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A New Synthesis of S-Arylthiabenzene Analogues using Grignard Reaction[1]

It has been well known that the synthetic method of thiabenzenes was until now the sole reaction between thiopyrylium salts and aryllithiums.[2] However, in the reaction of 2-thianaphthylium salts (Ia, b, c, d) having aryl group at 1-position with arylmagnesium bromide, a very interesting result, compared with the corresponding 1-thianaphthylium salt (IV)[3] and with simple 2-thianaphthylium salt (V) as shown in Chart 1, was recognized in this communication.

We wish to report here the first example of synthesis of S-arylthiabenzene analogues by Grignard reaction of the corresponding thiopyrylium salts. We also report mechanisms for the formation of 1,2-diaryl-2-thianaphthalenes (II) and 1,2-diaryl-2-thiochromenium perchlorates (III) by the above reactions.

The treatment of 1-phenyl-2-thianaphthylium perchlorate (Ia) with phenylmagnesium bromide[4] in ether under an N_2 stream at room temperature gave 1,2-diphenyl-2-thianaphth-

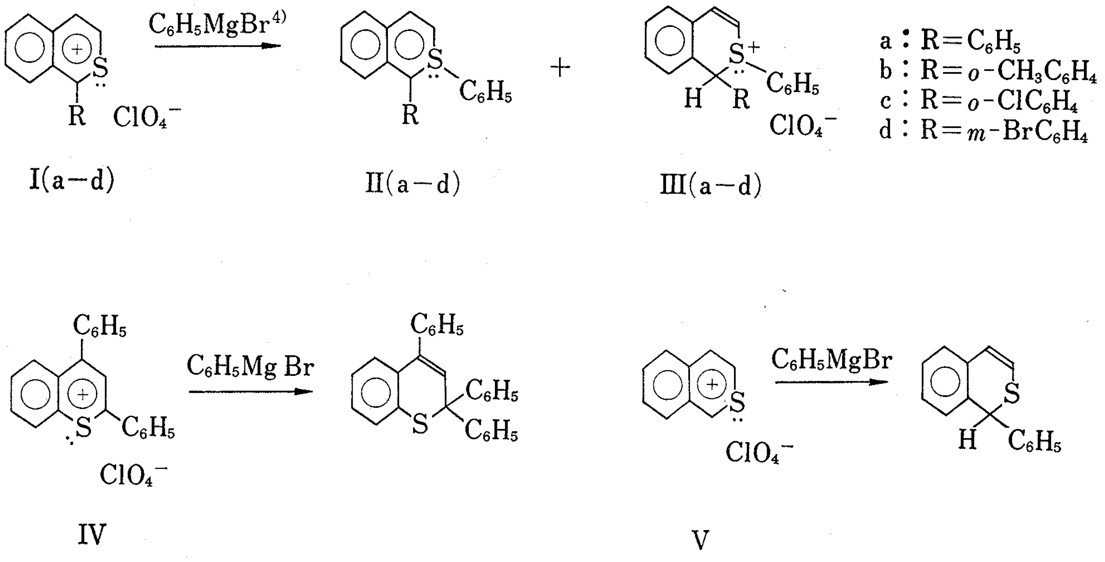

Chart 1

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[1] A part of this work was presented at the Third International Congress of Heterocyclic Chemistry, Sendai, Aug. 1971, Abstracts of Papers, p. 579, and then considerably examined to find this novel synthesis of the thiabenzene analogues.

[2] *a*) G. Suld and C.C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961); *b*) M. Hori, T. Kataoka, Y. Asahi and E. Mizuta, *Chem. Pharm. Bull.* (Tokyo), **21**, 1692 (1973).

[3] M. Hori, T. Kataoka and H. Shimizu, *Chem. Pharm. Bull.* (Tokyo), **22**, 2485 (1974).

[4] In the case of methyl- or isopropylmagnesium halide, Ia did not give any S-alkyl-2-thianaphthalene derivatives but only 1-methyl-1-phenyl-, VIa (54%, bp 135° (1 mmHg), NMR ($CDCl_3$) δ: 6.90—7.50 (9H, m, aromatic H), 6.75 (1H, d, $J=10$ Hz, C_4–H), 6.36 (1H, d, $J=10$ Hz, C_3–H), 1.95 (3H, s, CH_3)) or 1-isopropyl-1-phenyl-2-thiochromene, VIIa (36%, mp 90°, NMR ($CDCl_3$) δ: 7.00—7.60 (9H, m, aromatic H), 6.56 (1H, d, $J=10$ Hz, C_4–H), 6.45 (1H, d, $J=10$ Hz, C_3–H), 2.90 (1H, m, CH_3–$C\underline{H}$–CH_3), 1.30 (3H, d, $J=7$ Hz, CH_3), 0.88 (3H, d, $J=7$ Hz, CH_3)), respectively.

alene, IIa (28%, mp 87° (decomp.), NMR ($CDCl_3$) δ: 6.75—7.80 (m, aromatic H), UV λ_{max}^{EtOH} mμ (log ε): 254 (4.10) in long tail curve)[3] as brown powder besides 1,2-diphenyl-2-thiochromenium perchlorate, IIIa (35%, mp 168° (decomp.), IR ν_{max}^{KBr} cm^{-1}: 1090 (ClO_4^-), NMR (CF_3COOH) δ: 8.11 (1H, d, J=9 Hz, C_4–H), 6.93—7.92 (14H, m, aromatic H), 6.50 (1H, d,d, J=9, 1.5 Hz, C_3–H), 6.22 (1H, d, J=1.5 Hz, C_1–H))[5] as white needles from dichloromethane-ether. The same types of reaction products, IIb (26%, mp 83° (decomp.)), IIc (22%, mp 88° (decomp.)) and IId (47%, mp 118° (decomp.)) besides IIIb (23%, mp 155° (decomp.)), IIIc (34%, mp 179° (decomp.)) and IIId (only a trace) were respectively obtained from Ib—d under the above conditions. In these reactions, electron spin resonance (ESR) absorptions for free radicals were observed in analogy with the reactions of thioxanthylium salts and organometallic reagents.[2b]

In order to elucidate the mechanism of the reaction between I and organometallic reagents, the reactions of IIIa with various bases were attempted and interesting results as shown in Chart 2 were obtained.

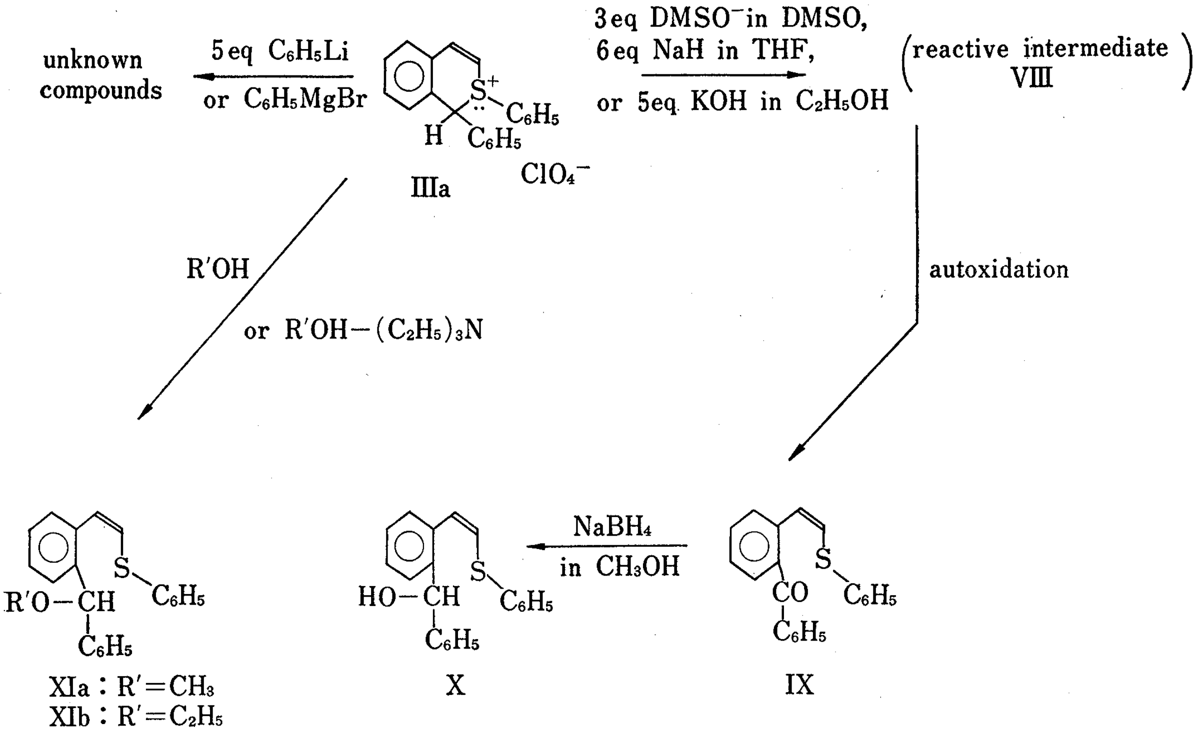

Chart 2

Treatment of IIIa with excess strong bases such as 3 eq sodium dimethylsulfinate in dimethylsulfoxide (DMSO), 6 eq sodium hydride in tetrahydrofuran (THF) or 5 eq potassium hydroxide in ethanol under an N_2 stream at room temperature, formed a ring opening compound, *o*-(ω-phenylthiostyryl) phenyl ketone, IX (bp 235° (4 mmHg), IR ν_{max}^{neat} cm^{-1}: 1660 (CO), NMR ($CDCl_3$) δ: 7.70—8.00 (3H, m, aromatic H), 6.85—7.67 (11H, m, aromatic H), 6.72 (1H, d, J=10 Hz, olefinic H), 6.42 (1H, d, J=10 Hz, olefinic H), 66%, 65%, or 58%, respectively). IX gave *o*-(ω-1-phenylthiostyryl) phenylmethanol, X (88%, bp 230° (4 mmHg), IR ν_{max}^{neat} cm^{-1}: 3360 (OH), NMR ($CDCl_3$) δ: 7.00—7.65 (14H, m, aromatic H), 6.79 (1H, d, J=10 Hz, olefinic H), 6.50 (1H, d, J=10 Hz, olefinic H), 6.08 (1H, s, $\underline{H}$–C–OH), 2.00 (1H, broad s, OH)) by sodium borohydride reduction in methanol, and the reaction of IIIa to IX seems to proceed *via* base catalyzed autoxidation of purple reaction intermediate, VIII

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5) The reaction of Ia and phenylmagnesium bromide has been reported to form only IIIa (C.C. Price and D.H. Follweiler, *J. Org. Chem.*, 34, 3202 (1969)).

(low mp, NMR ($CDCl_3$) δ: 6.50—8.00 (m, aromatic H))[6] as shown in Chart 2.

On the other hand, IIIa reacted with excess phenyllithium or phenylmagnesium bromide to form an unknown compound[7] as colorless powder (42.7%, mp 79° (decomp.), UV $\lambda_{\text{max}}^{\text{EtOH}}$ mμ: 290) or yellow powder (33.4%, mp 90° (decomp.), UV $\lambda_{\text{max}}^{\text{EtOH}}$ mμ: 258), respectively. These unknown compounds show UV spectra different from that of IIa.

Further, IIIa was made to react with methanol or ethanol for two days under an N_2 stream at room temperature to form another ring opening products, XIa (93%, bp 180° (4 mmHg), NMR ($CDCl_3$) δ: 7.05—7.70 (14H, m, aromatic H), 6.82 (1H, d, J=10 Hz, olefinic H), 6.48 (1H, d, J=10 Hz, olefinic H), 5.50 (1H, s, O–C–H), 3.40 (3H, s, OCH_3)) or XIb (92%, bp 196° (4 mmHg), NMR ($CDCl_3$) δ: 7.15—7.69 (14H, m, aromatic H), 6.84 (1H, d, J=10 Hz, olefinic H), 6.49 (1H, d, J=10 Hz, olefinic H), 5.61 (1H, s, O–C–H), 3.55 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 1.27 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$)), respectively, and this reaction was accelerated by the presence of triethylamine which belongs to weak base.

The results described in this communication could support that radical and ionic reactions exist each independently in the reactions between I and organometallic reagents.[8]

Further studies of the scope and limitation of the title synthesis are now in progress.

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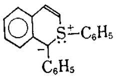
6) The unstable intermediate (VIII) is hardly attributable to the ylidic structure, 

because the doublet bands of the proton at C-3 in the ylide could not be observed in an olefinic region in the NMR spectrum even during the reaction mentioned above.

7) This result could be explained as follows. Preferentially, sulfonium salts react with phenyllithium to give the corresponding σ-sulfuranes as intermediates in the reactions, which will be collapsed to afford the various compounds. On the contrary, phenylmagnesium bromide attacks the carbon atom adjacent to the trivalent sulfur atom and also couples with the trivalent sulfur atom to cause the ligand exchange reaction (M. Hori, T. Kataoka, H. Shimizu and M. Miyagaki, *Chem. Pharm. Bull.* (Tokyo), **22**, 1171, 2004, 2014, 2020, 2030 (1974)).

8) All new compounds had satisfactory analytical data to support the assignment.

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Stable S-Alkylthiabenzenes. Synthesis of 2-Methyl-1-phenyl-2-thianaphthalene[1]

There has been much interest recently in the synthesis of stable S-alkylthiabenzenes. Hortmann and Harris[2] recognized generation of a very unstable 1-methyl-3,5-diphenylthiabenzene (II) by the treatment of 1-methyl-3,5-diphenyl-2*H*-thiinium tetrafluoroborate (I) with *t*-butyllithium in dimethylsulfoxide (DMSO)-d_6 in a standard nuclear magnetic resonance (NMR) tube under an N_2 stream but were not able to isolate it in 1970. Therefore, no reports have been published on the pure synthesis of stable S-alkylthiabenzenes so far.

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1) A part of this work was presented at the Third International Congress of Heterocyclic Chemistry, Sendai, Aug. 1971, Abstracts of Papers, p. 579.

2) A.G. Hortmann and R.L. Harris, *J. Am. Chem. Soc.*, **92**, 1803 (1970).