Journal of Chromatography, 347 (1985) 297–302
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 035

Note

Separation of isomeric halogenobicyclononene carbonitriles

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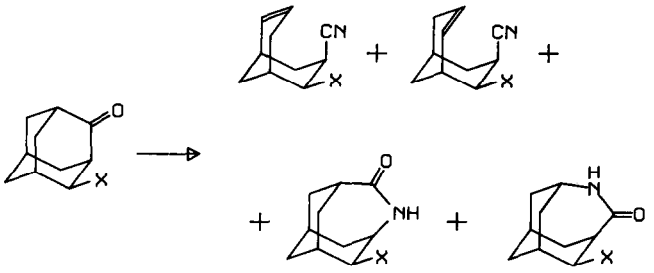
(Received July 17th, 1985)

The Schmidt reaction of 4-substituted adamantanones yields a mixture of two 4-halogenobicyclononene carbonitriles and two halogenoazahomoadamantanones[1] (see Scheme 1); the halogenoazahomoadamantanones were separated by medium-pressure liquid chromatography using silica gel and a light petroleum–acetone mixture[2]. We have applied both analytical and preparative high-performance liquid chromatography (HPLC) to the analysis and preparative separation of isomeric halogenobicyclononene carbonitriles and methanesulphonatobicyclononene carbonitriles.



Scheme 1.

EXPERIMENTAL

Analytical HPLC

The retention times and analyses of the fractions obtained from the preparative separation were carried out on a Varian 8500 liquid chromatograph (Varian, Palo Alto, CA, U.S.A.). A 250 × 4 mm I.D. column packed with silica gel (8 μm) (Sila-

0021-9673/85/$03.30

TABLE I

ANALYTICAL CHROMATOGRAPHY

Mobile phase: *n*-pentane–acetone (*a*:*b*).

No.	*Compound*	*a* = 99, *b* = 1			*a* = 97, *b* = 3		
		T_r (*s*)	*k'*	α	T_r (*s*)	*k'*	α
1	6-*endo*-Chlorobicyclo[3.3.1]non-2-en-7-carbonitrile	1996	23.3	1.15	565	8.11	1.09
2	6-*endo*-Chlorobicyclo[3.3.1]non-3-en-7-carbonitrile	2286	26.7		609	8.82	
3	6-*endo*-Iodobicyclo[3.3.1]non-2-en-7-carbonitrile	1672	19.4	1.14	493	5.85	1.07
4	6-*endo*-Iodobicyclo[3.3.1]non-3-en-7-carbonitrile	1892	22.1		521	6.24	
	Unidentified	1126	12.7	1.53	362	4.84	1.35
	Unidentified	1678	19.5	1.15	468	6.55	1.28
5	6-*endo*-Bromobicyclo[3.3.1]non-2-en-7-carbonitrile	1918	22.4	1.14	581	8.37	1.09
6	6-*endo*-Bromobicyclo[3.3.1]non-3-en-7-carbonitrile	2182	25.6		630	9.16	
		a = 90, *b* = 10					
7	6-*endo*-Methanesulphonoxybicyclo[3.3.1]non-2-en-7-carbonitrile	998	11.5	1.02	–	–	–
8	6-*endo*-Methanesulphonoxybicyclo[3.3.1]non-3-en-7-carbonitrile	1021	11.8		–	–	–

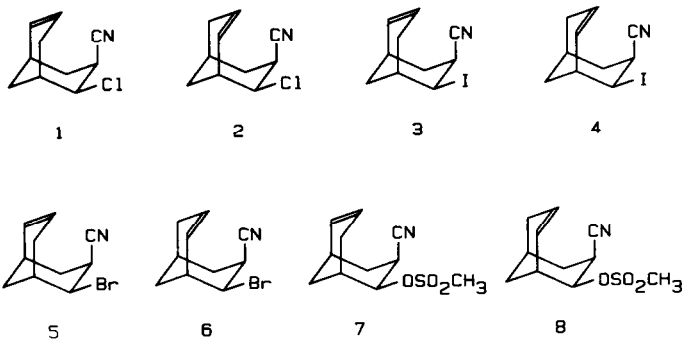


Fig. 1. The structures of the investigated compounds.

sorb; Lachema, Brno, Czechoslovakia), an Optilab 902 B refractive index detector (Tecator, Sweden) and a TZ 4221 strip-chart recorder (Laboratorní přístroje, Prague, Czechoslovakia) were used. Sample injection was performed by the stop flow technique with a 5-μl syringe (Hamilton, Bonaduz, Switzerland). Mixtures of *n*-pentane and acetone in different proportions (see Table I) were used as the mobile phase at a flow-rate of 100 ml/h.

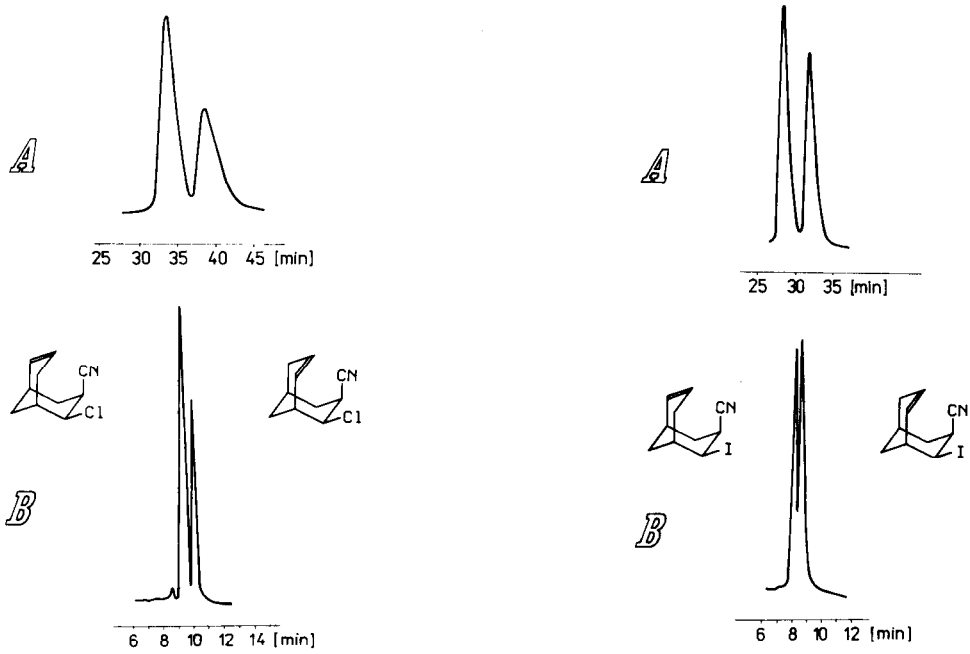


Fig. 2. Analytical separation of chlorobicyclononene carbonitriles. Column: 250 × 4 mm I.D., packed with 8-μm silica. Mobile phase: (A) *n*-pentane–acetone (97:3, v/v); (B) *n*-pentane–acetone (99:1, v/v). Flow-rate: 100 ml/h. Refractive index detector.

Fig. 3. Analytical separation of iodobicyclononene carbonitriles. Conditions as in Fig. 2.

TABLE II

PREPARATIVE SEPARATION

Mobile phase: *n*-pentane–acetone (97:3, v/v).

No.	*Compound*	*Amount separated (mg)*	*Yield (mg)*	*Purity (%)*
1	6-*endo*-Chlorobicyclo[3.3.1]non-2-en-7-carbonitrile	300	179	95
2	6-*endo*-Chlorobicyclo[3.3.1]non-3-en-7-carbonitrile		110	88
3	6-*endo*-Iodobicyclo[3.3.1]non-2-en-7-carbonitrile	400	212	92
4	6-*endo*-Iodobicyclo[3.3.1]non-3-en-7-carbonitrile		169	82

Separation of individual compounds

The preparative separations were carried out on a 300 × 17 mm I.D. stainless-steel column, with a conical inlet part (designed and manufactured in our laboratory[3,4]), slurry packed with 8.5-μm irregular silica gel (Silasorb). The pump was an LC-XPD (Pye Unicam, Cambridge, U.K.), operated at 600 ml/h. A refractive index detector (Varian) was used. The mobile phase used was *n*-pentane–acetone (97:3, v/v). Sample injection was performed using a loop injector (Rheodyne, U.S.A.) equipped with a 200-μl sample loop. A 500-μl injection syringe (Hamilton) was used. The fractions were collected manually according to the shape of the chromatographic curve.

RESULTS AND DISCUSSION

Analytical retention data of the separated bicyclononene derivatives are listed in Table I. The structures of the investigated compounds are shown in Fig. 1.

Although the compounds were not separated satisfactorily by thin-layer chro-

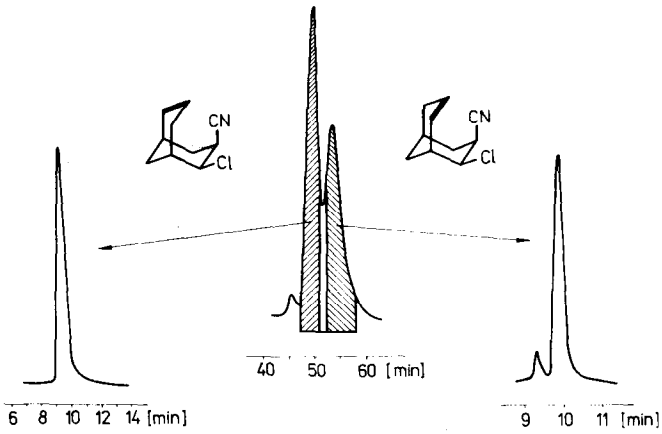


Fig. 4. Preparative separation of chlorobicyclononene carbonitriles and analysis of the fractions obtained. Preparative: column, 300 × 17 mm I.D., packed with 8.5-μm silica; mobile phase, *n*-pentane–acetone (97:3, v/v); flow-rate, 600 ml/h. Analytical: column, 250 × 4 mm I.D., packed with 8-μm silica; mobile phase, *n*-pentane–acetone (97:3, v/v); flow-rate, 100 ml/h.

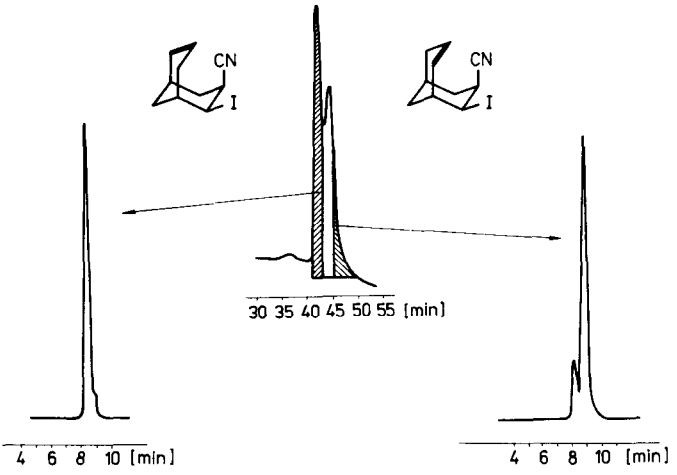
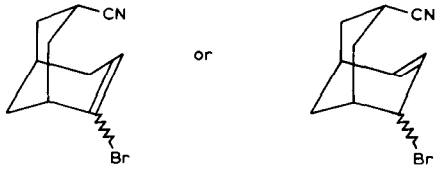


Fig. 5. Preparative separation of iodobicyclononene carbonitriles and analysis of the fractions obtained. Conditions as in Fig. 4.

matography (TLC)[2], the mobile and stationary phases used in TLC were chosen for HPLC.

The analytical separations of isomeric chlorobicyclononene carbonitriles, using two different mobile phases, are shown in Fig. 2. The separation of isomeric iodobicyclononene carbonitriles, using the same mobile phases, are shown in Fig. 3. The identifications of the structures of both iodoisomers were confirmed by NMR spectroscopy[5] after their separation by preparative HPLC. Other compounds were identified on the basis of their chromatographic behaviour.

Two compounds with unidentified structures accompanying the bromobicyclononene carbonitriles are considered to have one of the following structures:



The amounts separated, yields and purities of compounds obtained by preparative HPLC are listed in Table II. Fig. 4 shows the preparative separations of chlorobicyclononene carbonitriles, including a description of the collected fractions and their HPLC analysis. Fig. 5 shows similar results for iodo derivatives.

Although analytical HPLC using a mobile phase with a lower content of acetone yields better separations, owing to the lability of the compounds a mobile phase with a higher content of acetone (3%) was chosen for the preparative separation. The purity of the individual compounds obtained was sufficient for the subsequent NMR investigation[5].

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