Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Suzuki, A. , Kunieda, N. and Kinoshita, M.(1978) 'Reaction Products of Thioanisole with formaldehyde', Journal of Macromolecular Science, Part A, 12: 8, 1143 — 1149
To link to this Article: DOI: 10.1080/00222337808063180
URL: http://dx.doi.org/10.1080/00222337808063180

J. MACROMOL. SCI.–CHEM., A12(8), pp. 1143-1149 (1978)

Reaction Products of Thioanisole with Formaldehyde

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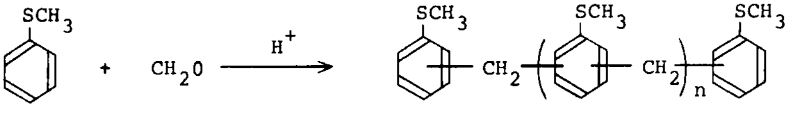
ABSTRACT

The acid-catalyzed condensation reaction of thioanisole (I) with formaldehyde was carried out in benzene in the presence of p-toluenesulfonic acid. Two compounds, a dimer (II) and a trimer (III) of thioanisole linked by a methylene group, were isolated from the reaction mixture as main products on the initial stage of this reaction.

INTRODUCTION

During the course of our studies on the acid-catalyzed reaction of aromatic compounds containing a sulfur atom with formaldehyde [1-4], previously, we have reported that four poly(methylene diphenyl sulfides), $C_6H_5{-}S{-}C_6H_4{-}(CH_2{-}C_6H_4{-}S{-}C_6H_4)_n{-}CH_2{-}C_6H_4{-}S{-}C_6H_5$ (n = 0, 1, 2, 3), were isolated as the products on the initial stage of the reaction [1]. Hamamura et al. [5] have reported that thiophenol reacted with formaldehyde in the presence of acid catalyst to give the resin. Moreover, we have found, by kinetic studies, that the effect of substituents on benzene ring of several homologous compounds of diphenyl sulfide such as C_6H_5X (X: OCH_3, SCH_3, OC_6H_5, SC_6H_5, CH_3, C_6H_5) in the acid-catalyzed reaction with formaldehyde was unified with Brown-Okamoto's σ^+ values ($\rho = -5.76$) [2, 3]. Actually, the rate of the reaction of thioanisole was found to be about fourteenfold faster than that for diphenyl sulfide, which is attributed to the large negative σ^+ value (-0.604) [6] for the methylthio (CH_3S–) group. This fact prompted us to examine the acid-catalyzed reaction of thioanisole with formaldehyde. In this paper, we wish to report on the reaction products which were obtained on the initial stage of the reaction of thioanisole with formaldehyde in the presence of p-toluenesulfonic acid as a catalyst.



II; n = 0, III; n = 1,

and oligomer

EXPERIMENTAL

General

IR spectra were taken with a Jasco IR-G type spectrometer. NMR spectra were determined with a Hitachi Perkin-Elmer R-20 spectrometer with tetramethylsilane as the internal standard. The melting points were taken on a Yanaco MP-type apparatus. The molecular weights were taken on a Knauer vapor-pressure osmometer with benzene as solvent at 45°C. Thin-layer chromatography (TLC) was carried out on silica gel (Merck, GF254) with the use of carbon tetrachloride as the developing solvent.

Materials

Thioanisole was prepared by the methylation of thiophenol with dimethyl sulfate in alkaline solution, according to the method of Suter and Hansen [7]; bp 82-83°C/18 Torr. (lit. [7] bp 58-60°C/6 Torr). α-Polyoxymethylene of commercial grade was used as formaldehyde source.

TABLE 1. Reaction of Thioanisole with Formaldehyde at 80°C

No.	Thioanisole (g)	F (g)[a]	Solvent (ml)[b]	Catalyst (g)[c]	Time (hr)	Yield (g)[d]
1	4.32	4.08	B, 50	Ts, 1.0	19	4.05
2	6.20	7.34	B, 100	Ts, 2.0	35	6.12
3	13.6	13.5	A, 80	H_2SO_4, 1.0 ml	8	11.2

[a] F = α-polyoxymethylene.
[b] Solvents: B = benzene, A = CH_3COOH.
[c] Catalyst: Ts = p-toluenesulfonic acid.
[d] Yield of the reaction product.

Reaction of Thioanisole with Formaldehyde

Adequate amounts of thioanisole, α-polyoxymethylene, p-toluenesulfonic acid, and benzene were placed in a three-necked flask fitted with a stirrer, a thermometer, and a condenser. The mixture was stirred at 80°C. After completion of the reaction, the mixture was poured into a large amount of ice water, neutralized with an aqueous solution of sodium carbonate, and extracted with benzene. The benzene layer was condensed under reduced pressure to obtain the resinous products. The conditions of the reaction are listed in Table 1.

Separation of the Reaction Products

By means of column chromatography on silica gel (Mallinckrodt, 100 mesh) with carbon tetrachloride as eluent, the reaction products were fractionated into four fractions. The R_f values and weight percent of the components in the resinous products are listed in Table 2.

RESULTS AND DISCUSSION

At first, the acid-catalyzed reaction of thiophenol with formaldehyde was carried out in benzene at 80°C to obtain the resinous products. From the reaction products, two fractions were separated by column chromatography on silica gel, by using carbon tetrachloride as eluent. IR spectra of these fractions exhibited no absorptions at 2550 cm^{-1}

TABLE 2. Separation of the Reaction Products

Fraction[a]	R_f[b]	Amount present in the reaction products (%)	Appearance
1	0.80	9.3	Liquid
2	0.54	34.8	Viscous liquid
3	0.25	20.7	Viscous liquid
4	<0.20	35.2	Viscous liquid

[a] Separated from the reaction products (2.00 g) of run 2 in Table 1 by column chromatography.

[b] Determined by TLC on silica gel using carbon tetrachloride as the developing solvent.

due to the mercapto group. In NMR spectra (in $CDCl_3$), two compounds obtained from the first fraction and the second fraction showed signals at 4.30 ppm and at 4.30 and 4.02 ppm due to methylene protons, respectively. Moreover, by elemental analyses, these compounds are assumed to be $C_6H_5{-}S{-}CH_2{-}(C_6H_4{-}S{-}CH_2)_n{-}S{-}C_6H_5$ (n = 0, 1).

ANALYSIS. Calcd for $C_{13}H_{12}S_2$, n = 0: C, 67.20%; H, 5.21%. Found: C, 66.73%; H, 4.96%. Calcd for $C_{20}H_{18}S_3$, n = 1: C. 67.75%; H, 5.12%. Found: C, 67.43%; H, 4.97%.

When thioanisole was treated with formaldehyde in benzene in the presence of p-toluenesulfonic acid, the reaction took place readily to yield the resinous products. Thin-layer chromatography (TLC) showed four spots (see Table 2). These components were fractionated by column chromatography.

From the second fraction, a viscous material was obtained. Crystallization from petroleum ether yielded the compound II as colorless needles with the melting point of 64-66°C. The IR spectrum of II has marked absorptions at 2900 and 1400 cm^{-1}, at 1340 cm^{-1}, and at 740 cm^{-1} due to methylene, methyl, and $-S-$ groups, respectively. The NMR spectrum (Fig. 1) shows signals at 2.37 ppm, at 3.80 ppm, and at 7.00 ppm (in CCl_4) due to methyl, methylene, and phenyl protons, respectively. From these results, the compound II was assumed to be a dimer of thioanisole linked by a methylene group. The elemental analysis and the molecular weight measurement of II were identical with those of methylenebisthioanisole.

ANALYSIS. Calcd for $C_{15}H_{16}S_2$ (II): C, 69.23%; H, 6.16%; MW, 260. Found: C, 68.87%; H, 6.19%; MW, 266.

Supposing two methylthio groups on the compound II are situated

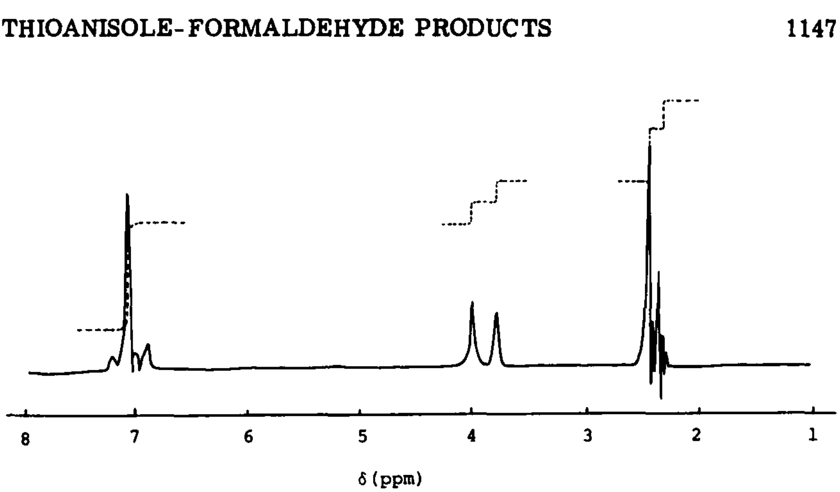
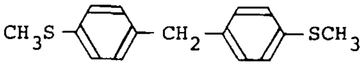


FIG. 1. NMR spectrum of compound II.

at the asymmetrical positions, the NMR spectrum of II should exhibit two kinds of signal due to methyl protons of the methylthio groups. Thus, the compound II is assumed to be either o,o'- or p,p'-methylene linked compound. However, from the fact that the absorptions due to ν(CH) of benzene ring were observed at 800 and 780 cm^{-1}, it may be concluded that the compound II is p,p'-methylenebisthioanisole as shown below.



II

Crystallization of the third fraction from n-hexane yielded compound III as colorless needles with a melting point of 45-46°C. The IR spectrum of III has marked absorptions at 2900, 1470, and 1400 cm^{-1}, at 1320 cm^{-1}, and at 740 cm^{-1} due to methylene, methyl, and –S– groups, respectively. The NMR spectrum (Fig. 2) shows signals at 2.32 and 2.37 ppm, at 3.77 and 3.93 ppm, and at 7.00 ppm (in CCl_4) due to methyl, methylene, and phenyl protons, respectively. The elemental analysis and the molecular weight measurement of III were identical with those of a trimer of thioanisole with the methylene linkage.

ANALYSIS. Calcd for $C_{23}H_{24}S_3$ (III): C, 69.70%; H, 6.06%; MW, 396. Found: C, 69.50%; H, 6.11%; MW, 396.

As shown in the NMR spectrum of III, compound III exhibited two kinds of signal to methylene protons at 3.77 ppm and at 3.93 ppm, and the ratio of area of these signals was 1:1. The signals due to

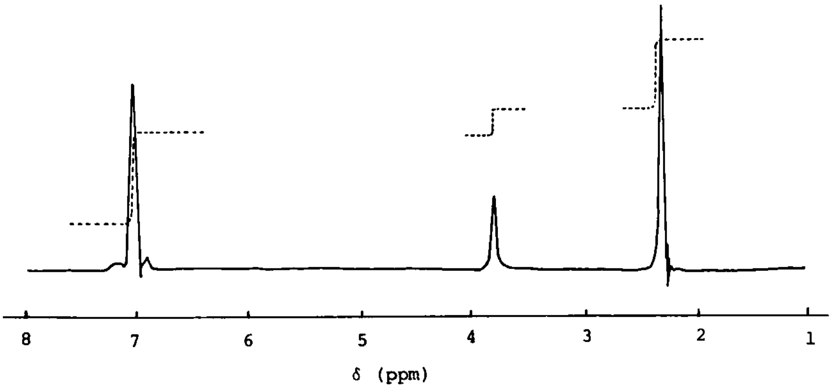
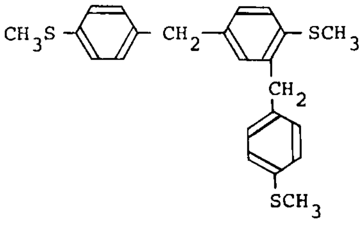


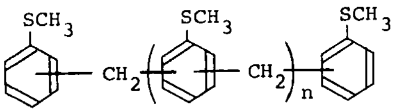
FIG. 2. NMR spectrum of compound III.

methyl protons were also observed at 2.32 ppm and at 2.37 ppm, and the ratio of area of these signals was 1:2. This fact indicates that two methylene groups in III are linked at two different positions on the benzene ring. Accordingly, the compound III may be thought to be the p,p',o-methylene-linked trimer of thioanisole as shown below.



III

The viscous material from the fourth fraction had a molecular weight of 663. This material is a mixture of methylene-linked compounds with n = 2-4 in the following structural formula:



The compound obtained from the first fraction was a liquid. The IR spectrum was identical with that of recovered thioanisole.

More detailed studies for the structural implications of the fourth fraction and the physical property of the resin will be subject of a forthcoming paper in this series.

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Accepted by editor April 15, 1978
Received for publication June 6, 1978