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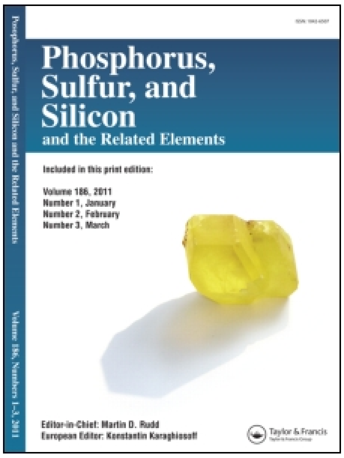

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Synthesis and Structure of 1,8-Dimethoxy-10-methyl-9-methylene-9H-thioxanthenium Salt—Possibility of Hypervalent Bonding Through O–C–O (?)

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*1,8-dimethoxy-10-methyl-9-methylene-9H-thioxanthenium salt (**4**) was prepared and the structure was determined by X-ray analysis to show the bond length between O—C is 2.80 A. This is too long to effect a hypervalent bonding. Bis[(1,8-dimethoxy) thioxanthylidene]allene (**5**) was prepared to be a symmetric compound in solution. Methylation of **5** with Meerwein reagent afforded S-monomethylated product (**6**) in solution and **6** gradually decomposed to C (or S)-monoprotonated allene (**7**), which was separately prepared as stable compound.*

Keywords 1,8-Dimethoxythioxanthylidene; (bisthioxanthylidene)allene; hypervalent bonding; methylation; protonation

Based on our recent success preparing pentacoordinated hypervalent carbon species (**1**: 10-C-5) using 1,8-dimethoxyanthracene skeleton,[1] we started to try to prepare hexacoordinate carbon species (**2**: 12-C-6) using an allene skeleton bearing 9-thioxantylidene rings at both ends.

First, we tried to prepare half part of **2**, 1,8-dimethoxy-10-methyl-9-methylene-9H-thioxanthenium salt (**4**) according to the scheme below.

9-Methylene compound (**3**) was prepared by the reaction of 1,8-dimethoxythioxanthone with methyl Grignard reagent followed by dehydration with hydrochloric acid. Then, **3** was methylated to give the

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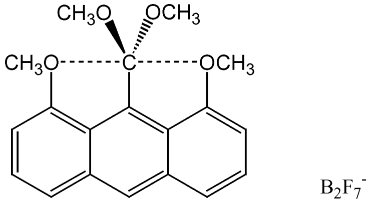

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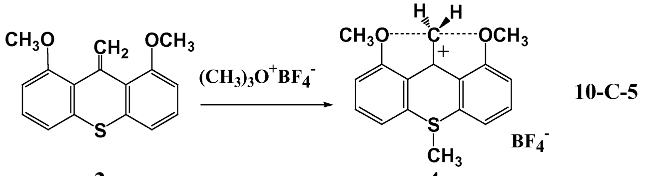
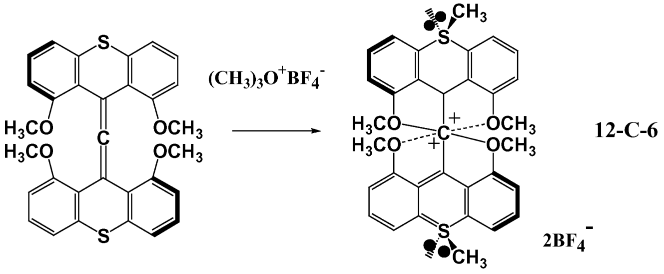


3 **4**

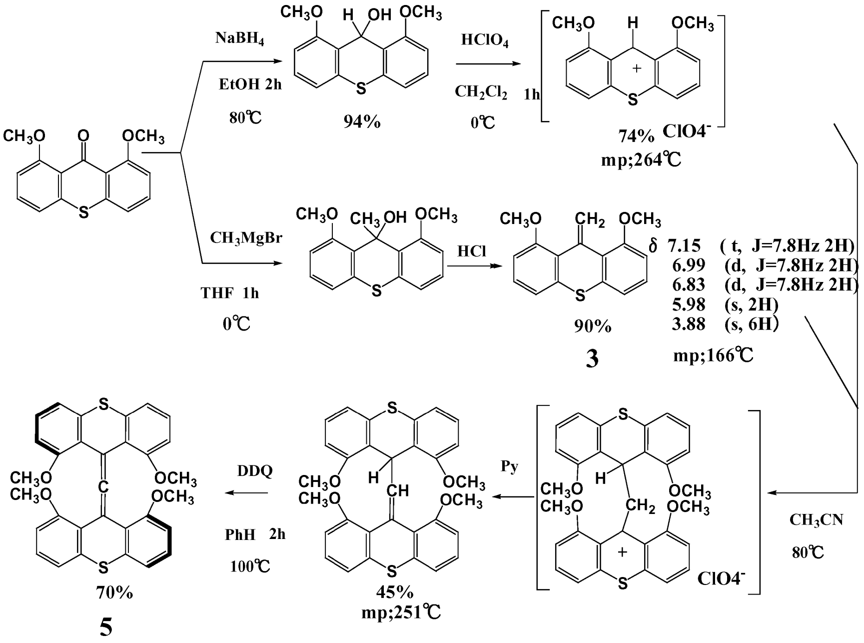


5 **2**

desired **4**, where hypervalent bonding was expected to form between O—C—O at 1, 9, and 8 positions.

However, X-ray analysis of the structure of **4** shows the distance of C—O is 2.80 A, which is too long for hypervalent bonding. Also the methyl on the sulfur and the methylene groups are facing each other, and the methylenethiacyclohexadiene ring is not planar and is considerably bent, as shown above.

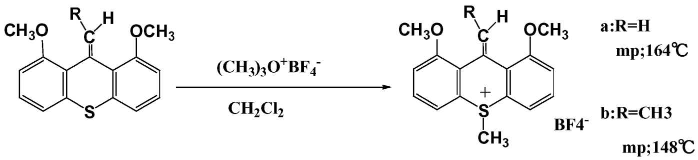
Second, the allene compound bearing four methoxy groups (**5**) was prepared by the reactions of thioxanthylium salt and the methylene compound (**3**), followed by deprotonation with pyridine and dehydrogenation with DDQ. The compound **5** showed only one methoxy group in H^1-NMR ($CDCL_3$). The methylation of **5** with Meerwein reagent in CD_2Cl_2 showed the formation of monomethylated species (**6**) in solution. The compound **6** is stable at room temperarutre for 3–4 hours and slowly decomposed to the monoprotonated species (**7**). When **6** is



δ 7.15 (t, J=7.8Hz 2H)
6.99 (d, J=7.8Hz 2H)
6.83 (d, J=7.8Hz 2H)
5.98 (s, 2H)
3.88 (s, 6H)
mp;166℃

δ 7.09 (t, J=7.8Hz 4H)
6.87 (d, J=7.8Hz 4H)
6.74 (d, J=7.8Hz 4H)
3.51 (s,12H)

mp;239℃



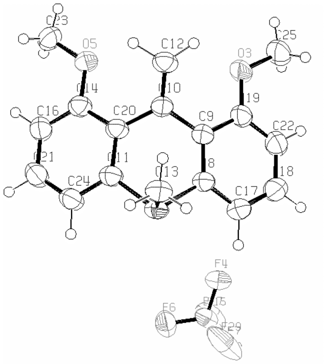
3 4

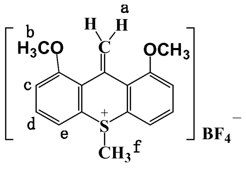
a:R=H
mp;164℃

b:R=CH3
mp;148℃

heated at 40°C, **6** gives **7** quickly. The compound **7** was prepared by the protonation of **5** with aqueous HBF_4 separately and is a stable compound (C or S-monoprotonated).

The lower chart of the two above shows **7**. The upper set of 1H NMR chart shows the presence of a mixture of **6** and **7**. By subtracting these, we can assign S-Me, two O-Me singlets, and a broad singlet for the two O-Me groups. Peaks at aromatic regions are acceptable as **6**. We are continuing the research to generate and prepare the hexacoordinate



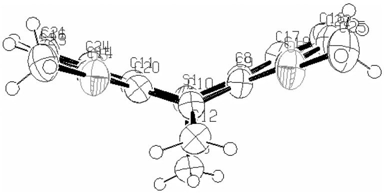


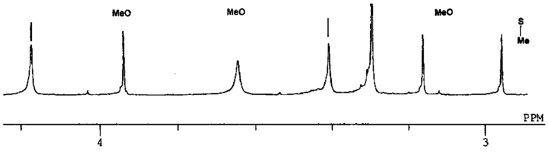
4

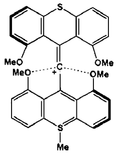
NMR

δ 7.73	(d,	J=8.3Hz	Hc	2H)
δ 7.53	(t,	J=8.3Hz	Hd	2H)
δ 7.31	(d,	J=8.3Hz	He	2H)
δ 6.66	(s,	Ha	2H)	
δ 3.99	(s,	Hb	6H)	
δ 3.26	(s,	Hf	3H)	

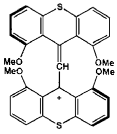
A	C-O	2.80Å
B	C-C	2.56Å
C	C-C	1.34Å



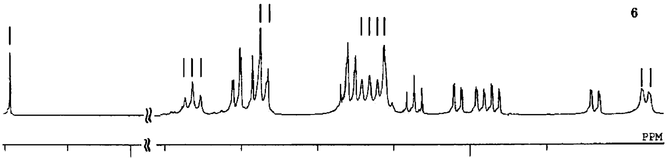


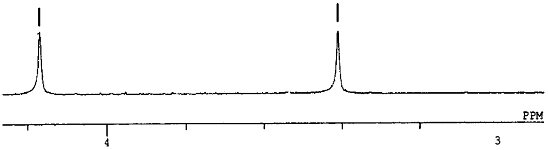


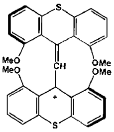
6



7







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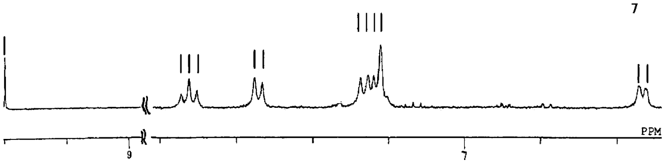

carbon species (***12-C-6***) by dimethylation (**2**), diacylation of **5,** and so forth.

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