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Rearrangement of Aryl Sulfides in the Presence of Aluminum Chloride[*1]

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Aluminum chloride-catalyzed rearrangement of aryl sulfides leads to thermodynamically controlled equilibrium mixtures at room temperature. On treatment of *o*-, *m*- or *p*-tolyl phenyl sulfide without solvent, the isomer distribution converges to an equilibrium point, 17% *ortho*, 47% *meta* and 36% *para* isomer by intramolecular isomerization. Intermolecular disproportionation by methyl-group exchange to produce diphenyl sulfide and ditolyl sulfide accompanied isomerization. In addition, a new type of aromatic rearrangement, intermolecular disproportionation by exchange of the arylthio group, was found to occur simultaneously giving benzene, toluene and thianthrene derivatives. The rate of this reaction is slower than that of the methyl rearrangement. A similar treatment of α-naphthyl phenyl sulfide gave the β-isomer from intramolecular isomerization and diphenyl sulfide, naphthalene, thianthrene and benzene from intermolecular disproportionation. The mechanisms of the rearrangement of aryl sulfides are discussed.

In recent years, several kinds of aromatic rearrangement have been elucidated with the development of analytical methods such as gas chromatography and infrared spectroscopy. Various types are recorded in reports and monographs.[1] In particular, the acid-catalyzed rearrangements of alkyl groups in aromatic hydrocarbons and of halogen atoms in halogenoaromatic compounds, involving the Reverdin and Jacobsen rearrangements, have been discussed in detail. However, no rearrangement of aryl sulfides has yet been described.

Preceding communications on iron catalyzed aromatic sulfuration have shown that the direct sulfuration of the aromatic nucleus with sulfur chlorides in the presence of a trace amount of ironpowder provides a convenient method for the preparation of symmetrical sulfides, and the reaction proceeds through thiosulfenyl chloride and sulfenyl chloride as intermediates.[2-3]

$$\mathrm{ArH} + \mathrm{S}_x\mathrm{Cl}_2 \xrightarrow{\mathrm{Fe}} \mathrm{ArSSCl} \longrightarrow \mathrm{ArSCl} \xrightarrow[\mathrm{Fe}]{\mathrm{ArH}} \mathrm{ArSAr}$$

$x = 1$ or 2

Similarly the iron-catalyzed reaction with various types of sulfenyl chlorides as starting materials provides a facile synthetic route for unsymmetrical aryl sulfides.[4] During the course of an extensive study on aromatic sulfuration with various types of catalysts, methyl and arylthio substituents in tolyl

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[*1] This investigation was presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1969.

[1] a) H. J. Shine, "Aromatic Rearrangement," Elsevier, Amsterdam (1967); b) D. A. McCaulay, "Friedel-Crafts and Related Reactions," Vol. II, Part 2, ed. by G. A. Olah, Interscience, New York (1964), p. 1049; c) M. J. S. Dewar, "Molecular Rearrangement," Part 1, ed. by P. de Mayo, Interscience, New York (1963), p. 295; d) H. Suzuki, *Yuki Gosei Kagaku Kyokai Shi*, **23**, 713 (1965).

[2] T. Fujisawa, N. Ohtsuka, T. Kobori and G. Tsuchihashi, *Tetrahedron Lett.*, **1968**, 4533.

[3] T. Fujisawa, T. Kobori and G. Tsuchihashi, *ibid.*, **1969**, 4291.

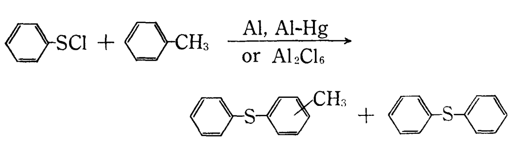
[4] T. Fujisawa, T. Kobori, N. Ohtsuka and G. Tsuchihashi, *ibid.*, **1968** 5071.

TABLE 1. REACTION OF BENZENESULFENYL CHLORIDE WITH TOLUENE

Catalyst	Wt %	Tolyl phenyl sulfide yield %	*ortho*	*meta* mol %	*para*	Diphenyl sulfide yield %
Fe	0.6	10	33	—	67	—
Fe	13.9	28	33	—	67	—
$FeCl_3$	0.6	10	33	—	67	—
$FeCl_3$	13.9	18	33	—	67	—
Al	1.4	—	—	—	—	—
Al	4.2	22	30	21	49	6
Al	13.9	22	26	26	48	4
Al_2Cl_6	1.4	16	36	—	64	—
Al_2Cl_6	4.2	20	31	8	61	2
Al_2Cl_6	13.9	43	22	35	43	17
Al_2Cl_6	27.8	42	17	41	42	16
Al-Hg	1.4	16	36	—	64	—
Al-Hg	4.2	26	34	21	45	5
Al-Hg	13.9	36	31	18	51	7

phenyl sulfides were found to rearrange in the presence of aluminum chloride. In the present experiments the rearrangement of aryl sulfides in the presence of aluminum chloride was investigated.

The products and isomer ratios from the reaction of toluene with benzenesulfenyl chloride depend on the kind and amount of the catalysts used. When iron catalysts such as iron powder or ferric chloride, are used, the products are *o*- and *p*-tolyl phenyl sulfides. The total yield increases with the increase of the amount of catalyst, and the *ortho-para* isomer ratio remains unchanged. On the other hand, in the case of aluminum catalysts such as aluminum metal, aluminum amalgam or aluminum chloride, the *meta* isomer is formed along with the other isomers, while the isomer ratios vary with the amount of the catalyst used. The formation of diphenyl sulfide in fair yield was simultaneously observed. The data for the reaction of toluene with benzenesulfenyl chloride in the presence of various types of catalysts are shown in Table 1. The product yields and isomer ratios were determined by glpc. The results suggest that intramolecular and intermolecular methyl group migration in the initially formed product mixture lead to the observed mixture of tolyl phenyl sulfide isomers and diphenyl sulfide. To confirm this hypothesis, each isomer of tolyl phenyl sulfide was chosen as a starting material and its rearrangement in the presence of aluminum chloride was studied.



Several common solvents were investigated under various conditions to determine how readily the dissolved tolyl phenyl sulfides undergo rearrangement. Representative runs are collected in Table 2. It is worth noting that no rearrangement took place in certain solvents under mild conditions (at room temperature).

Thus, *p*-tolyl phenyl sulfide was recovered after treatment in ether or acetonitrile and only very slowly changed in carbon tetrachloride or nitrobenzene. In petroleum ether, although the products after a 20 hr reaction time could be clearly distinguished by glpc analysis, other peaks appeared at the same region of the peaks of the tolyl phenyl sulfides in the glpc chart after a 40 hr reaction time and quantitative analysis became impossible. This seemed to be attributable to disproportionation between the sulfides and the petroleum ether. The intramolecular rearrangement was readily observed in diphenyl sulfide as solvent, but intermolecular rearrangement, disproportionation, could not be detected in this case. The equilibrium amounts of the sulfide isomers found after a 40 hr reaction time may characterize the equilibrium point when only the intramolecular isomerization took place. Since the tolyl phenyl sulfide isomer compositions were different when the disproportionation was occurring simultaneously, the rearrangements were carried out without solvent in order to observe both features of the reaction. Although the rearrangement occurred readily without solvent at room temperature, addition of a trace amount of water as cocatalyst resulted in an extremely rapid reaction lasting 30 min. After 2 hr, results were the same with or without the addition of water.

Thus, the tolyl phenyl sulfide isomer compositions were obtained by treating stirred mixtures of the sulfides with aluminum chloride (20 : 1 molar ratio) at room temperature in the presence of a drop of water, added by a microsyringe. The mixtures soon became homogeneous liquids and changed to viscous liquids after 72 hr making stirring by magnetic stirrer very difficult. At certain intervals, samples were withdrawn from the reaction mixtures,

TABLE 2. SOLVENT EFFECT IN REARRANGEMENT OF *p*-TOLYL PHENYL SULFIDE WITH Al_2Cl_6 CATALYST AT ROOM TEMPERATURE

Solvent	Product wt% reaction time, 20 hr					Product wt% reaction time, 40 hr				
	Diphenyl sulfide	Tolyl phenyl sulfide *o*-	*m*-	*p*-	Ditolyl sulfide	Diphenyl sulfide	Tolyl phenyl sulfide *o*-	*m*-	*p*-	Ditolyl sulfide
Carbon disulfide	16	15	7	59	3	28	8	15	35	14
Benzene	26	3	11	57	4	36	7	16	32	9
Chloroform	20	4	12	52	12	24	4	14	46	12
Diphenyl sulfide	—	23	46	31	—	—	33	46	21	—
Petroleum ether	20	2	6	60	9					
Carbon tetrachloride	4	—	—	96	—	3	—	—	97	—
Nitrobenzene	1	—	1	98	—	1	—	1	98	—
Diethyl ether	—	—	—	100	—	—	—	—	100	—
Acetonitrile	—	—	—	100	—	—	—	—	100	—
Toluene	16	13	13	52	12					

TABLE 3. ISOMERIZATION OF TOLYL PHENYL SULFIDES WITH $Al_2Cl_6 \cdot H_2O$ CATALYST AT ROOM TEMPERATURE

Isomer	Reaction time	% tolyl phenyl sulfide isomer distribution *ortho*	*meta*	*para*
ortho	5 min	71	25	4
	10	66	29	5
	15	54	39	7
	30	33	58	9
	1 hr	18	69	13
	2	19	66	15
	6	16	61	23
	26	13	53	34
	48	15	49	36
	168	17	47	36
meta	5 min	14	82	4
	10	14	80	6
	15	15	78	7
	30	21	69	10
	1 hr	16	71	13
	2	16	67	17
	6	13	67	20
	26	12	51	37
	48	12	51	37
	168	17	47	36
para	5 min	0	1	99
	10	0	1	99
	15	0	2	98
	30	0	3	97
	1 hr	3	8	89
	2	4	13	83
	6	5	29	64
	26	12	48	40
	48	14	48	38
	168	17	47	36

hydrolyzed by addition of water and extracted with ether. The samples were then analyzed by glpc.

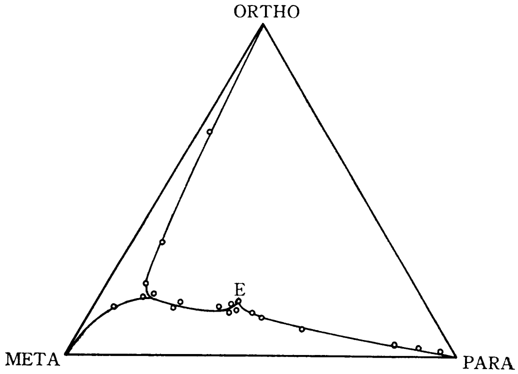


Fig. 1. *Ortho*, *meta* and *para* isomer equilibrations in isomerization of neat tolyl phenyl sulfides with $Al_2Cl_6.H_2O$ catalyst at room temperature.

The results are given in Table 3. Three runs are plotted in triangular coordinates[5] in Fig. 1.

The *ortho* isomer trajectory starts asymptotically to the 0% *para*-isomer side and the *meta* isomer trajectory starts asymptotically to the 0% *para* isomer side. Both trajectories combine after a 1-hr reaction time and then drift toward the *para* isomer side. After 168 hr, the joint trajectory meets the *para* trajectory at the thermodynamically controlled equilibrium point, in which the sulfide isomer compositions were *ortho* 17%, *meta* 47% and *para* 36%. This corresponds to a *meta*/*para* ratio of 1.3 and *ortho*/*para* ratio of 0.5. The most rapid rearrangement is shown to be the *ortho*→*meta* migration. The pattern of the triangular composition diagram resembles that for the acid-catalyzed isomerization of xylene[6] rather than that for isomerization of bromotoluene,[7] previously reported.

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5) R. H. Allen, T. Alfrey, Jr., and L. D. Yats, *J. Amer. Chem. Soc.*, **81**, 42 (1959).

6) R. H. Allen and L. D. Yats, *ibid.*, **81**, 5289 (1959).

7) J. W. Crump and G. A. Gornowicz, *J. Org. Chem.*, **28**, 949 (1963).

TABLE 4. EQUILIBRIUM COMPOSITIONS OF DISUBSTITUTED BENZENES

Substituents in ring		Reaction temperature	Catalyst	% Composition			Ratio *m/p*
				ortho	*meta*	*para*	
Me	PhS	room	$Al_2Cl_6 \cdot H_2O$	17	47	36	1.3
Me	Me	30	$Al_2Br_6 \cdot HBr$	12	72	16	4.5[a]
Me	Et	room	$Al_2Cl_6 \cdot HCl$	7	66	27	2.4[b]
Me	*i*-Pr	room	$Al_2Cl_6 \cdot HCl$	2	69	30	2.3[c]
Me	*t*-Bu	25	$Al_2Cl_6 \cdot H_2O$	0	64	36	1.8[d]
Et	Et	25	$Al_2Cl_6 \cdot H_2O$	3	69	28	2.5[e]
i-Pr	*i*-Pr	25	$Al_2Cl_6 \cdot H_2O$	0	67	33	2.1[f]
t-Bu	*t*-Bu	25	$Al_2Cl_6 \cdot H_2O$	0	52	48	1.1[g]
Br	Br	30	$Al_2Br_6 \cdot H_2O$	4	62	34	1.8[h]
Me	Br	30	$Al_2Cl_6 \cdot H_2O$	37	45	18	2.5[i]

a) K. S. Pitzer and D. W. Scott, *J. Amer. Chem. Soc.*, **65**, 803 (1943).
b) R. H. Allen, *ibid.*, **82**, 4853 (1960).
c) Ref. 5.
d) G. A. Olah, M. W. Meyer and N. A. Overchuck, *J. Org. Chem.*, **29**, 2310 (1964).
e) G. A. Olah, M. W. Meyer and N. A. Overchuck, *ibid.*, **29**, 2313 (1964).
f) G. A. Olah, M. W. Meyer and N. A. Overchuck, *ibid.*, **29**, 2315 (1964).
g) Ref. 8.
h) G. A. Olah, W. S. Tolgyesi and R. E. A. Dear, *J. Org. Chem.*, **27**, 3455 (1962).
i) Ref. 9.

The initial point at which the two *ortho* and *meta* trajectories become associated is considered to be close to the equilibrium point which would be observed if intramolecular rearrangement only took place.

A comparison of the rearrangement of tolyl phenyl sulfides to that of other disubstituted benzenes, which have been previously described, is summarized in Table 4.

The rearrangement of an alkyl group on the benzene nucleus in the presence of an acid-catalyst is well known: Xylenes are isomerized at room temperature and give a *meta/para* ratio of 4.5. This reaction has been shown to proceed by an intramolecular 1,2-shift mechanism.[6] Attachment of more bulky alkyl groups to the benzene nucleus gives a smaller *meta/para* ratio. Thus, the value became smaller in the order methyl, ethyl, isopropyl, *t*-butyl. When two *t*-butyl groups are substituted on the nucleus, the *meta/para* ratio is 1.1. In this case, the reaction is known to proceed by intermolecular rearrangement involving a π-complex at the transition state.[8] Halogen atoms can also move their position on the benzene nucleus in the presence of acid-catalysts by an electrophilic attack mechanism of halogen cation.[9] In the case of bromotoluene, the *meta/para* ratio is 2.5.

The value 1.3 for the *meta/para* ratio in the rearrangement of tolyl phenyl sulfides is fairly close to that for di-*t*-butylbenzenes mentioned above. This indicates that isomerization and disproportionation occur simultaneously in the rearrangement. The relative amounts of tolyl phenyl sulfide and of diphenyl sulfide and ditolyl sulfide, which are products of the intermolecular exchange of the methyl group, *versus* the reaction time (taking the sum of the amounts of the three compounds concerned as 100%) are summarized in Figs. 2—4.

The amount of diphenyl sulfide increases with reaction time, but the yield of the corresponding ditolyl sulfide is maximal at a 6-hr reaction time and thereafter diminishes. The ratio of diphenyl sulfide to tolyl phenyl sulfides converges to about 3.9. This failure in material balance of the methyl group

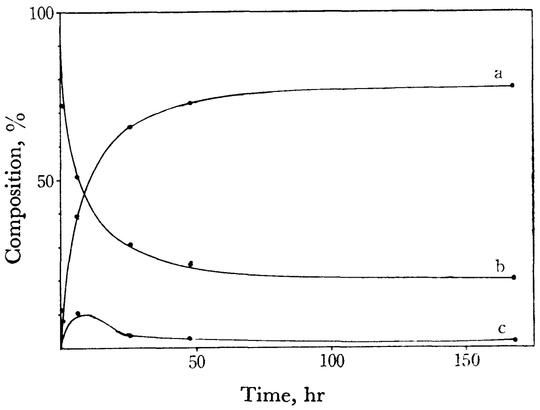

Fig. 2. Disproportionation of neat *o*-tolyl phenyl sulfide with $Al_2Cl_6 \cdot H_2O$ catalyst at room temperature.
a: diphenyl sulfide, b: tolyl phenyl sulfide, c: ditolyl sulfide

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[8] G. A. Olah, C. G. Carlson and J. C. Lapierre, *J. Org. Chem.*, **29**, 2687 (1964).

[9] G. A. Olah and M. W. Meyer, *ibid.*, **27**, 3464 (1962).

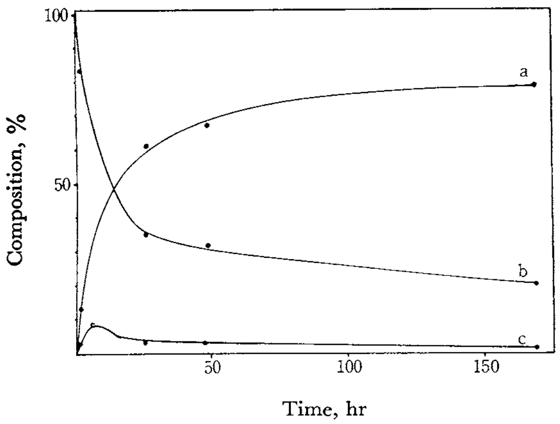

Fig. 3. Disproportionation of neat *m*-tolyl phenyl sulfide with $Al_2Cl_6 \cdot H_2O$ catalyst at room temperature.
a: diphenyl sulfide, b: tolyl phenyl sulfide, c: ditolyl sulfide

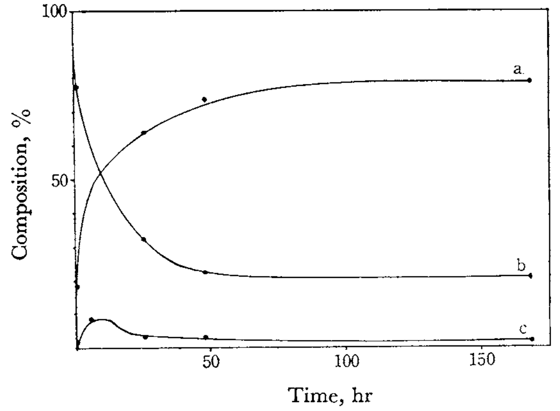

Fig. 4. Disproportionation of neat *p*-tolyl phenyl sulfide with $Al_2Cl_6 \cdot H_2O$ catalyst at room temperature.
a: diphenyl sulfide, b: tolyl phenyl sulfide, c: ditolyl sulfide

may be due to the formation of polymethyl derivatives of the sulfides, which also occurs in the case of the Jacobsen rearrangement.[10] In fact, the formation of trimethyldiphenyl sulfide and tetramethyldiphenyl sulfide could be observed on glpc analyses, but they also gradually diminished after a maximum at 6-hr reaction time.

The poor material balance for the methyl group might also suggest other products. Careful examination of the product analyses revealed bond fission between the aryl group and the sulfur atom of the sulfide as well as rearrangement of the methyl group: thianthrene, toluene and benzene were observed among the products from the tolyl phenyl sulfides. The relative amounts of these compounds are shown in Figs. 5—7.

Among the products, the proportion of polymethyl derivatives of thianthrene increased with long reaction times. Although these compounds were obtained by glpc separation, each isomer could not be isolated and the methyl-group positions could not be determined.

As mentioned above, the intermolecular methyl group rearrangement of tolyl phenyl sulfide gives diphenyl sulfide and ditolyl sulfide (Eq. (1)), while a similar arylthio group rearrangement affords benzene, toluene and thianthrene derivatives (Eq. (2)). Thus, in order to compare the rates of these two rearrangements, the ratio of the sum of mole fractions of benzene and toluene, which are formed by the arylthio migration, to the mole fraction of

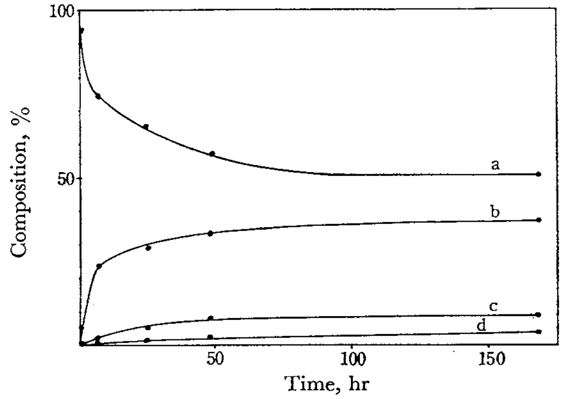

Fig. 5. Disproportionation of arylthio groups in neat *o*-tolyl phenyl sulfide with $Al_2Cl_6 \cdot H_2O$ catalyst at room temperature.
a: diaryl sulfides (diphenyl sulfide+tolyl phenyl sulfide+ditolyl sulfide), b: toluene, c: thianthrene, d: benzene

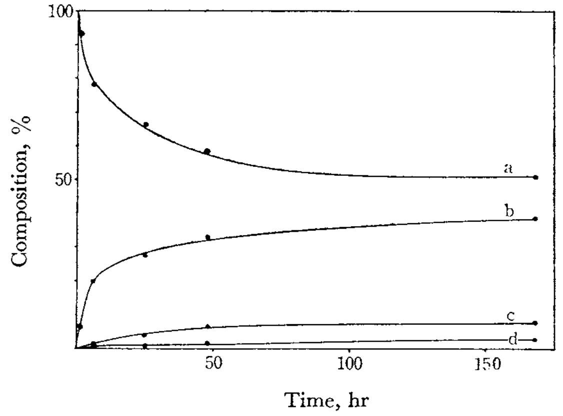

Fig. 6. Disproportionation of arylthio groups in neat *m*-tolyl phenyl sulfide with $Al_2Cl_6 \cdot H_2O$ catalyst at room temperature.
a: diaryl sulfides (diphenyl sulfide+tolyl phenyl sulfide+ditolyl sulfide), b: toluene, c: thianthrene, d: benzene

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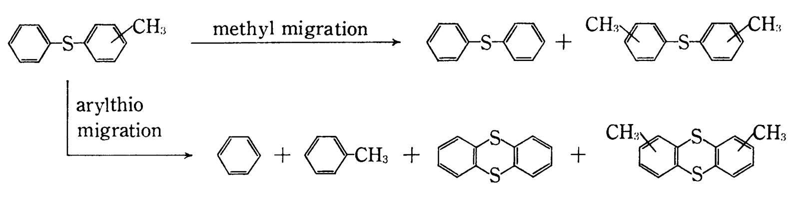
[10] *e. g.*, R. Goto, *Kagaku to Kogyo*, **17**, 25 (1964).



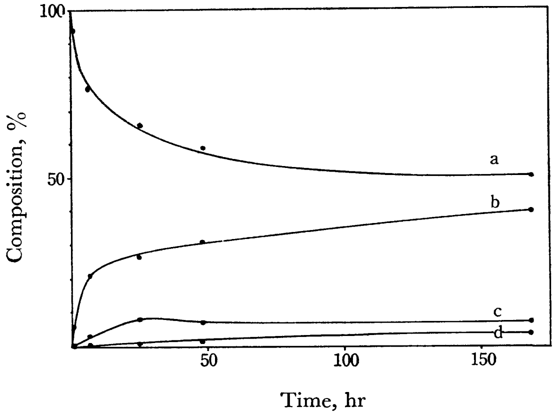


Fig. 7. Disproportionation of arylthio groups in neat *p*-tolyl phenyl sulfide with $Al_2Cl_6 \cdot H_2O$ catalyst at room temperature.
a: diaryl sulfides (diphenyl sulfide+tolyl phenyl sulfide+ditolyl sulfide), b: toluene, c: thianthrene, d: benzene

diphenyl sulfide, which results from the methyl migration, was calculated and is given in Table 5. The values of the ratio converge to about 0.9 after long reaction times in all cases, regardless of the choice of the isomer of tolyl phenyl sulfide as starting material. Table 5 also indicates that the amount of diphenyl sulfide formed is larger than that of arenes in the initial stages of the reaction, which shows that the methyl rearrangement proceeds faster than the arylthio rearrangement in the disproportionation of tolyl phenyl sulfide.

TABLE 5. RATIO OF THE SUM OF MOLE FRACTIONS OF BENZENE AND TOLUENE TO THE MOLE FRACTION OF DIPHENYL SULFIDE IN THE ALUMINUM CHLORIDE CATALYZED DISPROPORTIONATION OF TOLYL PHENYL SULFIDES

Reaction time	Tolyl phenyl sulfides		
	ortho	*meta*	*para*
10 min	0.2	—	0.3
30	0.3	0.1	0.4
1 hr	0.3	0.2	0.5
6	0.4	0.5	0.6
26	0.6	0.6	0.6
48	0.7	0.7	0.7
168	0.9	0.9	0.9

This Lewis acid-catalyzed arylthio group rearrangement has not been reported and is thus a new type of aromatic rearrangement. The most striking characteristic of this rearrangement is that it proceeds at room temperature. In order to make a further study of it, the rearrangement of α-naphthyl phenyl sulfide in the presence of aluminum chloride at room temperature was tried. β-Naphthyl phenyl sulfide, the product of intramolecular rearrangement, increased rapidly at first ($\alpha/\beta = 59/41$ at 1 hr), then exceeded the amount of α isomer (11/89 at 24 hr), but the ratio of α and β isomers eventually approached 50 : 50 after about 72 hr (Table 6).

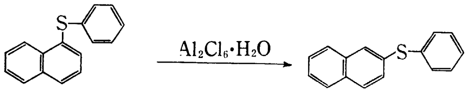


TABLE 6. ISOMERIZATION OF α-NAPHTHYL PHENYL SULFIDE WITH $Al_2Cl_6 \cdot H_2O$ CATALYST AT ROOM TEMPERATURE

Time, hr	0	1	6	24	72
α/β	100/0	59/41	15/85	11/89	50/50

As regards intermolecular rearrangement, the formation of diphenyl sulfide, naphthalene, thianthrene, diphenyl disulfide and benzene were ob-

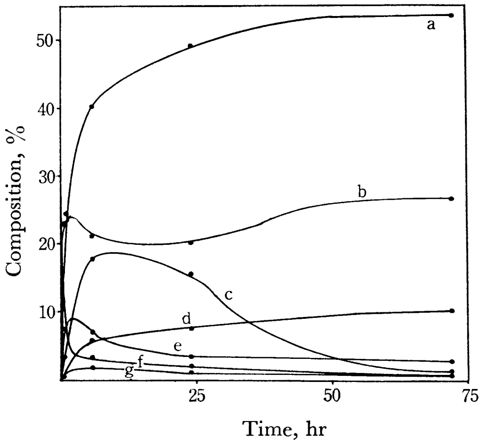
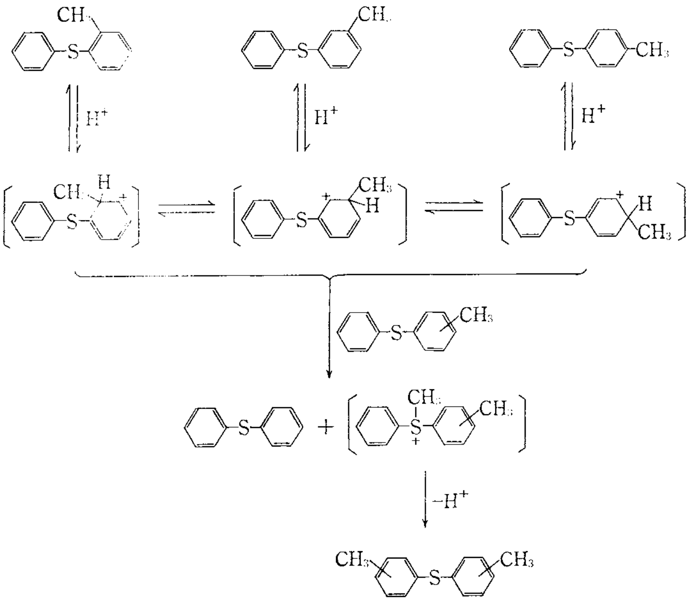


Fig. 8. Disproportionation of α-naphthyl phenyl sulfide with $Al_2Cl_6 \cdot H_2O$ catalyst at room temperature.
a: diphenyl sulfide, b: naphthalene, c: β-naphthyl phenyl sulfide, d: thianthrene, e: diphenyl disulfide, f: α-naphthyl phenyl sulfide, g: benzene

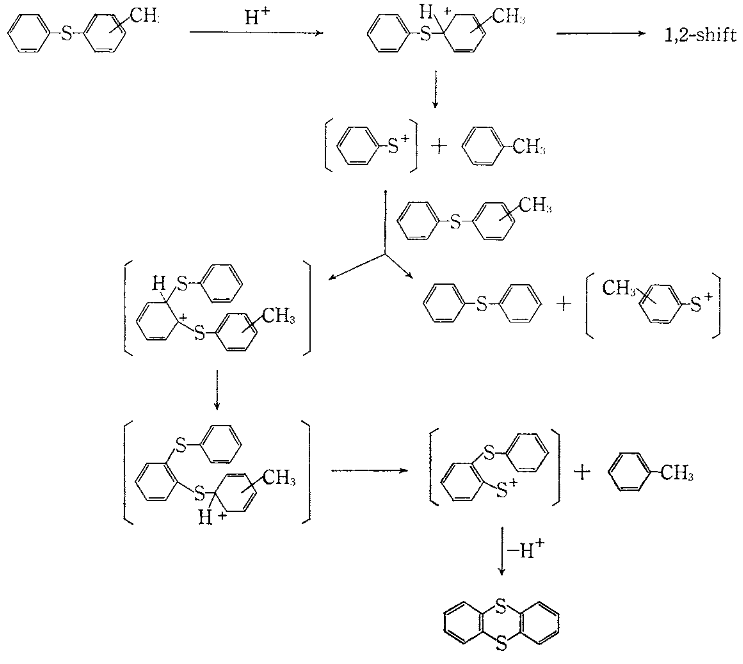
served, together with the decrease of naphthyl phenyl sulfide, as shown in Fig. 8. Other unidentified products observed by glpc, are probably thianthrene type products of naphthalene, and dinaphthyl sulfide, *etc.*

From the results, the isomerization and disproportionation of methyl and arylthio substituents were found to take place simultaneously on treatment of aryl sulfides with aluminum chloride. The mechanisms of the migrations may be as follows:



The proton attacks the position bonded to the methyl group of the aromatic nucleus to make σ-complexes, which are in equilibrium with each other *via* intramolecular 1,2-methyl shifts. In the case of intermolecular rearrangement, the complexes react with another tolyl phenyl sulfide to give diphenyl sulfide and ditolyl sulfide, which proceeds by way of a sulfonium-cation type intermediate.

On the other hand, the protonation at the position of the nucleus bonded to the sulfur atom may promote the intramolecular 1,2-arylthio shifts. The simultaneous bond fission between aryl group and



sulfur atom takes place yielding sulfenium cation.[11] This might be explained partly by the attack on a sulfur bearing carbon to yield another sulfenium cation and partly by the attack on the position *ortho* to the sulfur atom of another sulfide to give thianthrene derivatives, according to the above described routes.

The facility of the rearrangement is considered to be due to the easy protonation by electron-releasing effect of sulfur atom, and the sulfonium type intermediate through which the mobile substituents are able to migrate to the adjacent aromatic nucleus.

Experimental

Materials. Benzenesulfenyl chloride was prepared from thiophenol and chlorine according to the method of Lecher and Holschneider.[12] Most of the aryl sulfides, for reaction and for product analyses were prepared by the condensation of the aryl diazonium salt and the corresponding thiophenols, with modification of the procedure for diphenyl sulfide.[13] α-Naphthyl phenyl sulfide was prepared from α-bromonaphthalene and thiophenol.[14] Thianthrene was obtained as a by-product of the preparation of diphenyl sulfide.[15] The purity of all sulfides was determined by glpc. The following boiling points (melting points) for the sulfides are given: tolyl phenyl sulfides, *o*-, 104°C/0.15 mmHg; *m*-, 98°/0.1; *p*-, 99°/0.09; ditolyl sulfide, *p,p*-, (56—57°); *m,p*-, 114—124°/0.2; *o,p*-, 120—124°/0.15; *o,m*-, 118—124°/0.3; *m,m*-, 124—128°/0.2; naphthyl phenyl sulfides, α-, (42—43°); β-, (52—54°); thianthrene, (155—156°). Aluminum chloride was used as it was.

Reactions of Toluene with Benzenesulfenyl Chloride in the Presence of Various Types of Catalysts. To a solution of 46.0 g (0.5 mol) of toluene and 7.2 g (0.05 mol) of benzenesulfenyl chloride was added the catalyst given in Table 1. The reaction mixture was allowed to stand at room temperature with stirring for 7 hr. After removal of excess toluene, the residual oily product was fractionated by vacuum distillation and then analyzed by glpc (10% carbowax 20M, 1 m, 220°).

General Rearrangement Procedure. Aluminum chloride (0.0005 mol) was added to 0.01 mol of each isomer of tolyl phenyl sulfide in a flask equipped with magnetic stirrer and calcium chloride tube. One microliter of water was added as promoter. The reaction mixture was kept standing at room temperature with constant agitation. Samples were withdrawn periodically; the reaction was stopped by quenching with water. The organic materials were extracted with ether. The extracts were analyzed by glpc (10% carbowax 20M, 2m 220°). When a solvent was used, the concentration was 5×10^{-1}M and molar ratio of the sulfide to the catalyst 10 : 1.

In the case of rearrangement of α-naphthyl phenyl sulfide, carbon disulfide was used to obtain homogeneous liquid. Glpc analytical conditions were 10% QF-1, 1m, 180°.

Gas-liquid Partition Chromatographic Analysis. All analyses were carried out on a Hitachi Model K-53 Fractometer using a hydrogen flame-ionization detector. The accuracy of the gas-liquid partition chromatographic analytical method, as established from the analysis of isomer mixtures of known composition, was better than ±5 relative % for all products.

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11) An alternative mechanism may involve an intermediate π-complex, analogous to that proposed for the migration of *t*-butyl group (Ref. 8).

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