

CHROM. 3753

GAS CHROMATOGRAPHIC SEPARATION AND IDENTIFICATION OF DIMERIZATION PRODUCTS OF α -METHYLSTYRENE*

A. ŠVOB, DJ. DEUR-ŠIFTAR AND V. JARM

INA Institute, Zagreb (Yugoslavia)

(Received July 24th, 1968)

SUMMARY

α -Methylstyrene dimerization products have been separated and identified by gas chromatography.

Although isomeric compounds with a high number of functional groups in the molecule are involved here, the structure of the dimers and the type of the other dimerization products was successfully determined by means of Kovats' retention indices. The results obtained for the structure of the compounds examined are in good agreement with the results of analyses by spectrometric methods (N.M.R., I.R., U.V.).

INTRODUCTION

Dimerization of α -methylstyrene in sulphuric acid results in a compound which acts as a polymerization modifier and can exist in at least four isomeric forms: 1,1,3-trimethyl-3-phenylindane; 2,4-diphenyl-4-methyl-1-pentene; *cis*- and *trans*-2,4-diphenyl-4-methyl-2-pentene¹. Unsaturated isomers can act as polymerization modifiers but, it has been assumed that their activities, dependent on their structures, are different. The cyclic dimer 1,1,3-trimethyl-3-phenylindane is believed to be substantially inactive as a polymerization modifier. The composition of the mixture obtained through the dimerization of α -methylstyrene in sulphuric acid medium is not completely known. Gas chromatographic analysis of this mixture gave four peaks¹. The second and the third peak predominate and are incompletely separated, and at present it is not known which dimer gives rise to a particular peak. The author¹ assumes that the dominant peaks originate from unsaturated isomers.

This paper describes the complete analysis of the dimerization products of α -methylstyrene by gas chromatography. The components were identified by Kovats' retention indices, and the results obtained were confirmed by spectrometric methods.

The increment δI used for the determination of the compounds investigated represents the difference in dispersion behaviour of two different compounds, *viz.*: the compound examined and the "parent" compound, the latter closely being related to

* Presented at the 1st Yugoslav Symposium on Gas Chromatography, Zagreb, April 10-12, 1968.

the former. This increment is referred to in the literature as the factor of homomorphy², or functional index³.

The increment ΔI , defined as the difference of the retention indices for one and the same compound on polar and nonpolar stationary liquids, was used for the determination of oxidation products of dimerization.

EXPERIMENTAL

Dimerization of α -methylstyrene is effected by polymerization of α -methylstyrene with H_2SO_4 as catalyst and in the presence of the surface active agent Ambiteric D which forms an emulsion between the sulphuric acid and the monomeric α methylstyrene.

The dimer 1,1,3-trimethyl-3-phenylindane is prepared by dimerization of α -methylstyrene on zeolite⁴. Determination of the retention and functional indices was carried out on the commercially pure components (*n*-paraffins and other hydrocarbons used as "parent" and related compounds) and on the pure components of the mixture examined which were obtained by preparative gas chromatography. The gas chromatograph Varian Aerograph Model 1520 provided with an analytical and a preparative column was used for the work. The measurements of the retention times of the individual compounds, required for the determination of the retention indices of the components of the dimeric mixture, were made on analytical columns. The preparative column was used for the separation and isolation of the dimeric fraction in the α -methylstyrene dimerization product. The mixture of dimeric isomers examined had a high boiling point within a narrow range (299–302°). For such separations silicone columns SE-30 and DC 710 are suitable⁵⁻⁷. In our work the best separation of the α -methylstyrene dimers was obtained on an Apiezon L column.

As is shown in Fig. 1 six well separated components in the dimer fraction of the α -methylstyrene dimerization products are obtained.

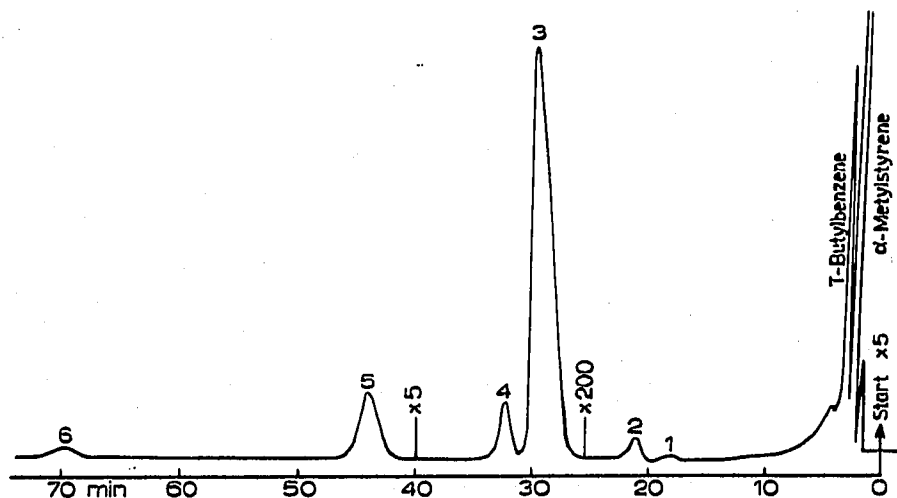


Fig. 1. Gas chromatogram of α -methylstyrene dimerization products (Apiezon L, 10%; Chromosorb W, 80–100 mesh; 1/8 in. \times 6 ft.; column temperature 200°; carrier gas flow rate 20 ml/min; carrier gas nitrogen; sample size 0.4 μ l).

For the preparative work a silicon rubber SE 30 column was used. The resolution obtained on the analytical SE-30 column was 94.6 %, and had a ten times shorter analysis time than the Apiezon L column, which is a real advantage. The analysis on the preparative column was performed under the following conditions:

Column 50 ft. \times 3/8 in. filled with 10 % SE 30 on Chromosorb A (20–30 mesh); carrier gas flow rate 400 ml/min; inlet pressure 60 p.s.i.g.; column temperature 240°; detector temperature 240°; injection block temperature 260°; sample size 1000 μ l. The isolated compounds were rechromatographed.

TABLE I

REDUCED RETENTION TIMES AND RETENTION INDICES OF THE DIMERIC COMPONENTS

| Component | SE 30 (180°) | | Emulphor (200°) | | Apiezon L (200°) | | $\Delta I = I^E - I^A$ |
|-----------|--------------|------|-----------------|--------|------------------|-------|------------------------|
| | T'_R (sec) | I | T'_R (sec) | I^E | T'_R (sec) | I^A | |
| 1 | 105 | 1555 | 244 | 2057.4 | 883 | 1723 | 334.4 |
| 2 | 138 | 1621 | 286 | 2102.0 | 1013 | 1756 | 346.0 |
| 3 | 225 | 1788 | 436 | 2221.2 | 1478 | 1843 | 378.2 |
| 4 | 240 | 1808 | 499 | 2254.6 | 1638 | 1866 | 388.6 |
| 5 | 305 | 1871 | 1276 | 2521.6 | 2618 | 1970 | 551.6 |
| 6 | 395 | 1938 | 1256 | 2516.0 | 3953 | 2061 | 455.0 |

RESULTS AND DISCUSSION

Table I shows the retention times and indices of the pure components of α -methylstyrene dimerization products, determined on three different columns: SE-30, Emulphor O and Apiezon L. The components of the dimeric mixture are designated with numbers, 1 to 6, according to the sequence of emergence of the peaks on the chromatogram. In the last column of Table I the increments ΔI for each component of the dimeric mixture are given.

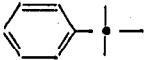
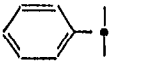
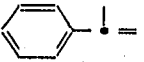
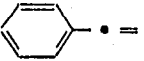
Table II shows the functional indices for methyl and phenyl groups which were obtained through the model compounds on the SE 30 column at 28°. It was found (see also WIDMER³) that there is no noticeable temperature dependence of the retention indices on this column. The functional index obtained in this work for the methyl group is in good agreement with the data obtained by WIDMER³. It was found that the phenyl group functional index changed depending on the type of carbon atom to which it is linked: e.g. quarternary or tertiary carbon atom, or double bond. The latter can again give a different value if a methyl group is found in its neighbourhood. Such cases were examined because in 2,4-diphenyl-4-methyl-1-pentene the phenyl group is linked to a quarternary carbon atom, while in 2,4-diphenyl-4-methyl-2-pentene the phenyl group is attached to a double bond in the neighbourhood of a methyl group.

The retention indices obtained for "parent" compounds of the isomeric dimers of α -methylstyrene were 489 for 1-pentene and 519 for 2-pentene which is in good agreement with the results obtained by WIDMER³ for the same compounds and column. On the basis of these data and the data for the functional indices of methyl

TABLE II

FUNCTIONAL INDICES

Column SE 30, 5%; column temperature 28°; 5 ft. \times 1/8 in; 20 ml N₂/min.

| Functional group | Functional index, δI |
|---|------------------------------|
| H ₃ C- | 70 |
|  | 610 |
|  | 616 |
|  | 622 |
|  | 636 |

and phenyl group (Table II), the retention indices for the dimers which should occur as the main products of α -methylstyrene dimerization¹ were calculated.

$$I_{2,4\text{-diphenyl-4-methyl-1-pentene}} = 1791$$

$$I_{2,4\text{-diphenyl-4-methyl-2-pentene}} = 1821$$

As shown in Table I the retention index of component 3 was $I = 1788$ and component 4 was $I = 1808$; thus it was concluded that component 3 is 2,4-diphenyl-4-methyl-1-pentene and component 4 is 2,4-diphenyl-4-methyl-2-pentene. As 2,4-diphenyl-4-methyl-2-pentene can exist in either *cis*- or *trans*-form, and the large substituents in the *cis*-form contribute less to the total value of the retention index⁸, the *cis*-isomer would be expected to have a shorter retention time than the *trans*-isomer. Hence, some of the previous components could belong to the *cis*-isomer. Component 2 was identified as the dimer 1,1,3-trimethyl-3-phenylindane with regard to the retention time of the pure compound. Thus, it can be assumed that component 1 is *cis*-2,4-diphenyl-4-methyl-2-pentene. The N.M.R. analysis confirmed that component 1 is the *cis*-isomer and component 4 is *trans*-2,4-diphenyl-4-methyl-2-pentene.

The difference in the retention indices on polar and nonpolar columns (ΔI) for the first four components is similar. However, the ΔI for components 5 and 6 is much higher implying the polar character of these components. The compounds are obviously of dimeric structure as they emerge from the column in the region of the other dimers. Thus it should be possible to calculate on the basis of the difference of the increments ΔI for hydrocarbon dimers (components 1-4) and the polar components 5 and 6, which group of compounds these components belong to. If the average value of ΔI of the first four components, 361.8 units, (corresponding to ΔI of compounds with two phenyl groups)⁹, is subtracted from the ΔI of components 5 and 6, the following values are obtained: $\Delta I'_{(5)} = 1898$ and $\Delta I'_{(6)} = 93.2$ units. The first value corresponds to compounds with a carbonyl group and the second to com-

pounds with an ether group. On the basis of results obtained by gas chromatography, the composition of the α -methylstyrene dimerization product is as follows:

- Component 1: *cis*-2,4-diphenyl-4-methyl-2-pentene(?)
- Component 2: 1,1,3-trimethyl-3-phenylindane
- Component 3: 2,4-diphenyl-4-methyl-1-pentene
- Component 4: *trans*(?)-2,4-diphenyl-4-methyl-2-pentene
- Component 5: ketone, aldehyde or ester
- Component 6: ether

The analysis of each separate component by N.M.R. spectrometry confirmed the above results¹⁰. Component 5, with help of elementary microanalysis and I.R. and U.V. spectrometric analysis, was identified as 1,3-diphenyl-3-methyl-2-butanone, but further identification of component 6 failed due to the instability of this compound.

TABLE III

QUANTITATIVE COMPOSITION OF VARIOUS SAMPLES OF α -METHYLSTYRENE DIMERIZATION PRODUCT

| Sample | Conditions of dimerization | Component (%) | | | | | |
|--------|--|---------------|------|-------|------|------|------|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| I | H ₂ SO ₄ : α MS = 4:1 50% H ₂ SO ₄ 50°, 4 h | 0.02 | 0.09 | 91.05 | 8.18 | 0.54 | 0.11 |
| III | H ₂ SO ₄ : α MS = 4:1 50% H ₂ SO ₄ 50°, 3.5 h | 0.02 | 0.08 | 91.53 | 7.86 | 0.41 | 0.09 |
| VI | H ₂ SO ₄ : α MS = 4:1 50% H ₂ SO ₄ 70°, 9 h | 0.02 | 0.09 | 91.70 | 8.13 | 0.03 | — |

A quantitative analysis of the α -methylstyrene dimerization product can be made by the method of normalization from the gas chromatographic data obtained by analysis on Apiezon L at 200° and 20 ml N₂/min (Fig. 1). The composition of the dimeric fraction was quantitatively determined without the light fraction which includes about 10% of α -methylstyrene. The results of the quantitative analysis for several dimer samples, obtained under various operating conditions of dimerization, are given in Table III. It is apparent from Table III that 2,4-diphenyl-4-methyl-1-pentene and *trans*-2,4-diphenyl-4-methyl-2-pentene are the main components under all conditions of dimerization, whereas *cis*-2,4-diphenyl-4-methyl-2-pentene, 1,1,3-trimethyl-3-phenylindane and oxidation products are present only in quantities less than 1%. By increasing the temperature and the duration of dimerization the quantity of oxidation products is considerably reduced.

REFERENCES

- 1 T. AITKEN, *Brit. Pat.* 979677, Jan. 6, 1965, Appl. Aug. 8, 1962.
- 2 G. SCHOMBURG, *J. Chromatog.*, 23 (1966) 1.
- 3 H. WIDMER, *J. Gas Chromatog.*, 5 (1967) 506.
- 4 N. M. SEIDOV, A. A. BAHŠI-ZADE, I. M. ČERNIKOVA AND Z. M. MELIKOVA, *Azerb. Khim. Zh.*, 5 (1962) 57.
- 5 G. M. PARKHURST, J. O. RODIN AND R. M. SILVERSTEIN, *J. Org. Chem.*, 28 (1963) 120.
- 6 A. ZWIERZAK AND H. PINES, *J. Org. Chem.*, 28 (1963) 3392.
- 7 D. BRAUN AND W. MEIER, *Angew. Makromol. Chem.*, 1 (1967) 17.
- 8 J. JONAS, M. KRATOCHVIL, H. GROSS AND J. JANAK, *Collection Czech. Chem. Commun.*, 31 (1966) 2399.
- 9 A. WEHRLI AND E. KOVATS, *Helv. Chim. Acta*, 42 (1959) 2709.
- 10 A. ŠVOB AND B. ČERNICKI, *Chimia*, in press.

J. Chromatog., 38 (1968) 326-331