equilibrated with the silver fluoborate irrigant. After the solvent front had reached close to the lower end of the papers, these were dried by hanging them for about a minute in an atmosphere saturated with thionyl chloride vapors, followed by brief heating on a hot plate at about 80°. After repeated treatment with thionyl chloride and drying, the papers were passed rapidly and at an even rate through a 5–10% solution of antimony pentachloride in chloroform. After marking the spots, the papers were heated as before as this tended to intensify the color. Excessive heating had to be avoided since this gave a dark background.

The detection of the spots was quite critical and depended much upon the experience of the operator. Attempts were made simply to dry the papers at an elevated temperature prior to the antimony pentachloride treatment, but this often gave unsatisfactory results, probably because of the volatility of the samples. All operations were carried out in subdued daylight. The finished chromatograms darkened if exposed to strong daylight but otherwise they remained almost unchanged over a long period of time.

Column Chromatography.—Polyvinyl chloride powder (Wackerchemie, Germany, 72 g.) was shaken with hexane (25 ml.) in 80% aqueous methanol (400 ml.) saturated with hexane. The slurry was freed from trapped air bubbles by brief stirring under slightly reduced pressure and then added in portions to a chromatographic tube. After each addition part of the solvent was drained off while a slight positive air pressure was applied to the top of the column. The settled solid then was packed rather firmly with a plunger. The finished column (32 × 280 mm.) was washed with 90% aqueous methanol saturated with hexane, which then was replaced by the same irrigant as used for paper chromatography, but saturated with hexane.

A sample (3.00 g.) of a sesquiterpene mixture from *Juniperus thurifera*, b.p. 136–137°/25 mm., was extracted with ten 10-ml. portions of the irrigant, each being added to the column. Elution was continued with the same solvent at a rate of about 1.5 ml./min., the eluate being collected in 16-ml. portions. These were filtered through glass paper prior to determination of the optical rotation in a 2-dm. tube. The proper solutions were combined, diluted with water, and extracted with hexane. The hexane extracts were concentrated to give fraction x (0.28 g.), fraction y (0.31 g., thujopsene), fraction $z + u$ (0.80 g.), and fraction v (1.47 g., α-cedrene), indicating a total recovery of about 95%.

Since fraction $z + u$ contained some α-cedrene, material (1.65 g.) from two identical runs was rechromatographed in a similar manner, but with more of the stationary hexane phase (48 ml.) on the same amount of polyvinyl chloride powder (72 g.). The eluate was collected in 18-ml. portions. After determination of the optical rotation as before, aliquots from some of the tubes were diluted with water and extracted with hexane and the extracts were examined by vapor phase chromatography (Fig. 2). The usual work-up of the contents of tubes 39–47 afforded crude compound *Z* (73 mg.). The combined yield of compound *U* from tubes 64–69 was 298 mg. In addition there was recovered a mixture of compounds *Z* and *U* (950 mg.) and a mixture of compound *U* and α-cedrene (67 mg.).

Vapor Phase Chromatography.—A Pye argon chromatograph, cat. no. 12000, was used together with a Philips automatic compensator PR 2210 A/21. The column tube (length 1.20 m., i.d. 5 mm.) was packed with 100–115-mesh Silocel C 22 brick powder impregnated with 2,4-dinitrophenyl-2-naphthyl ether (15%) and dibenzylpyridine (a mixture of 2,4- and 2,6-isomers, 0.75%).[9] The column was charged with 0.025-μl. samples and was operated at 150°.

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[9] A. B. Groth, *Svensk Papperstid.*, **61**, 315 (1958).

The Thermal Decomposition of Thiolsulfonates. III. Phenyl and Carboethoxymethyl Esters of α-Toluenethiolsulfonic Acid

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Previous studies[1,2] have shown that at elevated temperatures in inert solvents various diphenylmethanethiolsulfonates undergo decomposition, principally according to equation 1. The rate of the reaction is notably faster in polar solvents (nitrobenzene, benzonitrile) than in nonpolar solvents (bromobenzene, methyl benzoate) and is also strongly dependent on the nature of R— in a manner directly proportional to the effect of R— on the acidity of the corresponding mercaptan, RSH.[3] The results clearly indicate that the sulfide sulfur atom apparently has considerable anionic character in the transition state of reaction 1.

$$(C_6H_5)_2CHSO_2SR \longrightarrow (C_6H_5)_2CHSR + SO_2 \qquad (1)$$

In addition, it was found[2] that benzyl α-toluenethiolsulfonate, $C_6H_5CH_2SO_2SCH_2C_6H_5$, undergoes a similar decomposition, whose rate is also faster in polar than nonpolar solvents, but whose rate in a given solvent is about 170 times less than that of the corresponding diphenylmethanethiolsulfonate. Since this rate difference is considerably less than the 10^4–10^5-fold differences normally observed between benzyl and benzhydryl derivatives in solvolysis reactions,[5] it was considered indicative that the aralkyl fragment has considerably less carbonium ion character in the transition state of the thiolsulfonate decomposition than is the case in such typical carbonium ion reactions as solvolysis.

However, because the previous results do not rule out the possibility that the α-toluenethiolsulfonate undergoes decomposition by a different mechanism than the diphenylmethanethiolsulfonates, one can argue that this last conclusion is somewhat tenuous. To put it on a firm foundation one needs to demonstrate that the dependence on R of the decomposition rates of a series of α-toluenethiolsulfonates, $C_6H_5CH_2SO_2SR$, parallels

(1) J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **82**, 6168 (1960).

(2) J. L. Kice, F. M. Parham, and R. M. Simons, *ibid.*, **82**, 834 (1960).

(3) Since the submission of the previous paper accurate values for the pK_a's of the various mercaptans RSH have become available.[4] It is significant that a plot for log k_1 for the decomposition rates of the thiolsulfonates in nitrobenzene at 142° *vs.* the pK_a's of RSH shows excellent linearity and has a slope of about 0.6.

(4) M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, and L. T. Ditsch, *J. Am. Chem. Soc.*, **82**, 4899 (1960).

(5) (a) A. Streitwieser, *Chem. Rev.*, **56**, 571 (1956); (b) S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

that observed with the diphenylmethanethiolsulfonates.

In the course of other work we have now had occasion to prepare two new α-toluenethiolsulfonates, the phenyl and carboethoxymethyl esters, and to study their decompositions. When taken together with the earlier results with the benzyl ester,[2] the present data permit one to conclude that the same basic mechanism is indeed operative in both the diphenylmethane- and α-toluenethiolsulfonate decompositions.

For the present work phenyl α-toluenethiolsulfonate was prepared from α-toluenesulfinic acid and benzenesulfenyl chloride using the general procedure outlined by Stirling[6] for the preparation of thiolsulfonates. For synthesis of the carboethoxymethyl ester we used the nucleophilic displacement of chloride ion from ethyl α-chloroacetate by potassium α-toluenethiolsulfonate. Because of the high reactivity of halides of this type in S_N2 displacement reactions[5a] this method is more successful here than has often been the case.

To ensure that the thermal decompositions of these esters took a course similar to that previously observed for benzyl α-toluenethiolsulfonate, the principal products of their decomposition in methyl benzoate solution at 172° were determined. The identified decomposition products of the phenyl ester (yields in mmole/mmole thiolsulfonate) were: sulfur dioxide (0.96); benzyl phenyl sulfide (0.80); diphenyl disulfide (0.03). The carboethoxymethyl ester gave: sulfur dioxide (1.00); ethyl S-benzylthioglycolate (0.52); some diethyl dithiodiglycolate was also formed but the exact amount could not be determined.

The decomposition rates of both esters were determined in methyl benzoate solution at 172° by measuring the rate of evolution of sulfur dioxide, using previously described[1,2] techniques. Good first-order kinetics were observed in each case. The results are shown in Table I, together with a rate constant for the benzyl ester extrapolated from data at higher temperatures.

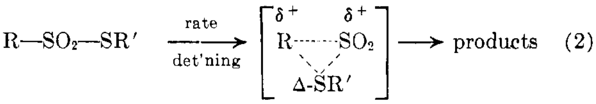
TABLE I

RATES OF DECOMPOSITION OF $C_6H_5CH_2SO_2SR$ IN METHYL BENZOATE AT 172°

R	$(PhCH_2SO_2SR)_0$, M	$k_1 \times 10^5$, sec.$^{-1}$
C_6H_5—	0.080	3.2
	.091	3.5
$EtOOCCH_2$—	.050	0.82
	.10	.81
$C_6H_5CH_2$—$_f$		.26[a]

[a] Rate constant for decomposition in chloronaphthalene at 172°. However, at 185° rate constants in chloronaphthalene and methyl benzoate are identical,[2] and previous work[2] has also suggested ΔH^* not noticeably solvent dependent.

The results in Table I show that the α-toluenethiolsulfonate decompositions also exhibit a pronounced dependence of rate on the nature of R, and that the nature of this dependence is again such as to parallel the effect of R on the acidity of RSH. To be sure, quantitatively the α-toluenethiolsulfonate decomposition in methyl benzoate seems to be somewhat less sensitive to changes in R, a plot of log k_1, *vs.* pK_a of RSH[4] having a slope of 0.4, rather than 0.6 as in the diphenylmethanethiolsulfonate decompositions in nitrobenzene. However, even so, the data still seem to require that in both cases the sulfide sulfur have appreciable anionic character in the transition state, and to argue that the basic mechanism of all the thiolsulfonate decompositions is essentially the same. Thus our original conclusion that the aralkyl group has considerably less carbonium ion character in the thiolsulfonate transition state than in such reactions as halide solvolysis remains unchanged. One mechanism consistent with this and the other evidence is, of course, that shown in equation 2 (for a fuller discussion of this and other possible mechanisms see ref. 1).[7]



$$R{-}SO_2{-}SR' \xrightarrow[\text{det'ning}]{\text{rate}} \left[\begin{array}{ccc} \overset{\delta+}{R} & \cdots & \overset{\delta+}{SO_2} \\ & \Delta\text{-}\dot{S}R' & \end{array}\right] \longrightarrow \text{products} \qquad (2)$$

Experimental

Phenyl α-Toluenethiolsulfonate.—α-Toluenesulfinic acid was prepared from α-toluenesulfonyl chloride[10] in the following manner. Sodium sulfite (0.2 mole) was dissolved in 125 ml. of water. The solution was placed in a separatory funnel, 19.1 g. of the sulfonyl chloride (0.1 mole) added, and the mixture shaken. The pH of the solution was tested frequently, and whenever it dropped below 10, 1 ml. of 50% sodium hydroxide was added. After 0.5 hr. all the sulfonyl chloride dissolved. The solution was then cooled and acidified with 60% sulfuric acid. A crystalline material first separated which then redissolved when more sulfuric acid was added. A total of about 70

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(6) C. J. M. Stirling, *J. Chem. Soc.*, 3597 (1957).

(7) Recent work by Martin, Tuleen, and Bentrude,[8] and Bartlett and Ruchardt[9] shows that the rates of certain perester decompositions exhibit considerable dependence on solvent ionizing power[8] and perester structure,[9] approaching to some degree that observed for reactions involving ion-pair intermediates; yet, from other evidence, these perester decompositions clearly involve formation of free radicals. Both groups[8,9] have explained these phenomena as arising from substantial contributions from structures of type ii to the resonance hybrid for the transition state.

$$\underset{\text{i}}{[R_1^{\cdot}\text{--}CO_2\text{--}{}^{\cdot}OR_2} \longleftrightarrow \underset{\text{ii}}{R_1^{+}\text{--}CO_2\text{--}\overset{-}{:}OR_2]}$$

A referee has pointed out that a similar explanation might apply to the thiolsulfonate decomposition, especially since our principal evidence against the involvement of radicals—the failure of the thiolsulfonates to initiate styrene polymerization—is not entirely unambiguous. This is indeed true. However, in the absence of definite *positive* evidence for the intermediacy of radicals in the thiolsulfonate decomposition, we feel it would be premature at present to advocate such a mechanism in preference to those already suggested.[1]

(8) J. C. Martin, D. L. Tuleen, and W. G. Bentrude, *Tetrahedron Letters*, 229 (1962).

(9) P. D. Bartlett and C. Ruchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

(10) B. G. Boldyrev and Iu. I. Kofman, *J. Gen. Chem. USSR*, **20**, 1761 (1950).

ml. of acid was used. Some of the sulfinic acid precipitated from the final solution. This was filtered off, and the filtrate was extracted with three 30-ml. portions of ether. The solid sulfinic acid was dissolved in these ether extracts, and these were then washed with water, dried, and the ether removed to leave an oil which crystallized on standing in a vacuum desiccator, giving 7.4 g. (47%) of α-toluenesulfinic acid, m.p. 64–69° (lit.,[11] 61–63°).

Benzenesulfenyl chloride[12] (1.45 g., 0.01 mole) was dissolved in 90 ml. of benzene and this solution was shaken for 1 hr. in a separatory funnel with a solution of 1.56 g. (0.01 mole) of α-toluenesulfinic acid in 60 ml. of water. The layers were then separated; the benzene layer was washed first with 25 ml. of saturated sodium bicarbonate, then with water, and was finally dried over sodium sulfate. Removal of the benzene under reduced pressure gave a crystalline residue. This was recrystallized twice from ethanol, giving 1.5 g. (57%) of phenyl α-toluenethiolsulfonate, m.p. 110–111°. Its infrared spectrum showed the expected strong sulfonyl group absorptions at 1325 and 1125 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58; S, 24.26; Found: C, 58.83; H, 4.48; S, 24.51.

Carboethoxymethyl α-Toluenethiolsulfonate.—Potassium α-toluenethiolsulfonate was prepared by the procedure of Boldyrev and Kofman.[10] The salt (0.79 g., 3.5 mmoles) was dissolved in a solution consisting of 30 ml. of purified acetone and 1.5 ml. of water. The solution was filtered and 0.43 g. (3.5 mmoles) of ethyl chloroacetate was added. The solution, which began to deposit potassium chloride almost immediately, was allowed to stand at room temperature for 24 hr. The precipitated potassium chloride was then filtered off, the acetone–water removed under reduced pressure, and the residue taken up in 20 ml. of chloroform. The chloroform solution was dried over sodium sulfate, the chloroform removed, and the solid residue was recrystallized from ethanol. There was obtained 0.42 g. (44%) of carboethoxymethyl α-toluenethiolsulfonate, m.p. 75–76°.

Anal. Calcd. for $C_{11}H_{14}O_4S_2$: C, 48.15; H, 5.14; S, 23.38. Found: C, 47.95; H, 5.12; S, 23.36.

Procedure for Kinetic Runs.—This was the same as that previously described[1,2] as was also the purification of the solvent employed.

Identification of Decomposition Products.—In each case product studies were carried out using the reaction solutions remaining at the end of a kinetic run. The methyl benzoate solvent was removed by fractional distillation under reduced pressure through a short Vigreux column.

In the case of the phenyl ester the residue from the distillation was crystallized from 80% ethanol, yielding a portion of the *benzyl phenyl sulfide* in a quite pure state, m.p. 42–43°, identified by mixed melting point and infrared comparison with a known sample.[13] The filtrate was evaporated, and the residue was chromatographed on acid-washed alumina (50 g./g. residue). Elution with hexane and various hexane–benzene mixtures gave, first, a small amount of *diphenyl disulfide,* identified by comparison with a known sample, followed by the remaining benzyl phenyl sulfide. From a run involving 4.0 mmoles of thiolsulfonate there was obtained 3.2 mmoles of sulfide and 0.13 mmole of the disulfide. The amount of sulfur dioxide evolved was 3.84 mmoles.

With the carboethoxymethyl ester the residue was chromatographed directly. Trial experiments with synthetic mixtures had shown that it was possible to separate mixtures of ethyl S-benzylthioglycolate, diethyl dithiodiglycolate, and methyl benzoate in this manner if the column was eluted first with hexane, then with hexane–benzene containing gradually increasing amounts of benzene, and finally with pure benzene. From a run involving 1.37 g. of thiolsulfonate there was obtained 0.543 g. of liquid having an infrared spectrum identical with that of a known sample[14] of ethyl S-benzylthiolglycolate. The identity of this material was confirmed by basic hydrolysis to the known[14] S-benzylthioglycolic acid, m.p. 64–65°. The only other product fraction from the chromatography (0.25 g.) was eluted at the point where diethyl dithiodiglycolate would be expected to appear. However, although its infrared spectrum suggested it might contain some of this material, there was clearly much of this fraction which was not the disulfide since acid hydrolysis, which on a known sample of diethyl dithiodiglycolate[15] easily afforded dithiodiglycolic acid, m.p. 108–109°, gave only an oil which resisted all attempts at crystallization.

Acknowledgment.—This work was supported by National Science Foundation Grant NSF G-19503.

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[11] B. Holmberg, *Arkiv. Kemi, Min., Geol.*, **14A**, No. 8 (1940).

[12] H. Lecher and F. Holschneider, *Ber.*, **57**, 755 (1924).

[13] R. Pummerer, *ibid.*, **43**, 1406 (1910).

[14] R. Lesser and A. Mehrlander, *ibid.*, **56**, 1643 (1923).

[15] T. S. Price and D. F. Twiss, *J. Chem. Soc.*, **93**, 1645 (1909).

Derivatives of Oxytryptophol[1]

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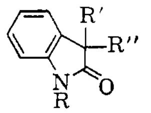
In connection with our general study of the chemistry of oxindole compounds[3] it was of interest to synthesize oxytryptophol (Ia). Whereas none of the routes which were investigated led to the desired compound, the reactions involved are of intrinsic interest and form the basis of the present report.



Ia. R = R″ = H, R′ = $(CH_2)_2OH$
b. R = R″ = H, R′ = Et
c. R = Et, R′ = R″ = H
d. R = $(CH_2)_2OH$, R′ = R″ = H
e. R = $(CH_2)_2Br$, R′ = R″ = H
f. R = Me, R′ = $(CH_2)_2Br$, R″ = H
g. R = R″ = H, R′ = $(CH_2)_2OC_6H_5$

Hydrogenation of 3-(α,β-dihydroxyethylidene)-oxindole (IIa), the product of a Claisen condensation of oxindole and ethyl glycolate whose infrared and ultraviolet spectral properties now confirmed its previously suggested structure,[4] has been reported[4] to lead to unidentifiable products. When on repetition of this experiment similar difficulties were encountered, IIa was acetylated and the resulting diacetate (IIb) hydrogenated

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[1] This work was supported in part by a grant (MY-1301) by the Public Health Service, U.S. Department of Health, Education, and Welfare.

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[3] E. Wenkert, J. H. Udelhofen, and N. K. Bhattacharyya, *J. Am. Chem. Soc.*, **81**, 3763 (1959), and previous papers.

[4] L. Horner, *Ann.*, **548**, 117 (1941).