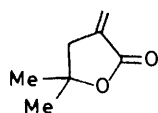


Sultone Formation from 2,4,6-Tri-isopropylbenzenesulphonic Acid

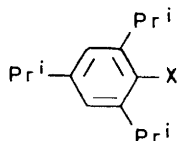
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2,4,6-Tri-isopropylbenzenesulphonic acid decomposed in the presence of oxygen giving 2,4,6-tri-isopropyl-1, α -sultone; a mechanism involving arylsulphonyl and peroxyarylsulphonyl radicals and intramolecular hydrogen atom abstraction is suggested.

RECENTLY we have applied the Shapiro reaction in the synthesis of α -methylene- γ -lactones. Typically, reaction of the 2,4,6-tri-isopropylbenzenesulphonyl hydrazone of 2-hydroxy-2-methylpentan-4-one with *n*-butyllithium, carbon dioxide, and trifluoroacetic acid in sequence gave 5,5-dimethyl-3-methylenetetrahydrofuran-2-one (1) (74%).¹ The by-product 2,4,6-tri-

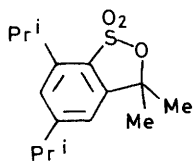


(1)



(2)

- a; X = SO₂H
 b; X = SO₂NHNH₂
 c; X = SO₂Cl
 d; X = SO₂[•]
 e; X = SO[•]
 f; X = S[•]
 g; X = SO₂I
 h; X = SO₂[•]
 i; X = $\begin{array}{c} \text{O} \\ \parallel \\ \text{S}-\text{OEt} \end{array}$
 j; X = $\begin{array}{c} \text{O} \\ \parallel \\ \text{SO}_3\text{Et} \end{array}$
 k; X = $\begin{array}{c} \text{O} \\ \parallel \\ \text{S}-\text{P}(\text{OEt})_2 \end{array}$
 l; SO₂OO[•]



(3)

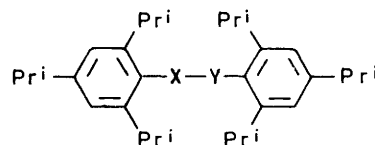
propylbenzenesulphonic acid (2a) partially decomposed in the presence of acid. Chromatography was required to separate the methylene lactone (1) from a minor aromatic product. Herein is described a study of this unexpected product, the sultone (3).

RESULTS AND DISCUSSION

2,4,6-Tri-isopropylbenzenesulphonylhydrazine (2b) was slowly decomposed by triethylamine. Subsequent acidification gave, after 5 d, the sultone (3) (28%) as a crystalline solid, m.p. 124–127 °C. Both microanalysis and the mass spectrum (M^+ 282.1294) were in excellent agreement with a composition of C₁₅H₂₂O₃S. The i.r. spectrum showed the absence of OH and the presence of the -SO₂-O- unit (1 330 and 1 190 cm⁻¹). The ¹H and ¹³C n.m.r. spectra were most informative. Clearly the molecule possessed only two isopropyl functions [δ_{H} 1.33 (12 H, 2 overlapping doublets, *J* 7 Hz), 3.03 (1 H, septet,

J 7 Hz), and 3.6 (1 H, septet, *J* 7 Hz); δ_{C} 23.29 (q), 23.67 (q), 29.58 (d), and 34.54 (d)], and was unsymmetrical. The low-field methyl resonance [δ_{H} 1.8 (6 H, s), δ_{C} 89.89 (s)] indicated an *ortho*-fused isopropoxy-sulphonyl function. Thus formulation as sultone (3) was unambiguous. Most probably sultone (3) arose *via* aerial oxidation of the sulphonic acid (2a).

Zinc-dust reduction² of 2,4,6-tri-isopropylbenzenesulphonyl chloride (2c) gave the sulphonic acid (2a). Identity and purity were confirmed by microanalysis, homogeneity by t.l.c., spectral characteristics, and by analogy with literature data.² The mass spectrum showed ions derived from the thiosulphonate (4a) and disulphide (4b), clearly arising from decomposition in the probe. Of note, ions at *m/e* 267 (2d), 251 (2e), 235 (2f), and 203 (C₁₅H₂₃⁺) were observed; these were common to many sulphonic acid derivatives in the sequel. With careful exclusion of oxygen, 2,4,6-tri-isopropylbenzenesulphonic acid (2a) [λ_{max} 273 (ϵ 1 400) and 282 nm (1 200)] was photolysed (≥ 316 nm)³ in the presence of 2,2'-azobis-(2-methylpropionitrile) (hereinafter referred to as the initiator) [λ_{max} 345 nm (ϵ 12)] for 3 h. Chromatography gave the disulphide (4b) (3%) and thiosulphonate (4a) (58%). Assignment of structures followed from microanalyses, spectral data, and comparisons with literature data.⁴ Further experiments are tabulated and only selected experiments are described in the Experimental section.



(4)

- a; X = S, Y = SO₂
 b; X = Y = S
 c; X = Y = SO₂

The sulphonic acid (2a) decomposed in the dark under argon without initiator giving the same two products. Clearly under these conditions the well known⁵ sulphonic acid disproportionation giving the thiosulphonate (4a) was observed. In the presence of oxygen, initiated photolysis of the sulphonic acid (2a) gave the sultone (3) (34%). In no instance was the sultone (3) detected in anaerobic reactions. Sultone (3) was also formed under oxygen without initiation on photolysis or in the dark.

TABLE

Reactions of 2,4,6-tri-isopropylbenzenesulphonic acid (2a) and *S*-2,4,6-tri-isopropylphenyl 2,4,6-tri-isopropylbenzene thiosulphonate (4a)

Reaction	Starting material/ mmol	Time	Reaction conditions *	Isolated products
1	0.99	3 h	O ₂ , initiator (2.1 equiv.), <i>hν</i>	sultone (3) 34%
2	0.69	3 h	Ar	thiosulphonate (4a) 53%, disulphide (4b) 7%
3	0.99	3 h	Ar, initiator (2.1 equiv.), <i>hν</i>	thiosulphonate (4a) 58%, disulphide (4b) 6%
4	0.60	2 h	O ₂ , <i>hν</i>	sultone (3) 29%
5	0.38	2 h	O ₂	sultone (3) 23%
6	0.40	16 h	O ₂	sultone (3) 33%
7	1.0	(a) 15 min (b) 2 h	(a) N ₂ , NaHCO ₃ (1 equiv.), I ₂ (1.06 equiv.) (b) O ₂ , <i>hν</i>	sulphonylsulphone (4c) 20%
8	1.0	(a) 15 min (b) 2 h	(a) N ₂ , NaHCO ₃ (1 equiv.), I ₂ (1.0 equiv.) (b) O ₂ , <i>hν</i>	sultone (3) 8%, sulphonylsulphone (4c) 6%
9	0.99	3.5 h	O ₂ , initiator (2.1 equiv.), (EtO) ₃ P (4.7 equiv.), <i>hν</i>	sultone (3) 11%, hydroxysulphonate (5) 11%, sulphinate (2i) 10%
10	0.52	2 d	O ₂ , (EtO) ₃ P (11.7 equiv.)	sulphonate (2j) 41%, phosphate (2k) 13%, sultone (3) 9%, sulphinate (2i) 9%
11	0.076	4.5 h	O ₂ , initiator (1.5 equiv.), <i>hν</i>	sultone (3) 51%, thiosulphonate (4a) 20%
12	0.18	2 d	air, CF ₃ CO ₂ H (14 equiv.)	thiosulphonate (4a) 98%
13	0.10	4 h	O ₂	thiosulphonate (4a) 100%

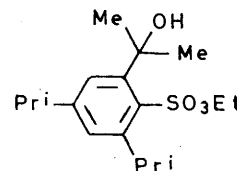
* Reactions 1—10 refer to the sulphonic acid (2a) and reactions 11—13 to the thiosulphonate (4a). In reaction 11, the yield of sultone (3) refers to a 1 : 1 stoichiometry. All reactions were carried out in the dark unless stated to the contrary; photolyses (*hν*) conditions are described in the Experimental section. The reactions were conducted whilst bubbling oxygen (O₂), argon (Ar), nitrogen (N₂), or air through the solutions. Reactions 1—6 and 9—13 were carried out in benzene as solvent; reactions 7 and 8 in water-benzene.

Prolonged reaction in the dark gave the sultone (3) in 33% yield.

Arylsulphonyl iodides are readily homolysed on photolysis giving arylsulphonyl radicals.⁶ The sulphonic acid (2a) rapidly reacted with iodine in the presence of sodium hydrogencarbonate. Subsequent photolysis of the presumed arylsulphonyl iodide (2g) under oxygen gave in low but variable yield the sultone (3). A new compound was also isolated, microanalytically pure, and assigned as the disulphone (4c). Clearly the arylsulphonyl radical was unable to abstract hydrogen atoms efficiently *via* an intramolecular pathway.

Sulphonic acid (2a) was decomposed in the presence of triethyl phosphite in order to capture any alkyl hydroperoxide intermediates. Photolysis in the presence of initiator and triethyl phosphite under oxygen gave a mixture of products. Chromatography gave the sultone (3) (11%). A more polar alcohol (ν_{\max} 3 530 and 3 500—3 150 cm⁻¹) (C₁₇H₂₈O₄S) (11%) was also isolated, the n.m.r. spectrum of which showed the presence of two non-equivalent isopropyl functions [δ_{H} 1.3 (12 H, d, *J* 8 Hz), 2.9 (1 H, septet, *J* 8 Hz), and 4.01 (1 H, septet, *J* 8 Hz)] and one 1-hydroxy-1-methylethyl function [δ_{H} 1.8 (6 H, s)]. The molecule was most reasonably the ethyl arylsulphonate (5). Fragmentations in the mass spectrometer at 313 ($M^+ - \text{Me}$) and 310 ($M^+ - \text{H}_2\text{O}$) were in agreement. A third product (10%) showed properties consistent with the sulphinate (2i) (ν_{\max} 1 130 cm⁻¹ with the absence of an intense band at 1 350—1 300 cm⁻¹, M^+ 296). Reaction of the sulphonic acid (2a) with triethyl phosphite in the dark under oxygen gave the sultone (3) (9%), the sulphinate (2i) (9%), ethyl 2,4,6-tri-isopropylbenzenesulphonate (2j) (41%), and *OO*-diethyl *S*-(2,4,6-tri-isopropylphenyl) thiophosphate (2k) (13%). Both microanalysed satisfactorily, and showed molecular ions in the mass spectra and intact 2,4,6-tri-

isopropylphenyl functions in the n.m.r. spectra. Presumably both the sulphinate (2i) and thiophosphate (2k) arose *via* the thiosulphonate (4a) and an Arbusov-like reaction; this has precedent in the literature.⁷ Alternatively, ethylation of sulphonate anions would have provided the ethyl arylsulphonates (2j) and (5). The introduction of



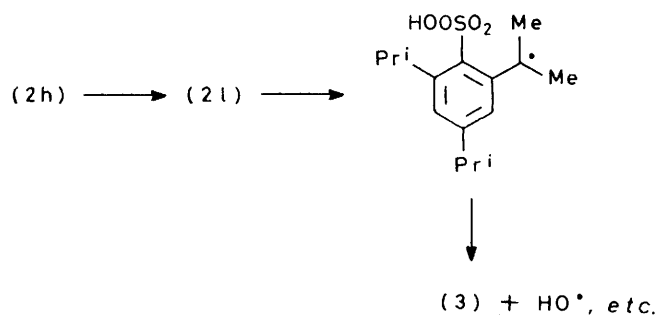
(5)

the hydroxy-function in sulphonate (5) was consistent with interception of a hydroperoxide by triethyl phosphite.

The thiosulphonate (4a) was examined as a precursor of the sultone (3). In the dark under oxygen, or in air in the presence of trifluoroacetic acid the thiosulphonate (4a) was recovered unchanged. However, on photolysis in the presence of initiator and oxygen the sultone (3) (51%) was formed and thiosulphonate (4a) (20%) recovered unchanged.

The conversion of benzenesulphonic acid into benzenesulphonic acid by oxygen has been reported by Horner and Basedow.⁸ The reaction was accelerated by photolysis and proposed to proceed by a chain-radical pathway *via* the benzenesulphonyl radical and peroxybenzenesulphonic acid. Intermediacy of the peroxybenzenesulphonic acid was consistent with *in situ* oxidation of dibenzyl disulphide to the sulfoxide. Consistent with these observations and the results in the Table, sultone (3) most probably arose by a radical pathway. In the absence of initiator radical (21) is capable of intramolecular hydrogen-atom abstraction giving the 2-arylpropyl

radical (as in the Scheme). Hydrogen-atom abstraction *via* a 7-membered transition state has precedent.⁹



SCHEME

EXPERIMENTAL

M.p.s were determined on a Kofler hot stage. I.r. spectra were recorded as Nujol mulls (solids) or in carbon tetrachloride solution (oils). U.v. and n.m.r. spectra were recorded as ethanol and deuteriochloroform solutions respectively. All reactions were carried out at room temperature unless stated to the contrary. Organic extracts were dried over sodium sulphate. Solvents were re-distilled; light petroleum refers to the reagent with b.p. 40–60 °C. Both t.l.c. and p.l.c. were carried out on Merck Kieselgel GF₂₅₄; developing solvents are given in parentheses. Photolyses were carried out using Pyrex apparatus with an externally cooled 125-W high-pressure mercury-arc lamp; a 1-cm 0.1M solution of naphthalene in light petroleum (b.p. 60–80 °C) cut out light below 316 nm.³

Preparation of 2,4,6-Tri-isopropyl-1,α-sultone (3).—2,4,6-Tri-isopropylbenzenesulphonylhydrazine (2b) (286 mg) in dichloromethane (15 ml) and triethylamine (0.50 g) were stirred for 5 d. Trifluoroacetic acid (1.2 g) was added and after 5 d the mixture was evaporated and chromatographed on Kieselgel H (20 g) to give (eluant light petroleum) an oil (2 mg) and [eluant dichloromethane–light petroleum (0 : 1–4 : 1)] the sultone (3) (77 mg, 28%), m.p. 124–127 °C (from light petroleum); ν_{\max} . 1 605w (C=C), 1 330s (–SO₂–O), 1 300w, 1 255w, 1 220w, 1 190s (–SO₂–O), 1 155w, 1 125m, 1 105w, 1 090w, 1 050w, 970w, 940w, 905w, 890w, 865m, 840w, 800m, and 760w cm⁻¹; λ_{\max} . 266 (ε 680) and 275 nm (670); δ_{H} 1.33 (12 H, t, *J* 7 Hz, CHMe₂), 1.80 (6 H, s, O-CMe₂), 3.03 (1 H, septet, *J* 7 Hz, *o*-CHMe₂), 3.60 (1 H, septet, *J* 7 Hz, *p*-CHMe₂), 7.03 (1 H, d, *J* 1 Hz), and 7.34 (1 H, d, *J* 1 Hz); δ_{C} 156.55 (s, 4-C), 145.83 (s, 2-C), 144.84 (s, 6-C), 128.05 (s, 1-C), 125.19 (d, 3-C), 117.02 (d, 5-C), 89.89 [s, 2-C(O–)Me₂], 34.54 (d, 4-CHMe₂), 29.58 (d, 6-CHMe₂), 28.65 [q, 2-C(O–)Me₂], 23.67 (q, 6-CHMe₂), and 23.29 (q, 4-CHMe₂); *m/e* 282 (*M*⁺), 267 (100%), and 175 (Found: C, 63.8; H, 7.85; S, 11.3%; *M*⁺, 282.1294. C₁₅H₂₂SO₃ requires C, 63.8; H, 7.85%; S, 11.35; *M*, 282.1290).

Preparation of 2,4,6-Tri-isopropylbenzenesulphonic Acid (2a).—Zinc dust (1.34 g) was added during 5 min to a suspension of 2,4,6-tri-isopropylbenzenesulphonyl chloride (2c) (3.03 g) in boiling water (25 ml). After 5 min the mixture was cooled, and the solid filtered off, suspended in water (40 ml), and boiled with sodium carbonate (1.6 g) for 20 min. The suspension was cooled, filtered, and the residue leached with water (2 × 5 ml). The filtrate was washed with dichloromethane (2 × 30 ml), cooled to 0 °C, and concentrated hydrochloric acid (1.7 ml) in water (50 ml) added. After 30 min the solid was filtered off, and recrystallised

without warming from aqueous methanol to give 2,4,6-tri-isopropylbenzenesulphonic acid (2a) (0.89 g, 33%) as white needles, m.p. 84.5–87 °C (lit.,² 80–81 °C); ν_{\max} . 3 050w, 2 500m, br, 1 770w, 1 600m, 1 570m, 1 430m, 1 340w, 1 320w, 1 300w, 1 260w, 1 240w, 1 190w, 1 170w, 1 115w, 1 135w, 1 100w, 1 075s, 1 055s, 1 015s, 940w, 920w, 880m, 845m, 820s, 760w, 720w, 665w, and 655m cm⁻¹; λ_{\max} . 273 (ε 1 400) and 282 nm (1 200); δ 1.15–1.5 (18 H, m), 2.9 (1 H, septet, *J* 8 Hz), 4.15 (2 H, m), 7.10 (2 H, s), and 10.7 (1 H, br s); *m/e* 502 (aryl-SO₂S-aryl), 470 (aryl-S₂), 438 (aryl-S-aryl), 284, 267, 251, 235, 221, 183, 151, 149, 91, 43, and 41. A further recrystallisation gave material with m.p. 87–88 °C (Found: C, 66.9; H, 9.05. Calc. for C₁₅H₂₄O₂S: C, 67.1; H, 9.0%).

Photolysis of 2,4,6-Tri-isopropylbenzenesulphonic Acid (2a).—Dry benzene (10 ml) was deoxygenated with argon for 3 h and dry 2,4,6-tri-isopropylbenzenesulphonic acid (2a) (265 mg) and 2,2'-azobis(2-methylpropionitrile) (340 mg) were added. The solution was deoxygenated for 10 min and photolysed for 3 h. Evaporation and chromatography on Kieselgel H (18 g) gave (eluant light petroleum) di-(2,4,6-tri-isopropylphenyl) disulphide (4b) (14 mg, 6%), m.p. 88–91 °C (lit.,^{4a} 91–92 °C); ν_{\max} . (CCl₄) 3 050w, 2 960s, 2 930m, 2 810m, 1 600m, 1 465m, 1 425m, 1 385m, 1 365m, 1 315w, 1 170w, 1 100w, 1 060w, 940w, and 880w cm⁻¹; δ 0.9–1.3 (36 H, 2 d, *J* 7 and 6 Hz), 2.85 (2 H, m), 3.5 (4 H, septet, *J* 6 Hz), and 6.9 (4 H, s); *m/e* 470 (*M*⁺), 235 (100%), 217, 183, 151, 149, 119, 117, 43, and 41 (Found: C, 76.75; H, 10.0. Calc. for C₃₀H₄₆S₂: C, 76.55; H, 9.85%) and [eluant dichloromethane–light petroleum (0 : 1–1 : 0)] *S*-2,4,6-tri-isopropylphenyl 2,4,6-tri-isopropylbenzenethiosulphonate (4a) (143 mg, 58%), m.p. 109–111 °C (from aqueous methanol) (lit.,^{4b} 108.5–110 °C); ν_{\max} . 3 050w, 2 960s, 2 930m, 2 900m, 2 870m, 1 600w, 1 560w, 1 460m, 1 425m, 1 380m, 1 360m, 1 320m, 1 250w, 1 190w, 1 160m, 1 140s, 1 100w, 1 070w, 1 060w, 1 030w, 940w, 880m, 840w, 790s, 765s, and 650s cm⁻¹; δ 0.8–1.35 (36 H), 2.80 (2 H, m), 3.7 (4 H, m), and 6.8–7.0 (4 H, 2 s); *m/e* 502 (*M*⁺), 470, 438, 303, 236, 235 (100%), 221, 193, 151, 85, 83, 43, and 41 (Found: C, 71.6; H, 9.3. Calc. for C₃₀H₄₆O₂S₂: C, 71.65; H, 9.2%).

Preparation and Decomposition of 2,4,6-Tri-isopropylbenzenesulphonyl Iodide (2g).—2,4,6-Tri-isopropylbenzenesulphonic acid (2a) (268 mg), sodium hydrogencarbonate (84 mg), and iodine (254 mg) in benzene (5 ml) and water (6 ml) were stirred under nitrogen for 15 min. T.l.c. [light petroleum–dichloromethane (1 : 1)] indicated a single product (*R_F* 0.8). The solution was photolysed for 2 h under oxygen when the initial product had completely decomposed. The aqueous phase was extracted with diethyl ether (3 × 50 ml) and the combined organic phase was dried, evaporated, chromatographed on Kieselgel H (18 g) [eluant light petroleum–diethyl ether (1 : 0–7 : 3)], and separated by p.l.c. [two developments in diethyl ether–light petroleum (1 : 19)] to give [*R_F* 0.6, dichloromethane–light petroleum (1 : 1)] di-(2,4,6-tri-isopropylbenzene)sulphonyl sulphone (4c) (53 mg, 20%), m.p. 117–118 °C (from aqueous methanol); ν_{\max} . (CCl₄) 3 050w, 2 970w, 2 930w, 2 880w, 1 600m, 1 550w, 1 465m, 1 450m, 1 430m, 1 390m, 1 375m, 1 370m, 1 335m, 1 265s, 1 170m, 1 155m, 1 135m, 1 125m, 1 105w, 1 070w, 1 060w, 1 020w, 935w, 895w, 885w, and 700m cm⁻¹; δ 1.3 (18 H, 2d, *J* 7 Hz), 2.95 (1 H, septet, *J* 7 Hz), 4.1 (2 H, septet, *J* 7 Hz), and 7.23 (2 H, s); *m/e* 470, 267, 252, 251, 235, 233, 204, 189 (100%), 187, 161, 149, 105, 91, 85, 71, 69, 64, 57, 43, and 41 (Found: C, 67.4; H, 8.8. C₃₀H₄₆O₄S₂ requires C, 67.4; H, 8.65%).

Photolysis of 2,4,6-Tri-isopropylbenzenesulphinic Acid (2a) with Triethyl Phosphite.—2,4,6-Tri-isopropylbenzenesulphinic acid (2a) (264 mg), 2,2'-azobis-(2-methylpropionitrile) (340 mg), and triethyl phosphite (0.80 ml) in dry benzene (10 ml) were photolysed under oxygen for 3.5 h. Chromatography on Kieselgel H (20 g) and repeated p.l.c. [diethyl ether–light petroleum (1 : 3—1 : 4)] gave 2,4,6-tri-isopropylphenyl ethoxy sulphoxide (2i) (27 mg, 10%) as an oil; ν_{\max} . 2 970s, 2 930s, 2 880m, 2 250w, 1 715w, 1 600m, 1 570w, 1 460m, 1 430m, 1 390m, 1 370m, 1 345m, 1 325w, 1 265w, 1 245w, 1 200w, 1 175w, 1 160w, 1 130s, 1 105m, 1 075w, 1 065w, 1 020s, 940w, 920w, 885s, 845w, 820w, 805w, 770w, 730m, 700m, 670w, and 650m cm^{-1} ; δ 1.2—1.35 (18 H, m), 1.4 (3 H, t, *J* 7 Hz, CH_2Me), 3.9 (1 H, septet, *J* 7 Hz), 3.95—4.45 (4 H, m), and 7.2 (2 H, s); *m/e* 296 (M^+), 279, 267, 251, 233 (100%), 191, 149, 120, 71, 57, 47, 43, and 40 (Found: C, 69.0; H, 9.6. $\text{C}_{17}\text{H}_{28}\text{O}_2\text{S}$ requires C, 68.85; H, 9.5%), sultone (3) (30 mg, 11%), and ethyl 6-(1-hydroxy-1-methylethyl)-2,4-di-isopropylbenzenesulphonate (5) (37 mg, 11%) (R_F 0.25, dichloromethane) as an oil; ν_{\max} . (film) 3 530m, 3 500—3 150m, br, 3 080w, 3 050w, 2 970s, 2 930s, 2 880 m, 1 710w, 1 600m, 1 570m, 1 510w, 1 470m, 1 430m, 1 420w, 1 390m, 1 370m, 1 355m, 1 335m, 1 260m, 1 200m, 1 180s, 1 155m, 1 125m, 1 100m, 1 070m, 1 010m, 965w, 940w, 910m, 885m, 875w, 840w, 790m, 780m, 755w, 735w, 700w, 685m, and 665m cm^{-1} ; δ 1.3 (12 H, d, *J* 8 Hz), 1.4 (3 H, t, *J* Hz, CH_2Me), 1.8 (6 H, s, OCMe_2), 2.9 (1 H, septet, *J* 8 Hz), 4.01 (1 H, septet, *J* 8 Hz), 4.27 (2 H, q, *J* 7 Hz, CH_2Me), 5.65 (1 H, s, OH), and 7.3 (2 H, s); *m/e* 313 ($M^+ - \text{Me}$), 310 ($M^+ - \text{H}_2\text{O}$), 282, 281, 267 (100%), 249, 203, 175, 161, 156, 145, 129, 115, 105, 97, 91, 71, 69, 59, 55, 43, and 40 (Found: C, 62.1; H, 8.6. $\text{C}_{17}\text{H}_{28}\text{O}_4\text{S}$ requires C, 62.15; H, 8.6%).

Dark Reaction of 2,4,6-Tri-isopropylbenzenesulphinic Acid (2a) and Triethyl Phosphite.—Triethyl phosphite (0.50 g) was added to 2,4,6-tri-isopropylbenzenesulphinic acid (2a) (154 mg) in dry benzene (5 ml) and the mixture was oxygenated in the dark for 6.5 h. Sulphinic acid (2a) still remained (t.l.c.) thus more triethyl phosphite (0.50 g) was added and the reaction continued for 2 d. Evaporation, chromatography on Kieselgel H (18 g) (eluant diethyl ether) and p.l.c. [two developments in diethyl ether–petroleum (1 : 3)] gave

the sulphinate (2i) (15 mg, 9%), the sultone (3) (15 mg, 9%), ethyl 2,4,6-tri-isopropylbenzenesulphonate (2j) (73 mg, 41%), m.p. 59—60 °C (from light petroleum at –30 °C); ν_{\max} . (CCl_4) 2 960m, 2 930m, 2 910w, 2 890w, 2 870m, 1 600m, 1 460m, 1 425m, 1 380m, 1 365m, 1 350m, 1 335m, 1 300w, 1 230w, 1 195m, 1 180s, 1 170m, 1 155m, 1 135w, 1 105w, 1 070w, 1 060w, 1 040w, 1 010w, 940m, 910m, 905m, 880m, 685w, and 660m, cm^{-1} ; δ 1.3 (18 H, d, *J* Hz), 1.35 (3 H, d, *J* 7 Hz), 2.85 (1 H, m), 3.9—4.0 (2 H, m), 4.25 (2 H, q, *J* 7 Hz), and 7.35 (2 H, s); *m/e* 312 (M^+), 297, 283, 269, 267, 266, 265, 251, 218, 202, 187, 159, 145, 131, 117, 105, 19, 43, and 41 (Found: C, 65.15; H, 9.05. $\text{C}_{17}\text{H}_{28}\text{O}_3\text{S}$ requires C, 65.35; H, 9.05%), and *OO-diethyl S-(2,4,6-tri-isopropylphenyl) thiophosphate* (2k), 27 mg, 13%) as an oil; ν_{\max} . 3 030w, 2 960s, 2 930m, 2 905m, 2 890m, 2 870m, 1 595w, 1 460m, 1 440w, 1 425w, 1 390m, 1 380m, 1 300m, 1 350w, 1 315w, 1 245m, 1 185w, 1 170w, 1 095w, 1 045s, 1 020s, 965m, 955m, 940m, and 865w cm^{-1} ; δ 1.2 (18 H, d, *J* 7Hz), 1.25 (6 H, t, *J* 6 Hz), 2.8 (1 H, m), 3.75—4.4 (6 H, m), and 7.05 (2 H, s); *m/e* 372 (M^+), 357, 355, 341, 339, 329, 281, 264, 236, 234, 203 (100%), 191, 187, 149, 43, and 40 (Found: C, 61.3; H, 9.0. $\text{C}_{19}\text{H}_{33}\text{O}_3\text{PS}$ requires C, 61.25; H, 8.95%).

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