filtrate was treated in the same manner as was IVb. There was thus obtained, through the lead mercaptide intermediate, Vc (0.2 g.) as yellow needles, m.p. 55–58°, which, because of their rapid oxidation, were not obtained analytically pure but were quantitatively converted by hypoiodite to bis-(4-methyl-2-nitrophenyl) disulfide, m.p. 174–175°; the melting point was not depressed by admixture with an authentic sample.[17]

Acetylation of IIIb.—IIIb was formed, in a manner analogous to III, by the piperidine-catalyzed addition of 3-methoxythiophenol (IIb)[3] to I; there was thus obtained a 35% crude yield of IIIb, m.p. 72–75°. Without further purification, IIIb (3.3 g.) was acetylated under the same conditions as III, except that the reaction mixture was stirred for at least 0.5 hr. at −10° before it was worked up. There was thus obtained β-(3-nitrophenyl)-β-(4-acetyl-3-methoxyphenylthio)-propiophenone (IVd) (2.6 g.); colorless crystals, m.p. 120–121°.

Anal. Calcd. for $C_{24}H_{21}O_5SN$: C, 66.20; H, 4.86. Found: C, 66.30; H, 4.83.

IVd (0.8 g.) was converted through the lead mercaptide intermediate to Vd (0.3 g.) in the same manner as was given for IVb. Because of its ready oxidation Vd, m.p. 75–80°, was not obtained in a pure form but was converted by a hot solution of ferric chloride in acetic acid to bis-(4-acetyl-3-methoxyphenyl) disulfide; colorless crystals, m.p. 179–180°.

Anal. Calcd. for $C_{18}H_{18}O_4S_2$: C, 59.66; H, 5.01. Found: C, 59.75; H, 5.29.

ROCHESTER, N. Y.

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(17) M. T. Bogert and R. W. Allen, *Ind. Eng. Chem.*, **18**, 532 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE]

Thiapyran Derivatives. IV. Some Symmetrical 2,6-Disubstituted Tetrahydrothiapyrans and 1,1-Dioxides

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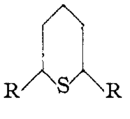
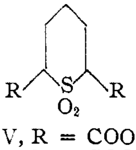
RECEIVED MAY 2, 1953

Some new symmetrical 2,6-disubstituted tetrahydrothiapyrans and related 1,1-dioxides have been prepared and characterized. The preparation of α,ε-dibromopimelic acid has been reinvestigated and a stereochemically pure form of this compound has been isolated and identified as the *meso* isomer.

While searching for intermediates which might prove useful in the synthesis of certain thiapyran derivatives, we have had occasion to prepare a number of new tetrahydrothiapyrans and tetrahydrothiapyran 1,1-dioxides, some of which have been described in the preceding papers in this series.[1] The present communication describes the preparation of some symmetrical 2,6-disubstituted tetrahydrothiapyrans (I–III) and 1,1-dioxides (IV–VI) which were obtained in the course of this work but which have not previously been reported.



I, R = COOH
II, R = $COOCH_3$
III, cyclic anhydride of I



IV, R = COOH
V, R = $COOCH_3$
VI, R = Br

The dicarboxylic acid I and its dimethyl ester II were prepared by the action of sodium sulfide on α,ε-dibromopimelic acid (VII) and methyl α,ε-dibromopimelate (VIII), respectively, under conditions similar to those previously employed[2,3] in the synthesis of the analogous 2,5-disubstituted thiophanes. A consideration of the stereochemical factors involved in cyclizations of this type shows that the *meso*-dihalides should lead to *cis* products, while the racemic dihalides should furnish the *trans* isomers. These results have been verified in the thiophane series,[2,3] where both the *meso* and the racemic forms of α,δ-dibromoadipic acid were available for cyclization. In the present investigation, however, an examination of the literature failed to provide any information on the stereoisomeric forms of α,ε-dibromopimelic acid. In 1895, Willstätter[4] reported, in what appears to be the only published reference to this compound, the isolation of almost quantitative yields of crude α,ε-dibromopimelic acid from the reaction between pimelic acid and excess bromine in the presence of red phosphorus. Willstätter's purified product is described as a colorless crystalline compound with m.p. 140–142°, but no indication is given as to whether this product was a *meso* form, a racemic form or a mixture of diastereomers.

Since it seemed desirable to employ a definite stereoisomeric form[5] of the dibromoacid in the cyclization reaction, we have reinvestigated the preparation of this compound and, by slightly altering Willstätter's original procedure, have succeeded in isolating and characterizing a stereochemically pure product. In our method the diacid chloride of pimelic acid, prepared by the action of thionyl chloride on the acid, was treated with slightly more than the theoretical amount of bromine, and the resultant dibromodiacid chloride was converted to the dibromoacid by reaction with hot formic acid.[6] The crude product (m.p. *ca.* 135–145°) which crystallized out of the reaction mixture on cooling was recrystallized repeatedly from formic acid until it gave a constant m.p. of 154.5–155°; no material comparable to Willstätter's 140–142° product was isolated at any stage of the purification, although the experiment was repeated many times. Attempts to isolate the other (presumably lower melting and more soluble) isomer from the combined mother liquors from the above operations were unsuccessful. Rapid concentration or removal of the solvent furnished

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(1) E. A. Fehnel and M. Carmack, THIS JOURNAL, **70**, 1813 (1948); E. A. Fehnel and P. A. Lackey, *ibid.*, **73**, 2473 (1951); E. A. Fehnel, *ibid.*, **74**, 1569 (1952).

(2) A. Fredga, *J. prakt. Chem.*, **150**, 124 (1938).

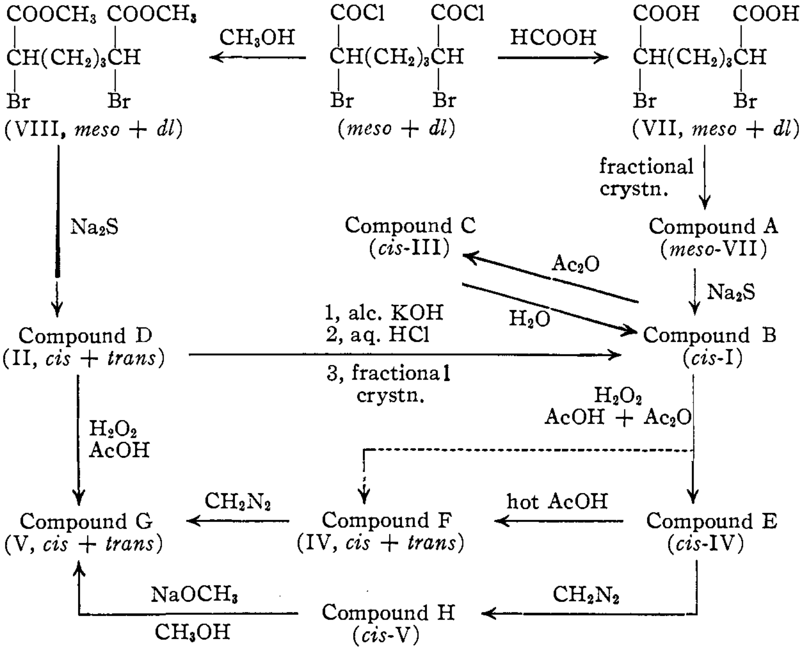
(3) R. J. Turner and A. J. Hill, *J. Org. Chem.*, **14**, 476 (1949).

(4) R. Willstätter, *Ber.*, **28**, 655 (1895).

(5) *I.e.*, either *meso* or racemic.

(6) *Cf.* the preparation of α,δ-dibromoadipic acid, H. R. Le Sueur *J. Chem. Soc.*, **93**, 716 (1908).

only waxy solids with wide m.p. ranges and low neutralization equivalents, indicating extensive contamination of the mixed isomeric dibromoacids with the monobromoacid. On slow evaporation over a period of several months or merely on prolonged standing in a stoppered flask, these mother liquors were observed to deposit additional quantities of the 155° isomer, apparently as a result of the gradual conversion of the more soluble form into the less soluble form *via* inversion at one of the two asymmetric α-carbon atoms.



The configuration of this 155° isomer (compound A) may be deduced from a consideration of the stereochemical relations outlined in the accompanying reaction diagram. The heterocyclic dicarboxylic acid (compound B) obtained on treatment of compound A with aqueous sodium sulfide underwent dehydration in boiling acetic anhydride to give a cyclic anhydride (compound C) from which the original acid B could be regenerated by the addition of water. Since the cyclic anhydride can have only the *cis* configuration and since no rearrangement is to be expected under the conditions employed for the hydrolysis of the anhydride to the diacid, compound B must be formulated as the *cis* isomer of tetrahydrothiapyran-2,6-dicarboxylic acid (*cis*-I). It follows, therefore, that the 155° isomer of α,ϵ-dibromopimelic acid must have the *meso* configuration and that Willstätter's product must have been either the racemic modification or, as seems more likely, a mixture of the *meso* and racemic forms.

The liquid dimethyl ester (VIII) of α,ϵ-dibromopimelic acid which was obtained on treatment of the dibromodiacid chloride with methanol undoubtedly consisted of a mixture of the *meso* and racemic forms,[7] and it seems probable, therefore, that the liquid dimethyl tetrahydrothiapyran-2,6-dicarboxylate (compound D) prepared from VIII by ring closure with sodium sulfide must also have consisted of a mixture of stereoisomers. Nevertheless, saponification of compound D in alcoholic potassium hydroxide and subsequent acidification of the potassium salt provided as the only isolable product the *cis* form of I, which was identified by comparison with compound B prepared directly from *meso*-α,ϵ-dibromopimelic acid. The yield of *cis*-I obtained in this way, however, was low, only about half of the ester (compound D) being accounted for, which suggests that a considerable amount of *trans*-I was formed but escaped detection due to its greater water solubility.[8]

The sulfide diacid (I) and diester (II) were oxidized to the corresponding sulfones (IV, V) by treatment with hydrogen peroxide in acetic acid. When this reaction was carried out with *cis*-I (compound B) under conditions designed to minimize the probability of *cis–trans* interconversion of the product, good yields of the sulfone diacid IV were obtained in what appeared to be a stereochemically pure form, m.p. 183–185° (compound E). Under less favorable conditions, the principal product was a waxy solid (compound F), m.p. *ca.* 100–130° from which no sharply melting material could be isolated, but which was identified on the basis of analytical results and chemical properties as a mixture of *cis*- and *trans*-IV. Since compound E is gradually transformed into a similar product on treatment with hot acetic acid, the *cis* configuration is clearly indicated for the 185° form of the sulfone diacid.

The apparent facility with which the *cis–trans* isomerization of IV can be effected is in accord with the observations of Ahlberg[9] and of Backer and Meyer[10] on the ease of racemization of optically active α-sulfonyldicarboxylic acids of the type $[RCH(COOH)]_2SO_2$. In polar solvents compounds of this type have been found to undergo loss of activity at a rapid rate, thus making the isolation of the pure stereoisomers a matter of considerable difficulty. Our inability to isolate the *trans* form of IV from compound F may reflect a similar high order of configurational instability in this series of heterocyclic α-sulfonyldicarboxylic acids, in conjunction with unfavorable solubility relationships between the *cis* and *trans* forms.

Like the corresponding diacid, the sulfone dimethyl ester V was obtained in two different forms, depending upon the method of preparation. Oxi-

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[7] *Cf.* E. Fischer, *Ber.*, **34**, 2543 (1901), regarding the composition of the corresponding diethyl ester.

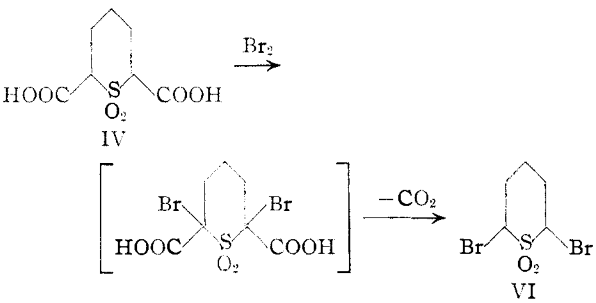
[8] Similar difficulties have been encountered by other workers in attempts to isolate the *trans* forms of the related cyclic dicarboxylic acids, cyclohexane-1,3-dicarboxylic acid [W. Goodwin and W. H. Perkin, Jr., *J. Chem. Soc.*, **87**, 841 (1905)] and tetrahydrofuran-2,5-dicarboxylic acid [H. R. Le Sueur and P. Haas, *ibid.*, **97**, 173 (1910)] from mixtures with the *cis* isomers.

[9] R. Ahlberg, *Ber.*, **55B**, 1279 (1922); *J. prakt. Chem.*, [2] **107**, 241 (1924); *Ber.*, **61B**, 811, 817, 827 (1928); *Svensk Kem. Tid.*, **44**, 48 (1932) [*C. A.*, **26**, 4060 (1932)].

[10] H. J. Backer and W. Meyer, *Rec. trav. chim.*, **46**, 212 (1927).

dation of the sulfide dimethyl ester (compound D) with hydrogen peroxide in acetic acid led to a low-melting form (compound G), m.p. 99–114° (mostly 99–100°), which remained unaffected by repeated recrystallization. A similar product was obtained when compound F was treated with diazomethane in ether solution. On the other hand, the action of diazomethane on compound E provided a high-melting form of the diester (compound H), m.p. 140–141°, which could be transformed into the low-melting form on treatment with methanolic sodium methoxide. These results are consistent with the configurational assignments indicated in the reaction diagram.

When an aqueous solution of *cis*-IV (compound E) was allowed to react with two equivalents of bromine at room temperature and the solution was then heated to promote decarboxylation of the unstable intermediate, a waxy solid was obtained which had a composition corresponding to that calculated for the expected α,α'-dibromosulfone VI.



As would be expected on the basis of Ramberg and Mellander's observation that the rates of bromination and racemization of α-sulfonylcarboxylic acids of the type $RSO_2CHR'COOH$ are the same,[11] the crude product appeared to consist of a mixture of *cis*- and *trans*-VI. A sharply melting and presumably stereochemically homogeneous form of VI was isolated after repeated fractional crystallization of the original product, but the available evidence does not permit any conclusion to be reached regarding the configuration of this isomer.

Experimental[12]

***meso*-α,ϵ-Dibromopimelic Acid (VII).**—A mixture of 67.5 g. (0.42 mole) of pimelic acid and 122 g. (1.03 moles) of thionyl chloride was heated under reflux on the steam-bath for 45 minutes, and the excess thionyl chloride was then distilled off under reduced pressure, the last traces being removed by entrainment with a small amount of chloroform.[13] The residual oil was treated on the steam-bath with 157 g. (0.98 mole) of bromine, which was added gradually over a 30-minute period, and heating was continued for another hour. The hot reaction mixture was then transferred to a separatory funnel and run slowly into 100 ml. of hot 98–100% formic acid at such a rate as to maintain a vigorous evolution of hydrogen chloride and carbon monoxide. When the addition was complete, the solution was refluxed gently for another 15 minutes before being cooled to room temperature. Crystallization was induced by scratching or seeding and was allowed to proceed overnight. The crude product was collected on a sintered glass funnel, washed with a little formic acid and dried; yield 68.6 g. (51%) of almost colorless, waxy crystals, m.p. *ca.* 135–145° with previous softening. Recrystallization of this material from a small amount of formic acid afforded 56.7 g. (42%) of colorless crystals which melted at 140–147° with slight previous sintering. Repeated recrystallization from formic acid eventually raised the m.p. to a constant value of 154.5–155°.

Anal. Calcd. for $C_7H_{10}Br_2O_4$: C, 26.44; H, 3.17; Br, 50.26; neut. equiv., 159.0. Found: C, 26.50; H, 3.39; Br, 50.26; neut. equiv., 159.4.

On standing in a stoppered flask for three months, the original formic acid filtrate slowly deposited another 30.8 g. (23%) of crude product, m.p. *ca.* 138–148° with previous softening. After two recrystallizations from formic acid this material melted at 151–153° and showed no m.p. depression when mixed with the *meso*-dibromoacid described above.

Methyl α,ϵ-Dibromopimelate (VIII).—Thirty-nine grams (0.24 mole) of pimelic acid was treated with 70 g. (0.59 mole) of thionyl chloride and 91 g. (0.57 mole) of bromine as in the above preparation, and the resultant dibromodiacid chloride was run slowly into 180 ml. of absolute methanol. After the initial vigorous reaction had subsided, the mixture was refluxed gently for several minutes and was then cooled and poured into 180 ml. of cold water. The lower oil layer was removed and the upper aqueous layer was extracted once with 290 ml. of ether. The combined organic phases were washed with dilute sodium bisulfite solution until free of bromine, then with sodium bicarbonate solution and finally with water. After drying over anhydrous magnesium sulfate, the ether was removed and the residual oil was distilled under reduced pressure to provide 73.3 g. (87%) of a slightly yellow oil, b.p. 185–192° at 12 mm. Redistillation of a portion of this material yielded an analytically pure middle fraction boiling at 188–190° at 12 mm.

Anal. Calcd. for $C_9H_{14}Br_2O_4$: C, 31.24; H, 4.08; Br, 46.20. Found: C, 31.06; H, 3.99; Br, 46.34.

***cis*-2,6-Tetrahydrothiapyrandicarboxylic Acid (I).**—An aqueous solution of the sodium salt of *meso*-α,ϵ-dibromopimelic acid was prepared by adding 20.7 g. (0.246 mole) of sodium bicarbonate to a suspension of 39.2 g. (0.123 mole) of pure *meso*-VII in 300 ml. of cold water. Pulverized sodium sulfide nonahydrate (31.2 g., 0.13 mole) was added to the resultant solution and the mixture was stirred until all the solid had dissolved. After standing for 18 hours at room temperature, the solution was acidified by the addition of 25 ml. of concd. hydrochloric acid and extracted with fifteen 35-ml. portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and evaporated to dryness on the steam-bath. The solid residue was recrystallized directly from 25 ml. of water to give 17.1 g. (73%) of colorless crystals, m.p 206–208°. Subsequent recrystallization from water raised the m.p. to 212–213°.

Anal. Calcd. for $C_7H_{10}O_4S$: C, 44.20; H, 5.30; neut. equiv., 95.1. Found: C, 44.44; H, 5.22; neut. equiv., 95.3.

***cis*-2,6-Tetrahydrothiapyrandicarboxylic Anhydride (III).**—One gram of *cis*-I was refluxed with 5 ml. of acetic anhydride for three hours, after which most of the excess reagent was removed by slow distillation over a two-hour period. Evaporation of the remaining acetic anhydride under reduced pressure left a waxy residue, which was extracted repeatedly with boiling ligroin (b.p. 90–120°) until the cold extracts no longer deposited crystals; yield 0.63 g. (70%) of colorless micro-crystalline powder, m.p. 168–169° with slight previous sintering. The m.p. was unchanged after recrystallization from cyclohexane.

Anal. Calcd. for $C_7H_8O_3S$: C, 48.82; H, 4.68; neut. equiv., 86.1. Found: C, 48.73; H, 4.89; neut. equiv., 86.3.

When 2.00 g. of the *cis*-anhydride (III) was dissolved in 4.0 ml. of hot water and the solution was cooled and filtered, 1.77 g. of colorless crystals were obtained which melted at 211–212° and showed no depression when mixed with the *cis*-acid (I) described above.

Dimethyl 2,6-Tetrahydrothiapyrandicarboxylate (II).—A mixture of 62.2 g. (0.18 mole) of methyl α,ϵ-dibromopimelate, 53 g. (0.22 mole) of pulverized sodium sulfide nonahydrate, 3 g. of sodium iodide, 380 ml. of methanol and 20 ml. of water was cooled in an ice-bath and stirred for a period of eight hours, after which it was allowed to stand at room temperature overnight. After removal of most of the

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(11) L. Ramberg and A. Mellander, *Arkiv Kemi, Mineral. Geol.*, **11B**, No. 31 (1934); *C. A.*, **28**, 4296 (1934).

(12) Microanalyses were performed by Clark Microanalytical Laboratory, Urbana, Ill.

(13) *Cf.* R. C. Fuson, C. L. Fleming, P. F. Warfield and D. E. Wolf, *J. Org. Chem.*, **10**, 126 (1945).

methanol under reduced pressure, the residual oil was diluted with *ca.* 500 ml. of water and extracted several times with ether. The combined extracts were washed with water, dried over anhydrous magnesium sulfate and distilled to provide 16.4 g. (42%) of colorless oil, b.p. 170–180° at 25 mm. The analytical sample was taken from the middle fraction (b.p. 161–163° at 13 mm.) of a subsequent distillation.

Anal. Calcd. for $C_9H_{14}O_4S$: C, 49.52; H, 6.46. Found: C, 49.57; H, 6.52.

Saponification of the dimethyl ester II was brought about by adding 16.3 g. (0.075 mole) of the crude product to a hot solution of 12.6 g. (0.225 mole) of potassium hydroxide in 100 ml. of methanol and refluxing the mixture for ten minutes after the initial exothermic reaction had subsided. The potassium salt which precipitated during the course of this reaction was collected, washed with methanol, and dried; yield 13.0 g. (65%). This material was dissolved in 30 ml. of cold water and the solution was acidified with 10 ml. of concd. hydrochloric acid. After crystallization was complete, the crude product was collected, washed once with a little water, and dried to provide 7.0 g. (76% from K salt, 49% from ester) of colorless crystals which melted at 204–208° and showed no depression when mixed with the *cis*-acid (I) described above.

***cis*-2,6-Tetrahydrothiapyrandicarboxylic Acid 1,1-Dioxide (IV).**—A mixture of 25 ml. of glacial acetic acid, 25 ml. of acetic anhydride and 8.1 ml. (0.071 mole) of 30% hydrogen peroxide was allowed to stand for three hours with occasional cooling to prevent the temperature from rising above 50°.[14] *cis*-2,6-Tetrahydrothiapyrandicarboxylic acid (6.48 g., 0.034 mole) was then added to the cold solution in small portions while keeping the temperature below 50°, and the reaction mixture was set aside at 0° for three days. During this time a portion of the product crystallized out of the solution; this was collected, washed with a little acetic acid, and dried to give 4.43 g. (58%) of colorless crystals, m.p. 183–185°. A second crop of crystals with similar m.p. was obtained by concentration of the mother liquors under reduced pressure and was added to the original product to give a combined yield of 6.69 g. (88%). When samples of this material were recrystallized from glacial acetic acid, the m.p. showed a tendency to decline somewhat and to become rather erratic (*e.g.*, 182–185°, 181–183°, 180–184°), presumably because of the isomerizing influence of the hot solvent on the configurationally unstable product (see below).

Anal. Calcd. for $C_7H_{10}O_6S$: C, 37.84; H, 4.54; neut. equiv., 111. Found: C, 37.76; H, 4.72; neut. equiv., 111.

The omission of the acetic anhydride in the above preparation or the use of unnecessarily prolonged reaction times or elevated temperatures resulted in lower yields of the product melting above 180°, the principal product in such experiments being a waxy solid with an indefinite m.p. in the region 100–130°. Recrystallization of this low-melting material from glacial acetic acid followed by careful drying over moist sodium hydroxide *in vacuo* failed to improve the m.p. or to cause any significant change in the neutralization equivalent (neut. equiv. calcd. for IV, 111; found, 112).

When 0.50 g. of the high-melting form of IV was dissolved in 5 ml. of glacial acetic acid and the solution was refluxed for one hour and evaporated to dryness on the steam-bath, 0.49 g. of waxy residue was obtained with characteristics identical to those described above for the low-melting form of IV.

Dimethyl 2,6-Tetrahydrothiapyrandicarboxylate 1,1-Dioxide (V).—To a solution of 10.0 g. (0.046 mole) of II in 40 ml. of glacial acetic acid there was added 11.4 ml. (0.10 mole) of 30% hydrogen peroxide while the mixture was cooled to prevent the temperature from rising above 50°. After the strongly exothermic reaction had subsided, the mixture was refluxed for several minutes to complete the reaction and the solvent was then distilled off under reduced pressure. The residual oil gradually crystallized on cooling to give a dark-colored waxy solid which was treated with Nuchar and recrystallized from methanol; yield, 8.0 g. (70%) of colorless crystals melting mostly at 89–92°. Repeated recrystallization from methanol raised the m.p. to 99–100°, with a small amount of material remaining unmelted until *ca.* 114°.

Anal. Calcd. for $C_9H_{14}O_6S$: C, 43.19; H, 5.64. Found: C, 43.42; H, 5.92.

A similar product was obtained when 6.1 g. (0.027 mole) of the low-melting form of IV described above was added to 100 ml. of an ether solution of diazomethane (*ca.* 0.06 mole) prepared according to the directions given by Arndt.[15] The ether-insoluble material was collected, washed with ether and recrystallized from methanol to yield 4.2 g. (69%) of colorless crystals which melted mostly at 97–99° with a small residue remaining unmelted until *ca.* 115°.

***cis*-Dimethyl 2,6-Tetrahydrothiapyrandicarboxylate 1,1-Dioxide (V).**—Finely powdered *cis*-IV (4.44 g., 0.020 mole) was treated with excess diazomethane (*ca.* 0.06 mole) as described above. The crude product melted at 126–130°; yield 3.94 g. (79%). Recrystallization from methanol raised the m.p. to 140–141°.

Anal. Calcd. for $C_9H_{14}O_6S$: C, 43.19; H, 5.64. Found: C, 43.31; H, 5.75.

A mixture of approximately equal parts of the dimethyl ester V prepared by oxidation of the sulfide (m.p. 99–100°) and the *cis*-dimethyl ester V prepared by methylation of the *cis*-diacid (m.p. 140–141°) melted at 100–116°, thus indicating that the 99–100° form of V is a eutectic mixture of the *cis* and *trans* isomers.

When 1.00 g. of *cis*-V was dissolved in 2.5 ml. of boiling methanol containing a trace of sodium methoxide (0.5 ml. of 1% sodium methoxide solution added to 2.0 ml. of methanol) and the solution was refluxed for 30 minutes, acidified with one drop of concd. sulfuric acid, and cooled, 0.82 g. of colorless needles, m.p. 97–99°, crystallized out. Subsequent recrystallization from methanol failed to alter the m.p. and no m.p. depression was observed on admixture with the sulfone diester V prepared by oxidation of the corresponding sulfide II.

2,6-Dibromotetrahydrothiapyran 1,1-Dioxide (VI).—Bromine (16.2 g., 0.101 mole) was added to a solution of 11.1 g. (0.050 mole) of *cis*-IV in 100 ml. of water and the mixture was allowed to stand at room temperature for 28 hours. During this time the bromine layer gradually disappeared and some carbon dioxide was evolved. The amber-colored solution was then boiled gently under reflux for 30 minutes to complete the decarboxylation and to remove a small amount of unreacted bromine. During this operation most of the product separated as a colorless oil phase, which on cooling slowly solidified. The waxy solid was collected, washed with water, and dried *in vacuo* over anhydrous calcium chloride; yield 10.8 g. (74%), m.p. *ca.* 95–135°. Repeated recrystallization of this product from 50% aqueous methanol provided 3.6 g. of feathery needles, which melted at 154–156°; subsequent recrystallization from a benzene–ligroin mixture provided an analytical sample melting at 155–156°.

Anal. Calcd. for $C_5H_8Br_2O_2S$: C, 20.56; H, 2.76; Br, 54.74. Found: C, 21.01; H, 3.05; Br, 54.60.

Acknowledgment.—The authors are happy to acknowledge the financial support of a portion of this work by a Frederick Gardner Cottrell grant from the Research Corporation.

SWARTHMORE, PENNA.

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[14] Several attempts to perform this oxidation by adding the hydrogen peroxide to a solution of the sulfide in an acetic acid–acetic anhydride mixture resulted in violent exothermic reactions which could not be controlled by cooling. The inverted method of mixing described above proved to be safer and generally more satisfactory for this preparation.

[15] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 166 (note 3).