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Note

Characterization of oxygen-containing adamantane derivatives by capillary gas chromatography

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The chemistry of adamantane has expanded rapidly in recent years, and increasing attention is being paid to adamantane derivatives. In particular, those derivatives containing oxygen appear to provide suitable intermediates for the preparation of adamantoid compounds with potential practical applications. Very few chromatographic data concerning adamantane derivatives have been published[1,2], and no data on oxygen-containing ditopic adamantane derivatives.

We have now investigated the chromatographic properties of all ditopic oxygen-containing adamantane derivatives on the non-polar phase OV-101 and on the medium polar phase polyphenyl ether 6 PPE. Based on Kováts indices, these measurements were carried out at temperatures of 200, 210 and 220°C. As "oxygen-containing" adamantane derivatives we denote such derivatives which contain the groups OH or C=O directly bound to the adamantane skeleton.

EXPERIMENTAL

The retentions of the adamantane derivatives were measured on a Varian 3700 gas chromatograph equipped with a flame ionization detector. The thermostat temperature was kept constant to ±0.2°C. The temperature at the sample inlet was 300°C in all cases. A fritted glass insert was used in the injection port, the splitting ratio being 100:1. Nitrogen was used as the carrier gas (*ca.* 0.5 ml/min) and as the make-up gas (30 ml/min) in all instances. Stainless-steel capillaries (50 m × 0.25 mm I.D., coated with OV-101 and with polyphenyl ether 6 PPE) were used for the analyses. The retentions of the compounds (which all were prepared in this Laboratory) were measured on both columns at 200, 210 and 220°C. The retention times were established using a CDS-111 computing integrator. Each sample was measured 3–5 times. The averages were rounded off to the nearest integer.

RESULTS AND DISCUSSION

The values of the Kováts indices together with their temperature increments on the non-polar phase OV-101 and on the medium polar phase 6 PPE are given in Tables I and II. The range of values on the non-polar phase OV-101 was approxi-

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TABLE I

KOVÁTS INDICES FOR THE OXYGEN-CONTAINING ADAMANTANE DERIVATIVES ON OV-101

*Compound**	*Temperature, T (°C)*			$10\left(\frac{\partial I}{\partial T}\right)$
	200	*210*	*220*	
1-Hydroxyadamantan-2-one	1550	1566	1578	14.0
1,2-Dihydroxyadamantane	1592	1597	1604	6.0
1,3-Dihydroxyadamantane	1473	1479	1493	10.0
5-Hydroxyadamantan-2-one	1516	1525	1531	7.5
1,4^{e}-Dihydroxyadamantane	1540	1551	1565	12.5
1,4^{a}-Dihydroxyadamantane	1544	1555	1569	12.5
Adamantane-2,4-dione	1539	1551	1558	9.5
4^{e}-Hydroxyadamantan-2-one	1607	1618	1625	9.0
4^{a}-Hydroxyadamantan-2-one	1607	1618	1625	9.0
2^{e},4^{e}-Dihydroxyadamantane	1610	1617	1624	7.0
2^{e},4^{a}-Dihydroxyadamantane	1609	1616	1623	7.0
2^{a},4^{a}-Dihydroxyadamantane	1623	1631	1645	11.0
Adamantane-2,6-dione	1498	1509	1513	7.5
6-Hydroxyadamantan-2-one	1610	1617	1624	7.0
2,6-Dihydroxyadamantane	1611	1618	1625	7.0

* e = Equatorial, a = axial.

TABLE II

KOVÁTS INDICES OF THE OXYGEN-CONTAINING ADAMANTANE DERIVATIVES ON 6 PPE

Compound	*Temperature, T(°C)*			$10\left(\frac{\partial I}{\partial T}\right)$
	200	*210*	*220*	
1-Hydroxyadamantan-2-one	1794	1804	1813	9.5
1,2-Dihydroxyadamantane	1887	1891	1896	4.5
1,3-Dihydroxyadamantane	1901	1908	1916	7.5
5-Hydroxyadamantan-2-one	1964	1974	1985	10.5
1,4^{e}-Dihydroxyadamantane	1976	1983	1991	7.5
1,4^{a}-Dihydroxyadamantane	1985	1991	1999	7.0
Adamantane-2,4-dione	1985	1997	2008	11.5
4^{e}-Hydroxyadamantan-2-one	2037	2049	2061	12.0
4^{a}-Hydroxyadamantan-2-one	2064	2084	2093	14.5
2^{e},4^{e}-Dihydroxyadamantane	2023	2036	2049	13.0
2^{e}.4^{a}-Dihydroxyadamantane	2033	2046	2060	13.5
2^{a},4^{a}-Dihydroxyadamantane	2040	2054	2068	14.0
Adamantane-2,6-dione	1985	1993	2000	7.5
6-Hydroxyadamantan-2-one	2059	2073	2086	13.5
2,6-Dihydroxyadamantane	2042	2051	2061	9.5

mately 130 units for all the 15 ditopic adamantane derivatives. The separation of 1,4^{e}-, 1,4^{a}-dihydroxyadamantane and adamantane-2,4-dione and the separation of 4^{e}- and 4^{a}-hydroxyadamantan-2-one, 2^{e},4^{e}-, 2^{e},4^{a}-dihydroxyadamantane, 6-hydroxyadamantan-2-one and 2,6-dihydroxyadamantane proved impossible. The calculated values can be broken down into several groups: 1,3-dihydroxyadamantane with the lowest index forms a "group" apart from the others, adamantane-2,6-dione comes next and the values 1516–1592 covering the 1,2 and the 1,4 derivatives and adamantane-2,4-dione is displaced even farther. The last group has values from 1607 to 1623 and includes hydroxyketones and diols in the positions 2,4 and 2,6. It can be concluded that the hydroxyketones and diols with both substituents on the secondary carbon atoms of the adamantane molecule have higher retention indices than the derivatives having one or both substituents on the tertiary carbon atoms. The presence of the keto group shifts the retention index towards lower values; this shift however is not very marked for derivatives having the substituents attached at the positions 2,4 and 2,6.

The situation changes when polyphenyl ether 6 PPE is used. The range of the retention indices is practically doubled, reaching approximately 270 units. The separation of 1,4^{a}-dihydroxyadamantane, adamantane-2,4-dione and adamantane-2,6-dione does not to occur in this case. The separation of 4^{e}-hydroxyadamantan-2-one, 2^{a},4^{a}-dihydroxyadamantane and 2,6-dihydroxyadamantane is also expected to be difficult. The results can be divided into two groups. The first group with the retention indices 1794–1985 includes the 1,2 derivatives, 1,3-dihydroxyadamantane, the 1,4 derivatives, adamantane-2,4-dione and adamantane-2,6-dione. The second group includes 2,4 and 2,6 derivatives with the exception of diones.

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