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Reactions of Organometallic Reagents with 2-Thiochromene 2-Oxides. A New Method of Synthesis of S-Arylthiabenzene Analogues

S-Arylthiabenzene analogues were synthesized by the reactions between 2-thiochromene 2-oxides and organometallic reagents such as aryllithiums and aryl Grignard reagents. The mechanism for the formation of the S-arylthiabenzene analogues was explained by postulating the formation of thiopyrylium ion as reaction intermediates.

There has been much interest in decet sulfur compounds, for example, stable thiabenzene,¹⁾ and σ -sulfuranes as intermediates.²⁾ Recently, we reported on the synthesis of S-alkylthiabenzene analogue by the reaction between 2-methyl-1-phenyl-2-thiochromenium perchlorate and a strong base.³⁾

In this communication, we wish to report the first examples of S-arylthiabenzene analogues synthesized by the reactions between 2-thiochromene 2-oxides and organometallic reagents such as aryllithiums and arylmagnesium bromides.

Thus, oxidation of 2-thiochromene with *m*-chloroperbenzoic acid in CH_2Cl_2 was made to give **1** (cf. Chart 1) as white needles, (yield 77%, mp 150°, IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1015 (S-O), NMR (CDCl_3) δ : 7.42 (4H, s, aromatic H), 7.23 (1H, d, $J=10$ Hz, $\text{C}_4\text{-H}$), 6.92 (1H, dd, $J=10$ and 1.5 Hz, $\text{C}_3\text{-H}$), 6.50 (1H, dd, $J=17$ and 1.5 Hz, $\text{C}_1\text{-H}$), 3.70 (1H, d, $J=17$ Hz, $\text{C}_1\text{-another H}$)) and then **1** was treated with phenylmagnesium bromide in ether-benzene under an N_2 stream at room temperature to form **2**^{4a)} (yield 63%, bp 154° (1 mmHg)) and a byproduct, **3**,^{4a)} as white needles (yield 0.8%, mp 200°), while a mixture of **1** with phenyllithium in the same condition gave only **4**^{1a)} as brown powder (yield 22.4%, mp 123° (decomp.)). Similarly, **2** was also converted to **5** as white needles by oxidation with *m*-chloroperbenzoic acid, with yield of 85%. It showed mp 124°, IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1030 (S-O), NMR (CDCl_3) δ : 7.54 (10H, m, aromatic H and $\text{C}_4\text{-H}$), 6.66 (1H, dd, $J=10$ and 1.5 Hz, $\text{C}_3\text{-H}$), 5.61 (1H, d, $J=1.5$ Hz, $\text{C}_1\text{-H}$).

Subsequently, carrying out the reactions of **5** with methyllithium and methylmagnesium iodide, **2** (yield 22% and 3%) and **6**^{4b)} (yield 5.7% and 15%, bp 135° (1 mmHg)), respectively, were obtained.

On the other hand, **5** was allowed to react with phenyllithium in ether-benzene under an N_2 stream at room temperature. Treatment of the resulting ether solution with H_2O -70% HClO_4 produced only **8a**^{1b)} with yield of 26%. However, treatment of **5** with phenylmagnesium bromide gave **9a**^{4a,4b)} as white needles (yield 0.5%, mp 168° (decomp.)) and **8a** with yield 57%. Similarly, when **5** was allowed to react with 3 eq. *p*-tolylmagnesium bromide, products were **8b** (yield 33.5%, mp 90° (decomp.)), NMR (CDCl_3) δ : 6.40-8.00 (15H, m, aromatic H), 2.32 (3H, broad s, CH_3) and **9b** as white plates (yield 3.6%, mp 163° (decomp.)), IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1090 (ClO_4^-)).

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Chart 1

a) ESR absorptions for free radicals were observed during the reactions.

The reason why the reaction of **5** against an aromatic Grignard reagent was different from that of **1** is attributable to the effect of phenyl group at 1-position of **5** having both steric and electromeric properties.

On the basis of above data, the formation of **8** and **9** can be explained by postulating the formation of thiopyrylium salts, **7**, as reaction intermediates, followed by the radical and ionic reactions, respectively, with excess organometallic reagents at the positive sulfur atom of **7** as shown in Chart 2.⁵⁾

Chart 2

a) ESR absorptions for free radicals were observed during the reactions in analogy with the reactions of thioxanthylum salts and organometallic reagents (M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.* (Tokyo), 12, 1692 (1973)).

Further work in thiopyran oxides of other ring systems is now under way.

Gifu College of Pharmacy
492-36, Mitahora, Gifu

MIKIO HORI
TADASHI KATAOKA
HIROSHI SHIMIZU

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5) The structures of all the new compounds were also confirmed by the elemental analysis.