

CHROMATOGRAPHIC SEPARATION OF AZAADAMANTANES AND THEIR DERIVATIVES IN A SYSTEM GAS-LIQUID*

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The Kováts indices and relative elution volumes were determined for 1-azaadamantane, 1,3-diaza-, 1,3,5-triaza-, 1,3,5,7-tetraazaadamantane and their derivatives on the stationary phases SE-30, OS-124, and polyethylene glycol, mol. wt. 1500, at 125, 160, 190, and 220°C.

Compounds containing the adamantane skeleton in their molecules have been extensively studied in the last few years. We are concerned particularly with derivatives containing nitrogen atoms directly in the adamantane skeleton. Gas-chromatographic analysis provides us in a short time with information about the purity of substances during the synthesis and identification of mixtures and intermediate products^{1,2}.

Relations between the structure and elution data of adamantanes and their hydroxy derivatives, ketones, halo derivatives, and acid esters are described in the previous papers^{3,4}. Chromatographic properties of other adamantane compounds produced in our laboratory are given in publication⁵⁻⁷. The detailed study⁸ deals with alkyladamantanes and hydrocarbons with the adamantoid structure. Further papers⁹⁻¹² are also concerned with chromatographic properties of adamantane hydrocarbons. From nitrogen derivatives of adamantane, 1-aminoadamantane has been determined as its N-trichloroacetyl derivative¹³. For the protection of the free amino group and an easier analysis of amines, the conversion of the amino group to the Schiff base has been recommended¹⁴.

EXPERIMENTAL

The purity of all compounds was followed by chromatography in a system gas-liquid and by mass spectrometry on an instrument LKB-9000.

Apparatus: The apparatus Chrom 31 (Laboratorní přístroje, Prague) with a flame ionization detector was used with nitrogen as the carrier, flow rate approximately 50 ml per minute. The injection chamber was partly filled with glass balls and heated to 270°C.

Columns and fillings: Stainless steel columns, inner diameter 6 mm and length 1.2 m, were used. The column A contained 5% wt. of the stationary phase SE-30 on Chromaton N-AW-DMCS

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TABLE I
Elution Data of Some Derivatives of Adamantane and Its Nitrogen Analogs

Compound	Column A	Column B	Column C
	125°C <i>I</i>	190°C <i>I</i>	160°C <i>r</i> _{1,2}
1-Azaadamantane	1 186	1 450	0·39
1,3-Diazaadamantane	1 224	1 575	0·60
1,3,5-Triazaadamantane	1 245 ^a	1 646	1·00
1,3,5,7-Tetraazaadamantane (urotropine)	1 224 ^a	1 661	1·26
7-Chloro-1,3,5-triazaadamantane	1 309	1 743	1·63
7-Bromo-1,3,5-triazaadamantane	1 385	1 855	2·63
7-Nitro-1,3,5-triazaadamantane	1 485	2 068	10·00
7-Amino-1,3,5-triazaadamantane	1 247 ^a	1 849	4·03
7-Methylamino-1,3,5-triazaadamantane	1 444 ^a	1 924	3·90
7-Dimethylamino-1,3,5-triazaadamantane	1 502 ^a	1 962	3·90
Adamantane	1 102	1 287	0·10
1-Bromoadamantane	1 352	1 706	0·76
1-Aminoadamantane	1 245	1 540	0·46
Eicosane	2 000	2 000	1·54
<i>V</i> _g ⁰ (1,3,5-Triazaadamantane), ml:	—	—	547

^a The compound displays a partly asymmetrical wave.

TABLE II
Relative Elution Volumes of 7-Amino-1,3,5-triazaadamantane Aldimines on the Column A at 220°C

Compound	<i>r</i> _{1,2}
(1,3,5-Triaza-7-adamantyliminomethyl)benzene	1·00
4-Chloro(1,3,5-triaza-7-adamantyliminomethyl)benzene	1·87
4-Methoxy(1,3,5-triaza-7-adamantyliminomethyl)benzene	2·40
4-Dimethylamino(1,3,5-triaza-7-adamantyliminomethyl)benzene	5·13
4-(1,3,5-Triaza-7-adamantyliminomethyl)pyridine	1·22
3-(1,3,5-Triaza-7-adamantyliminomethyl)pyridine	1·27
(1,3,5-Triaza-7-adamantyliminomethyl)propane	0·24
7-Hydroxylamino-1,3,5-triazaadamantane trimethylsilyl ether	0·24
7-(Aminoethyl)amino-1,3,5-triazaadamantane	0·38
Eicosane	0·63
<i>V</i> _g ⁰ [(1,3,5-Triaza-7-adamantyliminomethyl)benzene], ml	475

grain size 0.16–0.20 mm (Lachema, Brno). The weight of the packing was 12.3 g. The column B was packed with 10.9 g of Chromaton N-AW-HMDS, grain size 0.16–0.20 mm, wetted with 10% wt of the stationary phase OS-124 (Lachema, Brno). The column C contained 9.7 g of Chromaton N, grain size 0.20–0.25 mm wetted with 5% wt polyethylene glycol, mol. wt. 1500, and 1% potassium hydroxide.

Retention data. On the stationary phases OS-124 and SE-30 for compounds of lower molecular weight, the retention data are expressed through the Kováts indices. In the cases when the elution volumes of the compounds analyzed are essentially higher than that of eicosane, hence during the analysis on polyethylene glycol and for the aldimine group, the chromatographic properties of the compounds were expressed by the relative elution volumes.

Preparation of standard substances. Adamantane was a commercial chemical. 1-Bromo- and 1-aminoadamantane were available in the laboratory. 1-Azadamantane was prepared from 1,3,5-tris(bromomethyl)cyclohexane and ammonia according to the paper¹⁷. 1,3-Diazaadamantane was prepared according to¹⁸, 1,3,5-triazaadamantane was obtained from 7-bromo-1,3,5-triazaadamantane by dehalogenation by zinc in alkaline medium¹⁹. 7-Nitro-1,3,5-triazaadamantane was prepared from ammonium acetate, formaldehyde, and nitromethane¹⁹, 7-amino-1,3,5-triazaadamantane was formed by reduction of the former compound by zinc in alkaline medium¹⁹. 7-Bromo- and 7-chloro-1,3,5-triazaadamantane were prepared by the action of the corresponding haloacid in the presence of its salt and sodium nitrite on 7-amino-1,3,5-triazaadamantane¹⁹. 1,3,5,7-Tetrazaadamantane (urotropine) *p.a.* was a commercial chemical of Lachema.

A mixture of 7-methylamino- and 7-dimethylamino-1,3,5-triazaadamantane was prepared by hydrogenation methylation from formaldehyde and 7-amino-1,3,5-triazaadamantane according to Hodge²⁰. The product was not, however, uniform, and a mixture of mono- and dimethyl derivative, m.p. 90°C, containing about 70% of the dimethyl derivative, was obtained by crystallization from heptane. The chromatographic waves were identified by mass spectrometry.

Aldimines were obtained by the reaction of a mixture of 7-amino-1,3,5-triazaadamantane and the corresponding aldehydes, *i.e.* benzaldehyde, 4-chloro-, 4-methoxy-, and 4-dimethylaminobenzaldehyde, 3- and 4-pyridinealdehyde, and butyraldehyde¹⁹. The preparation of 7-hydroxylamino-1,3,5-triazaadamantane is described in the paper²¹. Its trimethylsilyl derivative was formed on the action of hexamethyldisilazane in the pyridine medium; it was not isolated and the solution served directly for chromatographic purposes. Its mass was verified by mass spectrometry. 7-(Aminoethyl)-amino-1,3,5-triazaadamantane was prepared from the nitrile of N-(1,3,5-triaza-7-adamantyl)aminoacetic acid by reduction by lithium aluminium hydride.

RESULTS AND DISCUSSION

The chromatographic data of the compounds studied in this work are summarized in Tables I and II. Our retention indices for adamantane and 1-bromoadamantane on the stationary phase SE-30 are in a good agreement with the values found previously⁴.

In the homologous series of azaadamantanes, the value of the retention index on the stationary phase SE-30 for 1,3,5,7-tetrazaadamantane is lower than for 1,3,5-triazaadamantane and equals that for 1,3-diazaadamantane. On the more polar stationary phase OS-124, the value of the index for 1,3,5,7-tetrazaadamantane is,

on the contrary, higher than for 1,3,5-triazaadamantane. The highest difference occurs then on the strongly polar polyethylene glycole (Table I) on account of hydrogen bonds between the nitrogen atoms of the compound analyzed and the stationary phase.

The difference between the values of the retention indices of 7-methylamino- and 7-dimethylamino-1,3,5-triazaadamantane decreases with increasing polarity of the stationary phase, for polyethylene glycol the retention volumes are equal; here the effect of the hydrogen bond between this stationary phase and the secondary amino group of 7-methylamino-1,3,5-triazaadamantane occurs to an enhanced extent.

TABLE III

Homomorphic Factors H for Azaadamantanes

$$H = I(\text{azaadamantane}) - I(\text{adamantane}).$$

Compound	Column A, 125°C	Column B, 190°C
1-Azaadamantane	84	163
1,3-Diazaadamantane	122	288
1,3,5-Triazaadamantane	143	359
1,3,5,7-Tetrazaadamantane	122	374

The change of polarity of the azaadamantanes accompanying the increase of number of nitrogen atoms in the molecule can be well characterized by means of the homomorphic factor^{15,16} H . Table III presents the H values related to adamantane. On both the phases SE-30 and OS-124 the value H per one nitrogen atom decreases, while the total polarity of the molecule increases. It can be assumed that with respect to the interaction with the stationary phase, the tertiary nitrogen atoms of the molecule are not equally effective.

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