*Pure & Appl. Chem.*, Vol. 61, No. 11, pp. 2059–2060, 1989.
Printed in Great Britain.


# Gas chromatography–mass spectrometry of stereoisomers of N-, O- and S-containing saturated tricyclic compounds

N.S. Kulikov and M.S. Bobyleva

Faculty of Chemistry, M.V. Lomonosov State University, 119899 Moscow, USSR

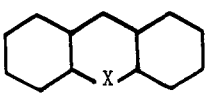
Abstract - A GC–MS study of mixtures of the stereoisomers of perhydroacridin, perhydroxanthene and perhydrothioxanthene has been carried out. Separation was accomplished on columns filled with graphitized thermal carbon black and WCOT capillary columns. The stereospecific features of the retention and the fragmentation of the stereoisomers under electron impact are discussed.

Structural elucidation of isomeric compounds poses many complicated problems in modern physical organic chemistry. The separation of their mixtures and isolation of every isomer in the individual form, an essential requirement for their study, is beset with many difficulties. NMR spectroscopy is a powerful tool in resolving the structures of the individual stereoisomers (most complicated of all isomers) but its application is limited when one deals with a mixture in which the amount of a particular stereoisomer is very low. GC–MS which combines a very high separative power of GC with a high sensitivity and informativity of MS in fact is the only available method for an investigation of multicomponent mixtures. The identification by this method is based on the retention indexes and/or mass spectra, provided these characteristics are sufficiently different. This implies, however, that some relevant *a priori* information is available and practically excludes an assignment of previously unstudied compounds.

One of the ways to get over this hindrance is the study of correlation between structure of stereoisomers, retention parameters and fragmentation pathways of molecular ions as well. Once these relations have been found, one can use them to enhance the diagnostic reliability and thereby to facilitate an assignment of stereoisomers.

Kiselev and coworkers had shown that the graphitized thermal carbon black (GTCB) is one of the most stereoselective adsorbent in GC. The retention on this adsorbent is mostly dependent on the dispersion intermolecular forces and is a function of three-dimensional structure of an adsorbate (ref. 1,2). Using adsorption columns with GTCB, Kiselev *et al.* were able to separate almost completely the mixtures of perhydroanthracene and perhydrophenanthrene isomers (ref. 3,4).

In the present GC–MS study the mixtures of stereoisomers of heterocyclic analogs of perhydroanthracene (PHA) have been investigated.




X=NH - perhydroacridin (PHAcr)
X=O - perhydroxanthene (PHX)
X=S - perhydrothioxanthene (PHTX)

The structures of the most abundant stereoisomers in the mixtures had been elucidated earlier by NMR spectroscopy (ref. 5,6). We have been unable to find any data in the literature on a GC–MS investigation of PHX and PHTX. Therefore, it was interesting to find out how many stereoisomers exist in mixtures being investigated and to examine the stereospecific characteristics of their retention on GTCB and of the fragmentation under electron impact.

For identification of unknown stereoisomers of saturated tricyclic heterocycles, an assumption was made that their adsorption on GTCB corresponds to the same relationships being established for the similar hydrocarbons (ref. 3,4). In Fig. 1a, as example, is shown the chromatogram of PHTX stereoisomers where one can see four resolved peaks. Unlike PHA which has five stable stereoisomers, its heteroanalogs theoretically should have six, two of these - trans-syn-cis and trans-anti-cis - characterised by similar geometrical structure differed from each other only by the position of heteroatom in the side rings. Therefore, these two stereoisomers cannot be separated on GTCB and eluted as one peak.

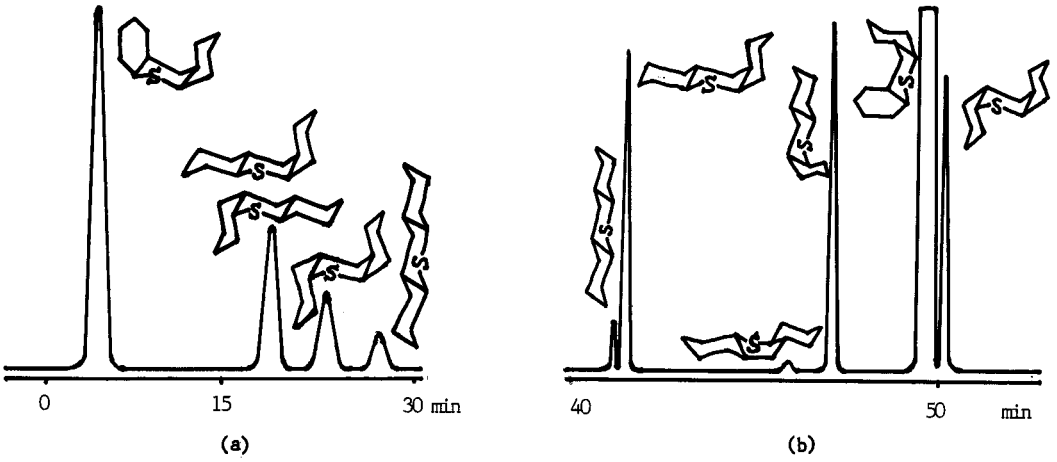
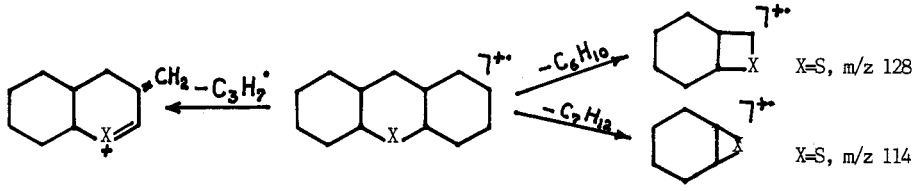



Fig. 1. Chromatogram of PHTX: (a) GTCB, 2m x 1mm, temperature programming 200° to 280°C, 10/min; (b) SP-1000, 50 m x 0.25 mm, temperature 145°C.

The use of the capillary column with SP-1000 liquid phase enabled us to find six stereoisomers of PHTX (Fig. 1b); five of PHX (trans-syn-cis) isomers are supposed to be unstable (ref. 7) and provided the possibility of investigation of their mass spectra, which considerably differ from the PHA ones. The fragmentation of the heterocyclic analogs of PHA is characterised by the predominant formation of the stable cation $[M-C_3H_7]+$, which at the same time reduces the intramolecular repulsion of the H...H pairs of the side rings (Scheme 1). This process suppresses the stereospecificity of fragmentation PHAcr and PHX isomers leading to similarity of the mass spectra.




Unlike PHAcr and PHX stereoisomers, the fragmentation of those of PHTX is characterised by the greater stereospecificity due to competing processes of fragmentation being accompanied by the rupture of the bonds of the middle ring and the formation of $[M-C_6H_{10}]+\cdot$(m/z 128), $[M-C_7H_{12}]+\cdot$(m/z 114) ions (Scheme 1). This results in different intensities of these peaks in the mass spectra of PHTX stereoisomers (Table 1). Peaks of these ions are more intensive in the mass spectra of trans-conjugated isomers at the same time as intensities of molecular ions and vice versa.

TABLE 1. Characteristic peaks in the mass spectra (70 eV) of the stereoisomers of PHTX. Intensities are given in % relative to the total ion current.

| m/z | 210 | 167 | 154 | 153 | 141 | 128 | 114 | 107 | 95 | 94 | 81 | 67 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| c-s-c | 17 | 16 | 1.2 | 1.2 | 4.6 | 2.5 | 3.0 | 1.6 | 4.1 | 3.6 | 7.4 | 4.5 |
| c-a-c | 19 | 16 | 1.2 | 1.5 | 5.5 | 2.6 | 4.1 | 1.7 | 4.1 | 4.4 | 8.0 | 4.6 |
| t-s-t | 12 | 4.2 | - | 3.3 | - | 5.8 | 16 | 2.6 | 4.1 | 3.4 | 11 | 4.0 |
| c-s-t | 12 | 13 | 1.9 | 0.7 | 4.3 | 7.3 | 5.8 | 1.8 | 3.8 | 4.4 | 7.5 | 4.0 |
| t-a-c | 12 | 11 | 2.2 | - | 5.9 | 10 | 6.9 | 2.0 | 3.9 | 5.2 | 8.4 | 4.1 |

## REFERENCES

1. N.N.Avgul, A.V.Kiselev and D.P.Poshkus, *Adsorption of Gases and Vapours on Homogeneous Surfaces*, p.31, Khimiya, Moscow (1975).
2. A.V.Kiselev, K.D.Shcherbakova et al., *J. Chromatogr. Sci.* 12, 788-790, (1974).
3. A.V.Kiselev, N.S.Kulikov and G.Curthoys, *Chromatographia* 18, 297-304, (1984).
4. A.V.Kiselev, V.I.Nazarova and K.D.Shcherbakova, *Chromatographia* 14, 148-154, (1981).
5. L.M.Yudovich, N.I.Smirnova et al., *Zhurn. Org. Khim.* 23, 2333-2335, (1987).
6. A.P.Krivenko, T.G.Nikolaev et al.,*Zhurn. Org. Khim.* 23, 1000-1003, (1987).
7. V.G.Kharchenko, L.M.Yudovich et al.,*Zhurn. Org. Khim.* 23, 576-581, (1987).