

- (13) This spectrum was obtained by allowing the reaction to proceed to completion under conditions where the methyl iodide distills from an open tube.

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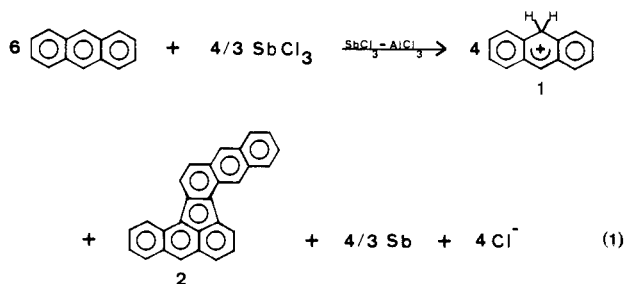
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Protonation of Some Arenes in an Aprotic Medium

Sir:

We have found that the dissolution of anthracene (up to 5 mol %) in an aprotic liquid, anhydrous SbCl_3 -10 mol % AlCl_3 , at 80–130 °C, results in the prompt formation of stable solutions of the 9-anthracenium ion (**1**) in 50–60% yields. The proton source for this novel reaction is the condensation-dehydrogenation of a part of the anthracene combined with the reduction of SbCl_3 to amorphous metal. The principal condensed product is anthra[2,1-a]aceanthrylene (**2**) and in terms of this product the overall reaction is as shown in eq 1. Under similar conditions 9,10-dimethylantracene (**3**) formed the 9H-9,10-dimethylantracenium cation (**4**) and naphthacene (**5**) formed the 5-naphthacenium cation (**6**), while naphthalene (**7**) was not protonated.



Previously, the protonation of anthracene and similar arenes had only been achieved by providing strong proton donors such as in superacid media¹ or with AlCl_3 -HCl.² In contrast, we deliberately suppressed such proton donors by working with carefully purified materials under clean argon atmospheres in glove boxes and vacuum-tight reaction vessels. Commercial 99.99% anhydrous SbCl_3 from three vendors was further purified by refluxing over Sb metal (to remove SbCl_5) followed by vacuum sublimation at 40 °C and then distillation under Ar in a sealed system to yield a colorless solid that melted at 73 °C to a colorless liquid. Aluminum chloride was made according to a published procedure³ from zone-refined 99.9999% Al and semiconductor-grade anhydrous HCl to yield a colorless solid.

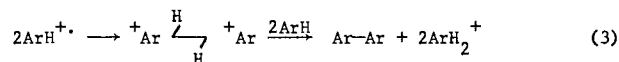
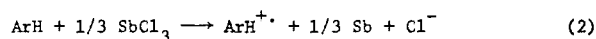
In our experiments, the formation of arenium ions was studied by ¹H NMR measurements on the melt both with and without a $(\text{CH}_3)_4\text{N}^+$ internal standard. The identity of **1** was confirmed from a comparison of its integrated ¹H NMR spectrum with that obtained from an authentic sample of 9-anthracenium heptachlorodialuminate,² $\text{C}_{14}\text{H}_{11}\text{Al}_2\text{Cl}_7$, in SbCl_3 without extra AlCl_3 . Cation **4** was identified by comparison with the published spectrum,⁴ and **6** was identified by comparison with the spectrum of **1**. These cations formed rapidly, in <10 min at 80–130 °C, and remained unchanged for some hours. The NMR spectra of other products, such as **2**, were not resolved but appeared as a broad, nondescript envelope in the aromatic region.

In the case of anthracene the reaction products from the NMR studies and from larger scale reactions performed in sealed glass ampules or Schlenk glassware were determined

following hydrolysis of the melt in 6 M HCl and dissolution of the organics in CH_2Cl_2 . The organic products were isolated by LC and identified by UV, NMR, and mass spectroscopy. Elemental Sb was analyzed by atomic absorption spectroscopy and X-ray diffraction. The identity and amounts of the products remained the same for all reaction conditions studied, 10–60 min at 80–130 °C. The mole ratio of **1**:**2**:Sb was found to follow the stoichiometry required by reaction 1.

In an earlier study⁵ we showed that anthracene and **5** in SbCl_3 without excess AlCl_3 undergo hydrogen redistribution reactions to form hydroaromatics (not found in the presence of excess AlCl_3) and condensed aromatics including three bianthracenes and **2**.⁶ Furthermore, no reduction of the SbCl_3 solvent was observed. Under the same conditions we found **7** to be unreactive.

The presence of excess AlCl_3 is necessary for reaction 1 to occur, and in our experiments the AlCl_3 /arene mole ratio was 2 or more. A consideration of published electrochemical data⁷ obtained in molten SbCl_3 implicates the arene radical cation as an intermediate in these self-protonation reactions. The results show that the role of the AlCl_3 is that of enhancing the oxidizing power of SbCl_3 . These facts can be accounted for by reactions 2 and 3.



On the basis of the electrochemical data,⁷ it can be shown that the presence or absence of excess AlCl_3 in SbCl_3 should affect reaction 2 in a way that parallels the influence of AlCl_3 on the protonation-solvent reduction reactions presented here. That is, for anthracene, **3**, and **5** at moderate concentration levels in SbCl_3 , reaction 2 is thermodynamically favorable with excess AlCl_3 present but unfavorable with AlCl_3 absent,⁸ whereas for **7** reaction 2 is not favorable whether AlCl_3 is present or absent.⁹ Enhancement of the oxidizing strength of SbCl_3 by added AlCl_3 arises from the reaction of AlCl_3 (or substances derived from it)¹⁰ with Cl^- released through the reduction of SbCl_3 .

We have recently obtained intense, well-resolved ESR spectra for the radical cations of anthracene, **3**, and **5** (but not **7**) formed from dilute solutions of the parent hydrocarbons in SbCl_3 - AlCl_3 melts without the addition of other oxidants. These and other data¹¹ indicate that reaction 2 occurs and is influenced by added AlCl_3 in at least qualitative agreement with what would be expected from the electrochemical measurements.

We have presented a novel arene self-protonation reaction in an aprotic SbCl_3 - AlCl_3 melt for which there is considerable evidence that the reaction proceeds through an oxidation of the arene to a radical cation by the SbCl_3 . The function of the AlCl_3 appears to be that of enhancing the oxidizing power of the SbCl_3 solvent. Our investigations of this chemistry continue, and a full report will soon be prepared.

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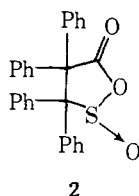
- (4) C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961).
 (5) M. L. Poutsma, A. S. Dworkin, J. Brynstad, L. L. Brown, B. M. Benjamin, and G. P. Smith, *Tetrahedron Lett.*, 873 (1978); A. S. Dworkin, M. L. Poutsma, J. Brynstad, L. L. Brown, L. O. Gilpatrick, and G. P. Smith, *J. Am. Chem. Soc.*, in press.
 (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.
 (7) P. Texier, *Bull. Soc. Chim. Fr.*, 4315, 4716 (1968).
 (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



The title compound **2** was prepared in one step (18% yield) by the treatment of 3,3,4,4-tetraphenylthiolactone⁹ (**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),

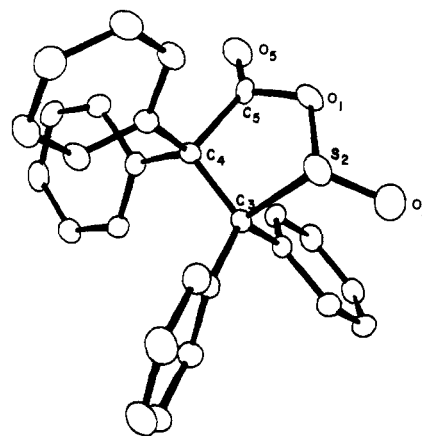
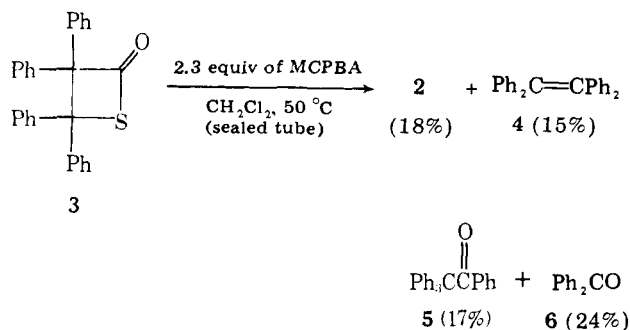


Figure 1. ORTEP drawing of the title compound showing numbering of ring.

~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 $\text{C}=\text{O}$ ¹² and $\text{S}=\text{O}$ 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 structure⁶ 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 $P2_1$ diffractometer (Mo $K\alpha$ 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 (MULTAN¹⁵) and refined by full-matrix least squares to $R = 0.072$ ($R_w = 0.065$) using 3383 unique reflections [$I > 3\sigma(I)$].

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 1). One mechanism involves the oxidation of compound **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 derivatives¹⁸ and of sulfones to sulfinate esters.^{13a,19}