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### Reactions and Mechanism of Bis(2,2'-Biphenylene)-Sulfurane with the Reagents Having Hydroxyl Group

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## REACTIONS AND MECHANISM OF BIS(2,2'-BIPHENYLYLENE)-SULFURANE WITH THE REAGENTS HAVING HYDROXYL GROUP

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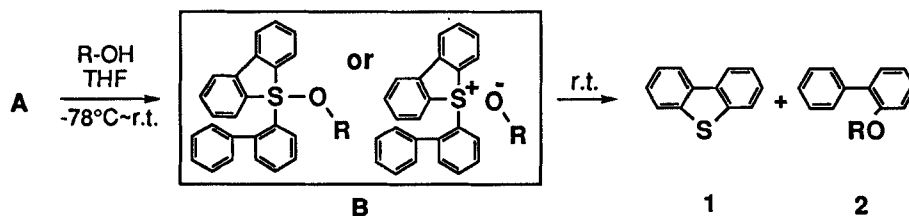
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**Abstract** Bis(2,2'-biphenylylene)sulfurane reacts readily with various alcohols, phenols, and thiols to give ligand coupling or ipso-substitution products under mild conditions via a two-step mechanism involving a  $\sigma$ -sulfuranes [10-S-4(C3O)] or correspondong sulfonium salts as intermediates.

### INTRODUCTION

Although the preparation and reactions of numerous sulfuranes have been examined by Martin and his co-workers using [10-S-4(C2O2)], there has been no report on the isolation of sulfuranes bearing four carbon ligands. Recently, we have succeeded in the preparation of bis(2,2'-biphenylylene)sulfurane (A) as a first example of [10-S-4(C4)] type sulfurane and determined its structure by X-ray crystallographic analysis.<sup>1)</sup> Tetraaryl-sulfuranes are generally unstable and are easily converted to the ligand coupling products by heating or decompose to the corresponding sulfonium salts by water. Therefore, a few studies on the reactivities of them have been reported. Here we report the new results on the reactions of bis(2,2'-biphenylylene)-sulfurane A stably isolated as tetraarylsulfurane with alcohols, phenols and thiols together with the mechanism for this reaction.

### RESULTS AND DISCUSSION




SCHEME 1 <sup>2)</sup>

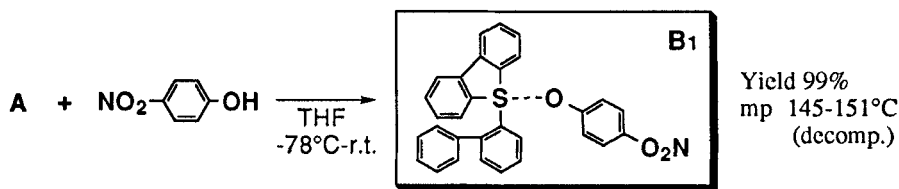
Sulfurane A reacted with alcohols and phenol to give the ligand coupling or ipso-

substitution products (1) and (2) as shown in Scheme 1 in quantitative yields (Table 1).

TABLE 1 Products from Reaction of A and R-OH

ROH	Yield(%)		
	1	2-BP-OR(2)	
MeOH	90	89	$\text{CH}_3\text{CHCH}_2$   OHOBP (3)
EtOH	87	89	$\text{CH}_3\text{CHCH}_2$   BPO OBP (4)
i-PrOH	92	93	$\text{CH}_2\text{CHCH}_2$   BPO OHOH BPO OHOBP (5)
t-BuOH	98	94	$\text{CH}_2\text{CHCH}_2$   BPO OHOH BPO OHOBP (6)
PhOH	96	97	$\text{CH}_2\text{CHCH}_2$   BPO OHOH BPO OHOBP (7)
$\text{CH}_3\text{CHCH}_2$   OHOH	99	80(3), 10(4)	$\text{CH}_2\text{OBP}$   H OBP (8)
$\text{CH}_2\text{CHCH}_2$   OH OHOH	99	26(5), 12(6), 17(7)	$\text{CH}_2\text{OBP}$   H OBP (8)
Glucose	99	90(8)	2-BP:  (8)

The reactivities of the alcohols (R-OH) were found to be in the following order, namely, R: Me > Et > i-Pr > t-Bu, by employing competitive reactions using a mixture of MeOH : EtOH, EtOH : i-PrOH and i-PrOH : t-BuOH. Not only mono, but also di-, tri- and even polyols such as glycerol and even glucose react with sulfurane A to give the respective polyol polybiphenyl ether. Furthermore, we tried to react with phenols having a nitro group as an electron-withdrawing group and succeeded in the isolation of the corresponding intermediate (B1) at room temperature (Scheme 2).



SCHEME 2

The isolated compound (B1) decomposed by heating to give the ligand coupling or ipso-substitution products quantitatively. The results demonstrate clearly that the mechanism for the present reactions proceeds by the proton-initiated ring opening of sulfurane A followed by the formation of intermediate B from which the ligand coupling or ipso-substitution takes place.<sup>3)</sup>

## REFERENCES

- Ogawa, S.; Matsunaga, Y.; Sato, S.; Iida, I.; Furukawa, N. *J. Chem. Soc. Chem. Commun.*, **1992**, 1141-1142.
- Furukawa, N.; Matsunaga, Y.; Sato, S. *SYNLETT*, **1993**, 655-656.
- Sato, S.; Furukawa, N. *Chem. Lett.*, **1994**, 889-892.