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INTRAMOLECULAR RHODIUM CARBENOID INSERTIONS INTO AROMATIC C-H BONDS. PREPARATION OF 1-CARBOALKOXY-1,3-DIHYDROBENZO[c]THIOPHENE 2,2-DIOXIDES

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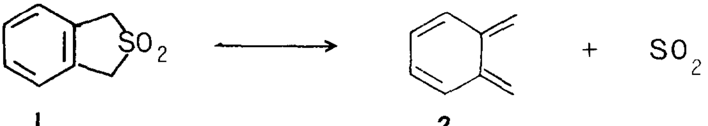
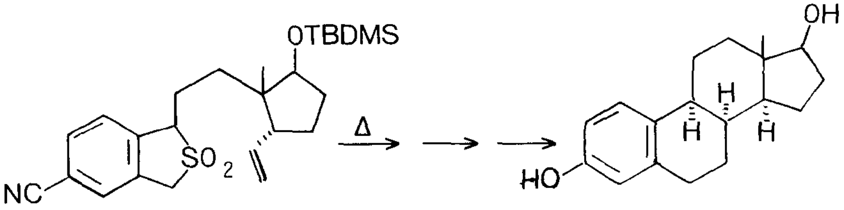
Abstract: Rhodium acetate catalyzed decompostion of various α-diazo-β-phenylmethane sulfonyl esters resulted in the formation of the title compounds in 40-50% yields.

1,3-Dihydrobenzo[c]thiophene 2,2-dioxides **1** are valuable precursors to o-quinodimethanes **2**. The synthetic utility of these sulfones is well documented.[1]



1 **2**

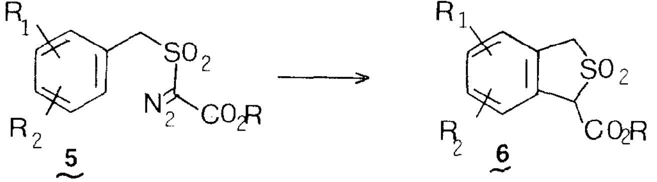
The intramolecular trapping of the o-quinodimethane intermediates, generated thermally from sulfones, is illustrated by the following synthesis of (+)-estradiol **4**.[2]



3 **4**

The parent sulfone **1** and aryl substituted derivatives are generally prepared by treatment of the appropriate 1,2-dihalomethylbenzenes with sodium sulfide, followed by oxidation.[3] Compounds such as **3** bearing suitable substituents on the heterocyclic ring may be obtained by alkylation via an alpha sulfonyl carbanion.[4] Regiochemical control can be a problem in the preparation of unsymmetrical compounds.[5]

We now wish to report a synthesis of these sulfones based on a rhodium acetate catalyzed decomposition of α-diazo-β-arylmethanesulfonyl esters 5,[6] compounds which are prepared in three steps from a wide array of readily available benzyl alcohols or halides.[7] The insertion reactions occur within two hours at room temperature in dry methylene chloride (0.2 M) in the presence of 5 mole % rhodium acetate, and give useful yields of 1-carboalkoxy-1,3-dihydrobenzo[c]thiophene 2,2-dioxides 6. (Table 1).



Formally, the products arise from the insertion of the carbenoid carbon into an ortho C-H bond. The structure of these products was readily deduced from their spectroscopic properties. In particular, the proton NMR specta showed a singlet (δ ≈ 5.1 ppm) and an AB quartet centered near 4.4 ppm due to the methine and methylene groups in 6, in addition to the appropriate ester and aromatic resonances. The mass spectra of 6 gave a strong molecular ion, and a strong, often base peak at M-64. Compounds such as 6 should be useful for the preparation of specifically substituted sulfones such as 3 by alkylation at either the methine or methylene carbon via a mono or dianion intermediate[8] followed by hydrolysis and decarboxylation.[9]

The reaction has a propensity to give products arising from attack at the carbon para to existing alkoxy substitution in cases where a competition between ortho and para is possible, (entry 5, 7). No isomeric by-products were detectable. The o-methoxy substituted aromatic (entry 4) gave no identifiable products, possibly due to competing oxygen ylide formation,[10] followed by decomposition. In contrast to the α-diazo esters, the α-diazo ketone (entry 9, R=CH_3) and sulfonyl diazomethane (entry 9, R=H) gave only intractable tars under the same conditions.

Other examples of intramolecular rhodium carbenoid insertions into aromatic C-H bonds are known. These include; insertion of α-diazo-β-ketoesters into an aryl C-H to yield substituted napthalenes;[11]

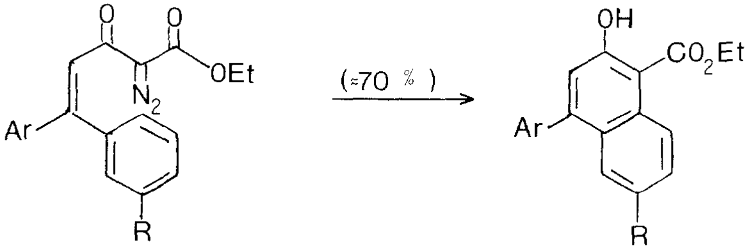
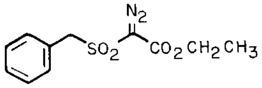
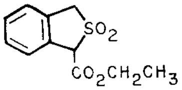
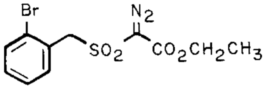
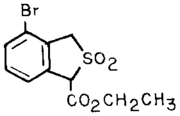
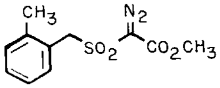
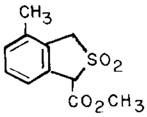
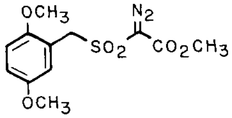
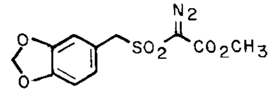
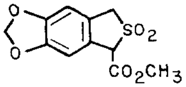
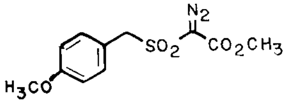
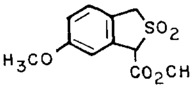
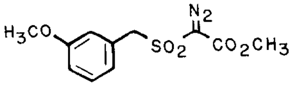
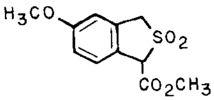
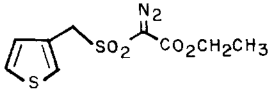
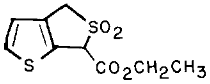
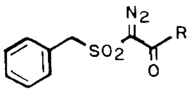


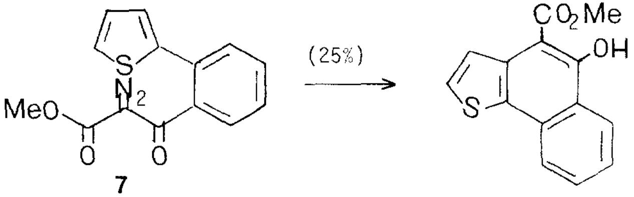
TABLE 1

ENTRY	DIAZOSULFONE	PRODUCT	YIELD[a] (%)	NMR[b]	
				CH	CH$_2$
1			46	5.00	4.43
2			48	5.10	4.43
3			14	5.00	4.30
4		—	—	—	—
5			47	4.90	4.26
6			45	4.96	4.33
7			42	4.90	4.30
8			49	5.03	4.26
9		—	—	—	—

a) isolated yields, following column chromatography

b) PPM from TMS in CDCℓ_3, 60 MHz.

insertion of α-diazo-β-ketoester **7** into the 3 position of a 2-substituted thiophene in competition with an aryl group;[12]



7

and the preferential insertion of α-ketodiazomethanes into the 2 position of an N-substituted pyrrole in competition with an aryl group.[13]

We are continuing our studies of the rhodium acetate catalyzed decomposition of sulfonyl substituted diazo compounds in order to prepare other heteroaromatic derivatives of 1, such as the thiophene derivative (entry 8), and SO_2 extrusion from these compounds.

ACKNOWLEDGEMENT. The financial support of NSERC (Canada) is gratefully acknowledged.

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5. This is not a problem in **3**, where the CN group acidifies the para methylene more than the meta group. Such a distinction would not be expected when CN is replaced by OMe.
6. The photochemical and thermal decomposition of sulfonyl diazomethanes has been studied. The reactions observed include insertions into aromatic and aliphatic C-H bonds and cyclopropanation of alkenes, alkynes and aromatics. (van Leusen, A.M., Strating, J., Quart. Rep. Sulfur Chem., 1970, 5, 67. Abramovitch, R.A., Alexanian, V., Smith, E.M., J. Chem. Soc. Chem. Comm. 1972, 893.)
7. The required α-diazoesters were prepared either by reaction of a benzylic alcohol with $HSCH_2CO_2R$ /ZnI_2 (Gauthier, J.Y., Bourdon, F., Young, R.N., Tetrahedron Lett., 1986, 27, 15.) or a benzyl halide with $HSCH_2CO_2R$ /base, followed by oxidation and diazo transfer with TsN_3/base (Regitz, M., Synthesis. 1972, 351.)
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9. Corey, E.J., Lowry, T.H., Tetrahedron Lett., 1965, 793, 803.
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