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COMPARISON OF ELECTRON-CAPTURE AND ELECTROLYTIC CONDUCTIVITY DETECTION FOR THE GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF SOME PERFLUORO DERIVATIVES OF FOUR AGRICULTURAL CHEMICALS

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SUMMARY

The gas chromatographic response of four perfluoro derivatives of four agricultural chemicals [diethylstilbestrol (DES), clopidol, linuron and carbofuran] was examined. The derivatives varied in fluorine content from 3 to 30 atoms per molecule. The sensitivities of the derivatives were found to be *ca.* 10-100 times greater by electron-capture detection than by electrolytic conductivity detection (halogen mode). The sensitivity also was found to increase with increasing fluorine content for all derivatives by electrolytic conductivity, whereas by electron capture, DES and clopidol exhibited similar responses with either the penta-, hepta- or pentadeca-fluoro derivatives. The sensitivity of linuron and carbofuran derivatives by electron capture varied with increasing fluorine content. For detection by electron capture, the hepta-fluorobutryl derivatives were preferred for DES and clopidol, and either the hepta-fluorobutryl or the pentadecafluorooctanoyl derivatives for linuron and carbofuran. For detection by electrolytic conductivity, the pentadecafluorooctanoyl derivatives were superior for all four compounds.

INTRODUCTION

Perfluoro derivatization of compounds containing an -OH or -NH moiety has proved to be very useful for sample analysis by gas chromatography (GC). Many types of compounds, such as amines, amides, phenols and alcohols, are susceptible to the reactions involved in the preparation of these types of derivatives. The advantages of this approach are that the derivatives have much improved chromatographic behavior and usually have increased sensitivity to electron-capture detection. The reactions have recently been included in reviews on chemical derivatization for GC^{1,2}. A number of authors compared several fluorinated anhydrides for derivatization of steroids³, phenols⁴ and carbamates⁵. The electron-capture response increased although not linearly with increasing fluorine content of the derivatives. Also, the increase in sensitivity was dependent upon the compound being derivatized. For example, the

heptafluorobutyryl (HFB) derivative of carbofuran (an N-methyl carbamate) was 5.2 times as sensitive as the corresponding trifluoroacetyl (TFA) derivative, while the HFB derivative of carbaryl (also an N-methyl carbamate) was only 2.2 times as sensitive as its TFA derivative⁵. The steroid testosterone showed a different ratio³. In this case the HFBA derivative was 100 times as sensitive as the TFA derivative.

Because of the influence of the parent compound on the electron-capture sensitivity of perfluoro derivatives, it was of interest to examine these reactions on compounds of interest to the present authors. Thus, the agricultural chemicals diethylstilbestrol (DES) (containing two phenolic OH groups), clopidol (one phenolic OH group), carbofuran (carbamate) and linuron (substituted urea) were chosen for the study. The electron-capture results were compared with results obtained from the same reactions by electrolytic conductivity detection (halogen mode). It was thought that the latter detector would be useful for the analysis of perfluoro derivatives since by its nature its sensitivity increases with increasing halogen content of the derivative. The present study also would serve to examine this effect further using fluorine as the halogen since little work on the response of the electrolytic conductivity detector to fluorine has been reported to date.

EXPERIMENTAL

Reagents and chemicals

The agricultural chemicals were analytical-grade materials obtained from commercial sources. The compounds examined were diethylstilbestrol (DES) (4,4'-dihydroxy- α,β -diethylstilbene), clopidol (2,6-dimethyl-3,5-dichloropyridin-4-ol), carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl-N-methylcarbamate), linuron [N-methyl-N-methoxy-N'-(3,4-dichlorophenyl)urea] and lindane (hexachlorocyclohexane) as a reference standard. Standard solutions were prepared in benzene at concentrations of 0.1 mg/ml. Clopidol, however, because of its generally poor solubility, was dissolved in acetonitrile to a concentration of only 20 $\mu\text{g}/\text{ml}$. These solutions were diluted as required for derivatization and gas chromatography.

All solvents were of glass-distilled residue-free grade. Trimethylamine (anhydrous, Eastman-Kodak, Rochester, N.Y., U.S.A.) in glass ampoules was cooled in ice-water and added with stirring to cool, tared benzene to produce a 0.1 M solution. The reagents used were trifluoroacetic anhydride (TFA) (Eastman), pentafluoropropionic anhydride (PFP) (PCR, Gainesville, Fla., U.S.A.), heptafluorobutyric anhydride (HFBA) (PCR) and pentadecafluoroundecanoic anhydride (PFO) (PCR). The reagents were used as received, except for PFO, which was refluxed with phosphorus pentoxide and redistilled before reactions were carried out⁶.

Gas-liquid chromatography (GLC)

All columns were constructed of borosilicate glass. The electrolytic conductivity results were obtained on a 1.3 m \times 4 mm I.D. column packed with 3% OV-1 on Chromosorb W HP (80-100 mesh). Helium was used as the carrier gas at a flow-rate of 40 ml/min.

Two columns were used for electron-capture analyses: a 1.8 m \times 4 mm I.D. column packed with 3% OV-1 on Chromosorb W HP (80-100 mesh), with a carrier gas (argon-methane, 95:5) flow-rate of 60 ml/min, was used for DES and clopidol

derivatives while a 1.3 m × 2 mm I.D. column packed with 1% SE-30 on Chromosorb W HP (80–100 mesh) at a carrier gas flow-rate of 20 ml/min was used for the derivatives of carbofuran and linuron. The column temperature varied depending upon the derivative being analyzed.

Electron-capture detection

A Hewlett-Packard 5713 gas chromatograph equipped with a ⁶³Ni pulsed detector operated at 250° was used. The injection port temperature was equal to or slightly higher than the column temperature. The attenuation used routinely was 32× on a 1.0-mV recorder (2.0 min/in.).

Electrolytic conductivity detection

A Tracor Microtek MT 220 gas chromatograph was fitted with a Coulson electrolytic conductivity detector set up for halogen analysis (reductive mode). The operating conditions were: pyrolysis furnace, 800°; transfer unit, 210°; d.c. bridge potential, 30 V. The attenuation was 4× for routine use with a 1.0-mV recorder (2.0 min/in.).

Derivative Preparation

DES and clopidol. A 1–10-μg amount of test compound in standard solution solvent was added to a 15-ml glass-stoppered or PTFE-lined screw-cap centrifuge tube. To this was added 0.1 ml of 0.1 M trimethylamine (TMA)–benzene and 20 μl of anhydride and the total volume was made up to 0.5 ml with benzene. The stoppered tubes were gently vortexed and permitted to stand at room temperature for 1 h, then 0.5 ml of benzene and 5 ml of water were added and the vessels shaken vigorously for 30 sec. After centrifugation for 5 min at 2270 g, the upper benzene layer was analyzed by GLC either directly or after dilution with benzene. For electrolytic conductivity analysis, the HFB and PFO reactions were shaken with two further 5-ml volumes of water to remove excess of reagent which affected this detector more than the electron-capture detector.

Carbofuran and linuron. These compounds were more difficult to derivatize than those described above. The reactions were the same with the exception that 50 μl of anhydride and 0.5 ml of 0.1 M TMA–benzene were added, the total volume was made up to 1.0 ml and the reactions were carried out at 70° for 1.5 h.

RESULTS AND DISCUSSION

Fig. 1 shows the structures of the compounds studied. Both phenolic –OH moieties of DES were derivatized by all reagents⁷. However, the *cis* and *trans* forms were separable by GLC, and two peaks were therefore always observed. Clopidol produced a single peak with all reagents but PFP, which consistently gave two peaks by both electron-capture and electrolytic conductivity detection. The reason for this was not investigated although the two peaks could be isomers. Both carbofuran and linuron were derivatized at the –NH moiety, producing single peaks with all reagents.

Table I lists the retention times and sensitivities of the derivatives by both detection methods. For peak-height measurements of the DES derivatives and PFP-clopidol, the largest peak (second peak for DES, second peak for PFP-clopidol) was

TABLE I
RETENTION TIMES AND SENSITIVITIES OF PERFLUORO DERIVATIVES

Compound	Derivative	Electrolytic conductivity detection			Electron-capture detection		
		Retention time (min)	Sensitivity PHt*	PA**	Retention time (min)	Sensitivity PHt*	PA**
DES	TFA	2.4/3.2	0.38	0.17	2.5/3.7	12	1.5
	PFP	2.4/3.4	1.1	0.20	2.6/4.0	83	15
	HFB	3.0/4.5	2.0	0.44	3.5/5.4	100	23
	PFO	3.4/5.4	2.5	0.86	3.4/5.3	71	21
Clopidol	TFA	2.1	1.8	0.21	2.8	167	24
	PFP	3.1/3.3	1.4	0.32	2.8/3.2	167	32
	HFB	5.2	2.5	0.74	4.5	250	45
	PFO	2.7	7.1	1.01	4.1	167	34
Lindane		6.0	1.4	0.31	4.5	83	20
Linuron	TFA	3.0	0.08	0.02	3.9	18	2.1
	PFP	2.8	0.28	0.09	3.6	25	4.8
	HFB	3.2	0.69	0.21	4.3	26	7.7
Carbofuran	PFO	3.9	1.7	0.60	4.8	50	13.3
	TFA	1.9	0.55	0.09	3.6	6	0.9
	PFP	1.8	1.0	0.17	3.4	15	2.3
	HFB	1.9	1.4	0.21	4.0	24	4.4
Lindane	PFO	3.9	2.0	0.51	3.7	71	11.0
		2.4	1.3	0.29	2.2	83	16.7

* PHt = peak height in inches per nanogram (of parent compound) corrected to 32 × (electron capture) and 4 × (electrolytic conductivity).

** PA = relative peak area per nanogram (of parent compound), corrected to 32 × (electron capture) and 4 × (electrolytic conductivity).

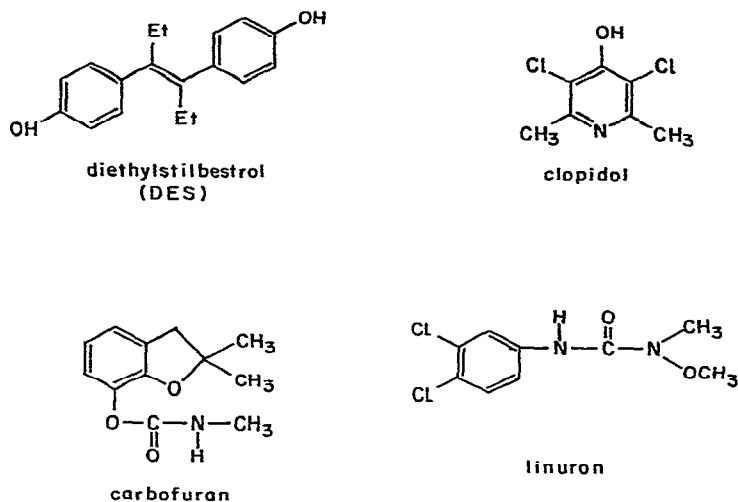


Fig. 1. Structures of the compounds studied.

chosen. Relative peak-area measurements included both peaks and were determined as the product of the peak height times the base width for a relative value, for all derivatives.

The electrolytic conductivity response generally increased with increasing number of fluorine atoms in the derivative. Thus, the PFO derivatives were most sensitive and the TFA derivatives the least sensitive. This pattern was evident for all four test compounds by both peak height and peak area. Generally the response per halogen per nanogram was similar for the derivatives with the exception of linuron. The TFA and PFP derivatives of this compound produced a much lower response compared with the same derivatives of the other test compounds. This might be a reflection of the poorer stability of these particular derivatives.

The electron-capture sensitivities of the linuron and carbofuran derivatives increased with increasing fluorine content. These results appear similar to those obtained in studies on similar derivatives of other compounds^{4,5}.

The stability of the compounds towards hydrolysis in the final benzene solutions increased with increasing molecular weight of the derivatives. The TFA derivatives of all compounds were the least stable and often were completely decomposed upon standing overnight. The HFB derivatives of linuron and carbofuran decomposed to the extent of *ca.* 30% after 3 days while their PFO derivatives decomposed to the extent of only 10% after 1 week.

For analysis using electron-capture detection it appears that the HFB derivatives are most useful for DES and clopidol since these gave the best sensitivities with very good peak shapes. The PFO derivatives are preferred for electrolytic conductivity analysis of the four compounds as well as for the electron-capture determination of linuron and carbofuran because they were the most sensitive. However, the HFB derivatives might be preferred for some compounds because of their better peak shape and greater volatility.

CONCLUSIONS

Electron-capture detection was found to be 10–100-fold more sensitive than electrolytic conductivity detection to the perfluoro derivatives of the agricultural chemicals examined. Of the derivatives studied, the PFO and HFB products are preferred because of their sensitivity and greater resistance to decomposition upon storage.

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