Communications to the Editor

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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 thiabenzenes,[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 ν_{max}^{KBr} cm^{-1}: 1015 (S–O), NMR ($CDCl_3$) δ: 7.42 (4H, s, aromatic H), 7.23 (1H, d, J=10 Hz, C_4–H), 6.92 (1H, dd, J=10 and 1.5 Hz, C_3–H), 6.50 (1H, dd, J=17 and 1.5 Hz, C_1–H), 3.70 (1H, d, J=17 Hz, C_1-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 ν_{max}^{KBr} cm^{-1}: 1030 (S–O), NMR ($CDCl_3$) δ: 7.54 (10H, m, aromatic H and C_4–H), 6.66 (1H, dd, J=10 and 1.5 Hz, C_3–H), 5.61 (1H, d, J=1.5 Hz, C_1–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 ν_{max}^{KBr} cm^{-1}: 1090 (ClO_4^-)).

1) *a*) C.C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2278 (1963); *b*) M. Hori, T. Kataoka, and H. Shimizu, *Chem. Pharm. Bull.* (Tokyo), **22**, 2485 (1974).

2) M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Chemistry Lett.*, **1972**, 515; B.M. Trost, R.W. LaRochelle, and R.C. Atkins, *J. Am. Chem. Soc.*, **91**, 2175 (1969); B.M. Trost and H.C. Arnt, *ibid.*, **95**, 5288 (1973).

3) M. Hori, T. Kataoka, H. Shimizu, H. Hori, and S. Sugai, The Third International Congress of Heterocyclic Chemistry, Sendai, Aug. 1971, Abstracts of Papers, p. 579 and also *Chem. Pharm. Bull.* (Tokyo), **22**, 2754 (1974).

4) *a*) C.C. Price and D.H. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969); *b*) M. Hori, T. Kataoka, H. Shimizu, and S. Sugai, *Chem. Pharm. Bull.* (Tokyo), **22**, 2752 (1974).

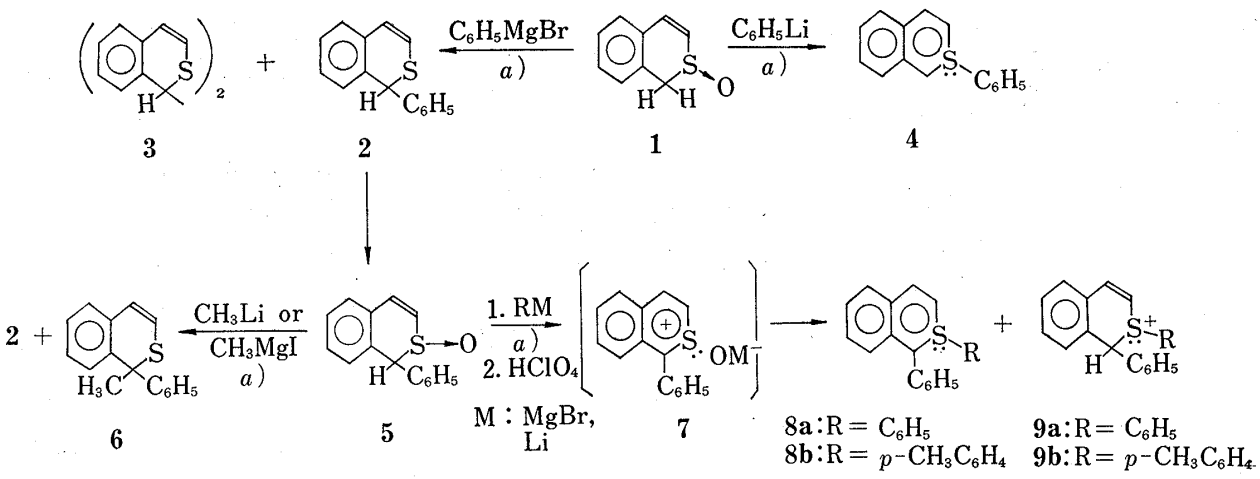

Chart 1

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]

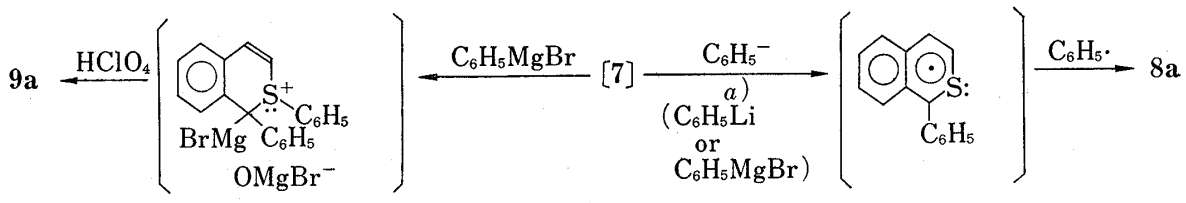

Chart 2

a) ESR absorptions for free radicals were observed during the reactions in analogy with the reactions of thioxanthylium 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.

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