SYNTHESIS OF FURAN-FUSED 3-SULFOLENE. A STABLE PRECURSOR TO FURAN ANALOGUE OF *o*-QUINODIMETHANE

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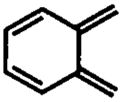
Abstract---Ultrasound-promoted zincation of 2-chloro-4-bromo-2-sulfolene (**10**) with benzoyloxyacetaldehyde (**6**), followed by base-induced hydrolysis, intramolecular conjugate addition and aromatization, gives the 3-sulfolene (**4**) which is a stable precursor to the furan analogue of *o*-quinodimethane.

The preparation and synthetic utility of *o*-quinodimethanes (**1**) have been extensively studied,[1] whereas their heterocyclic analogues (**2**) have received much less attention. In general, this type of highly reactive compounds are prepared from suitable precursors by 1,4-elimination or flash vacuum pyrolysis. For example, 2,3-dimethylene-2,3-dihydrofuran (**3**) has been obtained from the thermolysis of 2-benzoyloxymethyl-3-methylfuran[2] or similar compounds.[3] Since 3-sulfolenes are known to be excellent precursors to the corresponding dienes,[4] aromatic-fused 3-sulfolenes should be good precursors to *o*-quinodimethanes as well. An attractive approach to the preparation of **3** would be to synthesize the corresponding 3-sulfolene (**4**) by building a furan ring on a five-membered cyclic sulfone system.[5]



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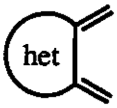

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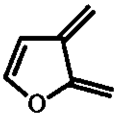

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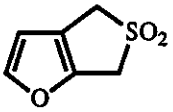

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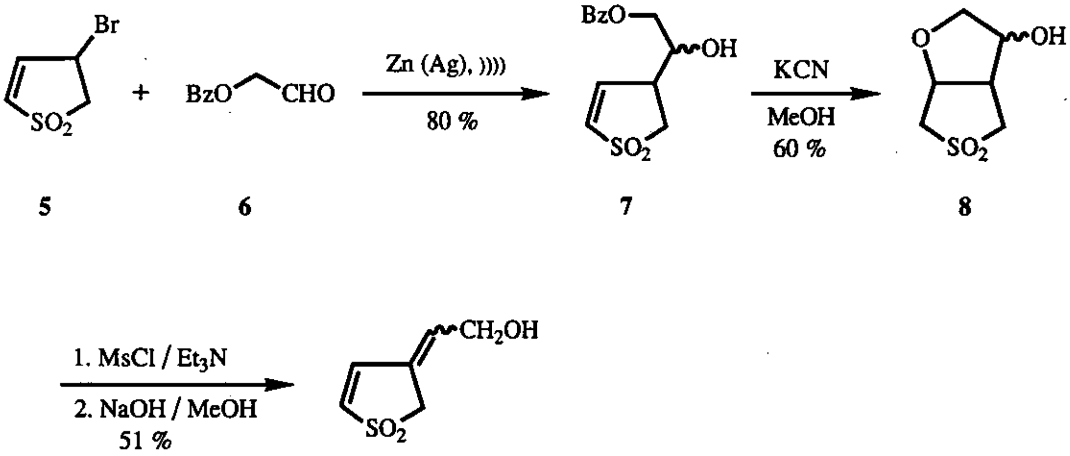
The reaction of the readily available 4-bromo-2-sulfolene (**5**)[6] with benzoyloxyacetaldehyde (**6**) (prepared from the ozonolysis of allyl benzoate followed by reductive workup with PPh_3) under the ultrasound-promoted zincation conditions[7] yielded **7** as a mixture of diastereomers in good yield (Scheme I). Treatment of **7** under mild basic conditions caused the hydrolysis of the benzoate and a spontaneous intramolecular conjugate addition to afford the bicyclic heterocycle (**8**). The remaining steps toward the synthesis of **4** were dehydration of **8** and the subsequent oxidative-aromatization. However, attempts toward this end were disappointing. For example, treatment of **8** with mesyl chloride in the presence of Et_3N followed by methanolic NaOH caused ring opening to give **9** which could not be recyclized after several tries.

Scheme I



5 **6** **7** **8**

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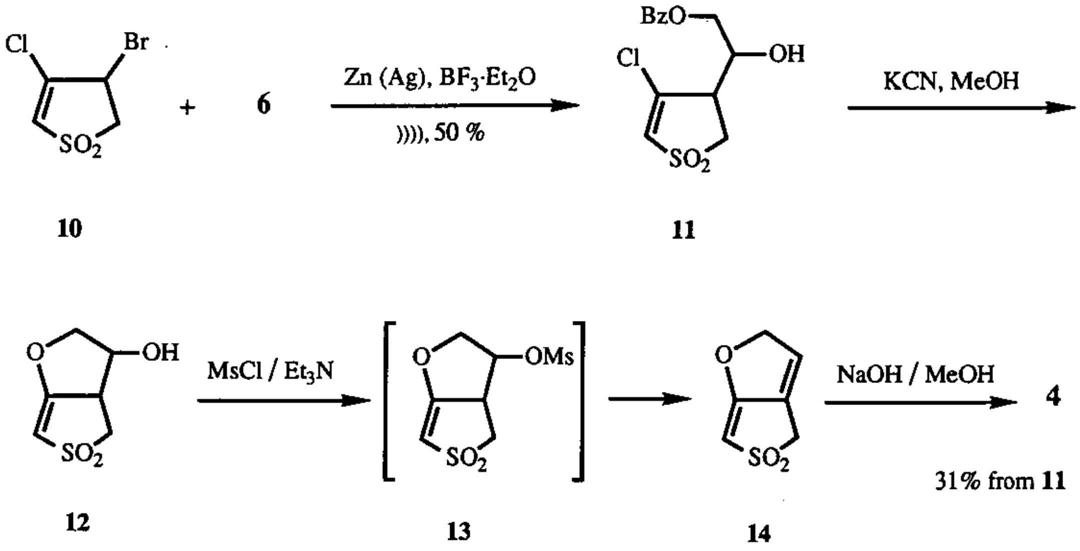
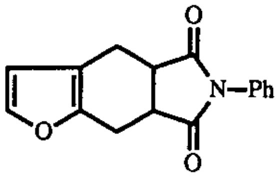
In order to avoid the undesired ring-opening reaction in the final step of Scheme I (**8** to **9**), 2-chloro-4-bromo-2-sulfolene (**10**)[8] was used as the starting material (Scheme II). Zincation of **10** with **6** in the presence of $BF_3 \cdot Et_2O$ produced **11** (in 50 % yield) which was hydrolyzed and cyclized to **12** by treatment with methanolic KCN. Treatment of **12** with MsCl in the presence of Et_3N gave the diene (**14**), presumably formed *via* the mesylate (**13**). The double bonds of **14** were isomerized with methanolic NaOH so that it was converted to the furan-fused 3-sulfolene (**4**). The ^1H nmr of compound (**4**) thus produced is identical to an authentic sample obtained by trapping **3** (generated in situ from the flash vacuum pyrolysis of 2-benzoyloxymethyl-3-methylfuran) with SO_2[9] [δ 4.24 (d, J=1.0 Hz, 2H), 4.27 (s, 2H), 6.44 (d, J=2.0 Hz, 1H), 7.52–7.54 (m, 1H)]. Compound (**4**) is a stable white solid (mp 84–85 °C). It is interesting to note that Et_3N converts the sulfur analogue of **13** directly to thiophene-fused 3-sulfolene without the need to use methanolic NaOH.[5a] The less ease of double bond isomerization of **14** to **4** should be due to the poorer aromaticity of furan than thiophene.

Scheme II



Heating a mixture of **4** and *N*-phenylmaleimide at 160 °C for 3 h yielded the cycloadduct (**15**) indicating that the furan *o*-quinodimethane (**3**) must have been formed as the intermediate. Thus, the very short reaction sequence shown in Scheme II conveniently leads to **4**, the stable precursor of **3**.



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9. We thank Professor C. H. Chou for providing the ^{1}H nmr spectrum of compound (**4**).

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