GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED BIPHENYLS

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(Received July 19th, 1961)

In the course of research it became necessary to establish a rapid and reliable analytical method for biphenyl, and the mono- and dichlorobiphenyls. Although infra-red methods were adequate for two or three component mixtures[1] we frequently had to deal with mixtures containing from 4 to 10 components. Gas chromatography provided not only a qualitative but also a quantitative method.

EXPERIMENTAL

Apparatus

A Barber-Colman Model 20 gas chromatograph equipped with a strontium-90 diode argon ionization detector was used.

Capillary columns

The 100-ft. stainless steel polypropylene glycol 750 (Dow Chemical Co.) column (PPG No. 1) was originally purchased from Barber-Colman. However, through ex-

TABLE I

Component	Relative retention time (biphenyl = 1)		
	PPG No. 1[a]	PPG No. 2[b]	Apiezon L[c]
A Biphenyl	1.00	1.00	1.00
B 2-Chlorobiphenyl	1.38	1.56	1.31
C 3-Chlorobiphenyl	1.82	2.20	1.83
D 4-Chlorobiphenyl	1.91	2.31	1.91
E 2,6-Dichlorobiphenyl	2.05	2.50	1.83
F 2,2'-Dichlorobiphenyl	2.13	2.64	1.80
G 2,5-Dichlorobiphenyl	2.29	3.00	2.41
H 2,4-Dichlorobiphenyl	2.29	3.00	2.48
I 2,3'-Dichlorobiphenyl	2.71	3.44	2.52
J 2,3-Dichlorobiphenyl		3.65	2.62
K 2,4'-Dichlorobiphenyl	2.92	3.74	2.69
L 3,5-Dichlorobiphenyl		3.85	3.44
M 3,3'-Dichlorobiphenyl	3.90	5.06	3.82
N 3,4-Dichlorobiphenyl		5.20	3.99
O 3,4'-Dichlorobiphenyl	4.20	5.45	4.03
P 4,4'-Dichlorobiphenyl		5.86	4.30

[a] 9 p.s.i.g., 165° [b] 36 p.s.i.g., 175° [c] 30 p.s.i.g., 185°

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tended use the coating was depleted. It was recoated in our laboratories by flushing through the capillary a 10% solution of Dow poly-propylene glycol 750 in *n*-pentane under 200 p.s.i.g. This recoated column is referred to as PPG No. 2 and is seen to differ significantly from PPG No. 1 (see Table I). The 200-ft. stainless steel Apiezon L column was purchased from Barber-Colman.

Instrument parameters

Injection port temperature, 270°; detector temperature, 240°; column temperatures between 165° and 185°; eluant pressure between 5 and 40 p.s.i.g.; scavenger flow, 150 ml/min; split flow, 300 ml/min measured as 10 p.s.i.g.; sample size 1.0 μl.

Quantitative analysis

An Ott compensating planimeter was used to measure peak areas, which were generally proportional to mole percent. However, to avoid errors due to deviations in linearity, standard mixtures were run concurrently to provide correction factors when necessary.

Chlorinated biphenyls

All of the mono and most of the dichlorobiphenyls have been adequately characterized and reported in the literature. Samples of 2,2'-; 2,4'- and 4,4'-dichlorobiphenyls were kindly supplied by Dr. A. M. ELLENBURG, Monsanto Chemical Co., St. Louis. All others were prepared by Gomberg techniques[2]. The 2,6-isomer was not isolated but was obtained in a Gomberg mixture and identified as described by WEINGARTEN[1]. The 2,3'- and 3,4'-isomers also were not isolated but were prepared in a Gomberg mixture and identified by relative abundance[1] and by analogy with relative retention times for other *o-p* pairs (*ortho* always preceded *para*).

RESULTS AND DISCUSSION

Biphenyl, the 3 monochlorobiphenyls and the 12 dichlorobiphenyls are nearly completely resolved by gas chromatography on a Barber-Colman Model 20 capillary column instrument. The results are summarized in Table I and Fig. 1.

On the whole we found the chlorobiphenyls to behave much like the methylbiphenyls as reported by BEAVEN *et al.*[3]. The components tend to form clusters according to the degree of *ortho* substitution. Dichlorobiphenyls with two *ortho* substituents have the lowest retention times, those with mixed *ortho* and *para* (*meta*) have intermediate retention times and those with only *para* and *meta* substituents have the longest retention times. This phenomenon has been correlated with conjugative effects[3]. We also found that vicinal substitution causes a higher retention time for the 2,3-isomer relative to the 2,3'-isomer[4] but not for the 3,4-isomer relative to the 3,4'-isomer.

The most valuable feature of the two columns used, PPG No. 2 and Apiezon L, is the manner in which they complement each other. On the Apiezon column the last of the monochlorobiphenyls overlaps the first of the dichlorobiphenyls and the 2,6-isomer has the same retention time as the 3-isomer. This region is completely resolved on the PPG column. The Apiezon column barely separates the 3,4- and 3,4'-isomers while the PPG completely resolves the two. On the other hand, the PPG column does not distinguish between the 2,5- and 2,4-isomers which the Apiezon resolves. The

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Apiezon also provides a more satisfactory separation of the 2,3- and 2,4′-isomers.

The most striking contrast between the columns is the reversal in position of the 2,6- and 2,2′-dichlorobiphenyls. On the Apiezon column the 2,2′-isomer has a lower retention time than the 2,6-isomer as well as the 3- and 4-monochlorobiphenyls. This sequence is completely reversed on the PPG column; both the 2,6- and 2,2′-isomers follow the monochlorobiphenyls and the 2,6-isomer preceeds the 2,2′-isomer. Another contrast involves the shift of the 3,5-isomer from the *m-p* cluster on the Apiezon column to the *o-p* cluster on the PPG.

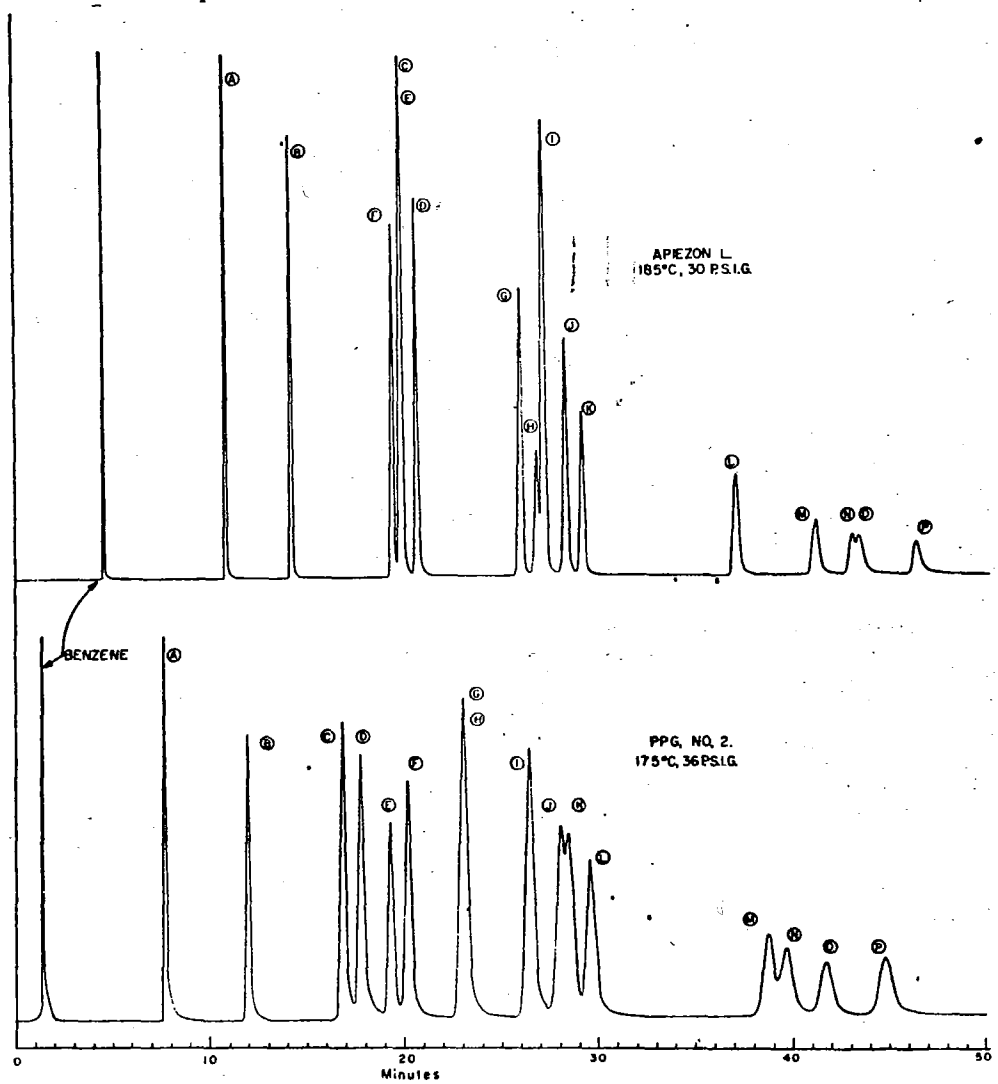

Fig. 1. For identification of peaks, see corresponding letters in Table I.

ACKNOWLEDGEMENT

The authors wish to thank DONALD R. BEASECKER and WILLIAM T. CAVE for many stimulating and useful discussions and GARY A. CLINEHENS for his valuable assistance.

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SUMMARY

Capillary column gas chromatography is reported as an analytical method for biphenyl, the 3 monochlorobiphenyls and the 12 dichlorobiphenyls. Two complementary columns were used permitting, in effect, total resolution.

RÉSUMÉ

La chromatographie en phase gazeuse, avec colonne capillaire, est proposée pour l'analyse de biphényles chlorés (biphényle, monochlorobiphényles, dichlorobiphényles). Deux colonnes complémentaires sont utilisées pour avoir une séparation totale.

ZUSAMMENFASSUNG

Beschreibung einer gaschromatographischen Methode mit Kapillarkolonne zur Analyse von chlorierten Biphenylen (Biphenyl, Monochlorbiphenyle, Dichlorbiphenyle). Durch Anwendung von 2 Zusatz-Kolonnen gelingt eine vollständige Trennung.

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3 G. H. BEAVEN, A. T. JAMES AND E. A. JOHNSON, *Nature*, 179 (1957) 490.
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Anal. Chim. Acta, 26 (1962) 391–394

Addendum

The purpose of this communication is to correct an error made in our paper **"Polarography of Some Pyridine and 1-Methylpyridinium Aldoximes"** which appeared in *Anal. Chim Acta*, 25 (1961) 281–288. On page 287 we make the following statement:

"... In alkaline solutions an alternate reaction pathway which involves saturation of the carbon-nitrogen double bond preceding the reductive splitting of the N-O bond is likely. The intermediate would be a hydroxylamine, R-CH_2-NHOH, instead of an imine. Since N-benzylhydroxylamine is reportedly reduced at more positive potentials in alkaline solutions than is benzaldoxime, while in acidic solutions it is reduced at more negative potentials, this alternate pathway appears feasible."

It has been called to our attention that N-benzylhydroxylamine is actually oxidized in alkaline solution, exhibiting an anodic wave, not a cathodic wave[1,2]. We must conclude that reduction of oximes via the hydroxylamine intermediate is unlikely.

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1 H. LUND, Personal Communication.
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Received December 18th, 1961

DSW 297234

STLCOPCB4067144