

CHROM. 9384

## Note

### High-performance liquid chromatographic analysis of the heptachloronaphthalenes present in Halowax 1051

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(Received June 3rd, 1976)

From gas chromatographic analysis<sup>1</sup> and from information supplied by the manufacturers<sup>2</sup>, it is well known that the main constituents of the mixture of polychloronaphthalenes commercially available as Halowax 1051 are octachloronaphthalene (90%) and heptachloronaphthalenes (10%). However, gas chromatography has not yet been able to separate the heptachloronaphthalenes into the 1H- and 2H-isomers<sup>1,3,4</sup>. Recently we have found<sup>4</sup> that high-performance liquid chromatography (HPLC) in the system silica gel/dry *n*-hexane allows a marginal separation of the heptachloronaphthalene isomers from each other and from octachloronaphthalene, and that the same applies to thin-layer chromatography in the reversed-phase system of Kieselguhr impregnated with paraffin oil/acetonitrile-methanol-acetone-water (20:20:9:1, v/v). Some further details of this study are reported in this paper.

#### MATERIALS AND METHODS

Halowax 1051 (Koppers, Pittsburgh, Pa., U.S.A.) is a mixture of polychlorinated naphthalenes with a chlorine content of *ca.* 70% and a melting point of about 185°. Octachloronaphthalene is a product from Analabs (North Haven, Conn., U.S.A.). *n*-Hexane (ChromAR; Mallinckrodt, St. Louis, Mo., U.S.A.) was used as the mobile phase in HPLC and was dried over molecular sieve 5A and degassed before use.

Small samples of the heptachloronaphthalenes were kindly provided by Dr. B. J. Wakefield (University of Salford, Salford, Great Britain). The following details are of interest<sup>3,5</sup>. Reduction of octachloronaphthalene with lithium aluminium hydride gives a heptachloronaphthalene displaying a <sup>1</sup>H NMR signal at  $\tau = 1.53$ . Fractional crystallization of Halowax 1051 from toluene and carbon tetrachloride gives a fraction rich in the other heptachloronaphthalene isomer ( $\tau = 2.15$ ).

HPLC was carried out on a Siemens S100 liquid chromatograph equipped with an automatic injection system (10  $\mu$ l) and a Zeiss PM2 DLC UV detector. The column was a stainless-steel tube, 25 cm  $\times$  3 mm I.D., pre-packed with 5- $\mu$ m Li-Chrosorb SI 60 silica gel (Merck, Darmstadt, G.F.R.). Development was carried out at a temperature of  $27 \pm 1^\circ$ . UV spectra were recorded on a Beckman Acta CIII spectrometer using cells with quartz windows.

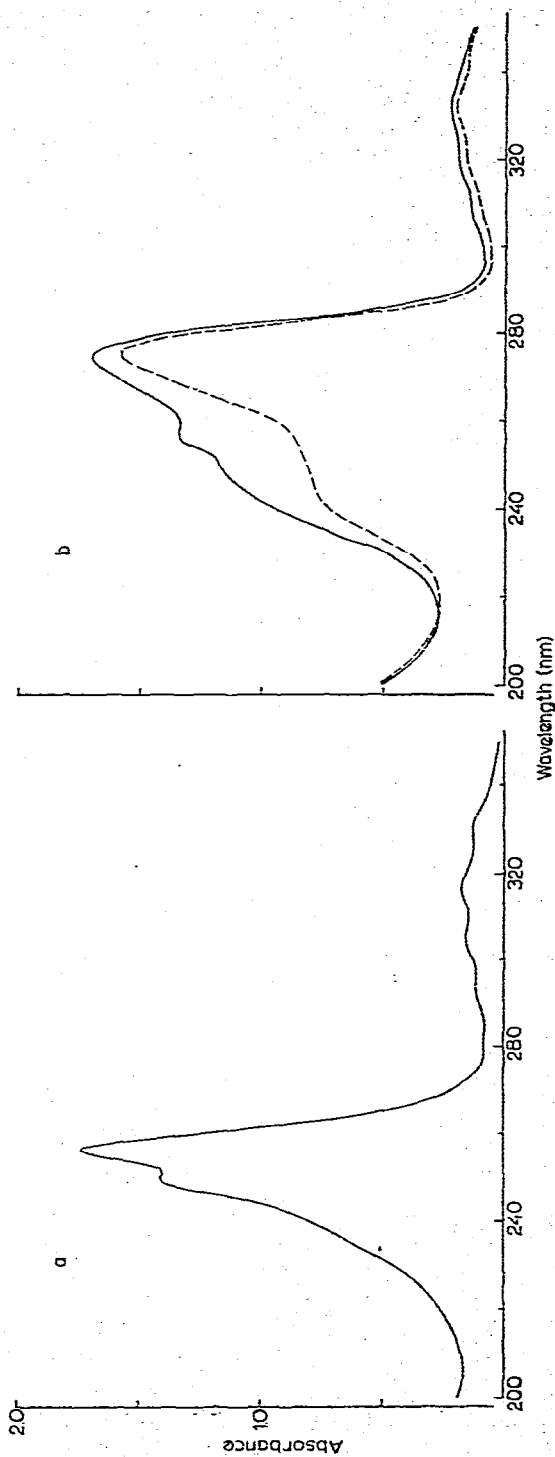


Fig. 1. UV absorption spectra of solutions in *n*-hexane of (a) heptachloronaphthalene (ca. 60 ppm) prepared by reduction of octachloronaphthalene and (b) Halowax 1051 (—) and pure octachloronaphthalene (---) (ca. 90 ppm each). Cell path, 2 mm.

## RESULTS AND DISCUSSION

It is well known that the wavelength of maximum absorption of the main or  $B_b$  band of polychloronaphthalenes shifts to the visible region with increasing introduction of chlorine atoms into the naphthalene nucleus. While naphthalene itself displays maximum absorption at 221 nm, Brinkman *et al.*<sup>4</sup> reported values of 223–225, 224–231, 233–235 and 238–245 nm for series of mono-, di-, tri- and tetrasubstituted chloronaphthalenes, respectively. Octachloronaphthalene has its maximum absorption at 275 nm. In good agreement with these data, the sample of heptachloronaphthalene prepared by reduction of octachloronaphthalene displays maximum absorption at 256 nm ( $\log \epsilon = 4.8$ ); its spectrum between 200 and 350 nm is shown in Fig. 1a. The UV spectrum of the sample of the other isomer is almost identical with that of Halowax 1051 shown in Fig. 1b; this result suggests the presence of a considerable amount of octachloronaphthalene in the sample. From Fig. 1b, it is also evident that the shoulder at 255–260 nm observed in the spectrum of Halowax 1051 is due to the presence of heptachloronaphthalene(s).

The spectral results were fully confirmed by HPLC analysis. With Halowax 1051, detection at 256 nm instead of at 275 nm effects a decrease in the peak height due to octachloronaphthalene ( $t_{\text{ret.}} = 1.65$  min), while the shoulder at  $t_{\text{ret.}} = 1.70$  min becomes more clearly visible (Fig. 2a). In order to achieve maximum resolution, chromatograms of the various samples were run at the relatively low flow-rate of *ca.* 0.2 ml·min<sup>-1</sup>; the results are shown in Fig. 2b. It can be concluded that the heptachloronaphthalene isomer prepared by reduction with lithium aluminium hydride is indeed an essentially pure product, while the sample of the second, more strongly retained, heptachloronaphthalene isomer still contains large amounts of octa- and the other heptachloronaphthalene.

Considering the assignment of the structure of the heptachloronaphthalene isomers, Wakefield and co-workers<sup>3,5</sup> stated that by analogy with the NMR spectrum of 1-monochloronaphthalene (3H,  $\tau = 2.5$ ; 8H,  $\tau = 1.85$ ) it seems clear that the compound from reduction with lithium aluminium hydride is the 1H-isomer, and the compound separated from Halowax 1051 is the 2H-isomer. However, they do not have any chemical proof for their assignment. Our UV spectral and HPLC data support the hypothesis of Wakefield and co-workers as discussed below. In HPLC in the system silica gel/dry *n*-hexane, it has been shown<sup>4</sup> that the introduction of chlorine atoms into the naphthalene nucleus in such a way that substitution occurs in the 1,8- and, although to a lesser extent, in the 2,3-positions strongly promotes retention. Therefore, one would expect the 1H-isomer, which has only one pair of chlorine atoms in the 1,8-position, to display less sorption than the 2H-isomer on to silica gel. Secondly, as for the UV spectra, it has been amply demonstrated<sup>4</sup> that  $\alpha$ -substitution causes a distinct bathochromic shift of the so-called  $L_a$  band, which is correlated to a localization of two  $\pi$ -electrons in *p*-positions and shows up in the 260–350-nm region. That is, the 2H-isomer, with its four  $\alpha$ -chlorine atoms, should display a larger red shift of the  $L_a$  band than the 1H-isomer, which possesses only three  $\alpha$ -chlorine atoms. Unfortunately, only one hepta-substituted isomer is available in pure form. Therefore, we must limit ourselves to a comparison of its UV spectrum with that of other polychlorinated naphthalenes that have four  $\alpha$ -chlorine atoms, such as 1,4,5,8-tetrachloronaphthalene and octachloronaphthalene. Data on the  $L_a$

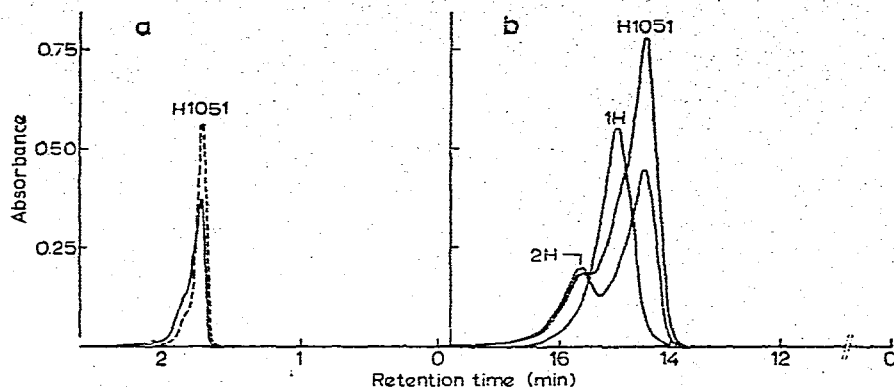


Fig. 2. HPLC of Halowax 1051 (H1051) and samples of heptachloronaphthalenes (1H and 2H) in the system silica gel (LiChrosorb SI 60)/dry *n*-hexane. Temperature,  $27 \pm 1^\circ$ . Flow-rate, (a) *ca.* 1.4 ml/min and (b) *ca.* 0.2 ml/min. Detection at 256 nm (—) and 275 (---) nm. For assignment of structure to the heptachloronaphthalenes, see text.

bands of the three compounds in question are given in Table I and indicate that the heptachloronaphthalene isomer considered here shows a distinctly smaller red shift than does octachloronaphthalene. It is even surpassed in this respect by 1,4,5,8-tetrachloronaphthalene, although it contains, next to the three (or four)  $\alpha$ -chlorine atoms, four (or three)  $\beta$ -chlorine atoms, which would be expected to effect an additional, although small, red shift of the  $L_a$  band. The isomer in question therefore probably contains only three  $\alpha$ -chlorine atoms, and is thus the 1H-isomer.

TABLE I

$L_a$  BAND MAXIMA OF POLYCHLORONAPHTHALENES

Substituted polychloronaphthalene	$\lambda_{max}$ (nm)
1,4,5,8-Tetra-	294, 307, 321, 336
Hepta*	293, 305, 316, 330
Octa-	310, 322, 332, 345

\* Prepared by reduction of octachloronaphthalene.

To summarize, the NMR evidence obtained by Wakefield and co-workers, as well as the HPLC and UV data reported here, strongly suggest that the heptachloronaphthalene isomer prepared by reduction of octachloronaphthalene is the 1H-isomer, and that obtained by crystallization from Halowax 1051 is the 2H-isomer. Regarding the isolation of pure 1H- and/or 2H-heptachloronaphthalene, preparative-scale HPLC might be useful. In agreement with an earlier observation<sup>4</sup>, it has been shown in our laboratory that reversed-phase HPLC has a high potentiality in the separation of highly chlorinated compounds, and surpasses HPLC in the system silica gel/dry *n*-hexane in this respect. Chromatography on a LiChrosorb RP-8 column (25 cm  $\times$  3 mm I.D.; Merck) with methanol-water (9-8:1-2, v/v) as the mobile phase yields

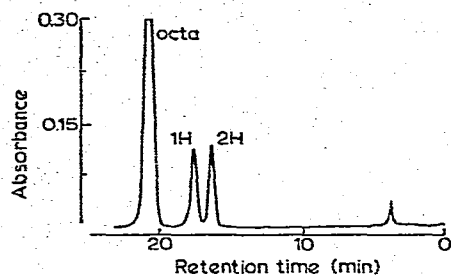


Fig. 3. HPLC of Halowax 1051 in the system LiChrosorb RP-8/methanol-water (8.5:1.5, v/v). Temperature,  $20 \pm 1^\circ$ . Flow-rate, *ca.* 0.9 ml/min. Detection at 230 nm.

excellent results. As the resolution and retention of the three substituted chloronaphthalenes increase with increasing water content of the mobile phase, the use of methanol-water (8.5:1.5, v/v) appears to be a good compromise for both analytical and preparative-scale work (Fig. 3).

The data on the hepta- and octachloronaphthalenes reported by Brinkman *et al.*<sup>4</sup> and obtained in the present work are summarized in Table II.

TABLE II

CHROMATOGRAPHIC AND SPECTRAL DATA OF HEPTA- AND OCTACHLORONAPHTHALENES

Substituted polychloronaphthalene	$R_F$ in reversed-phase TLC <sup>3</sup>	$t_{ret.}$ (relative) in GLC <sup>4</sup>	$t_{ret.}$ in HPLC (min)	$t_{ret.}$ in reversed-phase HPLC (min)	$\lambda_{max}$ (nm)
1H-Hepta-	0.23	0.63	1.70	18.6	256
2H-Hepta-	0.27	0.63	1.80	16	—
Octa-	0.19	1.00	1.65	21	275

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