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Note

Paper electrophoretic characterization of ethylenic compounds as dimethylsulphoniomethylthio derivatives

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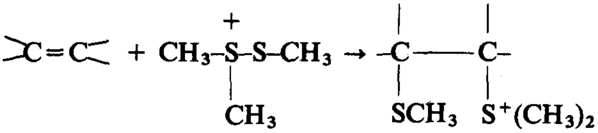
Although many methods have been developed for the examination of ethylenic compounds, such as gas and high-performance liquid chromatography, electrophoresis has not previously been applied, presumably on account of the difficulty of the preparation of suitable derivatives. In this investigation, based on the work of Helmkamp *et al.*[1] on preparative chemistry, it has been found that ethylenic compounds can be readily derivatized according to the reaction



$$>C{=}C< + CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{S}}-S-CH_3 \rightarrow -\underset{\underset{SCH_3}{|}}{\overset{|}{C}}-\!\!-\underset{\underset{S^+(CH_3)_2}{|}}{\overset{|}{C}}-$$

The compounds obtained are water soluble and can be easily detected after paper electrophoresis by using of Dragendorff's reagent. This approach is suggested for the identification of ethylenic compounds.

EXPERIMENTAL

Chemicals

Dimethylmethylthiosulphonium fluorosulphonate was prepared in this laboratory: 2.8 g (0.03 mole) of redistilled dimethyldisulphide were dissolved in 10 cm^3 of nitromethane and 2.85 g (0.025 mole) of methyl fluorosulphonate were added in one portion. The mixture was stoppered and swirled and, after 60 min, 30 cm^3 of diethyl ether was added to the yellow solution to precipitate the product. The solid was isolated by filtration, washed with 20 cm^3 of diethyl ether and air dried for about 1 min.

Methyl fluorosulphonate ("magic methyl") was obtained from E. Merck (Darmstadt, F.R.G.). All unsaturated compounds were of analytical-reagent grade and were purchased from Fluka (Buchs, Switzerland) and E. Merck. Nitromethane was obtained from POCh (Gliwice, Poland).

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Solutions

The pH 1.7 buffer solution was an aqueous solution of 0.05 mole/dm^3 orthophosphoric acid, 0.1 mole/dm^3 orthoboric acid and 10% (v/v) ethylene glycol.

Dragendorff's reagent was prepared by mixing 5 cm^3 of solution A and 5 cm^3 of solution B and adding 20 cm^3 of glacial acetic acid, followed by dilution with water to 100 cm^3. Solution A was 0.85 g of bismuth subnitrate dissolved in a mixture of 40 cm^3 of water and 20 cm^3 of glacial acetic acid. Solution B was 8 g of potassium iodide dissolved in 20 cm^3 of water.

Sample derivatization procedure

A 10^{-5} mole amount of unsaturated compounds in 0.1 cm^3 of nitromethane was placed in a small glass test-tube containing 0.2 cm^3 of a 1 mole/dm^3 nitromethane solution of dimethylmethylthiosulphonium fluorosulphonate. After the tube had been shaken and allowed to stand for 1 h, the sample was ready for electrophoretic separation.

Electrophoresis procedure

The apparatus for high-voltage electrophoresis (Type AEA; WSR, Olsztyn, Poland) was operated in accordance with the manufacturer's instructions. Whatman No. 1 chromatography paper (8 × 37 cm) was impregnated with orthophosphoric acid–orthoboric acid–ethylene glycol buffer solution by immersion in a trough, excess of solution being removed by blotting with filter-paper. Samples were applied 5 cm from the edge of the paper as 5-μl spots using a microsyringe. The safety case of the electrophoresis unit was then closed and a potential of 2000 V applied for 45 min. The paper was removed and, after spraying with Dragendorff's reagent, the compounds became visible as compact pink spots on a pale yellow background.

RESULTS AND DISCUSSION

The mobilities of the products obtained from the addition reactions of unsaturated hydrocarbons with the dimethylmethylthiosulphonium cation, relative to

TABLE I

MOBILITIES OF DIMETHYLSULPHONIOMETHYLTHIO DERIVATIVES RELATIVE TO $S(CH_3)_3^+$

No.	*Parent compound*	*Relative mobility*	*No.*	*Parent compound*	*Relative mobility*
1	2-Methyl-1-propene	0.52	11	1-Tetradecene	0.21
2	1-Pentene	0.52	12	1-Hexadecene	0.16
3	1-Hexene	0.49	13	1-Nonadecene	0.07
4	2-Hexene	0.51	14	Cyclopentene	0.62
5	2-Hexyne	0.59	15	Cyclohexene	0.58
6	1-Heptene	0.45	16	2-Phenyl-1-propene	0.55
7	1-Octene	0.42	17	Ethynylbenzene	0.52
8	1-Nonene	0.39	18	Limonene	0.47
9	1-Decene	0.36	19	α-Pinene	0.55
10	1-Dodecene	0.29			

TABLE II

MOBILITIES OF UNSATURATED COMPOUNDS AS DIMETHYLSULPHONIOMETHYLTHIO DERIVATIVES RELATIVE TO $S(CH_3)_3^+$

No.	*Parent compound*	*Relative mobility*
1	Allyl alcohol	0.64
2	Oleyl alcohol	0.00
3	Acrolein	0.56
4	Crotonaldehyde	0.53
5	Cinnamaldehyde	0.50
6	Acrylic acid	0.63
7	Crotonic acid	0.40
8	Acrylamide	0.53
9	Methyl acrylate	0.52
10	Ethyl acrylate	0.50
11	3,4-Dihydro-2*H*-pyrane	0.57

that of the trimethylsulphonium cation, are presented in Table I. The relative mobility data are average values of five measurements and in no instance was the variation between them greater than 0.02.

Tables II gives the mobilities of the products obtained in addition reactions of some compounds that contain double bonds with dimethylmethylthiosulphonium cation, relative to that of the trimethylsulphonium cation.

Based on this investigation, the proposed method can be used for the separation and identification of unsaturated hydrocarbons in non-aqueous solvents. The reaction of dimethylmethylthiosulphonium fluorosulphonate with unsaturated hydrocarbons is very rapid and the products are stable and can be separated by high-voltage paper electrophoresis. The stability of the derivatives was monitored for 2 weeks and no changes in the electropherograms were observed.

As shown in Table I, using this method straight-chain 1-alkenes containing up to nineteen carbon atoms in the molecule can be separated and identified. This method is useful for the separation and identification not only of unsaturated hydrocarbons, but also of unsaturated compounds containing other functional groups (see Table II).

REFERENCE

1 G. K. Helmkamp, B. A. Olsen and D. J. Pettitt, *J. Org. Chem.*, 30 (1965) 676.