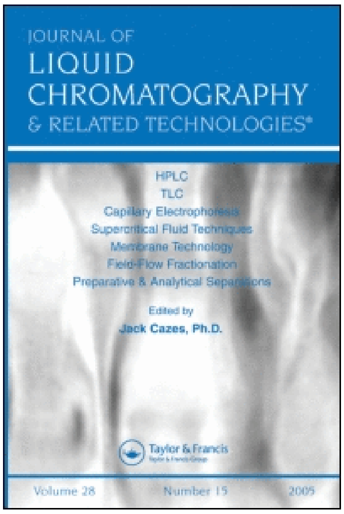

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A Direct Fractionation Procedure for the Quantitative Resolution of Triphenylphosphine-Desulfurization Products by Silica Gel Liquid Chromatography

Shoji Hara[a]; Kitaro Oka[a]
[a] Tokyo College of Pharmacy Horinouchi, Tokyo, Japan

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A DIRECT FRACTIONATION PROCEDURE FOR THE QUANTITATIVE RESOLUTION OF TRIPHENYLPHOSPHINE-DESULFURIZATION PRODUCTS BY SILICA GEL LIQUID CHROMATOGRAPHY

Shoji Hara and Kitaro Oka
Tokyo College of Pharmacy
Horinouchi, Hachioji, Tokyo 192-03, Japan

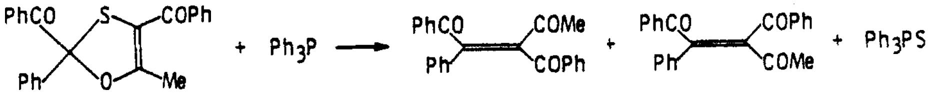
ABSTRACT

A direct fractionation procedure involving a high efficiency LC column was used to resolve and isolate the triphenylphosphine-desulfurization products from their crude reaction mixture. Elimination of the reagent and reagent-origin material, and quantitative resolution of a pair of the geometrical isomers in a silica gel binary solvent system were simultaneously accomplished.

INTRODUCTION

Desulfurization with triphenylphosphine has been widely used in synthetic organic chemistry. However, one of the disadvantages of this method is the difficulty found in the working-up procedures to separate excess reagent from the desired products. These components usually have similar solubilities in the organic solvents used for extraction and recrystallization, and, in the worst case, similar mobilities on silica gel LC.

One of the authors (Hara) has developed a direct fractionation procedure (DFP) for the reaction products to systematize and simplify the separation process in synthetic chemistry (1-4). This method has made it possible to obtain highly pure products in quantitative yields. We will report herein an application of the method to the isolation of triphenylphosphine-desulfurization products.



1 2 3 4 5

EXPERIMENTAL

The 1,3-oxathiol **1** (20 mg, 52 nmol) was dissolved in 2.5 ml of xylene containing Ph$_3$P (41 mg, 157 nmol) and the mixture was refluxed for 8 hrs. The resulting mixture was cooled and then put on a high efficiency column (Zorbax silica, Shimadzu Co., Kyoto; 9 mm I.D. x 50 cm) by on-column injection. The column was connected with a pump (Model KP-9H, Kusano Scientific, Tokyo) and RI detector (Model 110, Waters, Ma., USA). The solvent system was optimized to 13% v/v EtOAc in *n*-hexane. Flow rate was 3.8 ml/min. The capacity ratios of **3** and **4** were k_3 = 3.82 and k_4 = 4.64; separation factor α = 1.21. The yields were Ph$_3$P, 28 mg (100%); Ph$_3$PS, 13 mg (86%); **3**, 8 mg (43%); **4**, 3 mg (17%); and other small amounts of side products.

RESULTS AND DISCUSSION

The 1,3-oxathiol **1** was treated with a three molar equivalents of triphenylphosphine in refluxing xylene (5). The TLC analysis of the resulting mixtures showed three major spots which were assigned as the recovered reagent **2**, its thioxide **5**, and the plural products **3** and **4** together with several minor spots some of which overlapped the major spots (Figure 1). A trial fractionation of these components by conventional column liquid chromatography was unsuccessful. Thus we examined the direct fractionation procedure using

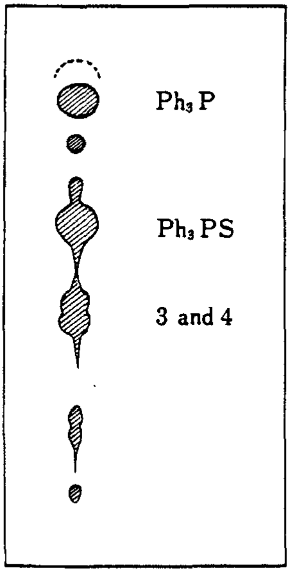


FIGURE 1

TL chromatogram of the reaction mixture developed with 20% v/v EtOAc in _n_-hexane and detected with UV lamp.

a highly efficient preparative silica gel column equipped with a differential refractometer to obtain fractions exhibiting the peaks of the solvent (xylene), triphenylphosphine, thioxide, several side products, and the desired main products. The silica gel-binary solvent system which was optimized by using TLC as the pilot technique (1) was adjusted. The main products were resolved with the separation factor of $\alpha = 1.21$ and were fractionated quantitatively. The chromatogram is shown in Figure 2 and the NMR spectra of these

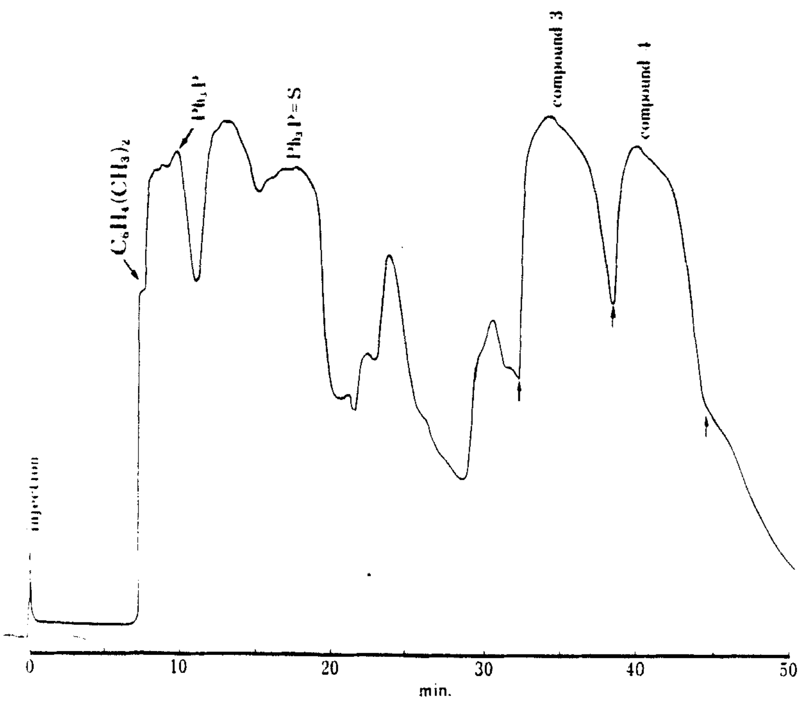


FIGURE 2

Preparative chromatogram of the reaction mixture on Zorbax silica column (9 mm I.D. x 50 cm) with 13% v/v EtOAc in n-hexane.

main products in Figure 3. The structures of the compounds **3** and **4** were assigned in relation of the olefin-geometrical isomers. Such a resolution of a pair of isomers has been known as a rather difficult problem in the chromatographic separations. DFP involves no pretreatment of the reaction mixtures so as to be simple and facile procedure to obtain the sample recovery with high purities and high yields.

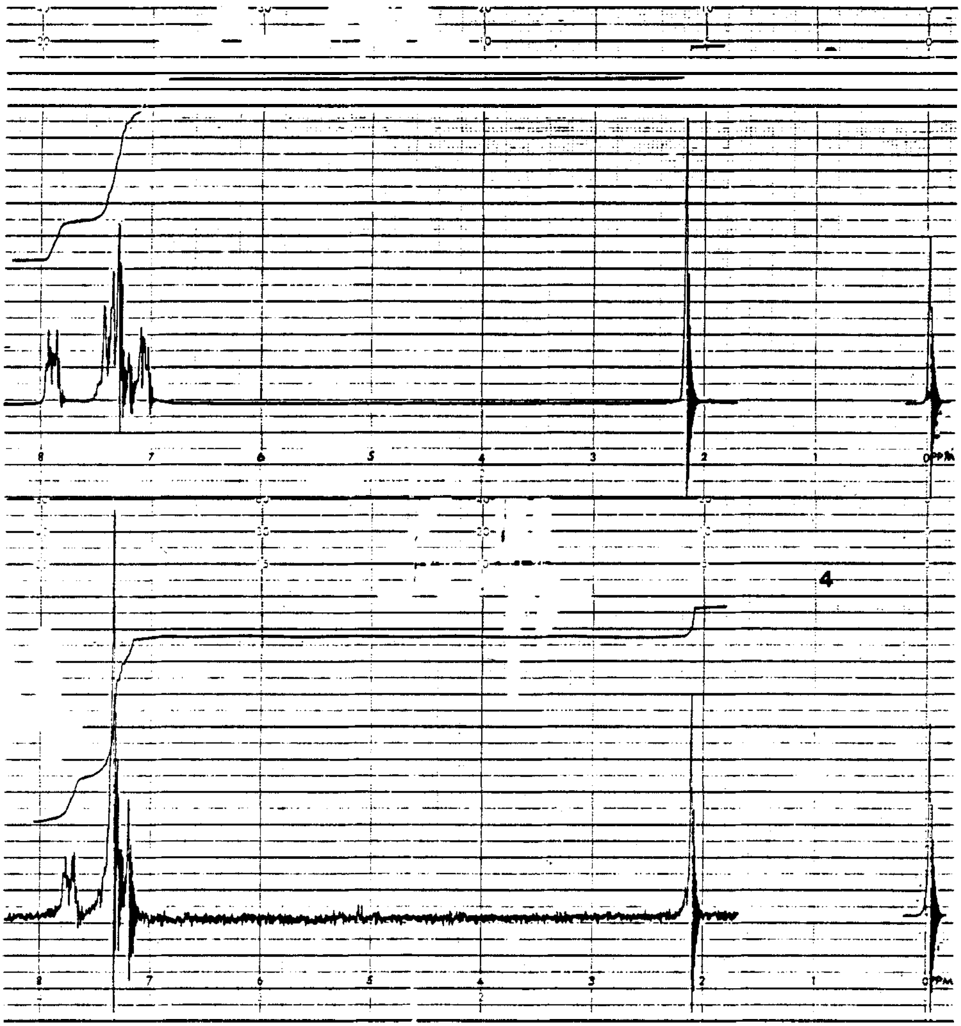


FIGURE 3

NMR spectra of the compounds 3 and 4 obtained in $CDCl_3$ solution and TMS as an internal standard at 100 MHz (JEOL-PS-100) aparatus.

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