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# Reactions of Sulfoxides Bearing ortho-Sulfur Functional Groups and Thianthrene Monooxide with Grignard Reagents

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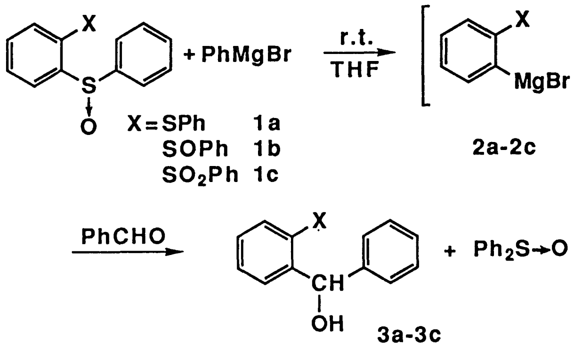
Diaryl sulfoxides bearing ortho-sulfur substituents react readily with Grignard reagents on the sulfur atom to produce the corresponding phenyl Grignard reagents bearing ortho-sulfur functional group. Furthermore, thianthrene monooxide was found to react with alkyl Grignard reagents affording o,o'-bis-Grignard reagent of diphenyl sulfide which was converted easily to Martin's sulfurane.

Sulfoxides have been known to undergo substitution reaction on the sulfinyl sulfur atom upon treatment with Grignard or organolithium reagents affording either one of the ligand exchange or ligand coupling products or simultaneously the both products.1) Therefore, the reactions are utilized as versatile procedures to prepare the coupling products such as bipyridyl derivatives2) or to eliminate the sulfinyl group from the organic compounds.3) Recently, as an alternative application of the reactions, the substitution reaction has been employed to generate the pyridyl Grignard reagents which are hardly prepared by the standard procedures.4) Furthermore, o-haloaryl phenyl sulfoxides have been found to react with alkyl Grignard reagents generating benzyne or pyridyne.5) In the course of studies on the substitution reactions of sulfoxides with Grignard reagents, we found that the sulfoxides bearing ortho-sulfenyl, -sulfinyl, or -sulfonyl substituent also undergo desulfinylation upon treatment with Grignard reagents eventually giving rise to the corresponding phenyl Grignard reagents bearing ortho-sulfur functional group. Furthermore, thianthrene monooxide was found to react readily with only alkyl Grignard reagents to afford o,o'-bis-Grignard reagent of diphenyl sulfide which was converted initially to diols and then to Martin's sulfuranes. This communication summarizes the preparation of several Grignard reagents bearing o-sulfur functional group and their application to organic synthesis.



Scheme 1.

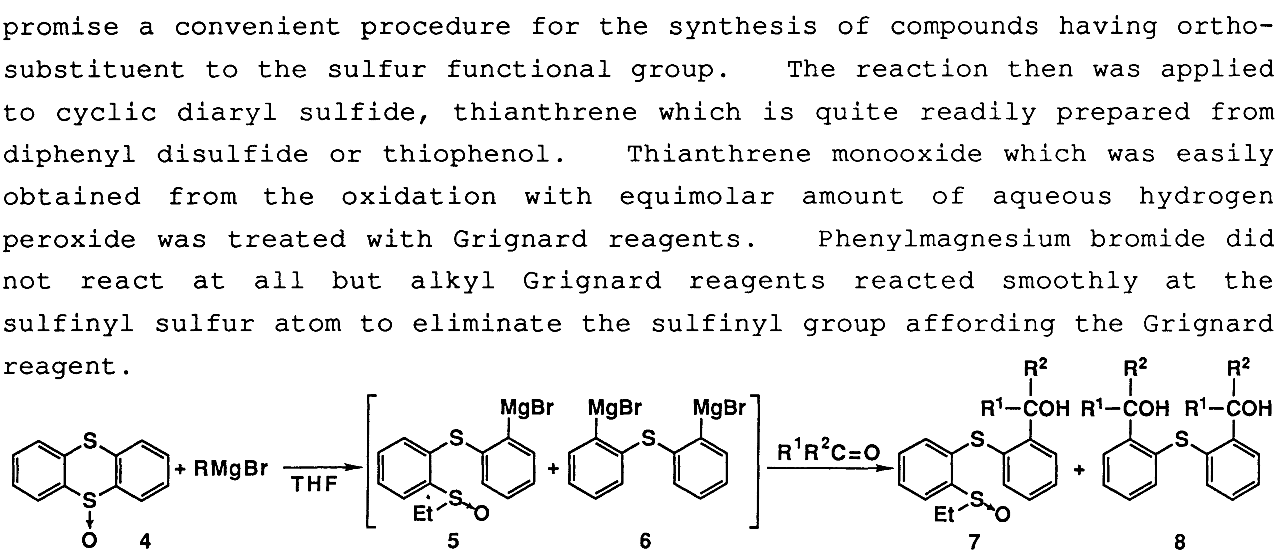
Table 1. Reactions of Sulfoxides Bearing ortho-Sulfur Functional Group with PhMgBr

| X | PhMgBr (equiv.) | Yield/% | | |
|---|---|---|---|---|
| | | **3** | $Ph_2S \rightarrow O$ | recov. |
| SPh (**1a**) | 1.0 | 77 | 81 | 0 |
| SOPh (**1b**) | 1.0 | 31 | 48 | 40 |
| SOPh (**1b**) | 2.0 | 76[1] | 99 | 0 |
| $SO_2Ph$ (**1c**) | 1.0 | 22 | 72 | 0[2] |

[1] Diastereomer ratio 4:1.

[2] Diphenyl sulfone 54%.

ortho-Phenylsulfenyl, -phenylsulfinyl, and -phenylsulfonyl phenyl sulfoxides (**1a**-**1c**) were prepared by the sequential oxidation of 1,2-bis-(phenylsulfenyl)benzene with m-chloroperbenzoic acid (mcpba). These compounds were treated with one equivalent of phenylmagnesium bromide except **1b** which required two equivalents of the Grignard reagent to perform the reaction. Formation of ortho-substituted Grignard reagents (**2a**-**2c**) was confirmed by treatment with benzaldehyde in tetrahydrofuran (THF) at room temperature. ortho-Substituted benzhydryl alcohols (**3a**-**3c**) were obtained in good yields except sulfone derivative (**1c**). The results are shown in Scheme 1 and summarized in Table 1. These data suggest that nucleophilic attack of Grignard reagent takes place easily on the sulfinyl sulfur atom to give ortho-sulfur functional phenylmagnesium bromide. Furthermore, the results reveal that the present reactions of **1a**-**1c** with Grignard reagent promise a convenient procedure for the synthesis of compounds having ortho-substituent to the sulfur functional group. The reaction then was applied to cyclic diaryl sulfide, thianthrene which is quite readily prepared from diphenyl disulfide or thiophenol. Thianthrene monooxide which was easily obtained from the oxidation with equimolar amount of aqueous hydrogen peroxide was treated with Grignard reagents. Phenylmagnesium bromide did not react at all but alkyl Grignard reagents reacted smoothly at the sulfinyl sulfur atom to eliminate the sulfinyl group affording the Grignard reagent.



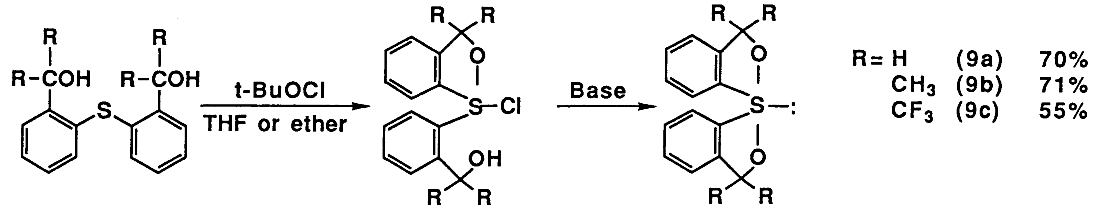
Scheme 2.

Table 2. Reactions of Thianthrene Monooxide (**4**) with Grignard Reagents

| Grignard reagent |  | Electrophile |  |  | Temp | Time | Yield/% |  |
|---|---|---|---|---|---|---|---|---|
| R | equiv. | $R^1$ | $R^2$ | equiv. | °C | h | **7** | **8** |
| Ph | 1.2 | Ph | H | 1.2 | r.t. | 6 | no reaction |  |
| Et | 1.5 | Ph | H | 1.5 | r.t. | 6 | 53 | 10 |
| Et | 1.2 | Ph | H | 1.2 | 0 | 6 | 91 | 8 |
| Et | 2.2 | Ph | H | 2.2 | r.t. | 7 | 14 | 30 |
| Et | 3.5 | Ph | H | 2.2 | r.t. | 6 | - | 51 |
| Et | 3.5 | p-$CH_3OC_6H_4$ | H | 2.2 | r.t. | 6 | - | 40 |
| Et | 3.5 | p-$ClC_6H_4$ | H | 2.2 | r.t. | 6 | - | 55 |
| Et | 3.5 | p-$CF_3C_6H_4$ | H | 2.2 | r.t. | 6 | - | 54 |
| Et | 3.5 | H | H | 2.2 | reflux | 8 | - | 41 |
| Et | 3.5 | $CH_3$ | H | 2.2 | reflux | 7 | - | 46 |
| Et | 3.5 | $CH_3$ | $CH_3$ | 2.2 | reflux | 10 | - | 18 |
| Et | 3.5 | $CF_3$ | $CF_3$ | 2.2 | reflux | 4 | - | 33 |
| Et | 3.5 | cyclopentanone |  | 2.2 | reflux | 10 | - | 10 |

Thianthrene monooxide (**4**) was treated with 1.2-1.5 equivalents of ethylmagnesium bromide in THF at room temperature or 0 °C to afford the ortho-sulfur substituted Grignard reagent **5** to which was added benzaldehyde in situ to result in the formation of alcohol **7** together with diol **8**. When 3.5 equivalents of ethylmagnesium bromide was treated with **4** and then with several aldehydes or ketones providing diols **8**. The results are shown in Scheme 2 and Table 2. The yields of diol **8** range from 10 to 55% depending on the aldehydes or ketones employed though the reactions were not optimized at present. In the case of the reactions of **4** with ketones shown in Scheme 2, small amount of ortho-substituted-phenyl phenyl sulfides ($R^1R^2C(OH)C_6H_4$-S-$C_6H_5$) were also detected. These results seem to indicate that in the reaction of **6** with ketones the steric hindrance by the one ortho-hydroxyl substituent prevents the approach of the 2nd ketone. Although the yields of diol **8** are not high, the present method is simple and therefore convenient to convert thianthrene monooxide to o,o'-diol of diphenyl sulfide in one step.

As a further extension of the present reactions, **8** was transformed to several Martin's sulfuranes **9** by treating **8** with tert-butyl hypochlorite (t-BuOCl) in THF and then with base according to the Martin's procedure.[6] The results thus obtained are summarized in Scheme 3.[7] The present method for preparation of Martin's sulfurane requires only three steps starting from thianthrene monooxide and hence is simple as compared with that of original method which requires six steps, for example, for preparation of **9a** and the reaction time is also shortened. Therefore, a combination of these



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Scheme 3.

procedures starting from thianthrene monooxide is promised to become one of the convenient method to prepare various sulfuranes and related compounds. Further extension of the reactions is in progress in this laboratory.

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7) **9a**; mp. 157-161 °C (lit. 158-161 °C), $^1$H-NMR(CDCl$_3$) $\delta$ 5.16(br s, 4H, CH$_2$), 7.12-7.50(m, 6H, m,p-ArH to S), 7.73-8.15(m, 2H, o-ArH to S). **9b**; mp. 155-156 °C (lit. 155-155.5 °C), $^1$H-NMR(CDCl$_3$) $\delta$ 1.52(s, 6H, CH$_3$), 1.62(s, 6H, CH$_3$), 7.00-7.60(m, 6H, m,p-ArH to S), 8.10-8.45(m, 2H, o-ArH to S). **9c**; mp. 159.5-161.5 °C (lit. 161-162 °C) $^1$H-NMR(CDCl$_3$) $\delta$ 7.58-7.80(m, 6H, m,p-ArH to S), 8.25-8.45(m, 2H, o-ArH to S). Anal. Found: C, 41.98; H, 1.67%. Calcd for $C_{18}H_8O_2SF_{12}$: C, 41.87; H, 1.56%.

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