J. Org. Chem. **1991,** *56,* 3263-3267

setting angles of 25 reflections. Data were corrected for Lorentz and polarization effects and for absorption by means of DIFABS[33] (based on spherical polar angles); the phase problems for all structures were solved directly, using MULTAN.[34] Hydrogen atoms were entered in calculated positions with isotropic temperature factors 1 Å^2 greater than that of the carbon atoms to which they are bound. Atomic scattering factors were taken from standard tables.[35] Enantiomorphs for **1e** and **3e** were not determined; however, the internal consistency of the pairs of chemically equivalent bond lengths and angles in each structure and the congruency of bond lengths and angles with other members of the family is sufficient evidence that neglect of enantiomorph determination has not led to systematic errors in metrical details that might compromise the conclusions reached in this study. In **3e**, the quality and extent of the data are such that anomalous scattering by S (under Cu K_α radiation) is barely significant. In **1e**, where the X-ray diffraction data set is more extensive than for **3e**, the anomalous scattering by S (under Mo K_α radiation), while (in principle) detectable, would lead to differences in bond lengths of no more than a few thousandths of an Å, a perturbation much less than that (0.05 Å, or $>5\sigma$) for which we have perceived structural differences to be significant.

Molecular Orbital Calculations. MNDO[36] calculations were performed with use of the MOPAC[37] program on a VAX 11/750 VMS computer. Initial bond lengths and angles were obtained from standard literature tables[38] and X-ray data. All geometric parameters were optimized with no specific assumptions; the keyword PRECISE was utilized—the maximum gradient at optimization was less than 5.0 for all conformers.

Molecular Diagrams. Three-dimensional representations of X-ray and MNDO structures were drawn with the PLUTO program (SDP, from Frenz and Associates and Enraf Nonius) interfaced to a Tektronix 4106 graphics terminal and a Tektronix 4662 plotter.

Chemistry. Sulfilimines **1e**–**3e** were prepared by the modified Chloramine-T method.[39] X-ray quality crystals were prepared by recrystallization from $CHCl_3/c\text{-}C_6H_{12}$ 1:1. Melting points (°C) and $\nu(S{=}N)$ (cm^{-1}) are as follows: **1e**, 169, 901; **2e**, 171, 923; and **3e**, 167, 924. Additional experimental data are summarized in the supplementary material section.

Acknowledgment. We gratefully acknowledge the assistance of Dr. Pedro Gomez-Romero and Dr. Miklos Kertesz, Georgetown University, for access to and use of PLUTO and MOPAC, respectively, and the Academic Computer Center, Georgetown University, for VAX computer time. The Bruker AM-300 WB NMR spectrometer utilized in this study was funded by NSF Grant CHE-8406088 and the W. M. Keck Foundation.

Supplementary Material Available: Comparative bond distances and angles vs similar derivatives, comparative bond distances and angles vs other nonsimilar tosylsulfilimines, átomic coordinates and anisotropic displacement parameters, hydrogen atom parameters, bond distances and angles, ASIS (^{1}H NMR) and ^{13}C NMR parameters, MNDO heats of formation, selected bond distances and angles, and optimized geometries (Cartesian coordinates) for **1e**, **2e**, and **3e** (22 pages). Ordering information is given on any current masthead page.

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(33) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158–66.

(34) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Universities of York, England and Louvain, Belgium, 1978.

(35) *International Tables for X-Ray Crystallography*, Vol. III; Kynoch Press: Birmingham, England, 1982.

(36) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–907. For a more recent update and review, see: (b) Dewar, M. J. S. *J. Mol. Struct.* **1983**, *100*, 41–50. For general overviews, see: (a) Sadlej, J. *Semi-Empirical Methods of Quantum Chemistry*; Ellis-Horwood, Ltd.: Chicester, 1985. (b) Clark, T. *A Handbook of Computational Chemistry*; Wiley-Interscience: New York, 1985; Chapter 4.

(37) MOPAC (MNDO version 3.00; QCPE publication #455); Stewart, J. P.; Frank J. Seiler Res. Lab., U.S. Air Force Academy, Colorado Springs, CO 80840.

(38) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons, Inc.: New York, 1985; pp 18–21, and references cited therein.

(39) (a) Svoronos, P. D. N.; Horak, V.; Zuman, P. *Phosphorus, Sulfur and Silicon* **1989**, *42*, 139–47. (b) Svoronos, P. D. N. Ph.D. Dissertation, Georgetown University, Washington, DC, December 18, 1980. (c) Svoronos, P. D. N.; Horak, V. *Synthesis* **1979**, 596–8.

Stilbenes from Sulfur-Mediated Dehydrodimerization of Substituted Toluenes

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When provision is made for removal of coproduct hydrogen sulfide, the reaction of sulfur with methyl *p*-toluate (MPT; **1**) at 280 °C leads to 70+% yields of the product dimethyl *trans*-4,4′-stilbenedicarboxylate (DMSC, **2**) if conversion of the MPT is restricted to ca. 10%. Diphenyl ether or excess MPT serves as the reaction solvent. Other products of the reaction include dimethyl 4,4′-bibenzyldicarboxylate (DBD, **3**), 1,2,3-tris(4-carbomethoxyphenyl)propane (**4**), 1,2,3-tris(4-carbomethoxyphenyl)propene (**5**; mixture of *E* and *Z* isomers), and 2,3,4,5-tetrakis(4-carbomethoxyphenyl)thiophene (**6**). The products are consistent with the reversible formation of 4-carbomethoxybenzyl radicals from sulfur and MPT where removal of the hydrogen sulfide drives the reaction forward.

Introduction

It has been known since early in this century that at least small quantities of stilbene can be isolated from the reaction products of toluene and sulfur[1] and that other aryl methanes are coupled by sulfur to the corresponding 1,2-diarylethylenes.[2] Processes for carrying out this reaction efficiently on toluene were described in a patent by Bhasin and Williamson.[3] Toland demonstrated that toluenes

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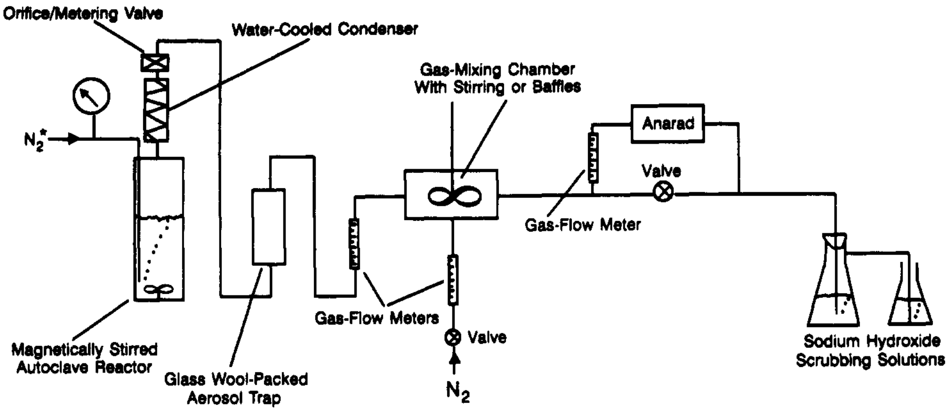
(1) Aronstein, L.; van Nierop, A. L. *Recl. Trav. Chim. Pays-Bas* **1903**, *21*, 488.

(2) Friedman, W. *Ber.* **1916**, *49*, 277, 1334, 1352, 1551.

(3) Bhasin, M. M.; Williamson, K. D. U.S. Patent 3548018, 1970.

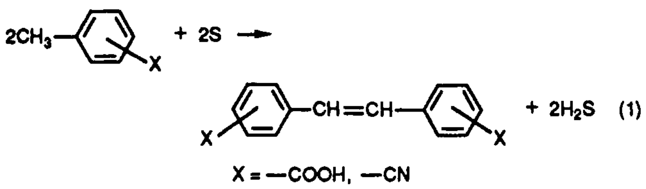
0022-3263/91/1956-3263$02.50/0



* N_2 Pressure-Regulated Nitrogen Sources

Figure 1. Typical configuration for sulfur/MPT reactions.

substituted with either carboxy or cyano groups can be utilized as substrates:[4-6]



Unexpectedly, it was discovered in these laboratories that the carbomethoxy group (X = $-COOCH_3$) is stable to the rather rigorous conditions (contact with sulfur at 280 °C) of the dehydrodimerization reaction. Thus, dimethyl *trans*-4,4′-stilbenedicarboxylate (DMSC), a building block for some novel polyester compositions,[7] is available in one step from methyl *p*-toluate. We have studied the characteristics of this reaction in some detail and report our findings herewith.

Experimental Section

General Procedure. NMR spectra of the isolated and synthesized standards were recorded in $CDCl_3$ solvent on JEOL spectrometers, Models GX-270 and GX-400. Liquid chromatographic (LC) analyses were performed on a Perkin-Elmer Series 3B instrument. The column was a 15-cm Waters NovaPak C18, and the gradient solvent was acetonitrile/water (50–99% AN) maintained at a flow rate of 2 mL/min. The UV detector was set at 235 nm.

Materials. Methyl *p*-toluate (MPT; **1**) was technical-grade material that had been distilled, allowed to crystallize, and then drained and washed of any residual meta isomer or methyl benzoate present; the melting point of the material was 37 °C. A few runs were made with Aldrich Gold Label MPT; no difference in reactivity was observed. Sulfur was Mallinckrodt sublimed USP grade. A few experiments were done with Aldrich Gold Label (99.999%) sulfur; no differences were observed in the reactivity of the two grades. Diphenyl ether was Eastman Kodak White Label grade material and was used directly. Nitrogen used for the gas sparging stream was from Air Products and listed as 99.99% or better. All other chemicals used were reagent grade or better.

Samples of reaction products were required for calibration of gas and liquid chromatographic analyses. Pure DMSC (**2**) was obtained by repeated recrystallization of reaction product from methyl benzoate, mp 235–237 °C (lit.[8] mp 234, 227–228 °C). Dimethyl 4,4′-bibenzyldicarboxylate (DBD; **3**) was obtained by hydrogenation of purified DMSC (5% Pd/C catalyst in methyl benzoate solvent, 110 °C, 150 psig H_2) and recrystallization of the product from ethanol, mp 117–120 °C (lit.[9] mp 117–118 °C).

1,2,3-Tris(4-carbomethoxyphenyl)propane and 1,2,3-Tris(4-carbomethoxyphenyl)propene (*E* and *Z* Isomers) ($Ar_3C_3H_5$ and $Ar_3C_3H_3$; 4, 5). These products were isolated from ~100 g of reaction product filtrate by first separating them from other materials with flash chromatography on silica gel. Solvent washings were made progressively more polar with heptane/ethyl acetate (98/2–0/100%) and then methylene chloride/acetonitrile (100/0–94/6) to elute a mixture of **4** and **5**. The individual components were separated from the flash chromatographic fraction by preparative LC with a C-18 column and acetonitrile/water elutant (gradient, 50–100% MeCN). A total of 66 mg of the saturated product were obtained as a semicrystalline solid: 1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.3 Hz, 6 H), 7.05 (overlap doublets, J = 7.6 Hz, 6 H), 3.86 (s, 3 H), 3.85 (s, 6 H), 3.21 (cx, 1 H), 3.07 (d, d, J = 17.0, 7.0 Hz, 2 H), 2.97 (d, d, J = 17.0, 8.2 Hz, 2 H); IR (film) 1715, 1605, 1435, 1280, 1180, 1110, 1020, 860, 775, 750, 710 cm^{-1}; mol wt by HRMS 446.1710, calcd for $C_{27}H_{26}O_6$ 446.1722. The unsaturated product, 44 mg of a solid was judged to be an *E*/*Z* mixture in approximately 60/40 ratio: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0–6.9 (cx, 12 H, aromatic, 1 H, vinyl), 6.56 (s, 1 H, vinyl), 4.18 (s, 2 H, benzyl), 3.90 (s, 3 H, CH_3O), 3.88 (s, 3 H, CH_3O), 3.86 (s, 3 H, CH_3O), 3.84 (s, 2 H, benzyl); IR (film) 1720, 1605, 1435, 1280, 1180, 1110, 775, 750, 710 cm^{-1}; mol wt by HRMS 444.1570, calcd for $C_{27}H_{24}O_6$ 444.1566.

2,3,4,5-Tetrakis(4-carbomethoxyphenyl)thiophene (Ar_4Thio; 6) was synthesized from DMSC by the following procedure: A 50-mL round-bottom flask was charged with 5.92 g (0.02 mol) of DMSC, 0.96 g (0.03 g atom) of powdered sulfur, and 24 mL of diphenyl ether solvent. The mixture was heated to 240 °C and held at this temperature while a slow purge of argon (ca. 0.1 SCFH) was delivered to the bottom of the flask. Evolution of hydrogen sulfide did not seem to be complete after 96-h reaction time, but workup was started with removal of the diphenyl ether solvent at 20 Torr with a hot air gun. The residue was taken up in 25 mL of hot acetone and allowed to cool; 0.5 g of unconverted DMSC could be recovered by filtration. The acetone was evaporated from the filtrate and the residue taken up in ~25 mL of hot ethyl acetate and methanol added to the point of incipient cloudiness. Cooling the mixture slowly near 0 °C precipitated ~3.5 g of yellow, crude product. Two additional recrystallizations from ethyl acetate yielded 0.73 g of light yellow crystals: mp 122–124 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 4 H), 7.81 (d, J = 8.3 Hz, 4 H), 7.26 (d, J = 8.3 Hz, 4 H), 7.01 (d, J = 8.3 Hz, 4 H), 3.90 (s, 6 H), 3.88 (s, 6 H); exact mass by

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[4] Toland, W. G.; Wilkes, J. B.; Brutschy, F. J. *J. Am. Chem. Soc.* **1953**, *75*, 2263.

[5] Toland, W. G.; Wilkes, J. B. *J. Am. Chem. Soc.* **1954**, *76*, 307.

[6] Toland, W. G. U.S. Patent 2688631, 1954.

[7] Jackson, W. J.; Morris, J. C. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1985**, *41*, 307.

[8] Fulton, J. D. *Brit. J. Pharmacol.* **1948**, *3*, 75. Hager, G. P.; VanArendonk, A. M.; Shonle, H. A. *J. Am. Chem. Soc.* **1944**, *66*, 1982.

[9] Sloan, G. J.; Vaughn, W. R. *J. Org. Chem.* **1957**, *22*, 750. Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691.

Table I. Reaction of Methyl *p*-Toluate ($ArCH_3$) with Sulfur, Diphenyl Ether Solvent[a] (Sulfur Added Batchwise at Start of Reaction)

	reactants and solvent, mol			reaction time,[b]	products, mol × 10^3 (% yields)						total	
run no.	$[MPT]_0$	$[S]_0$	$[Ph_2O]_0$	min	$(ArCH)_2$[c]	$(ArCH_2)_2$	$Ar_3C_3H_5$	$Ar_3C_3H_3$	Ar_4Thio	toluic acid	MPT,[d] mol × 10^3	H_2S, mol (% $[S]_0$)
007	2.00	0.50	2.00	210	119.2 (56.6)	41.5 (19.7)	6.9	8.9	13.0		420.8	0.45 (91)
035[e]	4.00	0.40	0	170	108.1 (57.4)	49.2 (26.1)	10.5	5.8	3.3		376.7	0.46 (115)
037[e,f]	4.00	0.80	0	200	179.8 (52.7)	89.0 (26.1)	18.3	12.3	13.1		681.8	
046	2.00	0.20	2.00	165	65.6 (69.3)	16.2 (17.1)	2.7	2.7	2.4		189.4	0.17 (85)
048	~2.00[g]	0.20	~2.00	200	66.7 (63.6)	20.1 (19.2)	4.5	2.9	3.5		209.8	0.18 (88)
071	2.00	0.20	2.00	180	68.0 (71.7)	11.0 (11.6)	3.3	4.6	2.0		189.8	0.19 (95)
037A	2.00	0.20	1.76	200	72.2 (70.3)	10.8 (10.5)	4.1	4.9	1.8	5.1	205.3	
044	1.00	0.20	2.65	150	73.4 (72.7)	10.6 (10.5)	3.7	4.0	1.8	3.3	201.6	
056	0.50	0.20	3.08	500	46.2 (64.1)	7.2 (10.0)	1.3	2.2	6.2	1.3	144.2	
073	4.00	0.40	0	140	116.9 (59.5)	30.6 (15.6)	13.5	12.3	5.1		392.8	0.37 (92)
079	4.00	0.20	0	80	68.1 (72.2)	11.7 (12.4)	4.1	4.1	1.1		188.6	0.18 (88)
051	4.00	0.20	0	150	71.6 (74.6)	6.2 (6.5)	3.2	3.3	1.7	10.1	192.1	
011[g]	4.00	0.20	0	220	80.6 (75.0)	7.6 (7.1)	3.1	5.7	1.4	6.2	214.7	
034[g]	2.00	0.14[h]	1.76	390	48.3 (83.3)	2.8 (4.9)		2.2	1.1	2.6	115.9	
134[i]	2.00	0.20	2.00	1440	14.5	91.2			~9			

[a] All reaction were run at 280 °C, 100 psig with N_2 sparging rate of 2.0 SCF/h unless otherwise noted. [b] Reaction was continued until H_2S concentration in nitrogen sparge gas was less than 0.1 vol %. [c] Ca. 19/20 of the stilbene product crystallized from the product mixture on cooling to ambient room temperature. This figure includes both dissolved and precipitated product. [d] Calculated from 2*([ArCH=CHAr] + [$ArCH_2CH_2Ar$]) + 3*([$Ar_3C_3H_5$] + [$Ar_3C_3H_3$]) + 4*[Ar_4Thio] + [Toluic Acid] (if listed). [e] Reactor pressure, 200 psig. [f] Nitrogen sparging rate, 3.0 SCFH. [g] Reaction temperature, 260 °C. [h] 0.20 mol sulfur charged to reactor, 0.06 mol determined to be in product filtrate by LC analysis. [i] No nitrogen sparge, closed reactor.

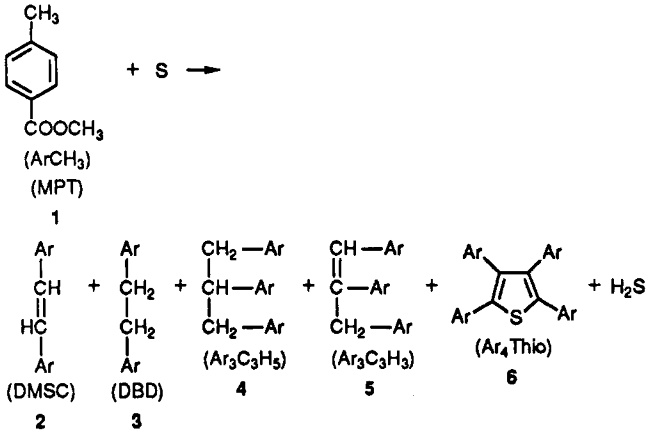
EI 620.1493, calcd for $C_{36}H_{28}O_8S$ 620.1497.

Apparatus and Procedure. Modest pressures are created by raising the principal reactant, MPT, to 280 °C; the vapor pressure of MPT is 3160 Torr = 61 psia = 46 psig at this temperature. The reaction was carried out, therefore, in an Aminco magnetically stirred autoclave with ancillary connections as shown schematically in Figure 1. In most runs, the reactants (MPT, sulfur, and diphenyl ether solvent) were charged to the reactor, which was pressured to a regulated 100 psig with nitrogen. Heat was then applied to the autoclave. The regulating valve on top of the condenser was adjusted to give a nitrogen thruput of 2.0 SCFH. After passing through an aerosol trap, the effluent gas was directed past a hydrogen sulfide measuring cell (Anarad Model Ar-440), which was calibrated for the 0–15 vol % concentration range. A gas dilution capability was included for the few instances when the concentration of hydrogen sulfide in the off-gas greatly exceeded 15%. Generally, much poorer reproducibility was the consequence of trying to bring the concentration back in range by additional nitrogen dilution. Effluent gas from the analyzer was scrubbed twice with 10% sodium hydroxide solution. At the end of a run, the sodium hydroxide solutions were combined, weighed, and sampled for sulfide analysis by titration.

Workup and Analyses. In general, all experiments were carried out with an excess of methyl *p*-toluate, and the reaction was continued until no more hydrogen sulfide (less than 0.1%) was being sparged from the reactor. At the conclusion of the reaction, the reactor was allowed to cool with stirring wherein the principal product, DMSC, readily crystallized out of the remaining MPT (or MPT–diphenyl ether mixture). The DMSC was collected by filtration, washed with methanol until free of MPT, dried, and weighed. Assays of the isolated DMSC by gas chromatography (GC) were usually performed, and high purities (98+%) were typical. A sample of the filtrate was analyzed by calibrated LC for residual DMSC, DBD, the triarylpropane and propenes, and the tetrarylthiophene. One filtrate was examined by an LC–MS technique for further minor reaction products. In addition to the previously listed products, only 2-(4-carbomethoxyphenyl)-5-carbomethoxybenzothiophene was tentatively identified. It is present at the lowest level of the identified products. The results of the above analyses on 22 runs are collected in Table I.

The readings of the hydrogen sulfide meter are indicative of the instantaneous reaction rate when combined with the measured flow rate from the reactor. Integration of hydrogen sulfide evolution rate vs time curves was used to confirm the total hydrogen sulfide evolution as determined from scrubber solution titrations as well as from sulfur charged to the system. (Most of the products of the reaction are non-sulfur containing.)

Scheme I. Reactants, Products, and Their Abbreviations



Results and Discussion

Product Analysis. The reactants, principal products and their abbreviations are illustrated in Scheme I. A summary of the product data and computed yields of DMSC and DBD is shown in Table I. In general, the yields from these batch runs are consistent with earlier experiments (results not shown) where reaction times were much longer, typically 12–20 h. Thus, the products of the reaction are stable at the reaction temperatures, and the results are not confounded by thermal degradation of the primary products. Usually, where MPT conversions are limited to 5 or 10%, DMSC yields are 70% or better and an additional 10% of the MPT consumed forms DBD. Thus, the reaction is moderately selective. Product qualities are excellent with the sulfur content of the DMSC, as collected directly from the product mixture, in the 100–200 ppm range. Higher conversions seem to accentuate the formation of DBD at the expense of DMSC and produce product of higher sulfur content.

The LC chromatogram of a typical product filtrate is shown in Figure 2. The major peaks were calibrated from synthesized or isolated standards (Experimental Section), but a few minor unassigned peaks remain in the LC trace. The only identified minor component (not shown in Figure 2) is the 2-(carbomethoxyphenyl)-6-carbomethoxybenzo-

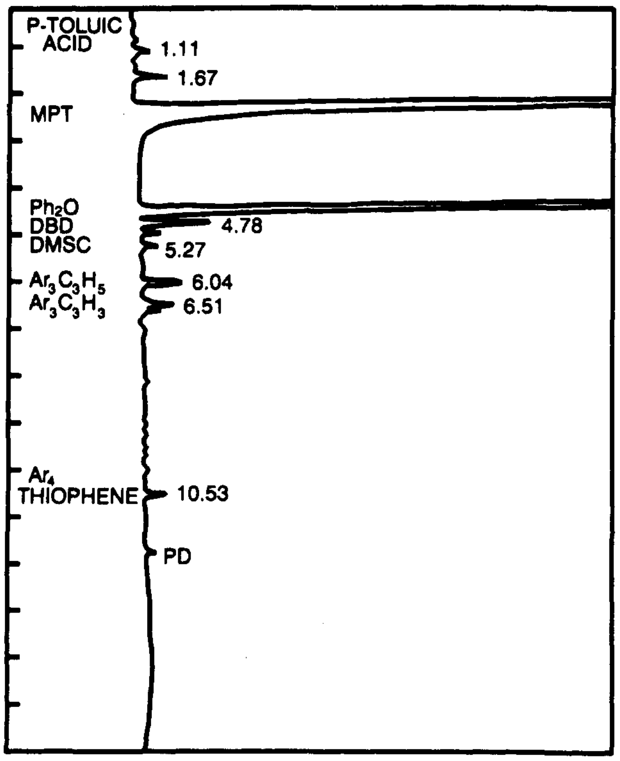


Figure 2. Liquid chromatogram of filtrate from run 037.

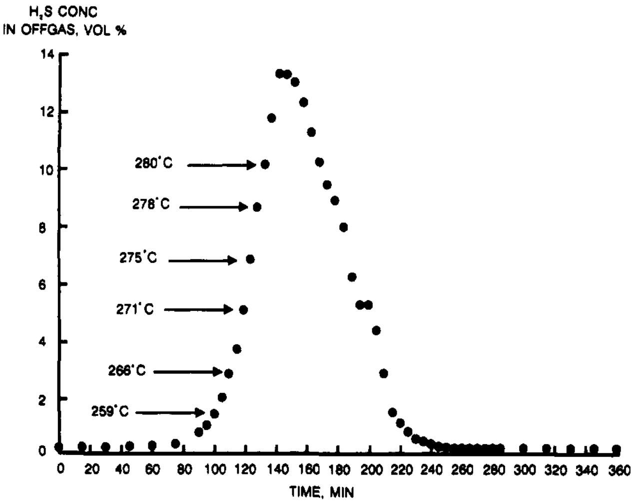


Figure 3. Dehydrodimerization of MPT, run 035.

thiophene as identified by LC/MS investigation. A synthesis of the "unsubstituted" analogue (2-phenylbenzothiophene) and comparison with product from a high conversion sulfur-toluene reaction was reported by Horton.[10] In the present case, the benzothiophene is a very minor product. The remaining minor products were present in too small amounts to give useful mass spectra for identification. In the runs listed in Table I, the total area of the unidentified components typically ranged from 10 to 15% of the area of the identified products. Depending on the identity of these minor products and their response in the LC detector, the yields of DMSC and DBD would need to be reduced accordingly when product analysis is complete.

No evidence was found for the presence of tetra(4-carbomethoxyphenyl)butane (or the associated butenes and butadiene). The analogous product is formed in the pyrolysis of bibenzyl[11] and is assumed to be the final, stable intermediate prior to the formation of the tetrarylthiophene product.

Table II. H_2S Evolution Data: Reaction of Methyl *p*-Toluate with Sulfur Added Batchwise at Start of Reaction

run	init reactor charge, mol			max rate,[a]	temp,	time,	H_2S evolved,[b]
no.	MPT	sulfur	Ph_2O	mL H_2S/s	°C	min	mol
201	1.0	0.1	1.0	0.71	296	90	0.074
035	4.0	0.4	0	2.1	281	145	0.34
036	2.0	0.4	2.0	2.1	295	175	0.28
037	4.0	0.8	0	2.2	282	170	0.67
046	2.0	0.2	2.0	0.65	281	195	0.18
048	~2.0	0.2	~2.0	2.0	284	175	0.37
071	2.0	0.2	2.0	1.2	280	90	0.26
073	4.0	0.4	0	3.4	277	80	0.55
079	4.0	0.2	0	2.7	281	50	0.27

[a] These are the maxima of curves such as Figure 3. Vol % H_2S has been converted to actual evolution rate by multiplying by the N_2 flow rate. [b] From integration of the H_2S evolution curves.

Chart I

bond	bond dissociation energy, kcal/mol
$ArCH_2$—H	85[a]
RS_x—H (R = 4-CB?)	92 $x = 1$ 70 x = 2 or higher
HS—H	92

[a] Toluene (no ring substitution).

Rates of the Sulfur-MPT Reaction. The availability of the Anarad H_2S-sensing meter offers the possibility of observing the qualitative kinetic behavior of the sulfur-MPT reaction. A typical profile of the hydrogen sulfide content of the nitrogen sparge stream vs reaction time is shown in Figure 3. As the temperature legends for some of the points show, the reaction is at least $^1/_3$ complete by the time the 280 °C set point is reached. The reactor's approach to 300 °C was usually so slow that most of the sulfur had been exhausted by the time 300 °C was reached. Some of the maximum rates attained by the batch runs are listed in Table II along with the reading of the reactor temperature probe. For the 280 °C set point runs, the evolution rate of hydrogen sulfide usually maximized at the time this temperature was reached.

The curves in Figure 3 can be integrated to give, with specification of the nitrogen flow rate, the amount of hydrogen sulfide evolved. This has been done for some of the batch sulfur runs, and the results are summarized in Table II. Agreement of these data with sulfur charged is less satisfactory than total hydrogen sulfide collected by the caustic scrubbers (last column, Table I).

In an attempt to run the reaction in an isothermal mode, some experiments were done by pumping a diphenyl ether solution of sulfur to the reactor after it had been brought to the desired reaction temperature (280 or 300 °C). These experiments have not been included in Table I. Two types of analysis of the hydrogen sulfide evolution data of these pumped runs both indicate that the reaction is near 0.5 kinetic order in total sulfur present. Attempts to determine the order of the reaction in MPT concentration from batch run data gave inconclusive results.

Mechanistic Considerations. No concise mechanistic pathway that leads to a kinetic expression and that predicts all the major products of the reaction is apparent. However, some likely elementary reactions of the system can be suggested.

All of the major products can be explained if an adequate supply of 4-carbomethoxybenzyl (4-CB) radicals is

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(10) Horton, A. W. *J. Org. Chem.* **1949**, *14*, 761.

(11) Poutsma, M. L. *Fuel* **1980**, *59*, 335.

available from the reactants. A problem in producing the 4-CB radicals arises from the bond dissociation data (Chart I).[12,13] Therefore, it is energetically unfavorable to produce the 4-CB radicals from MPT with anything but a simple thiyl radical; polymeric thiyl radicals are not expected to be the principal propagating radicals for the oxidation of the MPT. This viewpoint requires that some mechanism exists to degrade 4-CB polythiyl radicals to the monomer and that 4-CB mercaptan is a plausible intermediate in the reaction sequence. Benzyl mercaptan has been found

$$\mathrm{ArCH_3 + {\bullet}SCH_2Ar \rightleftharpoons ArCH_2{\bullet} + HSCH_2Ar} \tag{2}$$

$$\mathrm{ArCH_2{\bullet} + {\bullet}S_x{\bullet} \rightleftharpoons ArCH_2S_x{\bullet}} \tag{3}$$

$$\mathrm{ArCH_2S_x{\bullet} \rightleftharpoons ArCH_2S{\bullet} + {\bullet}S_{x-1}{\bullet}} \tag{4}$$

to undergo thermolysis readily to yield, among other things, stilbene; the carbon–sulfur bond dissociation energy was cited as being only 56 kcal/mol.[14] Of course, at least

$$\mathrm{ArCH_2SH \rightleftharpoons ArCH_2{\bullet} + {\bullet}SH} \tag{5}$$

$$\mathrm{{\bullet}SH + ArCH_3 \rightleftharpoons H_2S\uparrow + ArCH_2{\bullet}} \tag{6}$$

some polymeric sulfur radicals ($\bullet S_x \bullet$) must attack MPT to initiate the suggested sequence. Equations 2–6 provide a route to an equilibrium concentration of 4-CB radicals that may dimerize to give the DBD product observed.

$$\mathrm{2\ ArCH_2{\bullet} \rightarrow ArCH_2CH_2Ar} \tag{7}$$

The steps shown in eqs 2–7 are typical of the usual free-radical elementary steps, with the possible exception of reaction 5. A difficulty with the sequence is that decomposition (5) may not be rapid enough at 280 °C to account for the fact that the benzyl mercaptan does not accumulate and persist for the relatively short reaction periods of the reaction. In the gas phase, benzyl mercaptan was found to decompose completely in 2.25 h at 250 °C on 13X zeolite surfaces but only ~6.4%/h when in contact with alumina.[15] This latter reaction was postulated to be noncatalytic or thermal. We were unable to find liquid-phase decomposition data for benzyl mercaptan in toluene or other hydrogen donor solvent near the temperature of interest. Other reactions that utilize the radical intermediates of eqs 2–7 and that lead to DBD can be written but they are speculative at this time.

We have experiments, to be reported separately, that show that DBD in diphenyl ether solvent is rapidly dehydrogenated by elemental sulfur to DMSC and H_2S at temperatures as low as 260 °C. The selectivity of the

$$\mathrm{ArCH_2CH_2Ar + S \rightleftharpoons ArCH{=}CHAr + H_2S\uparrow} \tag{8}$$

dehydrogenation is high as long as conversion is held to 10% or less. Abstraction of one of the hydrogens from the DBD gives a plausible intermediate for the higher molecular weight products of the reaction.

The sulfur–MPT reaction with no removal of hydrogen sulfide was only briefly investigated. The major product appeared to be DBD, and DMSC became the minor product; in one experiment (run 134, Table I), the DBD/DMSC ratio was ~6.3/1 after 24 h of reaction. The maximum pressure attained (hydrogen sulfide plus MPT vapor pressure) was 80 psig. It has been noted previously that nonventing of hydrogen sulfide from toluene/sulfur or toluic acid/sulfur reactions promotes bibenzyl formation.[3,4]

Other Substrates. The sulfur-mediated dehydrodimerization reaction has some generality for the synthesis of stilbenes[16] but the rigorous conditions of the reaction limit the functional groups that can be present. Not surprisingly, the phenyl ester of *p*-toluic acid is a suitable substrate.[17] Of other alkyl esters of *p*-toluic acid only the ethyl ester showed some promise of applicability; higher esters are too readily attacked on the ester function by the sulfur intermediates.[18] Generally, the meta-substituted toluenes are suitable substrates if the reaction succeeds with the corresponding para isomer.[4–6,18]

Conclusion

The reaction of MPT with sulfur in the 260–300 °C temperature range leads to DMSC as the major product if coproduct hydrogen sulfide is stripped from the reaction mixture. Yields approaching 70% are attainable if conversion is limited to ~10% by using a limited charge of sulfur. Other identified products include the bibenzyl derivative, DBD, 1,2,3-tris(4-carbomethoxyphenyl)propane, an *E* and *Z* 1,2,3-tris(4-carbomethoxyphenyl)propene mixture, and 2,3,4,5-tetrakis(4-carbomethoxyphenyl)thiophene. 4-Carbomethoxybenzyl radical is a likely intermediate in the formation of the products.

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(12) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(13) Benson, S. W. *Thermochemical Kinetics, 2nd ed.*; John Wiley and Sons: New York, 1976; p 309.

(14) Fixari, B.; Abi-Khers, V.; LePerchec, P. *Nouv. J. Chim.* **1984**, *8*, 177.

(15) Venuto, P. B.; Landis, P. S. *J. Catal.* **1971**, *21*, 330.

(16) Becker, K. B. *Synthesis* **1983**, 347.

(17) Van Sickle, D. E.; Morris, J. C.; McCall, M. A.; Fleischer, J. C.; Walker, T. R. U.S. Patent 4789755, Dec 6, 1988.

(18) McCall, M. A.; Morris, J. C. Eastman Chemical Co. Research Laboratories, unpublished results.