks of the anologous ions in the spectra of 6-oxo-1,3-diazaadamantanes [1]. Peaks of F_{12} ions, which are due to cleavage of the N–N bond, are also present in the mass spectra of IIa,b. The subsequent fragmentation of the F_{12} ions is presented in Scheme 3.

Scheme 3



The compositions of the principal ions of II-VIII were confirmed by the high-resolution mass spectra.

The peculiarities of the mass-spectral fragmentation of functional derivatives of 1,3-diazaadamantane revealed in this research can be used to identify and establish the structures of compounds of similar series.

EXPERIMENTAL

The IR spectra were obtained with UR-20 and Specord 71 IR spectrometers (in mineral oil). The PMR spectra were obtained with Bruker WM-250 and Tesla-80 spectrometers (in $CDCl_3$) with hexamethyldisiloxane (HMDS) as the internal standard. The ^{13}C NMR spectra were obtained with a Bruker WM-250 spectrometer in $CHCl_3$ with $CHCl_3$ as the internal standard. The mass spectra were obtained with an LKB-2091 chromatographic mass spectrometer with direct introduction of the samples into the ion source; the accelerating voltage was 3.5 kV, the cathode-emission

Fragment Ions in the Mass Spectra of II-VIII

(% of the total ion current)

F_8	F_9	F_{10}	F_{11}	F_{12}	F_{13}	F_{14}	F_{16}	F_{15}
—	—	—	—	1,7	2,4	1,6	1,1	3,5
—	—	—	—	2,2	2,9	1,1	1,3	2,0
—	—	—	—	—	—	—	—	—
—	—	—	2,7	2,2	5,7	1,4	2,3	2,1
—	—	—	3,2	2,5	4,4	1,5	2,6	2,4
—	—	—	0,2	0,9	3,2	1,0	1,5	0,9
2,0	4,4	3,1	—	—	—	—	—	—
1,6	5,5	3,0	—	—	—	—	—	—
0,3	5,5	4,4	—	—	—	—	—	—
2,5	1,9	0.5	—	—	—	—	—	—
7,2	4,1	1,6	—	—	—	—	—	—
3,5	5,0	1,8	—	—	—	—	—	—
0,7	3,7	1,4	—	—	—	—	—	—
10,9	2,8	1,5	—	—	—	—	—	—

substituents.

current was 25 μA, the ionizing-electron energy was 70 eV, and the temperature of the ionizing chamber was 200°C. The high-resolution mass spectra were obtained with a Kratos MS-80 spectrometer with direct introduction of the samples into the ion source; the accelerating voltage was 3.0 kV, the cathode-emission current was 100 μA, the ionizing-electron energy was 70 eV, the temperature of the ionizing chamber was 150°C, and the standard was perfluorinated kerosene. Resolution $M/\Delta M = 7500$.

The characteristics of II-VIII are presented in Tables 1-4. The results of elementary analysis for C, H, and N were in agreement with the calculated values.

Adamantanones Ib,c and adamantanols VIIb,c were synthesized by the methods in [7], while adamantanone Ia was synthesized by the method in [1].

5,7-Dimethyl-6-oxo-1,3-diazaadamantane Hydrazone (IIa). A 2.00-g (11.1 mmole) sample of 5,7-dimethyl-6-oxo-1,3-diazaadamantane (Ia) in 10 ml of hydrazine hydrate was heated with gentle refluxing for 1 h, after which the reaction mass was evaporated in vacuo, and the solid residue was recrystallized from n-heptane.

Compound IIc was similarly obtained.

1,2-Bis(5-methyl-1,3-diaza-6-adamanylidene)hydrazine (IIb). This compound was obtained as in the case of IIa,c from 0.50 g (3.0 mmole) of adamantanone Ib and 5 ml of hydrazine hydrate and was recrystallized from toluene. ^{13}NMR spectrum: 170.2 [$C_{(6)}$], 70.7 [$C_{(2)}$], 63.5 [$C_{(4)}$, $C_{(10)}$], 56.3 [$C_{(8)}$, $C_{(9)}$], 38.0 [$C_{(5)}$], 31.4 [$C_{(7)}$], 17.6 ppm (CH_3).

5,7-Dimethyl-1,3-diazaadamantane (IIIa). A mixture of 1.00 g (5.15 mmole) of hydrazone IIa and 1.00 g of powdered potassium hydroxide was heated at 220-230°C for 1.5 h, after which the cooled mass was treated with dry ether (four 10-ml portions). The solvent was removed by distillation, and the dry residue was sublimed in vacuo.

Compound IIIc was similarly obtained.

5,7-Dimethyl-6-oxo-1,3-diazaadamantane Oxime (IVa). Solutions of 3.00 g (16.6 mmole) of adamatanone Ia in 10 ml of water, 1.59 g (22.9 mmole) of hydroxylamine hydrochloride in 8 ml of water, and 1.77 g (44.2 mmole) of sodium hydroxide in 4 ml of water was mixed, and the mixture was kept on a boiling-water bath for 6 h. The precipitate that formed when the mixture was cooled was removed by filtration, washed with 5 ml of cold water, and recrystallized from alcohol.

Compounds IVb,c were similarly obtained.

5,7-Dimethyl-6-amino-1,3-diazaadamantane (Va). A 30-ml sample of 50% aqueous sodium hydroxide solution was added with vigorous stirring in the course of 3 h to a suspension of 15 g of Ni–Al alloy and 5.00 g (25.6 mmole) of oxime Na in 25 ml of water, after which the mixture was maintained for another hour at 50-60°C. The product was extracted with ether (eight 20-ml portions), the extract was dried over NaOH, and the solvent was removed by distillation in vacuo.

Compounds Vb,c were similarly obtained.

5,7-Dimethyl-6-cyano-6-hydroxy-1,3-diazaadamantane (IVa). A 1.53-g (8.5 mmole) sample of adamantanone Ia and 3.62 g (42.5 mmole) of acetone cyanohydrin were refluxed in 15 ml of acetone for 6 h. The crystals that formed when the reaction mass was cooled were removed by filtration and recrystallized from ethyl acetate.

5,7-Dimethyl-6-hydroxy-1,3-diazaadamantane (VIIa). This compound was obtained by the method in [7] from 1.08 g (6.0 mmole) of adamantone Ia and 0.113 g (3.0 mmole) of sodium borohydride in 10 ml of ethanol. Recrystallization of the product from benzene gave 1.01 g (92.6%) of VIIa with mp 196-197°C (mp 196-197°C [18]).

5,7-Dimethyl-6-phenyl-6-hydroxy-1,3-diazaadamantane (VIIIa). A solution of 5.23 ml (33.3 mmole) of bromobenzene in 10 ml of ether was added with stirring to 0.46 g (66.6 mmole) of ground lithium in 10 ml of absolute ether. After 0.6 h, 1.00 g (5.6 mmole) of adamantanone Ia was added with stirring in the course of 0.25 h to the resulting solution, after which the reaction mass was stirred for another 4 h. The resulting precipitate was dissolved by adding 18% hydrochloric acid, and the aqueous layer was treated with ether (three 20-ml portions) and neutralized with potassium carbonate. The product was extracted with chloroform (four 10-ml portions), the extract was dried over magnesium sulfate, the solvent was removed by distillation, and the dry residue was sublimed in vacuo.

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SYNTHESIS OF N-(2-CHLOROPHENYLSULFONYL)-N'-(4-METHOXY-6-METHYL-1,3,5-TRIAZIN-2-YL)-UREA WITH A RADIOACTIVE LABEL

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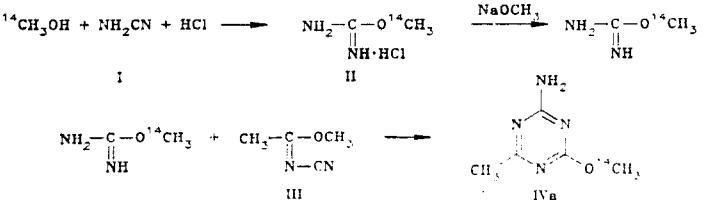
UDC 547.491.8'495.2:07:632.954

Methods for the introduction of a radioactive ^{13}C label into N-(2-chlorophenylsulfonyl)-N'-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea, which has herbicidal activity, are described.

N-(2-Chlorophenylsulfonyl)-N'-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (chlorosulfone, DPKh-4189, Glin) is one of the highly active herbicides that are of interest for agriculture [1, 2]. The aim of the present research was to synthesize the labeled (in various positions) herbicide that is necessary for the study of its behavior in environmental subjects.

The following reaction scheme was used to introduce a radioactive label into the methoxy group of the substituted aminotriazine [3, p. 84; 4]:



When equimolar amounts of methanol and cyanamide (I) are used in the first step of the synthesis, the yield of O-methylisourea hydrochloride (II) varies markedly, probably because

All-Union Scientific-Research Institute of Phytopathology, Moscow Oblast 143050. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 654-656, May, 1989. Original article submitted September 11, 1987.

0009-3122/89/2505-0547$12.50