

CHROM. 14,573

Note

Separation of triarylsulfonium salts by thin-layer chromatography

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(Received November 24th, 1981)

Triarylsulfonium salts are important as photoinitiators for cationic polymerization^{1–3}. The synthesis of these salts can often be accompanied by the formation of similar side products, occasionally in significant quantities³. Because of these considerations, a definite need exists to define the types and amounts of triarylsulfonium salts in these products.

Thin-layer chromatography (TLC) is usually a powerful tool for separating similar compounds, in this case for molecules which have similar aromatic moieties, but different polarities. While there has been some work on the chromatographic separation of alkylsulfonium iodides⁴ and phosphonium salts⁵, there has been no report on the separation of triarylsulfonium salts. A TLC separation was therefore developed to accomplish this task.

EXPERIMENTAL

Materials

Purified triarylsulfonium hexafluorophosphate salts were obtained from S. Schlesinger and W. Watt of American Can Company (Princeton, NJ, U.S.A.). Methanol and hydrochloric acid, 1.0 *N*, were obtained from Fisher Scientific (Springfield, NJ, U.S.A.). Hexafluorophosphoric acid, 65% solution in water, was obtained from Aldrich (Milwaukee, WI, U.S.A.). All reagents were of the highest purity available and used without further purification.

TLC plates were purchased from Whatman (Clifton, NJ, U.S.A.).

Methods

1.0% Methanolic solutions each of bis[4-(diphenylsulfonio)phenyl] sulfide dihexafluorophosphate (BDS), *S*-phenylthianthrylium hexafluorophosphate (SPT), triphenylsulfonium hexafluorophosphate (TPS) and diphenyl-4-thiophenoxyphenylsulfonium hexafluorophosphate (DPTS) were made up. These solutions were stored in the dark at 4°C prior to use.

Analytical TLC was performed using 250- μ m precoated silica gel K6 plates without any preconditioning. Samples (up to 500 μ g) were spotted on the plate with a

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disposable capillary tube. Similarly, preparative TLC was performed using 1000- μm precoated silica gel plates. In this case, samples were applied as streaks at the 2000 $\mu\text{g}/\text{cm}$ loading level.

Ascending development (to a distance about 10 cm above the starting line) was performed using methanol-water-1 *N* hydrochloric acid (90:10:5), in a well-equilibrated chromatographic tank. After solvent evaporation, visualization was accomplished by UV fluorescence quenching of the TLC plate phosphor (*caution*: HCl, HF and PF₅ vapors may be released on visualization). Although not used here, an alternative method of visualizing sulfonium compounds on the TLC plate is spraying with cobaltous ammonium thiocyanate solution^{6,7}. Zones containing onium compounds subsequently appear red.

Zones containing the separated triarylsulfonium compounds were scraped off and eluted with additional mobile phase solvent. Samples were not collected from zones exposed to UV radiation used in visualization. After evaporating the solvent, the solid products were redissolved in methanol. Purified hexafluorophosphate salts of the TLC separated components were isolated by precipitation following the addition of a stoichiometric excess of hexafluorophosphoric acid to the water diluted methanol solution (4 parts water to 1 part methanol). Infrared and proton nuclear magnetic resonance spectroscopic analysis and further TLC were performed to check for sample decomposition.

RESULTS AND DISCUSSION

The four standard triarylsulfonium compounds (Fig. 1) were separated with good resolution and minimal tailing (Table I). Preparative TLC was used to separate mg quantities of the triarylsulfonium compounds. The hexafluorophosphate salts of the separated components were recovered in each case and their IR spectra compared. Excellent IR spectral correlations before and after TLC were seen for each compound, indicating the absence of decomposition during the separation procedure.

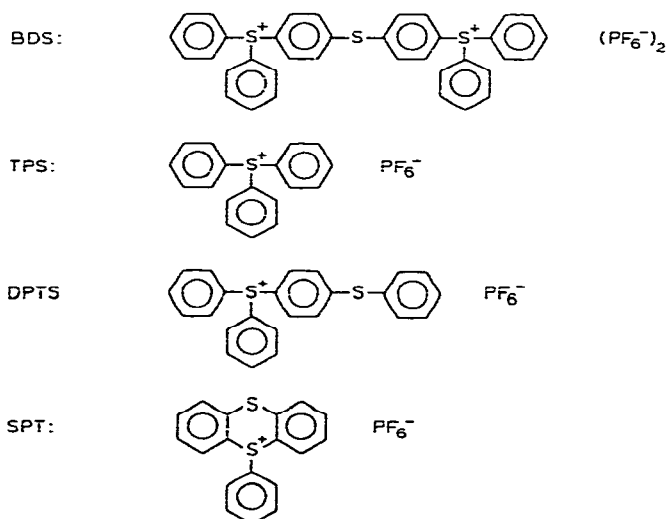


Fig. 1. Triarylsulfonium compounds separable by TLC.

The TLC artifact indicated in Table I is probably due to the formation of the so-called second solvent front. This effect occurs if the mobile phase contains a mineral acid, such as hydrochloric acid.

TABLE I
TLC RESULTS (R_F VALUES)

<i>Synthetic mixture</i>	<i>Identification</i>
0.14–0.26	TLC artifact
0.35	BDS
0.52	SPT
0.58	TPS
0.71	DPTS

The order of retention appeared to be related to the relative importance of the triphenylsulfonium (TPS) segment in the molecule. It was concluded that the more predominant the TPS segment, the greater is the compound's affinity for the silica gel stationary phase. Furthermore, the R_F values were found to be highly dependent on the pH of the mobile phase, tending rapidly towards zero as the pH exceeded 2.0 [BDS in methanol–water (90:10), pH adjusted with HCl to pH 1.0, $R_F = 0.35$; at pH 2.0, $R_F = 0.05$; for TPS at pH 1, $R_F = 0.58$; at pH 2, $R_F = 0.28$].

Spectroscopic analysis of the recovered compounds showed silica contamination and anionic exchange, *i.e.*, chloride substituting for hexafluorophosphate. Silica contamination of the isolated products is due to the appreciable solubility of silica in acidic methanol–water solvent. A significant portion of this solubilized silica probably exists as methyl esters of silicic acid. Thus, the isolation of pure TLC separated compounds must allow for the removal of these esters. Pure hexafluorophosphate salts were found to be obtainable by adding an excess of the hexafluorophosphate anion (see *Methods*).

ACKNOWLEDGEMENTS

The author thanks Mr. H. Pobiner for suggesting TLC as a potential method for separating these compounds, Drs. S. Schlesinger and W. Watt for samples of the triarylsulfonium salts and their helpful suggestions, Drs. F. Loprest, H. Hoffman and L. Schkolnick for their comments and support and the American Can Company for permission to publish this paper.

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