ml. of 4 *N* ethylamine in 95% ethanol was allowed to stand tightly stoppered for 7 days and there was obtained 30 g. of a solid melting at 104–118°. Ten grams of this solid recrystallized from 200 ml. of boiling water gave 3 g. of large prisms, m.p. 166–169°. Three recrystallizations from isopropyl alcohol raised the m.p. to 170–171°.

Anal. Calcd. for $C_{12}H_{18}N_2O_2$: C, 64.82; H, 8.16; N, 12.60. Found: C, 64.56; H, 8.00; N, 12.78.

PORTLAND 2, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

An Attempted Fries Reaction with Thiolesters. The Formation of Trithioörthoesters[1]

BY D. S. TARBELL AND A. H. HERZ[2]

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The Fries rearrangement of favorably substituted aryl thiolesters has not been realized, even in the presence of the strong Lewis acid, aluminum bromide. Instead, trithioörthoesters may be formed by partial cleavage of the thiolester, followed by the addition of the thiophenol to the ester carbonyl. Thus, phenyl thiolacetate upon treatment with boron fluoride or aluminum bromide yielded phenyl trithioörthoacetate (I). Structure I had been previously assigned to a compound obtained by the action of thiophenol on 1,1,1-trichloroethane; however, the product of that reaction has been shown to be 1,2-diphenylthioethane (VI). A number of orthotrithioesters have been prepared by treating an acyl chloride or thiolester with thiophenol in the presence of boron fluoride; similarly, a mixed orthothioester (II) was obtained by the action of *m*-thiocresol on phenyl thiolacetate. Since 4-acetylthiophenol and boron fluoride gave a mercaptole-type of condensation product, it is concluded that in general, under the acidic conditions of the Fries reaction, acylthiophenols would be expected to condense to polymercaptoles. The failure of the Fries reaction to occur is attributed to deactivation of the aromatic ring by contributions from resonance forms in which sulfur has expanded its valence shell.

Several reports[3] indicate that the Fries reaction has not been realized with esters of thiophenols, RCOSAr. We have reinvestigated this problem, because it seemed possible that the use of a very strong Lewis acid, such as aluminum bromide,[4] and a suitably substituted thiophenol ester, might bring about the desired rearrangements. Such a result would make possible a kinetic study of the reaction, and thus might yield some information about the mechanism of the Fries reaction with oxygen esters, which is not very well understood.[5] As indicated below, the reaction has not been successful in our hands, but under the experimental conditions used the aryl thiolacetates may be partially converted to aryl trithioörthoacetates, $CH_3C(SAr)_3$(I).

Treatment of analytically pure phenyl thiolacetate with boron fluoride, either alone or in acetic acid, yielded only a crystalline compound, of m.p. 145–146°. The composition of this material agreed with the phenyl trithioörthoacetate structure I, and its chemical properties supported this view; the latter included conversion by alcoholic mercuric chloride to phenylthiomercuric chloride, and and quantitative oxidation by peroxide to benzenesulfonic acid. Furthermore, the infrared and ultraviolet spectra (see Table I) of the 146° compound agreed very closely with those of phenyl trithioörthoformate,[6] $HC(SC_6H_5)_3$. However, structure I had been assigned to a compound of m.p. 71.5°, obtained by the action of 1,1,1-trichloroethane on thiophenol[7]; this product was reported to yield a trisulfone of m.p. 180°, which we were unable to obtain from the 146° compound.

$RC(SAr)_3$
I, Ar = C_6H_5, R = CH_3
II, $(Ar)_2$ = *m*-$CH_3C_6H_4$, Ar = C_6H_5, R = CH_3
III, Ar = *m*-$CH_3C_6H_4$, R = CH_3
IV, Ar = $CH_2C_6H_5$, R = CH_3
V, Ar = C_6H_5, R = C_6H_5

TABLE I

INFRARED ABSORPTION MAXIMA IN NUJOL

S, strong, M, medium, W, weak absorption

$(C_6H_5S)_3C—CH_3$		$(C_6H_5S)_3C—H$	
691 cm.$^{-1}$	M	691 cm.$^{-1}$	S
704	S	704	M
..		725	W
756	S	759	S
920	W	..	
999	W	999	W
1024	M	1024	M
1059	M	1059	M
1176	W	1176	W
1300	M	1300	W

ULTRAVIOLET ABSORPTION IN METHYLCYCLOHEXANE

$(C_6H_5S)_3C—CH_3$		$(C_6H_5S)_3C—H$	
mμ	log ε	mμ	log ε
Max. 236	4.161	Max. 236	4.115
Min. 257	3.779	Min. 256	3.991
Max. 268	3.843	Max. 264	4.009

It appeared probable, from a consideration of the m.p.'s, and the percentage compositions, that Laves' compounds were actually 1,2-diphenylthioethane,[8] m.p. 69°, (VI) and the corresponding disulfone,[9] m.p. 180°.

$$CH_3CCl_3 \xrightarrow{C_6H_5SH} C_6H_5SCH_2CH_2SC_6H_5 \qquad (VI)$$

This compound might have been formed from an

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(1) Presented at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

(2) Eastman Kodak Fellow, 1952–1953.

(3) (a) K. Auwers and F. Arndt, *Ber.*, **42**, 537 (1909); (b) H. Burton and P. F. Hu, *J. Chem. Soc.*, 601 (1948); (c) *cf.* G. B. Bachman and C. L. Carlson, THIS JOURNAL, **73**, 2857 (1951).

(4) *Cf.* (a) Pfeiffer and Haack, *Ann.*, **460**, 156 (1928); (b) D. P. Harnish and D. S. Tarbell, THIS JOURNAL, **70**, 4123 (1948); (c) D. S. Tarbell and J. C. Petropoulos, *ibid.*, **74**, 244 (1952).

(5) For review, see A. H. Blatt, in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 342; *cf.* D. S. Tarbell and P. E. Fanta, THIS JOURNAL, **65**, 2169 (1943), and C. R. Hauser and B. H. Man, *J. Org. Chem.*, **17**, 390 (1952).

(6) B. Holmberg, *Ber.*, **40**, 1740 (1907).

(7) E. Laves, *ibid.*, **25**, 353 (1892).

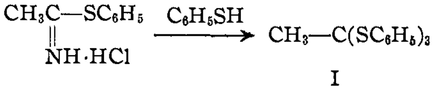
(8) E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 3189 (1928).

(9) (a) R. Otto, *Ber.*, **13**, 1280 (1880); (b) H. Gilman and N. J. Beaber, THIS JOURNAL, **47**, 1451 (1925).

impurity of 1,2-dichloroethane or 1,1,2-trichloroethane in the halide used,[10] or it might be the result of an elimination and recombination reaction, involving the elements of hydrogen chloride and thiophenol, and the reductive removal of chlorine by the latter.[11]

This alternative was shown to be the likely one by a repetition of Laves' experiments, using carefully purified 1,1,1-trichloroethane; the only product besides diphenyl disulfide which could be isolated was VI, which yielded the expected disulfone on oxidation. Mixed m.p.'s were taken with authentic samples of both VI and its disulfone.

The 146° compound was shown conclusively to have structure I by synthesis, following the general procedure for orthoacetates,[12] from phenyl iminothiolacetate and thiophenol.



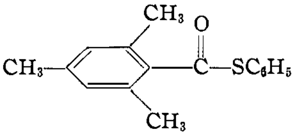
$$\underset{\text{NH·HCl}}{CH_3\overset{}{C}\text{—}SC_6H_5} \xrightarrow{C_6H_5SH} CH_3\text{—}C(SC_6H_5)_3$$

I

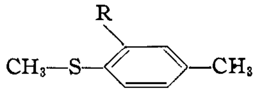
The formation of I from phenyl thiolacetate must involve a cleavage of part of the ester to yield thiophenol (or derivative), which then reacts further with the thiolacetate to yield I. This was supported by showing that the addition of thiophenol to phenyl thiolacetate increased the yield of I. Furthermore, treatment of phenyl thiolacetate with *m*-thiocresol and boron fluoride led apparently to a mixture of trithioörthoacetates, from which the mixed ester II, with one phenyl and two *m*-tolyl groups, was isolated by fractional crystallization. Presumably interchange of arylthio groups can occur in the presence of the acid catalyst.[13]

Attempts to carry out the Fries reaction on *m*-tolyl thiolacetate gave only starting material and tars. However, in the presence of *m*-thiocresol the corresponding trithioörthoacetate III was obtained; this was also formed directly from *m*-thiocresol, acetic anhydride and boron fluoride. Benzyl trithioörthoacetate (IV) was obtained similarly from benzyl thiolacetate,[14] benzyl mercaptan and boron fluoride; phenyl trithioörthobenzoate (V) was formed from phenyl thiolbenzoate (or, better benzoyl chloride), thiophenol and boron fluoride.[15] The action of aluminum bromide on phenyl thiolbenzoate and thiophenol leads to thianthrene.[16]

The preceding experiments made it clear that the action of strong Lewis acids on aryl thiolacetates may lead to partial cleavage to form thiophenol derivatives, which then add to the carbonyl group of unchanged ester to form the trithioörthoacetates. It appeared possible that the Fries reaction might be realized in an aryl thiolester in which addition to the carbonyl group would be unlikely for steric reasons. Since it is known that *p*-tolyl mesitoate readily undergoes the Fries reaction,[17] phenyl thiolmesitoate (VII) was prepared. This compound, as expected, was recovered unchanged after treatment with thiophenol and boron fluoride,



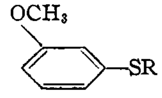
VII



VIII, R = H
IX, R = COCH$_3$

and hence does not form a trithioörthomesitoate; it was also recovered unchanged after heating with aluminum bromide at 153° for some time. The oxygen analogs of VII gave good yields of rearranged products[17] using aluminum chloride at 150°.

3-Methoxyphenyl thiol acetate (X) which was prepared because the benzene nucleus should be comparatively readily acylated,[18] was converted by zinc chloride, or by boron fluoride with or without acetic acid, to tars and to a green amorphous material from which it was not possible to isolate any thiophenol corresponding to a Fries rearrangement. The green solid appeared to be of high molecular weight, it was apparently neither a thioindigo,[19] because it was not reversibly reducible to a leuco compound, nor a sulfur dye,[20] because it did not dissolve in alkali sulfide. Neither did it appear to be a polymercaptole, since it remained unchanged after prolonged refluxing with mercuric chloride.[21]



X, R = COCH$_3$
XI, R = 2,4-(O$_2$N)$_2$C$_6$H$_3$

On the other hand, treatment of 4-acetylthiophenol with boron fluoride rapidly gave a very insoluble condensation product which, upon refluxing with an acidic mercuric chloride solution, reformed about 30% of the original 4-acetylthiophenol as the mercuric mercaptide. This indicates that the condensation product contained a large percentage of mercaptole linkages, and in general, makes it appear that if an acylthiophenol were formed under the acidic conditions of the Fries reaction, it would be expected to condense to a polymercaptole.[22]

The failure of any of the aryl thiolesters to undergo the Fries reaction emphasizes the contrast between sulfur and oxygen substituents on the aromatic ring, to which attention has been drawn previously.[3c,4c] The reason for this failure may be

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[10] *Cf.* A. C. Cope, THIS JOURNAL, **57**, 572 (1935), who clarified a similar situation by showing that the supposed phenyl orthoacetate obtained from phenol and 1,1,1-trichloroethane was actually 1,2-diphenoxyethane.

[11] There is ample analogy for this, *e.g.*, the work of R. Otto, (*J. prakt. Chem.*, [2] **40**, 505 (1889); *Ber.*, **27**, 3055 (1894)), on reactions between polyhaloalkanes and thiophenoxides or sulfinates.

[12] S. M. McElvain and W. J. Nelson, THIS JOURNAL, **64**, 1825 (1942).

[13] W. M. Mochel, C. L. Agre and W. E. Hanford, *ibid.*, **70**, 2268 (1948); M. Moura Campos and H. Hauptmann, *ibid.*, **74**, 2962 (1952).

[14] B. K. Morse and D. S. Tarbell, *ibid.*, **74**, 416 (1952).

[15] J. D. Kendall, U. S. Patent 2,389,153 (*C. A.*, **40**, 1540 (1946)), reported some alkyl trithioörthoacetates, $CH_3C(SR)_3$, from acetyl chloride, mercaptan and zinc chloride.

[16] J. J. B. Deuss, *Rec. trav. chim.*, **27**, 145 (1908).

[17] R. C. Fuson, S. L. Scott and S. B. Speck, THIS JOURNAL, **63**, 2845 (1941).

[18] This expectation was supported by the fact that, although thiophenol itself does not give nuclear acylation under Friedel–Crafts conditions,[3c] 3-methoxythiophenol yields 2-acetyl-5-methoxythiophenol; *cf.* German Patent 202,632 (*Chem. Zentr.*, **79**, II, 1659 (1908)).

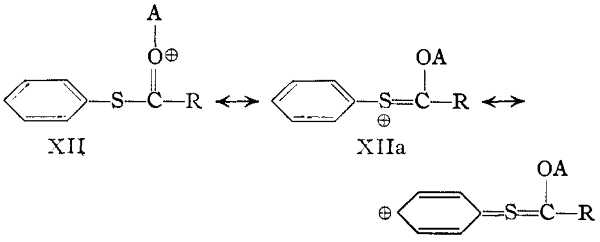
[19] D. K. Fukushima in Elderfield, "Heterocyclic Compounds," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 156.

[20] W. N. Jones, Jr., *Chem. Revs.*, **36**, 291 (1945).

[21] *Cf.* B. Holmberg, *J. prakt. Chem.*, **135**, 57 (1932).

[22] We are indebted to a referee for the suggestion that polymercaptoles might be formed in the Fries rearrangement of thiolesters.

that the Lewis acid A coördinates with the carbonyl oxygen of the ester; this product can have resonance contributions from structures such as XIIb (and the analogous ortho forms) in which the ring is deactivated, due to expansion of the valence shell of sulfur. This is not possible with the oxygen esters.



XII XIIa XIIb

It should be noted that a sulfur atom *per se* does not necessarily prevent electrophilic substitution in the aromatic ring; thus, methyl 4-methylphenyl sulfide (VIII) readily undergoes Friedel–Crafts acetylation[23] to form IX, in which substitution has occurred ortho to the sulfur. Structures analogous to XIIb might be written for the product of Lewis acid additions to VIII, but apparently they are not important enough to inhibit the Friedel–Crafts acylation reaction.

Experimental[24]

Phenyl Trithioörthoacetate (I). A. **From Phenyl Thiolacetate and** Boron **Fluoride.**—Freshly distilled phenyl thiolacetate[25] (5.0 g.) absorbed 1 equivalent of fluoride; after 14 hr. at room temperature, saturated aqueous sodium acetate solution was poured onto the dark yellow solid addition product. The mixture was extracted with benzene, then with ether, and from the extracts, after washing, drying and cooling, 0.2 g. of crystalline I was obtained identical with the material described below. The filtrate contained only thiophenol and starting material. Similar results were obtained by varying the reaction times and temperature, and by the use of aluminum bromide instead of boron fluoride.

B. From **Phenyl Iminothiolacetate Hydrochloride and Thiophenol.**—Phenyl iminothiolacetate hydrochloride[26] (1.5 g.) was heated with 15 cc. of thiophenol for 60 hr. on the steam-bath. The ammonium chloride (0.3 g., 70%) was collected, and the thiophenol was removed by distillation. The solid, deposited by the residual oil on cooling, after several recrystallizations from alcohol, weighed 0.3 g. and melted at 145–146°.

Anal. Calcd. for $C_{20}H_{18}S_3$: C, 67.75; H, 5.12; S, 27.13. Found: C, 68.08; H, 4.99; S, 26.3.

C. From **Phenyl Thiolacetate, Thiophenol and** Boron **Fluoride.**—From 5.0 g. of phenyl thiolacetate, 13.85 g. of thiophenol and 2.5 g. of boron fluoride, there was obtained, following procedure A, 8.2 g. (71%) of recrystallized product, m.p. 145–146°, undepressed upon admixture with samples prepared by procedures A and B.

Thiophenol (3.5 g.) and diphenyl disulfide (0.5 g.) were obtained from the filtrate.

Reactions of Phenyl Trithioörthoacetate (I).—This compound was recovered unchanged in 80% yield after refluxing with alcoholic alkali for 14 hr. Concentrated sulfuric acid in the cold gave a yellow color, which rapidly turned to a deep violet, similar to the color produced by sulfuric acid and thiophenol.

A mixture of 0.1 g. of the trithioörthoacetate and 1 g. of mercuric chloride, dissolved in the minimum amount of alcohol, were boiled for 2 min. The cooled solution deposited 0.28 g. (90%) of phenylthiomercuric chloride, decomposing at 194–195°. Recrystallization of this compound several times from alcohol yielded $(C_6H_5S)_2Hg$, m.p. 151–152°. Both compounds were identified by mixed m.ps. with authentic samples.[27]

The trithioörthoacetate (0.383 g.) and 2.8 cc. of 30% hydrogen peroxide were heated in 20 cc. of acetic acid on the steam-bath until the solvent had evaporated. The residue was titrated with 0.0997 *N* alkali, and consumed 32.5 cc.; the calculated value (for 3 moles of benzenesulfonic acid) was 32.6 cc. The sodium salt left after evaporating the water yielded S-benzylthiouronium benzenesulfonate, m.p. 148–149°, which gave no depression on mixed m.p. with an authentic sample.[28]

1,2-Bis-(phenylthio)-ethane from Thiophenol and 1,1,1-Trichloroethane. — Eastman Kodak Co. 1,1,1-trichloroethane was carefully fractionated and the fraction boiling at 74°, with n^{20}_{D} 1.4379, was collected.[29] This material (2.65 g.) was heated with 3.3 g. of thiophenol and 2 g. of sodium hydroxide in 10 cc. of water for 72 hr. The oily layer solidified on cooling and was removed by filtration; distillation of the filtrate yielded 1.1 g. of thiophenol. The solid was fractionally crystallized from alcohol, and yielded 0.2 g. of diphenyl disulfide (m.p. 60°), and 0.1 g. of 1,2-bis-(phenylthio)-ethane, m.p. 69–69.5°. Its identity was established by a mixed m.p. with an authentic sample,[8] and by oxidation with hydrogen peroxide in acetic acid to the 1,2-bis-(phenylsulfonyl)-ethane, m.p. 179–180°. This likewise gave no depression on mixed m.p. with an authentic sample.[9b] There was no evidence for the formation of the true trithioörthoacetate, m.p. 144–145°, described above.

m-**Tolyl Thiolacetate.**—*m*-Tolyl lead mercaptide (18.8 g.), prepared by adding an excess of lead acetate in 50% alcohol to *m*-thiocresol[30] (18 g.), was dissolved in 50 cc. of dry pyridine, and 20 cc. of acetic anhydride was added slowly. After the yellow lead mercaptide color had disappeared, the solution was heated on a steam-bath for 10 min., and poured into a mixture of ice and hydrochloric acid. After separating the layers, the water layer was extracted with ether, and the combined oil and ether washed until neutral. The solution was dried, the ether removed, and the residue was distilled, giving 11 g. (80%) of *m*-tolyl thiolacetate, as a colorless oil, b.p. 81–83° (1.6 mm.), n^{25}_{D} 1.5609.

Anal. Calcd. for $C_9H_{10}OS$: C, 65.03; H, 6.02. Found: C, 65.46; H, 6.27.

The yield was consistently low when the ester was prepared by the direct acetylation of *m*-thiocresol with acetyl chloride.

m-**Tolyl Trithioörthoacetate** (III).—Boron fluoride (0.9 g.) was bubbled into a mixture of 2 g. of *m*-thiocresol and 0.54 g. of acetic anhydride. The solution, which warmed up and turned yellow, was allowed to stand at room temperature for 48 hr., and then poured into cold 30% sodium hydroxide solution. The yellow solid (1 g.) which precipitated, yielded, after several crystallizations from alcohol, 0.65 g. (30%) of colorless needles, m.p. 117–118°.

Anal. Calcd. for $C_{23}H_{24}S_3$: C, 69.65; H, 6.10. Found: C, 69.75; H, 6.06.

The same compound was obtained from *m*-tolyl thiolacetate, *m*-thiocresol and boron fluoride in 17% yield, using the conditions described above for phenyl thiolacetate.

Phenyl-(bis-*m*-tolyl) Trithioörthoacetate (II).—Boron fluoride (1.1 g.) was bubbled into a mixture of 2.5 g. of phenyl thiolacetate and 5 g. of *m*-thiocresol. The solution became warm and turned orange; it was allowed to stand at room temperature for 48 hr. and was poured into saturated aqueous sodium acetate solution. The resulting oil was taken up in pentane, extracted with methanolic alkali and washed until it was neutral. It solidified, and the solid obtained (2 g.) yielded, after repeated crystallization from alcohol, 1 g. (16%) of colorless needles, m.p. 103–104°.

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(23) K. Auwers and F. Arndt, *Ber.*, **42**, 537 (1909).

(24) Analyses by Miss Claire King; m.ps. are corrected.

(25) W. Michler, *Ann.*, **176**, 177 (1875). To ensure complete absence of water and thiophenol, the once distilled phenyl thiolacetate was chilled, then recrystallized from *n*-pentane until addition of lead acetate in 50% alcohol gave no immediate yellow coloration. The phenyl thiolacetate was then redistilled, b.p. 82° (3 mm.), m.p. (uncor.) 18–19.5°, n^{20}_{D} 1.5700. The crystalline form of phenyl thiolacetate has not been previously reported.

(26) W. Autenrieth and A. Brüning, *Ber.*, **36**, 3464 (1903).

(27) H. Lecher, *ibid.*, **48**, 1425 (1915); **53**, 568 (1920).

(28) E. Chambers and G. W. Watt, *J. Org. Chem.*, **6**, 376 (1941).

(29) A. Turkevich and C. P. Smyth, THIS JOURNAL, **62**, 2468 (1940), report the same constants for this compound.

(30) *Org. Syntheses*, **27**, 81 (1947).

Anal. Calcd. for $C_{22}H_{22}S_3$: C, 69.06; H, 5.80. Found: C, 69.03; H, 5.84.

Benzyl Trithioörthoacetate (IV).—Boron fluoride (3.4 g.) was bubbled into a mixture of 7 g. of benzyl mercaptan and 7 g. of benzyl thiolacetate[14]; after three days at room temperature, 50 cc. of pentane was added to the dark orange mass, followed by 20 cc. of 30% methanolic potassium hydroxide. The latter was separated and discarded, and the pentane was washed, dried and removed, leaving 10 g. of brown oil which solidified on chilling. Recrystallization from methanol containing 5–10% of benzene gave 5 g. (45%) of colorless needles, m.p. 66–67°.

Anal. Calcd. for $C_{23}H_{24}S_3$: C, 69.65; H, 6.10. Found: C, 69.93; H, 6.12.

The nature of the compound of m.p. 46° reported by Laves[7] to be formed from sodium benzyl mercaptide and 1,1,1-trichloroethane, and considered by him to have structure IV, is uncertain.

Phenyl Trithioörthobenzoate (V).—A mixture of 6 g. of benzoyl chloride and 19 g. of thiophenol was saturated with boron fluoride and heated on the steam-bath for 45 min.; heating was accompanied by a loss of weight of 1.3 g., apparently due to loss of hydrogen chloride (1.5 g. is the theoretical loss). Boron fluoride was then bubbled into the cooled solution until the weight was 1.5 g. greater than the original. After two hours on the steam-bath and 24 hours at room temperature, the mixture was worked up as described in the preceding paragraph, yielding 5 g. of oil which solidified on chilling. Recrystallization from ethanol yielded 2 g. of white crystals, m.p. 86–87°.

Anal. Calcd. for $C_{25}H_{20}S_3$: C, 72.07; H, 4.84. Found: C, 72.03; H, 4.95.

Using the above procedure in the cold gave phenyl thiolbenzoate[31] in 53% yield. Phenyl thiolbenzoate, treated under the above conditions, was recovered unchanged; however, when a few cc. of ethyl ether was added to the reaction mixture and the mixture was saturated with boron fluoride, followed by heating for 2 hr. on the steam-bath, the desired compound (V) was obtained in 28% crude yield.

Phenyl Thiolmesitoate (VII).—Mesitoyl chloride[32] (12.5 g.) was mixed with 15 g. of thiophenol and, after evolution of hydrogen chloride had decreased, was heated for 30 min. on the steam-bath. The mixture was taken up in ether, washed with 20% alkali, then with water, dried and the solvent removed; the residue crystallized, and after recrystallization from methanol gave 14.5 g. (82%) of product, melting at 56–57°.

Anal. Calcd. for $C_{16}H_{16}OS$: C, 74.96; H, 6.29. Found: C, 74.63; H, 6.22.

Attempts to prepare the ester by Newman's method[33] were unsuccessful; in 100% sulfuric acid, thiophenol gives, in addition to diphenyl disulfide, a gum-like product. The ester VII was recovered unchanged after treatment with thiophenol and boron fluoride.

Attempted Fries Reaction on Phenyl Thiolmesitoate.—The ester VII (2.5 g.) was refluxed with 3 g. of aluminum bromide in carbon disulfide for 2 hr.; the solvent was removed and the residue was heated for 50 min. at 153°, but still very little hydrogen bromide was evolved. The mixture was worked up in the usual way by decomposing with ice–hydrochloric acid and extraction with ether. The residue was crystallized from methanol several times, and 80% of the starting material, identified by a mixed m.p., was obtained.

3-Methoxythiophenol was prepared from *m*-anisidine by the published procedure,[34] and had the following properties: b.p. 78° (4 mm.), $n^{20}D$ 1.5845.

Treatment with 2,4-dinitrochlorobenzene[35] yielded the hitherto unreported **3-methoxy-2′,4′-dinitrodiphenyl sulfide (XI)**, m.p. 133–134°.

Anal. Calcd. for $C_{13}H_{10}N_2O_5S$: C, 50.98; H, 3.29. Found: C, 51.31; H, 3.34.

2-Acetyl-5-methoxythiophenol was obtained in 8% yield from 3-methoxythiophenol and 2 moles each of acetyl chloride and aluminum chloride in carbon disulfide at 5° according to published directions.[18]

Treatment of 2-acetyl-5-methoxythiophenol with boron fluoride led to a brown tar, while action of aqueous alkali on this thiophenol gave a bright red, insoluble solid, apparently a thioindigo dye.[36] In ethanol solution in contact with air, 2-acetyl-5-methoxythiophenol was quantitatively oxidized to bis-(2-acetyl-5-methoxyphenyl) disulfide, m.p. 152–153°.

Anal. Calcd. for $C_{18}H_{18}O_4S_2$: C, 59.66; H, 5.01. Found: C, 59.69; H, 5.07.

3-Methoxyphenyl Thiolacetate (X).—3-Methoxyphenyl lead mercaptide, m.p. 157–158°, was prepared and then acetylated in a manner similar to *m*-tolyl lead mercaptide (see above); slightly yellow oil, b.p. 119° (5 mm.), $n^{20}D$ 1.5701.

Anal. Calcd. for $C_9H_{10}O_2S$: C, 59.32; H, 5.53. Found: C, 59.19; H, 5.43.

Treatment of the thiolacetate with an alcoholic solution of lead acetate rapidly formed the lead mercaptide.[37]

Action of Boron Fluoride on 3-Methoxyphenyl Thiolacetate (X).—3-Methoxyphenyl thiolacetate (5 g.) was exposed to boron fluoride; the solid, yellow addition compound which formed was dissolved in glacial acetic acid (3 g.), and more boron fluoride added until a total of 3 g. was taken up. After two weeks at room temperature, the deep yellow, viscous solution was poured into cold, saturated aqueous sodium acetate. A brown solid which separated was collected, dissolved in acetone with an intense green color; addition of diethyl ether precipitated it as a dark green, amorphous solid (2 g.). With shorter reaction times and in the absence of acetic acid, similar results were obtained.

Attempts to purify the green solid by repeatedly dissolving and reprecipitating it, caused the solid to become more and more insoluble. It is most soluble in pyridine and completely insoluble in hexane or sodium sulfide; in solution it turns brown upon the addition of alkali. The green solid decomposes above 215°, reduction with zinc in acetic acid discolors it irreversibly and the reaction products gave no positive test for sulfhydryl groups. The green solid was not changed after refluxing 24 hr. in an acidic mercuric chloride–ethanol solution.

4-Acetylthiophenol was prepared in 60% yield from *p*-aminoacetophenone in a manner analogous to the preparation of *m*-thiocresol[30] from *m*-toluidine. 4-Acetylthiophenol is a slightly yellow oil, b.p. 110° (2.5 mm.,[38] $n^{25}D$ 1.6181).[39]

Upon oxidation with ferric chloride in acetic acid, 4-acetylthiophenol yields bis-(*p*-acetylphenyl) disulfide; buff crystals, m.p. 99–100°.

Anal. Calcd. for $C_{16}H_{14}O_2S_2$: C, 63.57; H, 4.67. Found: C, 63.46; H, 4.82.

4-Acetylthiophenol (5 g.) in 12 cc. of dry ether was saturated with boron fluoride at 0–5° and then permitted to stand at room temperature for 24 hr. The solution, which had turned highly viscous, was then worked up in the usual manner and yielded 4.6 g. of red-brown amorphous powder. The powder was insoluble in common organic solvents and methanolic or aqueous alkali. Pyridine changed the solid's color to yellow; however, at about 200° it turned red-brown again and did not melt up to 260°.

A suspension of 1 g. of the red-brown powder in a solution of 1 g. of mercuric chloride in 25 cc. of ethanol and 2 cc. of concd. hydrochloric acid was refluxed for 24 hr. and filtered while hot. There was obtained 0.9 g. of black residue, not further investigated, and upon addition of water to the filtrate and chilling 0.6 g. of buff powder was obtained. This, after recrystallization from nitrobenzene, melted at 225–227° and gave no m.p. depression when admixed with authentic 4-acetylphenylmercuric mercaptide (see below).

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(31) R. Schiller and R. Otto, *Ber.*, **9**, 1635 (1876).

(32) *Org. Syntheses*, **21**, 77 (1941).

(33) M. S. Newman, THIS JOURNAL, **63**, 2431 (1941).

(34) F. Mauthner, *Ber.*, **39**, 3596 (1906), reports the b.p. as 224–225°.

(35) *Cf.* R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

(36) *Cf.* German Patent 198,509 (*Chem. Zentr.*, **79**, I, 2118 (1908)).

(37) G. Sachs, *Ber.*, **54**, 1849 (1921), observed that ethyl thiolacetate was rapidly split by mercuric acetate to yield ethyl mercaptides.

(38) G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 370 (1939), gave b.p. 142° (11 mm.).

(39) ADDED IN PROOF.—Further purification has yielded the material as a colorless crystalline solid, m.p. 27–28.5°.

4-Acetylthiophenol (1 g.) and 2 g. of mercuric oxide in 20 cc. of dry pyridine was heated 10 min. on a steam-bath; excess mercuric oxide was filtered off, and upon addition of water and chilling, 1.5 g. of buff flakes was obtained which, after recrystallizing from nitrobenzene, melted at 225–227°.

Anal. Calcd. for $C_{16}H_{14}O_2S_2Hg$: C, 38.20; H, 2.80. Found: C, 38.24; H, 3.05.

This mercuric mercaptide turns yellow upon heating and is readily soluble in cold pyridine.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

1,2-Bis-(arylsulfonyl)-ethenes in the Diels-Alder Reaction

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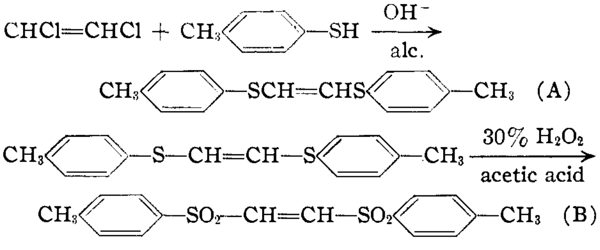
The preparation and Diels-Alder reactions of 1,2-bis-(phenylsulfonyl)-ethene and 1,2-bis-(*p*-tolylsulfonyl)-ethene are described. The compounds mentioned are presumably the *trans* isomers. They are reactive dienophiles toward cyclopentadiene, isoprene, butadiene and anthracene. No reaction with furan was observed.

The recent work of Snyder and Hallada,[1] dealing with the use of α,β-unsaturated sulfonyl compounds in the Diels-Alder reaction, has made presentation of our related work desirable. It has been possible to isolate both the *cis* and the *trans* isomers of bis-(*p*-tolylsulfonyl)-ethene, whereas the above authors worked with only one isomer. While the present work with the low melting form, which is, presumably, the *cis* compound,[2] is a duplication of their results and is not discussed further, the series of Diels-Alder adducts obtained from the "*trans*" form are new.

The original intention was to prepare a series of adducts with 1,2-bis-(phenylsulfonyl)-ethene, but poor yields of the intermediate 1,2-bis-(phenylmercapto)-ethene led to the use of 1,2-bis-(*p*-tolylsulfonyl)-ethene. However, the 1,2-bis-(phenylsulfonyl)-ethene isolated in the preliminary work was a high melting solid (229°). This fact led to the expectation that a high melting isomer of 1,2-bis-(*p*-tolylsulfonyl)-ethene should also exist. Previous authors[1,3] obtained only the low melting isomer by the reactions



Substitution of a longer reaction time in step A and use of glacial acetic acid in step B gave a mixture of disulfones which could be separated by their solubility differences.

The 1,2-bis-(arylsulfonyl)-ethenes were found to be highly reactive dienophiles in reactions with cyclopentadiene, isoprene, butadiene and anthracene. The reaction with furan does not occur in ether at room temperature, in refluxing benzene, or in benzene at 115°. The reaction with anthracene is of interest. Snyder and Hallada[1] report the isolation of two isomeric adducts of "*cis*" bis-(*p*-tolylsulfonyl)-ethene and anthracene, which were believed to be *meso* and racemic forms. In the present work, the "*trans*" bis-(*p*-tolylsulfonyl)-ethene gave only the lower melting compound, presumably the racemic mixture. In the previous work,[1] partial isomerization of the low melting bis-(*p*-tolylsulfonyl)-ethene by the heat necessary to secure reaction with anthracene evidently occurred, resulting in the two isomers obtained. This isomerization of the low melting compound lends further credence to the assignment of the *cis* structure to it, since the *cis* isomer is usually the labile form.[4]

The decomposition of butadiene sulfone in dibutyl ether to give butadiene usable in a Diels-Alder reaction constitutes an improvement, in our opinion, over the usual closed tube method of carrying out such reactions with butadiene, at least in the cases reported here.

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Experimental

1,2-Bis-(phenylsulfonyl)-ethene.—1,2-Bis-(phenylmercapto)-ethene (2.4 g., 0.01 mole), which had been prepared by the method of Cusa and McCombie,[5] was dissolved in 100 ml. of glacial acetic acid and the resulting solution heated to reflux temperature. Ten grams of 30% hydrogen peroxide was added and the refluxing continued for 2.5 hours. Refrigeration and filtration gave 1.1 g. of crystalline solid melting at 228°. Trituration with 95% alcohol gave 1.0 g. (32%) of solid melting at 229°.

Anal. Calcd. for $C_{14}H_{12}O_4S_2$: C, 54.52; H, 3.93. Found: C, 54.39; H, 4.01.

Reduction of this compound with zinc and glacial acetic acid gave the known 1,2-bis-(phenylsulfonyl)-ethane.[6]

1,2-Bis-(*p*-tolylmercapto)-ethene.—The method of Fromm and Seibert[3] was modified in this preparation. *p*-Toluenethiol (124.2 g., 1.0 mole) was added to 1440 ml. of 7% alcoholic potassium hydroxide in a three-neck flask equipped with stirrer, reflux condenser and addition funnel. The solution was heated to reflux, then *cis*-dichloroethylene (50 g., 0.52 mole) in 100 ml. of ethanol was added dropwise over a period of seventeen hours. After addition was complete, reflux was continued for two hours. The solution was filtered while hot. The salt residue was extracted twice with 100-ml. portions of boiling ethanol, and these extracts added to the filtrate. On cooling, **133 g.** of crude solid, m.p. 83–90°, was obtained (97.8%). Recrystallization from

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(1) H. R. Snyder and D. P. Hallada, THIS JOURNAL, **74**, 5595 (1952).

(2) H. Gilman, "Organic Chemistry," Vol. I, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 450.

(3) E. Fromm and E. Seibert, *Ber.*, **55**, 1014 (1922).

(4) Reference 2, p. 453.

(5) N. W. Cusa and H. McCombie, *J. Chem. Soc.*, 767 (1937).

(6) R. Otto, *Ber.*, **13**, 1280 (1880).