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(6) Although it is anticipated that a bianthracene is a precursor to **2**, none was found in the self-protonation reactions described here. These reactions were very much faster than the hydrogen redistribution reactions in $SbCl_3$ without $AlCl_3$ and probably passed through a bianthracene stage before our slow observational methods had time to sample the system.
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(8) This conclusion does not hold for highly dilute solutions of **3** and **5**. For such dilute solutions the electrochemical data imply that at equilibrium a substantial fraction of this arene will be oxidized even without $AlCl_3$ present. However, as the concentration of substrate is increased, Cl^- generated by solvent reduction suppresses this oxidation. Quantitative calculations based on the electrochemical values indicate that this suppression is substantial at the 1 mol % concentration level.
(9) Although $E_{1/2}$ has not been measured for **7** in $SbCl_3$, it has been measured in other solvents in which the relative oxidizability of other arenes is the same as in $SbCl_3$. These data leave little doubt about the predicted inertness of **7** toward oxidation by $SbCl_3$.
(10) Molten $SbCl_3$ is generally regarded as a leveling solvent for strong Lewis acids like $AlCl_3$, which are believed to react and form an equivalent amount of $SbCl_2^+$.
(11) These results are from a study by A. C. Buchanan, III, R. Livingston, A. S. Dworkin, and G. P. Smith that also includes other arenes, as well as studies of arenes in $SbCl_3$ without $AlCl_3$ and in $SbCl_3$ plus Cl^- donors. A paper is currently being drafted.

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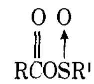
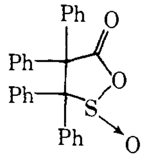
3,3,4,4-Tetraphenyl-1,2-oxathiolan-5-one 2-Oxide. Synthesis, Structure, and Selected Chemistry

Sir:

Considerable effort has been directed toward the preparation of stable mixed carboxylic-sulfinic acid anhydrides (**1**).[1-6] To date these attempts have been largely unsuccessful.[1-4,6] In this communication, we report the synthesis, properties, and structure of a stable member of this class of compounds, 3,3,4,4-tetraphenyl-1,2-oxathiolan-5-one 2-oxide (**2**).[8]

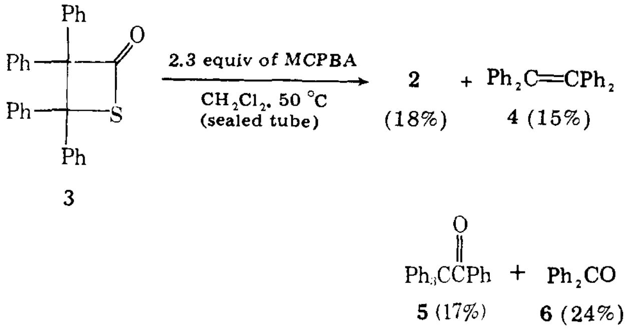

$RC(=O)OS(\rightarrow O)R'$

1



2

The title compound **2** was prepared in one step (18% yield) by the treatment of 3,3,4,4-tetraphenylthiolactone[9] (**3**) in methylene chloride with 2.3 equiv of *m*-chloroperbenzoic acid. Analysis by thin-layer chromatography prior to workup indicated the possible presence of compounds **2**, **4**, **5**, and **6** along with unreacted **3**. In an effort to minimize the decomposition of anhydride **2** during isolation, medium-pressure liquid chromatography (SiO_2, hexanes-methylene chloride (60:40), ~20 psi) was employed to isolate **2**.[10]



The infrared, ^1H and ^{13}C NMR, and mass spectral (CI and EI modes) properties along with elemental analyses (C, H, S) supported the proposed structure for anhydride **2**.[11] The infrared spectrum showed prominent bands at 1795 and 1100 cm^{-1} which can be assigned to the C=O[12] and S→O[13] groups, respectively. The proton decoupled ^{13}C NMR spectrum exhibited 16 different carbons in the aromatic region (127–141 ppm) as well as three additional peaks (67.8, 87.4, 173.2 ppm). The resonances at 67.8 and 87.4 ppm are comparable with those obtained for C-3 and C-4 of compound **3**.[9] The remaining absorption at 173.2 ppm has been assigned to the carbonyl carbon.[14] Mass spectrometry (CI mode) showed a molecular ion peak (P + 1) at *m/e* 425.

Cognizant of both the prior difficulties in assignment of structure[6] and the claims of the inherent instability of carboxylic-sulfinic acid anhydrides,[1] we felt it necessary to carry out a single-crystal X-ray structure determination. In particular, the observed spectral properties could be explained by several structures isomeric with **2**. Crystals of the title compound are monoclinic, space group $P2_1/n$, with $a = 9.130$ (2), $b = 13.711$ (3), $c = 16.988$ (2) Å; $\beta = 103.91$ (2)°. Intensity data were measured on a Syntex P2₁ diffractometer (Mo Kα radiation monochromatic with a graphite crystal) equipped with a low-temperature apparatus which kept the crystal cooled to 238 K. The structure was solved by direct methods (MULTAN[15]) and refined by full-matrix least squares to $R = 0.072$ ($R_w = 0.065$) using 3383 unique reflections [$I > 3\sigma(I)$].

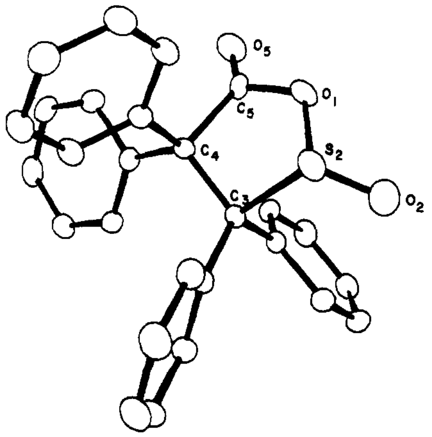
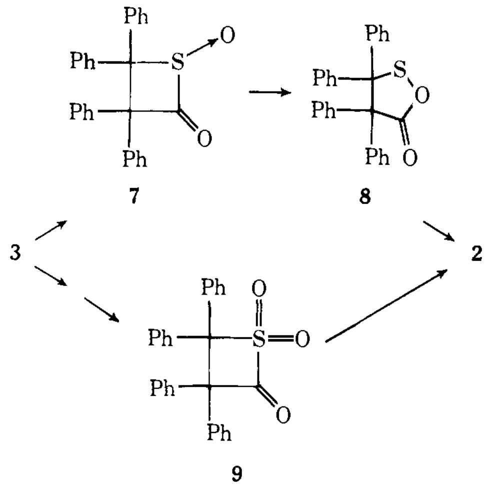


Figure 1. ORTEP drawing of the title compound showing numbering of ring.

The five-membered ring (see the ORTEP drawing, Figure 1, for numbering) has an envelope conformation, with O_1–S_2–C_4–C_5 in one plane; C_3 is −0.84 Å out of this plane, and the dihedral angle of the envelope is 133°. Important distances (ångstroms) and angles (degrees) follow: O_1–S_2, 1.680; S_2–O_2, 1.407; S_2–C_3, 1.916; C_3–C_4, 1.586; C_4–C_5, 1.611; C_5–O_5, 1.118; C_5–O_1, 1.385; C_5–O_1–S_2, 117.3; O_1–S_2–O_2, 105.4; O_1–S_2–C_3, 90.1; O_2–S_2–C_3, 110.7; S_2–C_3–C_4, 98.1; C_3–C_4–C_5, 103.6; C_4–C_5–O_1, 108.0; C_4–C_5–O_5, 127.9; O_5–C_5–O_1, 123.9. Crystallographic details will be furnished in a later paper.

Two reasonable pathways can be envisioned for the formation of compound **2** (Scheme I). One mechanism involves the oxidation of **3** with 1 equiv of peracid to give initially an α-keto sulfoxide **7**. Isomerization of **7** to the sulfenyl derivative **8**, followed by rapid oxidation at sulfur, would yield **2**.[16] Alternatively, successive oxidation of thiolactone **3** at sulfur with 2 equiv of peracid would lead to the α-keto sulfone **9**,[17] which then could rearrange to give anhydride **2**. Precedent exists for the isomerization both of substituted sulfoxides to sulfenyl derivatives[18] and of sulfones to sulfinate esters.[13a,19]

Scheme I



Preliminary experiments to determine the reactivity of **2** have been conducted. The anhydride **2** showed no evidence of decomposition at temperatures below 230 °C. Thermolysis of **2** at 240 °C (10 min) gave **4** (71%).[20] Mass spectral analysis of the gases liberated during thermolysis indicated that the major fragmentation pathway was the extrusion of SO_2 and CO rather than SO and CO_2.[21] Irradiation (medium-pressure mercury lamp, quartz, 1 h) of a degassed methylene chloride solution of **2** afforded exclusively 9,10-diphenylphenanthrene (73%).[20,23] Finally, treatment of anhydride **2** with an ether solution of $LiAlH_4$ (>10 equiv, 12 h) led to an immediate color change from colorless to blue to red and eventually to light green. Workup of the organic layer after addition of ethyl acetate and acidification with 6 N HCl led to a complex mixture (≥9 compounds by TLC). Purification by preparative thick-layer chromatography gave 2,2-diphenylethanol (50%).[20] The mechanism of these and related reactions are under investigation.

Acknowledgment. We (H.K., S.H.S.) thank the Robert A. Welch Foundation for its generous support of this research.

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(11) Physical and spectral properties of 3,3,4,4-tetraphenyl-1,2-oxathiolan-5-one 2-oxide (**2**): mp 233–235 °C dec from hexanes; IR ($CHCl_3$) 1795, 1182, 1100 cm^{-1}; NMR ($CDCl_3$) δ 6.70–7.46 (m); ^{13}C NMR ($CDCl_3$) 67.8, 87.4, 127.6, 128.0, 128.1, 128.3, 128.4, 128.7, 129.3, 129.6, 131.1, 131.7, 132.2, 132.3, 133.7, 135.6, 139.4, 140.1, 173.2 ppm; MS (CI mode) P + 1 peak at *m/e* 425; MS (EI mode) *m/e* (rel intensity) 362 (0.1), 360 (0.1), 333 (28), 332 (100), 289 (6), 255 (13), 254 (20), 250 (8), 241 (11), 178 (10), 176 (10), 166 (12), 165 (33), 126 (11), 77 (14). Anal. ($C_{27}H_{20}O_3S$) C, H, S.
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(20) The experimentally obtained material proved to be identical with an authentic sample.
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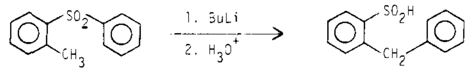
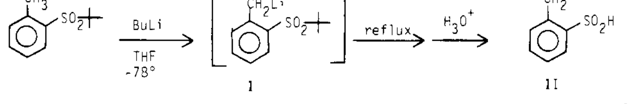
An Example of Alkyl Group Transfer in a Truce–Smiles Rearrangement

Sir:

The extensively studied Truce–Smiles rearrangement has previously involved only diaryl sulfones, as with phenyl *o*-tolyl sulfone to form *o*-benzylbenzenesulfinic acid.[1]



We report here the first example of such rearrangement in which the migrating group is alkyl rather than aryl. In the course of investigating several reactions of metalated *o*-tolyl *tert*-butyl sulfone, it was found that refluxing the lithiated species I in THF for several hours led to formation of *o*-neopentylbenzenesulfinic acid (II) (the yield of which was increased from 40 to 75% by lengthening reflux time from 2 to 8 h). The structure of the product II has been confirmed by NMR of the methyl sulfone derivative and NMR and mass spectrum of the 2-hydroxy-3,5-dichlorobenzyl sulfone derivative. Particularly noteworthy is the fact that the alkyl group being transferred is tertiary.[2]



This novel rearrangement can be rationalized in terms of an electron-transfer–radical-anion reaction pathway. The close proximity of the $-SO_2-$ group should facilitate transfer of an