was added. After 10 min., methylene chloride was added and the mixture was extracted several times with water and dried over magnesium sulfate. The solvent was evaporated and the products were chromatographed as usual.

The reaction with isopropyl bromide was carried out as described above. V.p.c. analysis of the initial reaction, however, showed that only *ca.* 2% of the phenol was alkylated. The product was therefore redissolved in DMSO and 0.1 mole of NaH, followed by 0.1 mole of isopropyl bromide, was added and the reaction was allowed to become neutral to indicating paper. Addition of NaH and DMSO was repeated seven times. The reaction mixture was then worked up as usual.

Coupling of Aromatic Rings. I. The Pyrolysis of Aryl Sulfides and Aryl Sulfones to Substituted Biphenyls

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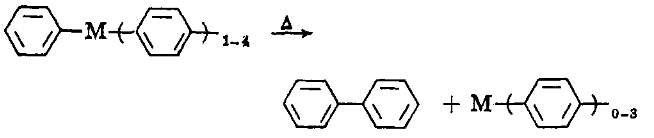
Pyrolysis of *p*-tolyl sulfide and *p*-tolyl disulfide on α-Fe embedded in a γ-Fe_2O_3 matrix yielded *p*-bitolyl in 60% conversion and 90% yield per pass. No decrease of activity for the catalyst was observed after *ca.* 50 passes, and no observable isomer redistribution preceded the coupling reaction. Pyrolysis of *p*-tolyl sulfone on alumina yielded *p*-bitolyl and a considerable amount of biphenyl. No observable isomer redistribution preceded this coupling reaction.

Pyrolysis of di- to pentaphenyl metalloids yielded biphenyl, frequently in high conversions.



M = Br,[1] I,[2] S,[3] Se,[3] P,[4] Sb,[5] As[6]

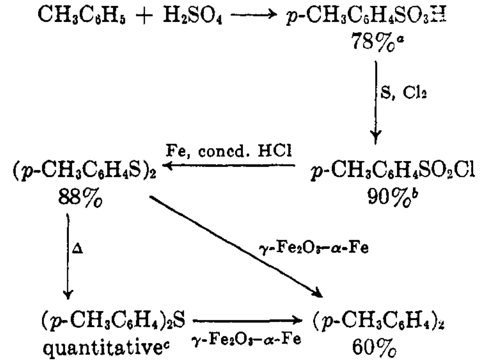
Bis(*p*-methoxyphenyl) sulfide when heated with Raney nickel gave *p,p'*-dimethoxybiphenyl in 50% conversion, and when *p*-tolyl disulfide was heated with Raney nickel, *p*-bitolyl was obtained in 84% conversion.[6] In our search for simple routes to substituted biphenyls proceeding with no isomer redistribution before the coupling step, pyrolysis of metalloids looked promising indeed. Unfortunately, most of the above starting materials require multistep syntheses and the elimination of sulfur with Raney nickel proceeded with a mild detonation, as also observed by others.[7] We have extended our search for new coupling reactions in two directions: (a) heterogeneous reactions in vapor phase on a solid catalyst support, and (b) homogeneous reactions in solution. In this paper we report two novel coupling reactions which proceed with the elimination of –S–, –S_2–, and –SO_2– linkages in vapor phase on solid supports to yield substituted biphenyls.

Results

Bitolyls from Tolyl Sulfides and Tolyl Disulfides.—The most economic conversion of toluene to *p*-tolyl sulfide or disulfide was obtained by the route summarized in Chart I.

Chart I

Synthesis of *p*-Bitolyl from *p*-Tolyl Sulfide and *p*-Tolyl Disulfide



[a] Reference 8, p. 461. [b] W. Meves and W. Ohse, German Patent 499,052; *Chem. Abstr.*, **24**, 4055 (1930). [c] Reference 12.

We have found that the reduction of *p*-toluenesulfonyl chloride with iron powder in concentrated hydrochloric acid yielded directly *p*-tolyl disulfide in 88% over-all conversion. Reduction of the sulfonyl chloride with iron powder in 75% sulfuric acid gave 20% of the *p*-tolyl disulfide and about 80% of the iron salts of *p*-toluenethiol. *p*-Toluenethiol was dimerized in quantitative conversions to *p*-tolyl disulfide in an alkaline aqueous solution using Cu^{II} ions and air or in a sulfuric acid solution employing Fe^{III} ions and air.[8]

Attempts to synthesize *p*-tolyl sulfide or disulfide directly from toluene and sulfur, sulfur dichloride, or disulfur dichloride in the presence of Lewis acids such as $FeCl_3$, $SbCl_5$, $AlCl_3$, and HF yielded smaller over-all conversions to the *para* derivative and the separation of the resulting isomers by distillation proved impractical.

When *p*-tolyl sulfide was heated with a tenfold excess of degassed Raney Nickel, *p*-bitolyl could be isolated in up to 84% conversion.[6] In our hands this dimerization reaction was very sensitive to the weight

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(1) A. P. Nesmeyanov, T. P. Tolstaya, and L. S. Isaeva, *Dokl. Akad. Nauk USSR*, **125**, 330 (1959); *Chem. Abstr.*, **53**, 19927 (1959).

(2) W. Baker, N. J. McLean, and J. F. W. McOmie, *J. Chem. Soc.*, 922 (1963).

(3) H. Hauptmann and W. F. Walter, *Chem. Rev.*, **62**, 347 (1962); G. R. Pettit and E. E. van Tamelen, *Org. Reactions*, **12**, 356 (1962).

(4) G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949).

(5) G. Wittig and K. Clauss, *ibid.*, **577**, 26 (1952).

(6) H. Hauptmann, B. Wladislaw, L. L. Nazario, and W. F. Walter, *ibid.*, **576**, 45 (1962).

(7) W. H. F. Sasse, *J. Chem. Soc.*, 3046 (1959).

(8) For discussion, see A. Schöberl and A. Wagner, "Methoden der organischen Chemie," Houben-Weyl, Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p. 60.

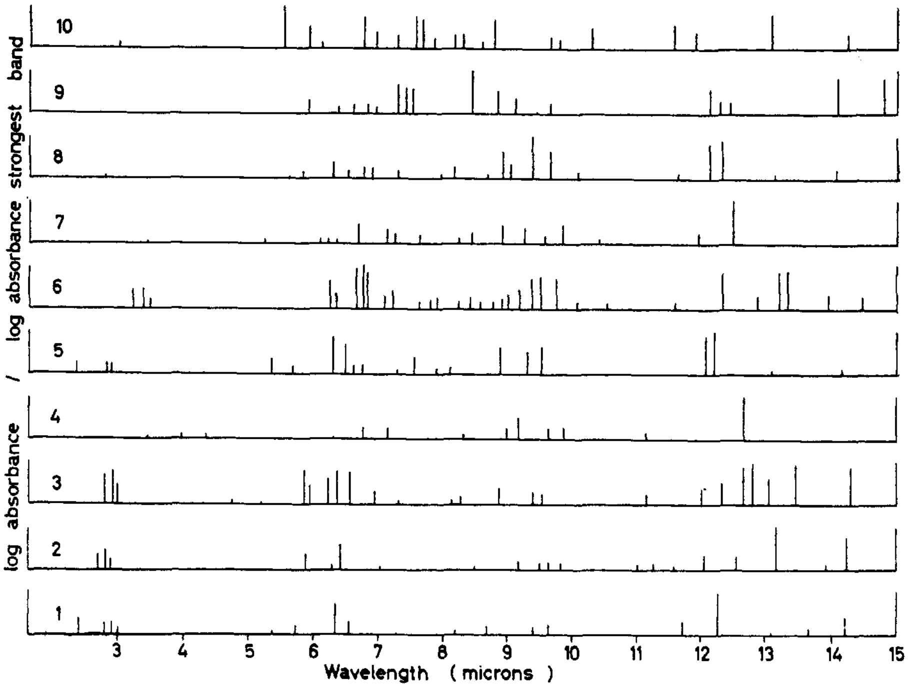

Figure 1.—Infrared spectra of intermediates employed. The band intensity was measured by the base-line method, and each band in a given compound was compared with the strongest band in the compound: 1, *p*-bitolyl (neat); 2, *o,p'*-bitolyl (neat); 3, *o,m'*-bitolyl (neat); 4, *p*-toluenethiol (KBr); 5, *p*-tolyl sulfide (KBr); 6, *o,p'*-tolyl sulfide (neat); 7, *p*-tolyl disulfide (KBr); 8, *p*-tolyl sulfoxide (KBr); 9, *p*-tolyl sulfone (KBr); and 10, *p*-bibenzoic acid dimethyl ester (KBr).

ratio of degassed Raney nickel to disulfide employed: at a 5:1 weight ratio the conversion to bitolyls was only 24%; the reaction also proceeded with a deflagration to mild detonation in an uncontrolled manner.

A substitute for the Raney nickel was therefore sought, preferably a substitute with active sites embedded into a solid support. Metallic iron was selected as the first candidate for a test.

Iron oxide is reduced to metallic iron at 300–800° when heated with hydrocarbons.[9] Metallic iron reacts readily with sulfur to yield iron sulfide[10] which can be "roasted" with air[11] to iron oxide to complete the cycle.

$$\mathrm{Fe} + \mathrm{S} \longrightarrow \mathrm{FeS}$$

$$4\mathrm{FeS} + 7\mathrm{O_2}\ (\mathrm{air}) \longrightarrow 2\mathrm{Fe_2O_3} + 4\mathrm{SO_2}$$

It is also known that aromatic disulfides yield sulfides when heated above 200–300°.[12]

When *p*-tolyl disulfide was dissolved in benzene and the solution was poured on a pelleted Fe_2O_3 support consisting mainly of α-Fe_2O_3 and γ-Fe_2O_3 heated to 450°, only *p*-tolyl sulfide was recovered as measured by a v.p.c. procedure. After repeated passes of *p*-tolyl sulfide and disulfide over the same catalyst in a temperature range of 400–850° and intermittent oxidation of the resulting iron sulfide with air, the catalyst became black and the pellets changed their shape into long sausages. Passage of *p*-tolyl sulfide and/or *p*-tolyl disulfide yielded *p*-bitolyl and starting material. Highest conversion to *p*-bitolyl was obtained when the catalyst bed was heated to 600°; a maximum conversion of 60% and over-all yields of 90% per pass were achieved. Results are summarized in Table I.

TABLE I

PYROLYSIS OF *p*-TOLYL SULFIDE ON γ-Fe_2O_3 AND α-Fe

Temp. of catalyst bed,[a] °C.	Products, % conversion[b]		
	Bitolyl	*p*-Tolyl sulfide	Biphenyl
400	Trace	~100	
500	50	49	
600	60	30	
700	Trace	Trace	>90

[a] Measured externally with a Pyro-vane. [b] Measured by v.p.c.

p-Bitolyl was determined in the reaction mixtures by using standard v.p.c. techniques to ±1%. To confirm these analyses the reaction products were separated by chromatography on alumina and isolated and their structures were confirmed by ultimate analysis and comparison of the infrared spectra with reference samples. Infrared spectra of intermediates and products investigated are summarized in Figure 1.

No isomer redistribution was observed as determined by the v.p.c. method employed, either in the pyrolysis of *p*-tolyl sulfide and disulfide to *p*-bitolyl or in the pyrolysis of *o,p'*-tolyl disulfide to *o,p'*-bitolyl. No decrease of the catalyst activity was observed after *ca.* 50 passes over the same catalyst. Furthermore, no formation of biphenyl was observed when benzene alone was pyrolyzed on the same catalyst heated up to 600°.

Examination of the catalyst (see Experimental Section) indicated that the α-Fe_2O_3 component of the initial catalyst was reduced to α-Fe embedded in the γ-Fe_2O_3 matrix. The X-ray diagrams of the initial catalyst and the "active" catalyst are given in Figures 2 and 3, respectively.

p-Biphenyls from *para*-Substituted Phenyl Sulfones.—*p*-Tolyl sulfone can be synthesized from toluene and concentrated sulfuric acid in conversions exceeding

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[9] H. H. Voge, *Catalysis*, 407 (1958).

[10] For discussion see J. B. McKinley, *ibid.*, 405 (1958).

[11] For summary of references, see Gmelin's "Handbuch der Anorganischen Chemie," Vol. 8, Ed. No. 9B, Verlag Chemie, Weinheim/Bergstrasse, 1953, p. 288.

[12] R. Mayer and H. J. Frey, *Angew. Chem.*, **76**, 861 (1964).

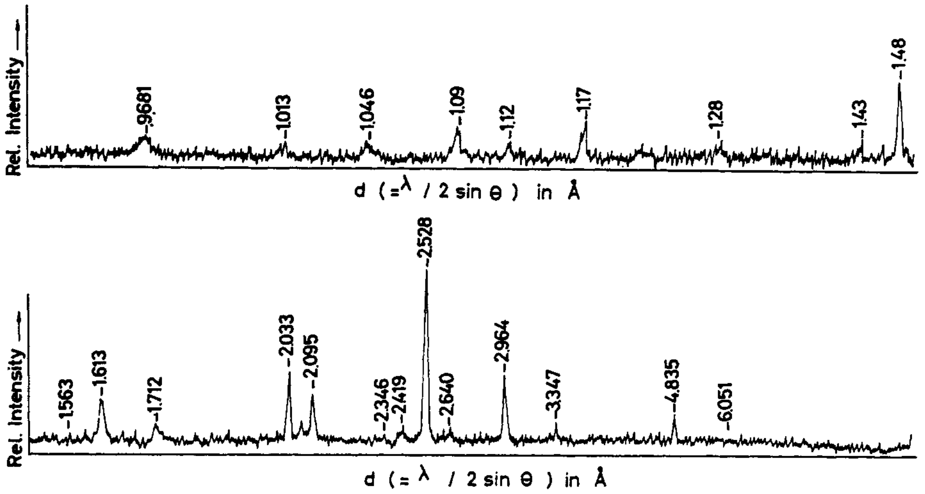


Figure 2.—X-Ray diagram of the Fe_2O_3 catalyst employed in the conversion of *p*-tolyl disulfide to *p*-tolyl sulfide: Co radiation Fe filter.

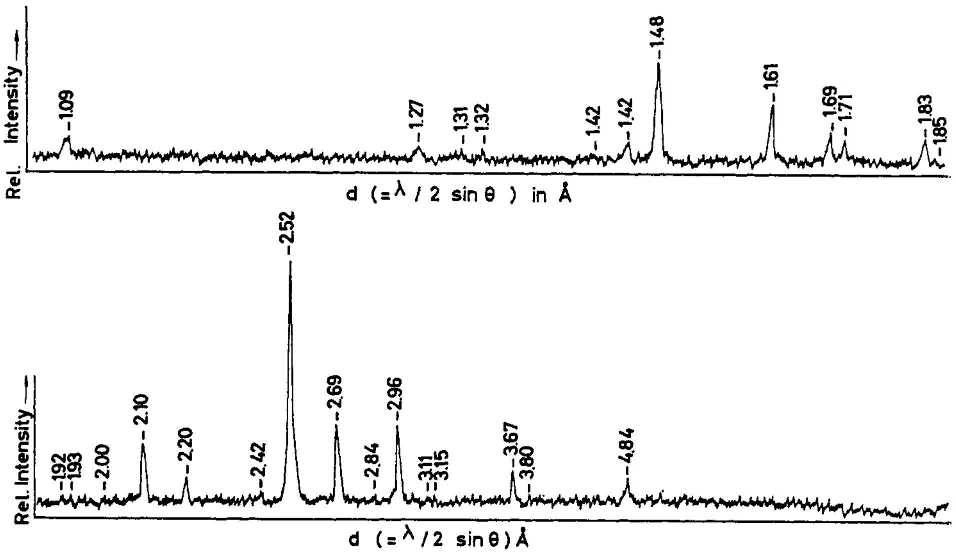
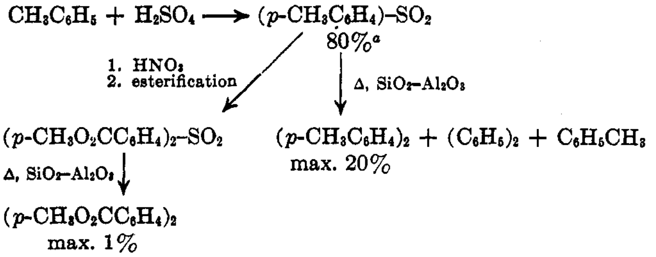


Figure 3.—X-Ray diagram of the γ-Fe_2O_3–α-Fe catalyst employed in the reaction of *p*-tolyl disulfide and *p*-tolyl sulfide to *p*-bitolyl: Co radiation, Fe filter.

80%.[13] An alternative attractive route to *p*-bitolyl would therefore be the pyrolysis of *p*-tolyl sulfone (Chart II).

Chart II

Synthesis of *p*-Bitolyl and *p*-Bibenzoic Acid Methyl Ester from *p*-Tolyl Sulfone



[a] Reference 13.

Aromatic sulfones are reported in the literature to be thermally stable compounds[14] and dimerization of aromatics *via* the elimination of SO_2 from an aromatic sulfone has apparently not as yet been achieved. On the other hand, sulfonyl chlorides do decompose thermally to free radicals.[15]

$$C_6H_5SO_2Cl \longrightarrow C_6H_5\cdot + SO_2Cl\cdot$$

When *p*-tolyl sulfone, dissolved in benzene, was dropped into a heated column packed with an alumina catalyst (Houdry Type S-65, Al_2O_3 12%, SiO_2 86%), the results shown in Table II were obtained.

Table II

Pyrolysis of *p*-Tolyl Sulfone on Aluminum Oxide–Silicon Dioxide

Temp., °C.[a]	Products, % conversion[b]		
	Biphenyl	*p*-Bitolyl	$p\text{-}CH_3C_6H_4SO_3H$
600	...	...	...
700	1	2	...
800	48	22	2
880	60	5	...

[a] Measured externally. [b] Measured by v.p.c.

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(13) H. Meyer, *Ann.*, **433**, 327 (1923).

(14) A. Schöberl and A. Wagner, ref. 8, p. 243.

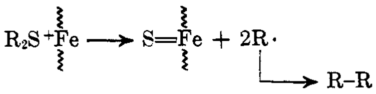
(15) (a) P. J. Bain, E. J. Blackman, W. Cummings, S. A. Hughes, E. R. Lynch, E. B. McCall, and R. J. Roberts, *Proc. Chem. Soc.*, 186 (1962); (b) A. Rieche and E. Naumann, *J. prakt. Chem.*, [4] **9** (**281**), 108 (1959).

Biphenyl and p-bitolyl were isolated from the reaction mixture by crystallization from methanol and were identified by admixture melting point with reference samples and by infrared spectra. The interesting observation evolving from this experiment is that little or no reorganization of the p-tolyl radical occurs *before* recombination to p-bitolyl, since no identifiable amounts of bitolyls other than p-bitolyl were observed in the vapor phase chromatograms of the reaction products. An attempt to pyrolyze solid p-tolyl sulfone on Houdry Al_2O_3–SiO_2 S-65 to reduce the formation of biphenyl at temperatures exceeding 800° did not give any identifiable amounts of p-bitolyl.

p-Bitolyl sulfone can be readily oxidized with nitric acid to the dicarboxylic acid which, on esterification with methanol, gives the dimethyl ester in 66% overall conversions. Interestingly enough, pyrolysis of the solid dimethyl ester on the same alumina above at 750° yielded trace quantities ($\sim$1%) of the p-bibenzoic acid dimethyl ester which was isolated from the reaction mixture by extraction with cold benzene.

Discussion

Alkyl and aryl sulfides are strong Lewis bases yielding with H^+ or alkylating agents deeply colored sulfonium ions R_2S^+H.[16] It is reasonable to assume that this is also the first step occurring on the Raney nickel and on the iron surface of the catalyst.[17] Upon heating, both S–C bonds appear to break simultaneously, presumably in a homolytic fashion, followed by rapid geminate recombination of the aromatic radicals generated in the following reaction.



$$R_2S^+Fe \longrightarrow S{=}Fe + 2R\cdot \longrightarrow R{-}R$$

Evidence[3] which supports the homolytic hypothesis is (a) Bonner's observation that an optically active center adjacent to the terminal carbon atom generated by the C–S bond scission does racemize, thus indicating the presence of an optically unstable radical,[18] and (b) the radical-transfer reaction.

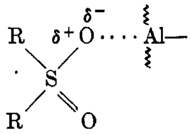
$$R\cdot + C_6H_6 \longrightarrow RH + C_6H_5\cdot$$

$$C_6H_5\cdot + C_6H_6 \longrightarrow C_6H_5C_6H_5 + H\cdot$$

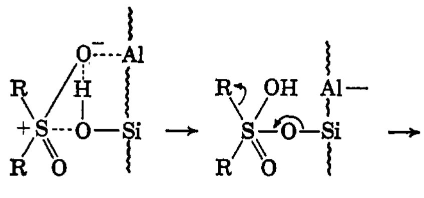
Surprisingly, no identifiable amounts of bibenzyl and methylbiphenyls were isolated. Also, our analytical method failed to detect any p-toluenethiol among the reaction products, which tends to support the hypothesis that the C–S bonds break simultaneously.

The important result of these experiments is that at low temperatures (500–600°) the C–S bonds appear to break simultaneously and that the recombination is much faster than either position isomerization of the radical or the radical-transfer reaction.[19] On the other hand, the precise nature of the reactions occuring on the catalyst surface requires more work to substantiate our working hypothesis discussed above.

The alumina surface contains both Lewis and Brønsted acid sites.[20] Lewis acid sites are generally assumed to be located on the Al ion embedded in the SiO_2 matrix, but Brønsted sites are probably present both on Al_2O_3 and on SiO_2 in the form of hydroxyls. Sulfones are weak bases, but apparently their base strength is sufficient to coordinate with the Lewis acid on the catalyst support in the transition state.



Support for the transition state pictured above is provided by the isolation of p-toluenesulfonic acid from the reaction mixture. The scission of the C–S bond must have occurred subsequently to a reaction of the sulfone group with a hydroxy group on the catalyst surface.



Reactions of hydrocarbons occurring on the alumina surface at low temperature are ionic reactions. At high temperatures the breakage of the C–S bonds in p-tolyl sulfone can best be understood as a free-radical process. At temperatures below 700° radical recombination leading to p-bitolyl without position isomerization prevails over independent destructions of the "free" p-tolyl radical. Above this temperature the radical is able to escape from the cage in which it was formed and undergoes secondary reactions, the main process being apparently a radical-transfer reaction. The preference for independent destruction of the "free" p-tolyl radical generated from p-tolyl sulfone as compared to that generated from the sulfide must be thought to show a less favorable stereochemistry of the transition state in the former reaction and its location at higher potential energy along the reaction coordinate. The C–S–C– angle in a sulfide is smaller than in the corresponding sulfone, indicating a more favorable transition state for the recombination process.[21]

Experimental Section

Synthesis of p-Tolyl Sulfide and p-Tolyl Disulfide.—To 800 ml. of concentrated hydrochloric acid were added 300 g.

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[16] G. Cilento, *Chem. Rev.*, **60**, 130 (1960); U. Schmidt, *Angew. Chem.*, **76**, 629 (1964). E.s.r. measurements of solutions of diaryl sulfides in concentrated sulfuric acid indicate that these may be radical ions: $R_2S^+\dot{H}$ rather than R_2S^+H only.

[17] G. M. Badger, N. Kowanko, and W. H. F. Sasse, *J. Chem. Soc.*, 2969 (1960); W. Hauptmann and B. Wladislaw, *J. Am. Chem. Soc.*, **72**, 707, 710 (1950).

[18] W. A. Bonner, *ibid.*, **74**, 1034 (1952).

[19] R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1953); *J. Am. Chem. Soc.*, **77**, 2042 (1955); *J. Phys. Chem.*, **65**, 763 (1961). See also D. H. Hey, M. J. Perkins, and G. H. Williams, *Tetrahedron Letters*, 445 (1963); J. F. Garst and R. S. Cole, *ibid.*, 679 (1963); G. A. Russel and R. F. Bridger, *ibid.*, 737 (1963).

[20] R. H. Griffith and J. D. F. Marsh, "Contact Catalysis," Oxford University Press, London, 1957, p. 229; L. A. Ignateva, P. G. Kryukov, and L. N. Konovalova, *Fiz. Probl. Spectroskopii, Akad. Nauk SSSR, Materialy 13-go (Trinadtsatgo) Soveshch.*, Leningrad, **2**, 59 (1960); *Chem. Abstr.*, **59**, 12305 (1963).

[21] W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., 1962, p. 18; W. R. Blackmore and S. C. Abrahams, *Acta Cryst.*, **8**, 329 (1955); J. Toussaint, *Bull. soc. chim. Belges*, **54**, 319 (1945); J. C. Sime and S. C. Abrahams, *Acta Cryst.*, **13**, 1 (1960).

of ice and 100 g. (0.525 mole) of *p*-toluenesulfonyl chloride, and the reaction mixture was stirred at 20°. Immediately 195 g. (3.5 moles) of iron powder was added in small batches over a period of 1 hr., whereby the temperature increased to 35–40°, and the reaction mixture foamed very considerably. The reaction mixture was stirred overnight at room temperature. The white solid floating on top of the reaction mixture was filtered and washed with water (82 g. wet). The solid was then washed with 500 ml. of warm 10% sodium hydroxide and subsequently with water; after drying in a vacuum oven, the weight of the insoluble material was 48.0 g. (FI). The sodium hydroxide soluble material was acidified with 50% hydrochloric acid whereby 9.0 g. precipitated (FII). After recrystallization from methanol FI melted at 43–44° (lit.[22] disulfide m.p. 45.2°). The infrared spectrum of this compound was identical with that of *p*-tolyl disulfide. After drying a sample of FII melted at 42° (lit.[23] m.p. 42–43° for *p*-toluenethiol) and the spectrum was identical with that of *p*-toluenethiol. Total conversion to products was 88%.

Dimerization of *p*-Toluenethiol to *p*-Tolyl Disulfide. A.—To 24.8 g. (0.2 mole) of *p*-toluenethiol in 800 ml. of water was added 8.8 g. (0.22 mole) of sodium hydroxide. After the solid dissolved in the solution, 0.5 g. of copper acetate was added and air was bubbled through the solution at 25° at a rate of 1000 cc./min. The disulfide which was filtered melted at 43–44°, after drying in a desiccator over concentrated sulfuric acid. The disulfide was further identified by admixture melting point with a synthetic sample, infrared spectrum, and v.p.c. elution (see below). Conversions to the disulfide were 43% after 1 hr. of bubbling air through the solution, 72% after 4 hr., and 100% after 24 hr.

B.—Into a 0.5 *N* sulfuric acid solution (80 ml.) containing 0.15 mole of Fe^{III} and 0.04 mole of *p*-toluenethiol was bubbled air at a rate of 2000 cc./min. for 16 hr. The temperature of the solution was maintained at 25°. The conversion to the disulfide was quantitative and appeared to be independent of the hydrogen ion concentration.

Pyrolysis of *p*-Tolyl Disulfide. Apparatus.—Into a 32-cm.-long tube furnace built in a vertical position was placed a quartz tube, 2.5 cm. in diameter, which was packed with pelleted catalyst. The column was packed with a catalyst bed, usually 15–20 cm. long. Through a ball joint the column was connected to a dropping funnel (500 ml.) equipped with an overflow and connected to a nitrogen line. The outlet of the catalyst tube was connected to a three-neck flask cooled with ice, which in turn was connected to two Dry Ice traps connected in sequence. The temperature of the catalyst column was measured in the *ca.* 3-mm. airspace between the tube and the furnace in the middle of the bed, and was controlled to *ca.* ±5° by a Pyrovane.

Catalyst.—Pure red oxide R-3098 (C. K. Williams Co., Easton, Pa.) was made into pellets of 5 mm. in diameter and 3 mm. long. Initially the catalyst was not active at all; however, after *ca.* two passes of 5 g. of *p*-tolyl disulfide in 100 ml. of benzene the catalyst turned black and the diameter of the pellets decreased. This catalyst converted *p*-tolyl disulfide to *p*-tolyl sulfide at 450° but *not* to *p*-bitolyl (catalyst A, Table III). When catalyst A was used at temperatures between 400 and 850° for the pyrolysis of *p*-tolyl disulfide and sulfide, each dissolved in benzene (see below); with intermittent "cleaning" of the catalyst for 10 min. at 500–600° with air, the pellets turned almost black, the diameter decreased to a steady 3 mm., and the pellet length increased to 6 mm. (catalyst B, Table III). Catalyst B was active in the desulfurization of *p*-tolyl disulfide to *p*-bitolyl. Some properties of the catalysts are shown in Table III.

TABLE III

PHYSICAL PROPERTIES OF Fe_2O_3 CATALYSTS

Catalyst	Surface area, m.²/g.	H_2O pore volume, cc./g.	X-Ray, relative intensity				Elements by fluorescence
			γ-Fe_2O_3	α-Fe_2O_3	α-Fe	Other[a]	
A	10.0	0.03	100	33	. . .	*ca.* 1	Fe, S, Ti, Pb
B	4.7	0.16	100	. . .	40	*ca.* 1	Fe, S, Ti, Pb

[a] The unassigned lines in catalyst A were different from those in catalyst B.

Analytical Procedures.—The instrument used was an Anacro II unit, Nester–Faust Co., Newark, Del., 8-ft. column, 20% silicon rubber, GC-22 on 60–80-mesh Super-Support. Instrument settings follow: injection port temperature, 320°; column temperature, 250°; cell temperature, 300; outlet temperature, 350°; and He flow, 40 cc./min.

The samples were made to a standard volume and the concentration of the bitolyl was measured quantitatively from a standard reference curve prepared from the following data: 0.67 mg. of *p*-bitolyl/ml. of benzene (relative peak height, 4.6), 1.37 (11.6), 2.68 (24.2), 4.02 (41.6), 13.4 (142.6), and 36.6 (346.0).

The compounds were eluted at the above instrument settings from the column as shown in Table IV.

TABLE IV

Compd.	Elution time chart units (rel.)
Biphenyl	15.0
p-Bitolyl	24.5
p-Tolyl sulfide	40.0
p-Tolyl disulfide	41.5
p-Tolyl sulfone	96.0

Typical Run.—*p*-Tolyl disulfide (2.5 g., 10 mmoles, Eastman Chemical Co.) was dissolved in 50 ml. of benzene and this solution was dropped into the quartz tube filled with 70–80 g. of a catalyst heated to 600°. (During the addition the N_2 flow through the system was 2000–3000 cc./min.) All of the benzene was added during a period of 30 min. The material eluted from the column was washed out of the traps; the solution was diluted to volume and was measured quantitatively by v.p.c. The reaction mixture consisted only of 40% *p*-bitolyl and 60% *p*-tolyl disulfide, no other isomers of bitolyl being present. (These isomers can be separated and identified quantitatively on the column described above if their ratio is not greater than 100:1.)

In a parallel run the trap condensates were dissolved in 50% benzene–petroleum ether (b.p. 30–60°) and poured onto a column prepared from Woelm neutral alumina (50 g.). Elution with benzene (200 ml.) yielded a solid, 868 mg. (47% conversion), which melted at 121–123° after recrystallization from methanol (lit.[24] for *p*-bitolyl m.p. 121°). Further elution of the column with chloroform yielded the recovered disulfide.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.36; H, 8.46.

The infrared spectrum in KBr was superimposable with the reference sample and the melting point was not depressed upon admixture with a reference sample.

Pyrolysis of Sulfones on SiO_2–Al_2O_3. A. Pyrolysis of *p*-Tolyl Sulfone.—The apparatus and analytical procedures used were the same as described above.

Catalyst was Houdry silica–alumina type S-65; surface area, 420 m.²/g.; pore diameter, 80 Å., 86% SiO_2; 12% Al_2O_3. Catalyst (80 g.) was packed into the column; N_2 flow was 2000–3000 cc./min.

Procedure.—*p*-Tolyl sulfone (5 g.) was dissolved in 100 ml. of benzene and the solution was dropped onto the solid support at a rate of 100 ml./hr. The solution was divided into four parts and was dropped onto the solid catalyst bed heated to the temperatures shown in Table V.

TABLE V

Column temp., °C.[a]	Products, % conversion[b]		
	FA	FB	FC
600	. . .	. . .	. . .
700	1	2	. . .
800	48	22	2
880	60	5	. . .

[a] Measured on the outside by Pyro-vane. [b] Measured by v.p.c.

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(22) Th. van Hove, *Bull. Acad. Roy. Belg., Classe Sci.*, [5] **12**, 929 (1927); *Chem. Zentr.*, **98**, II, 3, 51 (1927).

(23) See ref. 22.

(24) J. Zincke, *Ber.*, **4**, 397 (1871).

The pyrolysis products obtained at 800° were separated quantitatively on the v.p.c. column described above and were collected for analysis. FA, m.p. 71–72° (for biphenyl, lit.[25] m.p. 69–71°), 0.4 g., was identified as biphenyl by melting point of admixture with a synthetic sample, by infrared spectrum, and by elution behavior on a v.p.c. column.

Fraction B, 0.2 g., had a melting point, after recrystallization from methanol, of 119–120° (lit.,[24] for *p*-bitolyl, m.p. 121°). The melting point of this sample was not depressed upon admixture with *p*-bitolyl; its infrared spectrum and elution behavior from a v.p.c. column were identical with those of *p*-bitolyl.

FC was *p*-toluenesulfonic acid, m.p. 102 (lit.[26] m.p. 102). The sample was further identified by comparison of its infrared spectrum with that of a synthetic sample and by melting point of admixture.

B. Pyrolysis of Solid *p*-Carbomethoxyphenyl Sulfone.—Experimental arrangements were as in the previous experiment. The infrared spectra of the sample pyrolyzed at 750° indicated [total sample removed was 2.9 g. (wet), *ca.* 100%] that the $-SO_2-$ band at 7.80 μ decreased in relation to the $-CO_2CH_3$ band at 5.82 μ from a ratio of 0.97 to a ratio of 1.52. The reaction mixture was leached with 200 ml. of benzene for 2 days at 25°. The insoluble material was filtered and dried at 25° and 0.1 mm., yielding 30 mg., m.p. 230–232°. The infrared spectrum of this substance was identical with that of *p*-bibenzoic acid dimethyl ester, and the melting point of the sample was not depressed upon admixture with a reference sample.

Preparation of *p*-Carbomethoxyphenyl Sulfone.—The *p*-tolyl sulfone was oxidized according to the method of Bennett[27]: to 27.6 g. (0.1 mole) of *p*-tolyl sulfone was added 100 ml. of 35% nitric acid and the reaction mixture was heated in an autoclave with stirring for 3 hr. at 200° under an initial nitrogen pressure of 150 lb. The reaction mixture was cooled to room temperature, filtered, washed on the filter with water, and air dried: 35 g. (~100% conversion). Without further purification the solid was added to 300 ml. of methanol (absolute), 30 ml. of concentrated sulfuric acid was added, and the methanol–water mixture was gradually distilled off with intermittent addition of fresh absolute methanol. A total of 300 ml. of methanol was collected.

The reaction mixture was then cooled to room temperature and was filtered. The pinkish solid was extracted with benzene in a Soxhlet for 2 days and the benzene extracts were concentrated with nitrogen, cooled to 0°, and filtered, yielding 13.5 g. (0.040 mole) of the ester (after drying in a vacuum oven at 50° and 0.1 mm.), m.p. 192–196° (for the ester, lit.[27] m.p. 194°). The infrared spectrum exhibited a typical ester band at 5.79 μ.

Anal. Calcd. for $C_{16}H_{14}O_6S$: C, 57.48; H, 4.22. Found: C, 57.65; H, 4.53.

The benzene-insoluble material was treated with 0.2 mole of sodium bicarbonate in 200 ml. of water and the solution was filtered. The filtrates were acidified; the acid was filtered and was dried at 50° and 0.1 mm., giving 8.7 g. (0.026 mole) or 66% total conversion to both ester and acid.

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[25] F. J. Garrick, *Trans. Faraday Soc.*, **23**, 561 (1927).

[26] J. M. Crafts, *Ber.*, **34**, 1312 (1901).

[27] F. Bennett, unpublished results.

The Chlorination of Camphene

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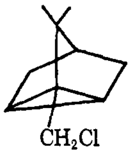
Chlorination of camphene with molecular chlorine in carbon tetrachloride at 0° gives a mixture of mono-, di- and polychlorides, the composition of which has been shown to vary systematically with the quantity of chlorine introduced. The main product found under all conditions studied is the Wagner–Meerwein related dichloride, *exo*-2,10-dichlorobornane (**5**). Primary monochloro products are camphene hydrochloride (**2**), 10-chlorotricyclene (**3**), and *cis*- and *trans*-8-chlorocamphene (**4**). An additional monochloride, *exo*-6-chlorocamphene (**6**), which is found in the liquid distillates of the product mixture, has been shown to result from thermal rearrangement of 10-chlorotricyclene. Details of the chlorination as well as physical and chemical properties of the products are discussed.

Work on the dark chlorination of camphene (**1**) dates back to 1919 when Langlois[1] reported that the main chlorination product is 8-chlorocamphene (**4**). Tishchenko[2] reinvestigated this system in 1953 and maintained that the liquid monochloro fraction reported by Langlois consisted of three compounds to which he assigned structures **3**, **4** and **9**. In addition he isolated a solid dichloride which he reported[3] as **5**. Tishchenko never obtained pure samples of the monochloro compounds but based his assignments on chemical conversions of mixtures of the three materials.



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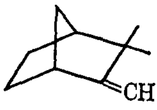

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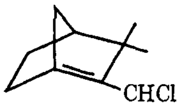

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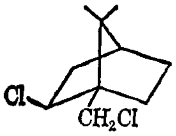

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In the case of **9**, for instance, he reported[2] having converted the chloride mixture to the corresponding alcohol, camphenol, from which he prepared a biphthalate derivative, which he subsequently oxidized to a diketo alcohol, $C_{10}H_{16}O_3$. That **9** was an allyl chloride was deduced from the observation that the product mixture contained very active chlorine.

In 1957 Chiurdoglu, *et al.*,[4] vigorously objected to Tishchenko's structure **9**, pointing out that it violated Bredt's rule. In the same publication these authors proposed the equally improbable structure **10** for Tishchenko's active chloride. They used infrared spectra as their main evidence.

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[1] G. Langlois, *Ann. chim.*, **12**, 193 (1919).

[2] D. Tishchenko, *Zh. Obshch. Khim.*, **23**, 1002 (1953); *J. Gen. Chem. USSR*, **23**, 1051 (1953).

[3] D. Tishchenko and I. Uvarov, *Zh. Obshch. Khim.*, **23**, 1407 (1953).

[4] G. Chiurdoglu, Ch. Goldenberg, and J. Gerraerts, *Bull. soc. chim. Belges*, **66**, 200 (1957).