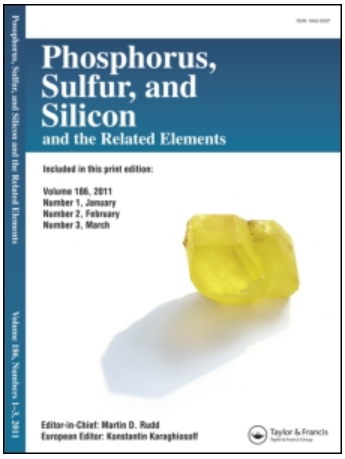

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Reactions and Mechanism of Bis(2,2'-Biphenylylene)-Sulfurane with the Reagents Having Hydroxyl Group

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

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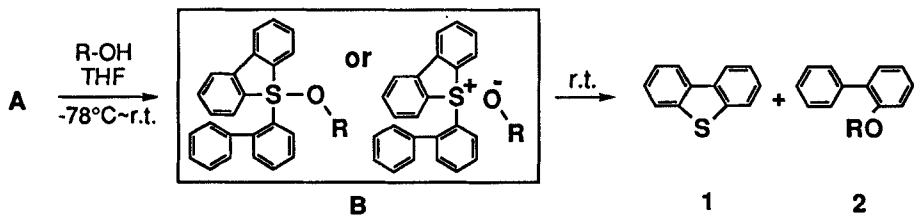
Abstract Bis(2,2'-biphenylylene)sulfurane reacts readily with various alcohols, phenols, and thiols to give ligand coupling or ipso-substitution products under mild conditions via a two-step mechanism involving a σ-sulfuranes [10-S-4(C3O)] or correspondong sulfonium salts as intermediates.

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.[1] 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 tetraarysulfurane with alcohols, phenols and thiols together with the mechanism for this reaction.

RESULTS AND DISCUSSION



SCHEME 1 [2]

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
EtOH	87	89
i-PrOH	92	93
t-BuOH	98	94
PhOH	96	97
CH_3CHCH_2 OHOH	99	80(**3**), 10(**4**)
CH_2CHCH_2 OH OHOH	99	26(**5**), 12(**6**), 17(**7**)
Glucose	99	90(**8**)

CH_3CHCH_2 OHOBP (**3**) CH_3CHCH_2 BPO OBP (**4**)

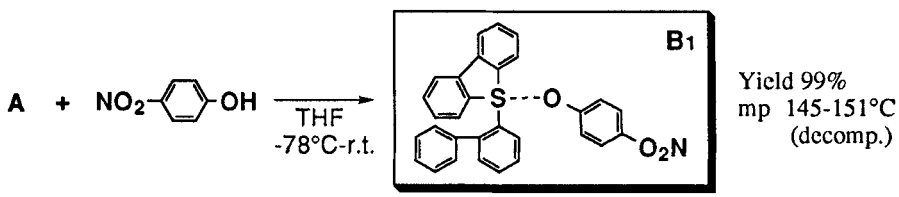
CH_2CHCH_2 BPO OHOH (**5**) CH_2CHCH_2 BPO OHOBP (**6**)

CH_2CHCH_2 BPOBPO OBP (**7**)

CH_2OBP H OH H OBP BPO OBP H OBP (**8**)

2-BP:

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 (**B**1) at room temperature (Scheme 2).



SCHEME 2

The isolated compound (**B**1) 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.[3)]

REFERENCES

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