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Note

Gas–liquid chromatography of the isomers of dichlorobenzophenone, di(chlorophenyl)methane and 1,1-di(chlorophenyl)ethane

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The identification and quantitative estimation of the six dichloro isomers of dichlorobenzophenone, the six dichloro isomers of di(chlorophenyl)methane and the six dichloro isomers of 1,1-di(chlorophenyl)ethane were required, because the dichloro isomers in the three series* were expected reaction products in a number of Friedel–Crafts syntheses. All six isomers of dichlorobenzophenone are known[1], but no attempts to identify and to estimate the six isomers in mixtures have been reported. Only four of the di(chlorophenyl)methane isomers and two of the 1,1-di(chlorophenyl)ethane isomers have been mentioned in the literature, but all six dichloro isomers in each of the three series have now been prepared by unambiguous synthetic routes[2]. Although several groups have used infra-red and ^{1}H nuclear magnetic resonance (NMR) spectroscopy to determine isomer ratios in compounds related to the present series[3–6], we found that these techniques, as well as that of mass spectroscopy, were of limited use. We did find, however, that ^{1}H NMR could be used to determine ratios between various groups of isomers in the di(chlorophenyl)methane and the 1,1-di(chlorophenyl)ethane series, *viz.* the groups (2,2′) to (2,3′ plus 2,4′) to (3,3′ plus 3,4′ plus 4,4′).

Since ^{1}H NMR could not be used to identify or to determine all the six isomers in any of the three series, we therefore studied the gas–liquid chromatographic (GLC) characteristics of the isomers in all three series.

EXPERIMENTAL

The apparatus used for the GLC analyses was a Perkin-Elmer F-11 instrument with a flame-ionisation detector. All analyses were carried out isothermally. The columns and operating conditions that were finally used for the analyses were as follows. For the dichlorobenzophenones a 2 m × 2 mm column of 2½% Carbowax 20M on 80–100 mesh Chromosorb W was used; the column temperature was 180°C, the injection temperature 200°C, nitrogen pressure was 24 p.s.i., air pressure 19 p.s.i.,

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* In each series, the aromatic nuclei are monosubstituted, making six possible dichloro isomers.

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hydrogen pressure 22 p.s.i., and the chart run at 5 mm per min. The column and operating conditions for the di(chlorophenyl)methanes were the same except that the column temperature was 160°C and the chart speed 15 mm per min. For analyses of the 1,1-di(chlorophenyl)ethanes a 2 m × 2 mm column of 6% diethyleneglycol succinate on 85–100 mesh Celite AW DMCS was used; the column temperature was 150°C, the injection temperature 200°C, nitrogen pressure 20 p.s.i., air pressure 24 p.s.i., hydrogen pressure 24 p.s.i., and the chart speed 5 mm per min.

For both qualitative and quantitative analyses, it was found convenient to use internal standards, making sure that no peaks were masked. The standards used were benzophenone for the dichlorobenzophenone and di(chlorophenyl)methane series and methyl stearate in the case of the 1,1-di(chlorophenyl)ethane series. Qualitative analyses were carried out by the addition of small amounts of the known dichloro isomers to an unknown mixture, in order to identify the various components present. The retention times of the six dichloro isomers in each series of compounds are given in Table I. In quantitative analyses, peak areas were calculated from the product of peak height and peak width at half peak height. It was found that in each series of isomers the areas were proportioned to the weights of isomers in the mixture, so that within each series the molar response of the six dichloro isomers was the same. The compounds (singly or as mixtures) were injected as 5% solutions in acetone (0.1 μl).

TABLE I

RETENTION TIMES OF THE DICHLORO ISOMERS IN THE DICHLOROBENZOPHENONE, DI(CHLOROPHENYL)METHANE AND 1,1-DI(CHLOROPHENYL)ETHANE SERIES

Isomer	*Retention time (min)*		
	Dichlorobenzophenone[*]	*Di(chlorophenyl)methane*[**]	*1,1-Di(chlorophenyl)ethane*[***]
2,2′	31.3	9.9	16.0
2,3′	33.0	11.4	17.8
2,4′	34.8	12.0	20.4
3,3′	36.8	12.7	23.0
3,4′	38.0	13.3	26.2
4,4′	41.6	13.9	28.8
Internal standard	20.0[§]	24.1[§]	14.1[§§]

[*] On 2½% Carbowax at 180°C.

[**] On 2½% Carbowax at 160°C.

[***] On 6% diethyleneglycol succinate at 150°C.

[§] Benzophenone.

[§§] Methyl stearate.

RESULTS AND DISCUSSION

The retention times given in Table I show that in all three series of compounds, the order of increasing retention time follows the sequence:

$$2,2' < 2,3' < 2,4' < 3,3' < 3,4' < 4,4' \qquad (1)$$

This agrees with previous work on related series. For example the retention times of dichlorobiphenyls on a large number of stationary phases always follow the above sequence[7,8]. In compounds of type YC_6H_4X, where X is F, Cl, Br or I and Y is $PhCH_2$ or CH_3, etc., the order of retention times quite generally is $1,2 < 1,3 < 1,4$, which again follows the pattern of sequence 1 (ref. 9). It seems possible, therefore, that the general sequence 1 could be assumed to hold in cases where authentic samples of all the isomers are not available. The only major exception to this general sequence, known to us, is that for the difluorobenzophenones retention times, on the same Carbowax column as used for the dichlorobenzophenones, are in the unusual order of $3,4' < 2,4' < 4,4'$ (ref. 2).

Quantitative analyses of the isomers within each series was helped by our observation that the molar responses of the six isomers were identical. In other related series this has not been found to be the case; Albro and Fishbein[7] observed that for the corresponding six isomers in the dichlorobiphenyl series, molar responses varied by up to about 20% (*i.e.* to within ±10%) between the various isomers. To some extent we were able to check our results against ^1H NMR analyses for the di(chlorophenyl)methanes and 1,1-di(chlorophenyl)ethanes. Details are in Tables II and III, for representative analyses. Agreement between the two methods is reasonably good and confirms our quantitative procedure. Since the ^1H NMR analyses are carried out with respect to the aliphatic proton signals of the $Ar{-}CH_2{-}Ar$ and $Ar{-}\overset{|}{C}H{-}Ar$ groups, the method is not applicable to the dichlorobenzophenones, and we were unable to use the NMR method as a check in this series.

TABLE II

ANALYSIS OF THE DI(CHLOROPHENYL)METHANE ISOMERS BY GLC AND ^1H NMR

Isomer	*Composition (%)*		
	GLC		*^1H NMR*
2,2′	9.3	9.3	9.2
2,3′	27.2	43.2	42.4
2,4′	16.0		
3,3′	20.1	47.5	48.4
3,4′	18.7		
4,4′	8.7		

TABLE III

ANALYSIS OF THE 1,1-DI(CHLOROPHENYL)ETHANE ISOMERS BY GLC AND ^1H NMR

Isomer	*Composition (%)*		
	GLC		*^1H NMR*
2,2′	5.2	5.2	4.6
2,3′	6.2	47.5	48.5
2,4′	41.3		
3,3′	0.2	47.3	46.9
3,4′	16.1		
4,4′	31.0		

We also tested the reproducibility of the quantitative analyses by repeated injections of a mixture of isomers. Some representative analyses of the 1,1-di(chlorophenyl)ethane isomers are given in Table IV, with different mixtures of the isomers obtained as reaction products. The reproducibility of the analysis varies somewhat from mixture to mixture, but in general the percentage composition of a mixture of all six isomers can be ascertained to within about one "absolute" percent.

TABLE IV

REPRODUCIBILITY OF ANALYSES OF THE 1,1-DI(CHLOROPHENYL)ETHANE ISOMERS BY GLC

Isomer	*Composition of mixture (%)**		
	A	*B*	*C*
2,2′	4.5 ± 0.3	4.2 ± 0.4	3.3 ± 0.4
2,3′	6.8 ± 0.9	5.9 ± 0.7	4.8 ± 0.6
2,4′	32.7 ± 0.7	35.4 ± 4.0	37.4 ± 1.8
3,3′	2.0 ± 0.5	1.3 ± 1.4	<1
3,4′	18.5 ± 0.4	17.1 ± 1.7	17.3 ± 1.1
4,4′	35.6 ± 1.4	35.8 ± 1.4	37.2 ± 1.4
Number of analyses	8	12	8

* Standard deviations are given in all cases. Note that mixtures A, B and C are not the same.

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