Novel Sultones. II. 1,4-Dialkyl-9-oxo-9*H*-indeno[1,2-*d*][1,2]oxathiin 3,3-Dioxides

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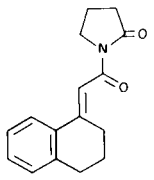
A new type of sultone, 1,4-dialkyl-9-oxo-9*H*-indeno[1,2-*d*][1,2]oxathiin 3,3-dioxides, can be readily synthesized by treating 3-hydroxy-3-phenylalkanoic acid with a mixture of acid anhydride and sulfuric acid. A mechanism for the formation of these sultones is proposed. A postulated intermediate in the preparation of the 1,4-dimethyl analog, 3-ethylideneindan-1-one, was prepared and subsequently converted to the same 1,4-dimethyl compound by the same reagents. Bromination of these sultones gave the 1-bromalkyl derivatives while treatment with hydrazine yielded pyrazolium sulfonates. Under different reaction conditions, 3-ethylidene-indan-1-one formed a pyrylium salt, which, in turn, was converted to a fused tricyclic pyridine derivative with ammonia.

Sultones, or oxathiin S,S-dioxides, can be considered as either the dioxides of cyclic thiotic acid esters or cyclic sulfonates. These compounds are usually formed by the elimination of water from the corresponding hydroxysulfonic acid, either by heat or by the action of a mixture of concentrated sulfuric acid and acetic anhydride (1-3). The latter agents have been particularly useful for the conversion of α,β-unsaturated ketones or related compounds into sultones. A synthesis of 2-[*N*-(2-pyrrolidonyl)]-5,6-dihydronaphth[2,1-*c*][1,2]oxathiin 4,4-dioxide (II), by the treatment of the imide I with a mixture of acetic anhydride and concentrated sulfuric acid, for example, has recently been reported from this laboratory (4).



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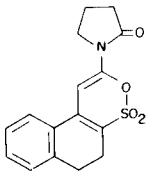
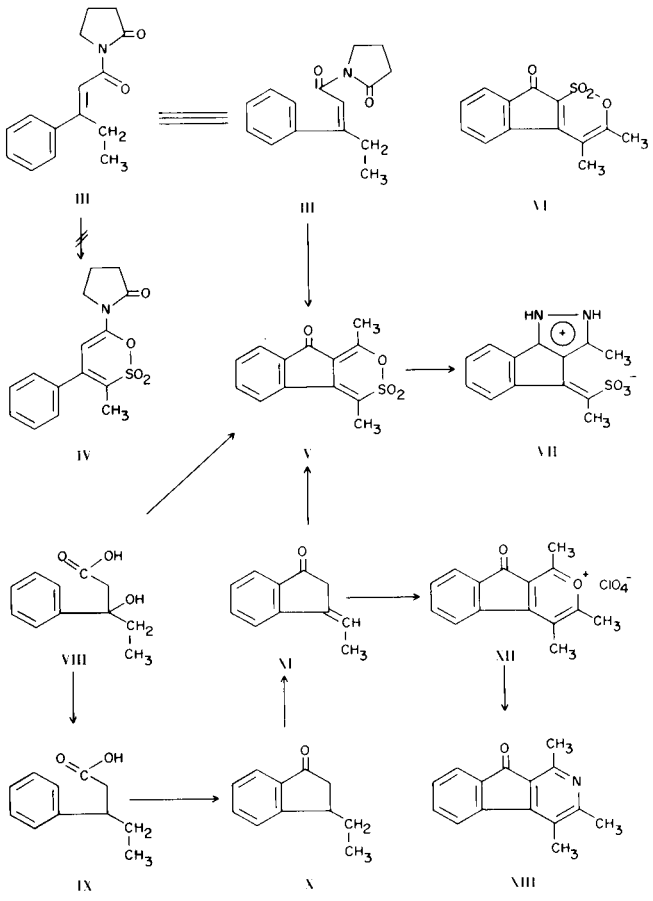


II

Treatment of the imide III, prepared from β-ethylcinnamic acid, with the same acid mixture yielded a product, which showed the expected ir absorption bands at 1655 cm^{-1} (>C=C<) as well as 1372 and 1186 cm^{-1} ($-SO_2-O-$ stretching) for a sultone. However, the compound contained no nitrogen. Its mass spectrum gave a molecular ion of m/e: 262 (100%) and M^+-SO_2 (5) at m/e: 198 (76%) [rather than m/e: 305, required for the anticipated *N*-pyrrolidinonyl-*o*-oxathiin dioxide (IV)] which, with the result of elemental analysis, revealed a molecular formula of $C_{13}H_{10}O_4S$. This information, together with the ultraviolet spectra (The uv spectra in ethanol or in *p*H 1 or 7 showed a single maximum peak at 256-257 nm. At *p*H 11, however, two new maxima appeared at 336 and 396 nm. The single maximum peak was restored upon acidification

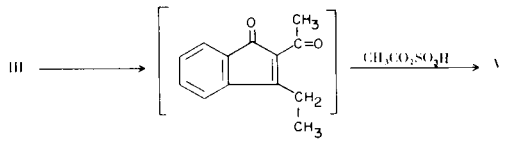


of the basic solution) and nmr data (a four-aromatic-proton multiplet at 2.23 τ and a six-proton singlet at 7.39 τ) suggested that the structure of the product is 1,4-dimethyl-9-oxo-9*H*-indeno[1,2-*d*][1,2]oxathiin 3,3-dioxide (V).

An alternative structure for this product, formula VI, was ruled out by the fact that a pyrazole derivative VII could be obtained by treatment of the product with hydrazine.

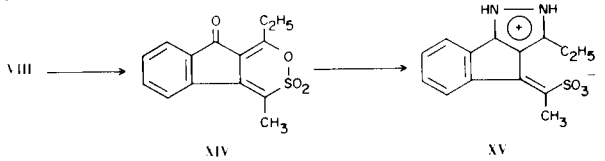
Since the yield of the sultone V from III was rather low, an alternative approach for the synthesis of V was studied. This was realized by heating 3-hydroxy-3-phenylvaleric acid (VIII) (6) in a mixture of acetic anhydride and sulfuric acid, and the desired compound V was obtained in 38% yield. In the latter reaction, 3-ethylidenindan-1-one (XI) may be considered a possible intermediate. Consequently, compound XI was prepared from VIII *via* 3-phenylvaleric acid (IX) (7) and 3-ethylindan-1-one (X) (8). Treatment of XI with acetic anhydride-sulfuric acid mixture gave the identical product V.

The aforementioned reactions indicate that formation of compound V from the imide III may involve, in the presence of the acetic anhydride-sulfuric acid mixture, cycliacylation of III with elimination of the pyrrolidone ring; this, in turn, was acetylated at the carbon atom α to the carbonyl group of the resulting 3-ethylindone intermediate. The newly formed α,β-unsaturated ketone then reacted in the usual way with the acetyl sulfuric acid to form the oxathiin dioxide ring system.



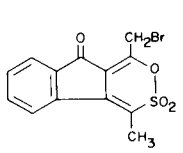
In the absence of a sulfonating agent, 3-ethylideneindan-1-one (XI) underwent a second acylation, at the position γ to the carbonyl function, and cyclized to a pyrylium salt, *viz.*, treatment of XI with a mixture of acetic anhydride and perchloric acid gave 9-oxo-9*H*-1,3,4-trimethyl-indeno[2,1-*c*]pyrylium perchlorate (XII). The structure of this pyrylium salt was substantiated by the fact that it was readily converted to 9-oxo-9*H*-1,3,4-trimethylindeno[2,1-*c*]pyridine (XIII) with aqueous ammonia (9).

In an analogous manner, treatment of 3-hydroxy-3-phenylvaleric acid (VIII) with a mixture of propionic anhydride and sulfuric acid readily yielded the corresponding ethyl sultone homolog XIV. The latter compound was transformed to the ethylpyrazole compound XV with hydrazine.

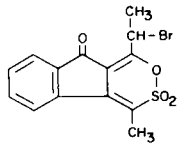


XIV XV

Bromination of these *o*-oxathiin dioxides took place with ease. Treatment of compound V with bromine at room temperature gave a monobromo derivative, the structure of which was assigned as XVI. The position of bromination was substantiated by a nmr spectrum study of the brominated product XVII, prepared from the corresponding ethyl homolog XIV.



XVI



XVII

Although these sultones are also formed by the reaction of α,β-unstaurated ketones with an acid anhydride-sulfuric acid mixture (1,3,4,10,11) the formation of these compounds is rather unique in that the original carbonyl function remains intact; *i.e.*, it is the acyl group from the acid reagent that is transformed into an integral portion of the sultone ring. In other cases (1,3,4,10,11) the ketonic group contributes as a portion of the sultone moiety. Sultones of this type, wherein a neighboring carbonyl function is adjacent to an *o*-oxathiin dioxide ring, are potential 1,3-diketones and may be useful in the synthesis of certain novel heterocyclic compounds.

EXPERIMENTAL

All melting points were taken on a Thomas-Hoover melting point apparatus and were corrected. The nmr spectra were determined on a Varian A-60 spectrometer. The mass spectra were obtained with a Varian Mat CH-4B Mass Spectrometer. Ir spectra were taken on a Perkin Elmer Infracord. The uv absorption spectra were determined with a Beckman DK-2 spectrometer.

N-(β-Ethylcinnamoyl)-2-pyrrolidone (III).

To a solution of β-ethylcinnamoyl chloride (prepared from 10 g. of β-ethylcinnamic acid and oxalyl chloride) in 100 ml. of benzene was added 15 g. of the sodium salt of pyrrolidone. The mixture was stirred for 1 hour then evaporated *in vacuo* to a thick oil. This was dissolved in 200 ml. of ether and extracted successively with water, saturated aqueous sodium bicarbonate, saturated aqueous sodium chloride, and water. The washed ether solution was dried (sodium sulfate), filtered, and concentrated to an amber oil which weighed 75 g. An analytical specimen was obtained by a short-path molecular distillation; ir: ν max 1733, 1694, 1678, 1600 cm^{-1}.

Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.75. Found: C, 74.34; H, 6.68; N, 5.63.

3-Hydroxy-3-phenylvaleric Acid (VIII).

A mixture of 65 g. of propiophenone, 80 ml. of ethyl bromoacetate, 62 g. of 20 mesh granular zinc, and 1 liter of dry tetrahydrofuran was placed under nitrogen in a dry, 5-liter three-necked round bottom flask equipped with a mechanical stirrer and two efficient reflux condensers. The mixture was stirred vigorously and gently warmed to initiate the reaction; it was then stirred for 30 minutes without external heat, then heated under reflux for 30 minutes. After cooling, the reaction mixture was decanted into

100 ml. of 50% aqueous acetic acid, and the excess zinc and the reaction flask rinsed thoroughly with fresh tetrahydrofuran. The combined tetrahydrofuran solution was evaporated *in vacuo* and the residue extracted with benzene (3 x 100 ml.). The benzene solution was washed successively with water, saturated aqueous sodium bicarbonate, saturated aqueous sodium chloride, then concentrated to a yellow oil. The oil was diluted with 250 ml. of ethanol and the solution refluxed under nitrogen as 100 ml. of 20% sodium hydroxide was added. The mixture was refluxed for 1 hour and the ethanol removed under reduced pressure. The resulting aqueous solution was diluted with 100 ml. of water, washed with ether, and filtered. The filtrate was cooled to 10° and acidified with 6*N* hydrochloric acid. The precipitated solid was collected by filtration, dried, and recrystallized from benzene to give 77 g. (82% yield) of VIII as fine, white needles, m.p. 119-121°. An additional recrystallization from benzene afforded an analytical sample, m.p. 120-121° (lit (6), m.p. 125°).

3-Phenylvaleric Acid (IX).

A mixture of 47.3 g. of VIII, 250 ml. of acetic acid, 1 ml. of 70% aqueous perchloric acid, and 2.5 g. of 10% palladium-on-charcoal was hydrogenated at 4 kg/cm^2 for 5 hours. The catalyst was removed by filtration (Celite) and the filtrate concentrated *in vacuo* to a viscous syrup. This was triturated with water and the resulting low melting solid collected by filtration and dried. It was purified by distillation at 113-115°/0.3-0.6 mm to give 42.6 g. of IX as a white, waxy solid, m.p. 61-63° (lit. (7), b.p. 142°/5 mm).

3-Ethylindan-1-one (X).

A mixture of 61 g. of IX and 550 g. of polyphosphoric acid was heated at 65-75° for 90 minutes (a rotating evaporator was used to turn the 1-liter round bottom reaction flask to effect mixing). The red reaction mixture was poured, with stirring, into 1-liter of ice and water. The aqueous suspension was extracted with ether (3 x 400 ml.). The combined ether solution was washed successively with water, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride. The washed ether solution was concentrated to one-third of its original volume, dried over sodium sulfate, filtered, and concentrated. The product was distilled at 86-94°/1 mm to give 49.5 g. (90% yield) of X. An analytical specimen was obtained by a second distillation *in vacuo*; ir: ν max 1722 cm^{-1}.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.30; H, 7.44.

3-Ethylideneindan-1-one (XI).

A stirred mixture of 12 g. of X and 17.8 g. of *N*-bromosuccinimide in 100 ml. of carbon tetrachloride was refluxed under a sun lamp for 25 minutes. It was then heated for an additional 8 hours. The resulting mixture was purified by chromatography on silica gel (310 g., 50 mm ID, hexane) to give 7.6 g. (48% yield) of XI (tlc homogeneous); nmr (deuteriochloroform): τ 2.20-2.75 (*m*, 4p, Ar-H), 3.73 (*m*, 1p, vinyl-H), 6.97 (*s*, 2p, -CH_2-), 8.18 (*d*, J = 7, 3p, -CH_3); ir: ν max 1711, 1270, 760 cm^{-1}.

A by-product was identified as 2-bromo-3-ethyl-1-indone, m.p. 78-79° (methanol): nmr (deuteriochloroform): τ 2.39-2.94 (*m*, 4p, Ar-H), 7.32 (*q*, 2p, J = 7, -CH_2-), 8.72 (*t*, J = 7, 3p, -CH_3); ir (Nujol): 1720 cm^{-1}.

Anal. Calcd. for $C_{11}H_9BrO$: C, 55.72; H, 3.83. Found: C, 56.01; H, 4.02.

1,4-Dimethyl-9-oxo-9*H*-indeno[1,2-*d*][1,2]oxathiin 3,3-Dioxide (V).

Method A.

To a cold mixture of 5 ml. of concentrated sulfuric acid and 20 ml. of acetic anhydride was added 6.16 g. of the imide III. The mixture was stirred and heated at 80° for 15 minutes, then poured onto 200 ml. of ice and water. A light yellow precipitate was formed which was collected by filtration to give 0.32 g. of V, m.p. 180-181°; nmr (deuteriochloroform): τ 2.23 (*m*, 4p, Ar-H), 7.39 (*s*, 6p, -CH_3); ir (chloroform): ν max 1725, 1655, 1372, 1186, 885 cm^{-1}; uv: λ max (ethanol): 257 nm (log ϵ 4.65); λ max (*p*H 1 or 7): 256 nm (log ϵ 4.65); λ max (*p*H 11): 258 (log ϵ 4.42), 336 (4.12) and 396 nm (3.98); mass spectrum (70 ev, 50°), m/e: 262 (M^+, 100%), 198 (M^+-SO_2, 76%), 183 (M^+-SO_2-CH_3, 33%), 155 (M^+-SO_2-$COCH_3$, 43%), 127 (M^+-SO_2-CH_3-$COCH_3$, 33%).

Anal. Calcd. for $C_{13}H_{10}O_4S$: C, 59.53; H, 3.84. Found: C, 59.39; H, 3.85.

Method B.

A mixture of 10 g. of 3-hydroxy-3-phenylvaleric acid (VIII) in 20 ml. of concentrated sulfuric acid was stirred for 1 hour in an ice bath. To this solution was added, with cooling, 80 ml. of acetic anhydride. The acidic solution was stirred at 0° for 10 minutes and at room temperature for 30 minutes. It was then heated at 75-80° for another 30 minutes and poured with stirring onto 1-liter of crushed ice. The resulting yellow precipitate was collected by filtration and washed well with water. The solid was dissolved in 100 ml. of chloroform. The chloroform solution was dried (sodium sulfate), filtered, and the filtrate was slurried with 20 g. of silica gel. This was again filtered and the silica gel washed with fresh chloroform. The combined chloroform solution was evaporated to dryness. The residue was recrystallized from ethyl acetate to give 4.4 g. of beige needles, m.p. 178-180°. An additional 0.8 g. of product, m.p. 178-180°, was isolated from the filtrate to give a total yield of 38% of V. Two additional recrystallizations from ethyl acetate gave an analytical sample as white needles, m.p. 180-181°. The product was found to be identical with that prepared by Method A.

Method C.

A mixture of 1.56 g. of 3-ethylideneindan-1-one (XI), 3.6 g. of acetic anhydride and 1.1 g. of concentrated sulfuric acid was stirred for 90 minutes at room temperature. The reaction mixture was poured onto 50 ml. of ice and water and the product collected by filtration. Recrystallization from a mixture of chloroform and ethanol gave 0.21 g. of a light yellow compound, m.p. 177-178°. The product was found to be identical with that prepared by the two preceding procedures.

1-Ethyl-4-methyl-9-oxo-9*H*-indeno[1,2-*d*][1,2]oxathiin 3,3-Dioxide (XIV).

This compound was prepared from 10 g. of 3-hydroxy-3-phenylvaleric acid (VIII), 23 ml. of concentrated sulfuric acid and 135 ml. of propionic anhydride by a procedure similar to that described in Method B for the synthesis of the corresponding dimethyl homolog V. Recrystallization from acetone-hexane gave 1.35 g. of XIV as yellow needles, m.p. 160-161°. An analytical sample was obtained by a repeated recrystallization from the same solvent pair, m.p. 163-164°; nmr (deuteriochloroform): τ 1.95-2.46 (*m*, 4p, Ar-H), 6.97 (*q*, 2p, J = 7 Hz, -CH_2-), 7.43 (*s*, 3p, -CH_3), 8.80 (*t*, 3p, J = 7 Hz, -CH_3); ir (chloroform): ν max 1725, 1653, 1368, 1188, 883 cm^{-1}; uv: λ max (ethanol): 257 nm (log ϵ 4.57); λ max (*p*H 1 or 7): 258 nm (log ϵ 4.57); λ max (*p*H 11): 246 (log ϵ 4.33), 257 (4.33), 352 (3.98), and 386 nm

(3.90); mass spectrum (70 ev, 75°): 276 (M^+, 100%), 212 (M^+ -SO_2, 29%), 197 (M^+-SO_2-CH_3, 74%), 183 (M^+-SO_2-C_2H_5, 10%), 169 (M^+-SO_2-$COCH_3$, 34%), 141 (M^+-SO_2-CO-$COCH_3$, 18%).

Anal. Calcd. for $C_{14}H_{12}O_4S$: C, 60.86; H, 4.38. Found: C, 60.83; H, 4.39.

9-Oxo-9*H*-1,3,3-trimethylindeno[2,1-*c*]pyrylium Perchlorate (XII).

A mixture of 24 g. of X and 35.6 g. of *N*-bromosuccinimide in 200 ml. of carbon tetrachloride was heated at reflux by means of a sun lamp for 1 hour and by an electric mantle for 8 hours. The reaction mixture was filtered and the filtrate concentrated *in vacuo*. The resulting oil was dissolved in 100 ml. of ethyl acetate and the solution was added to a cold (0-5°) mixture of 200 ml. acetic anhydride, 23 ml. of 70% aqueous perchloric acid, and 300 ml. of ethyl acetate. To the solution was added enough ethyl acetate to make a total volume of 2 liters. The mixture was stirred at 0-5° for 30 minutes then allowed to warm to room temperature; stirring was continued for 4 hours. A brown precipitate, which formed during this period, was collected by filtration and washed with ethyl acetate to give 8.7 g., m.p. 208-210°. The filtrate, after standing for 24 hours, yielded an additional amount (8.5 g. m.p. 215-216°) of product resulting in a total yield of 39%. An analytical sample was obtained by recrystallization once from acetic anhydride-ethyl acetate and once from acetonitrile-ethyl acetate as green, lustrous platelets, m.p. 222-223° dec., nmr (trifluoroacetic acid): τ 1.82 (*m*, 4p, Ar-H), 6.73 (*s*, 3p, -CH_3), 6.82 (*s*, 3p, -CH_3), 7.00 (*s*, 3p, -CH_3); ir (Nujol): ν max 1710, 1628, 1090, 898, 750, 625 cm^{-1}.

Anal. Calcd. for $C_{15}H_{13}O_2{\cdot}ClO_4$: C, 55.48; H, 4.04. Found: C, 55.72; H, 3.85.

9-Oxo-9*H*-1,3,4-trimethylindeno[2,1-*c*]pyridine (XIII).

A mixture of 6.34 g. of the pyrylium perchlorate and 200 ml. of concentrated aqueous ammonia was heated on a steam bath for 30 minutes then cooled in an ice bath. The brown solid was collected by filtration, washed with water, and dried to give 4.62 g. of crude XIII. Chromatography on basic alumina (140 g., 4 cm ID, prepared in 1:1 benzene-chloroform) with the same solvent pair gave 3.28 g. (74% yield) of XIII as cream colored powder, m.p. 151-152°. Three recrystallizations from methanol afforded an analytical sample as light yellow needles, m.p. 151-152°; nmr (deuteriochloroform): 2.22-2.49 (*m*, 4p, Ar-H), 7.30 (*s*, 3p, -CH_3), 7.46 (*s*, 3p, -CH_3), 7.60 (*s*, 3p, -CH_3); ir (Nujol): ν max 1690, 1572, 903, 743 cm^{-1}; uv λ max (ethanol): 252 (log ϵ 4.96), 292 3.76), 303 (3.89), 330 (3.76), and 348 nm (3.78); mass spectrum (70 ev, 150°): m/e 223 (M^+, 100%), 194 (25%), 181 (15%), 152 (29%).

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.49; H, 5.89; N, 6.15.

3-Methylindeno[1,2-*c*]pyrazolium 4-Ethylidene-1′-sulfonate (VII).

To 20 ml. of 98% hydrazine was added, with stirring, 5 g. of V. After 5 minutes the warm solution was diluted with 30 ml. of water and acidified with 250 ml. of 2*N* aqueous hydrochloric acid. The resulting clear yellow solution was warmed on a steam bath whereupon a precipitate formed. It was collected by filtration and washed successively with water, methanol, and ether. An off-white powder (4.4 g.) was obtained, m.p. 238-240°. An analytical sample was prepared by adding dilute aqueous hydrochloric acid to a filtered solution of the crude product in pyridine. The white needles obtained by two such purifications melted at 252-254°; nmr (pyridine-d_5): τ 2.40-2.66 (*m*, 4p, Ar-H), 6.40 (*s*, 3p, -CH_3), 6.72 (*s*, 3p, -CH_3); ir: 3300, 2565, 1185, 1040 cm^{-1}, uv λ max (ethanol): 242 (log ϵ 4.50), 250 (4.55), and 291 nm (4.17).

Anal. Calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14. Found: C, 56.98; H, 4.61; N, 10.36.

3-Ethylindeno[1,2-*c*]pyrazolium 4-Ethylidene-1′-sulfonate (XV).

A suspension of 0.4 g. of XIV in 7 ml. of 95% hydrazine was warmed gently on a steam bath until a clear solution was obtained. It was diluted with 30 ml. of water, acidified with 200 ml. of 6*N* hydrochloric acid, and warmed briefly on a steam bath whereupon a precipitate formed. This was collected by filtration and washed successively with water, methanol, and ether to give 0.3 g. of XV as a white powder, m.p. 215°. An analytical specimen was prepared by precipitation as in the case of VII, m.p. 216-217°.

Anal. Calcd. for $C_{14}H_{14}N_2O_3S{\cdot}\frac{1}{2}H_2O$: C, 56.17; H, 5.05; N, 9.36. Found: C, 56.37; H, 5.36; N, 9.15.

1-Bromomethyl-4-methyl-9-oxo-9*H*-indeno[1,2-*d*][1,2]oxathiin 3,3-Dioxide (XVI).

To 10 g. of bromine cooled at 0° was added 5 g. of V. The mixture was stirred vigorously with a glass rod while allowed to warm to room temperature. When the mixture solidified, 20 ml. of chloroform was added and the suspension was evaporated on a steam bath under reduced pressure. The resulting yellow solid was recrystallized from ethyl acetate to give 5.5 g. (85% yield) of XVI, m.p. 153-157°. An analytical specimen was obtained by an additional recrystallization from ethyl acetate, white needles, m.p. 163-164°; ir (deuteriochloroform): ν max 1722, 1656, 1372, 1266, 1191, 896, 887 cm^{-1}; uv λ max (ethanol): 264 (log ϵ 4.62), 255 nm (4.11); λ max (*p*H 1 or 7): 265 (4.62), 295 nm (4.14); λ max (*p*H 11): 265 (log ϵ 4.41), 358 (4.02), 400 (4.00); nmr (deuteriochloroform): τ 2.8 (*m*, 4p, Ar-H), 5.30 (*s*, 2p, -CH_2Br), 7.34 (*s*, 3p, -CH_3).

Anal. Calcd. for $C_{13}H_9BrO_4S{\cdot}\frac{1}{4}H_2O$: C, 45.17; H, 2.77. Found: C, 45.27; H, 2.72.

1-(1-Bromoethyl)-4-methyl-9-oxo-9*H*-indeno[1,2-*d*][1,2]oxathiin 3,3-Dioxide (XVII).

A solution of 0.75 g. of XIV in 3 ml. of chloroform was added to 1 g. of cold bromine. Absolute ethanol (3 ml.) was then added and the mixture stirred at room temperature for 15 minutes. It was heated on a steam bath under reduced pressure until a solid residue was obtained. The crude product was recrystallized from ethyl acetate to yield 0.22 g. of a yellow powder which was homogeneous on tlc (silica gel-chloroform). Recrystallization from ethyl acetate-hexane gave an analytical specimen as white granular crystals, m.p. 183-184°; ir (chloroform): ν max 1716, 1650, 1600, 1190, 1130, 1040, 890 cm^{-1}; uv λ max (ethanol): 263 (log ϵ 4.52), 295 nm (4.01); nmr (deuteriochloroform): τ 1.87-2.48 (*m*, 4p, Ar-H), 3.83 (*q*, 1p, J = 7 Hz, -CH-Br), 7.35 (*s*, 3p, -CH_3), 8.07 (*d*, 3p, J = 7 Hz, -CH_3).

Anal. Calcd. for $C_{14}H_{11}BrO_4S$: C, 47.34; H, 3.12. Found: C, 47.74; H, 3.48.

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