(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 λ_{max}^{EtOH} mμ: 290) or yellow powder (33.4%, mp 90° (decomp.), UV λ_{max}^{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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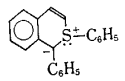
6) The unstable intermediate (VIII) is hardly attributable to the ylidic structure, 
because the doublet bands of the proton at C-3 in the ylide could not be observed in an olefinic region in the NMR spectrum even during the reaction mentioned above.

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.

[Chem. Pharm. Bull. 22(11)2754—2757(1974)]

UDC 547.81.04

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.

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).

In this communication, we wish to report the first example of the synthesis of a stable S-alkylthiabenzene analogue.

Although the reaction of 9-phenyl-10-alkylthioxanthenium salts (III) with strong bases did not give thiabenzene analogues (IV) but Stevens-type rearranged products (V),[3] S-methylthioxanthenium tetrafluoroborates (VIa, b, c), having an alkyl group at 2-position, were made to react with potassium *t*-butoxide in DMSO to afford the compounds,[4] VIIIa (9%, mp 118.5°, NMR ($CDCl_3$) δ: 6.66—7.50 (12H, m, aromatic H), 2.33 (3H, s, C_2–CH_3), 2.01 (3H, s, C_9–CH_3)), VIIIb (13%, mp 91°, NMR ($CDCl_3$) δ: 6.68—7.56 (12H, m, aromatic H), 2.65 (2H, q, J= 7.5 Hz, $C\underline{H}_2CH_3$), 2.03 (3H, s, C_9–CH_3), 1.20 (3H, t, J=7.5 Hz, $CH_2C\underline{H}_3$)) and VIIIc (18%, mp 92°, NMR ($CDCl_3$) δ: 6.70—7.59 (12H, m, aromatic H), 2.06 (3H, s, C_9–CH_3), 1.30 (9H, s, $(CH_3)_3C$)) and the mixtures,[5] VIIa (75%, mp 47—52° (decomp.), NMR ($CDCl_3$) δ: 6.68—7.50 (m, aromatic H), 2.33 (s, C_2–CH_3), 2.24 (s, S–CH_3)), VIIb (39%, an oil, NMR ($CDCl_3$) δ: 6.68—7.60 (m, aromatic H), 2.63 (q, J=7.5 Hz, $C\underline{H}_2CH_3$), 2.26 (s, S–CH_3), 1.22 (t, J=7.5 Hz, CH_2-

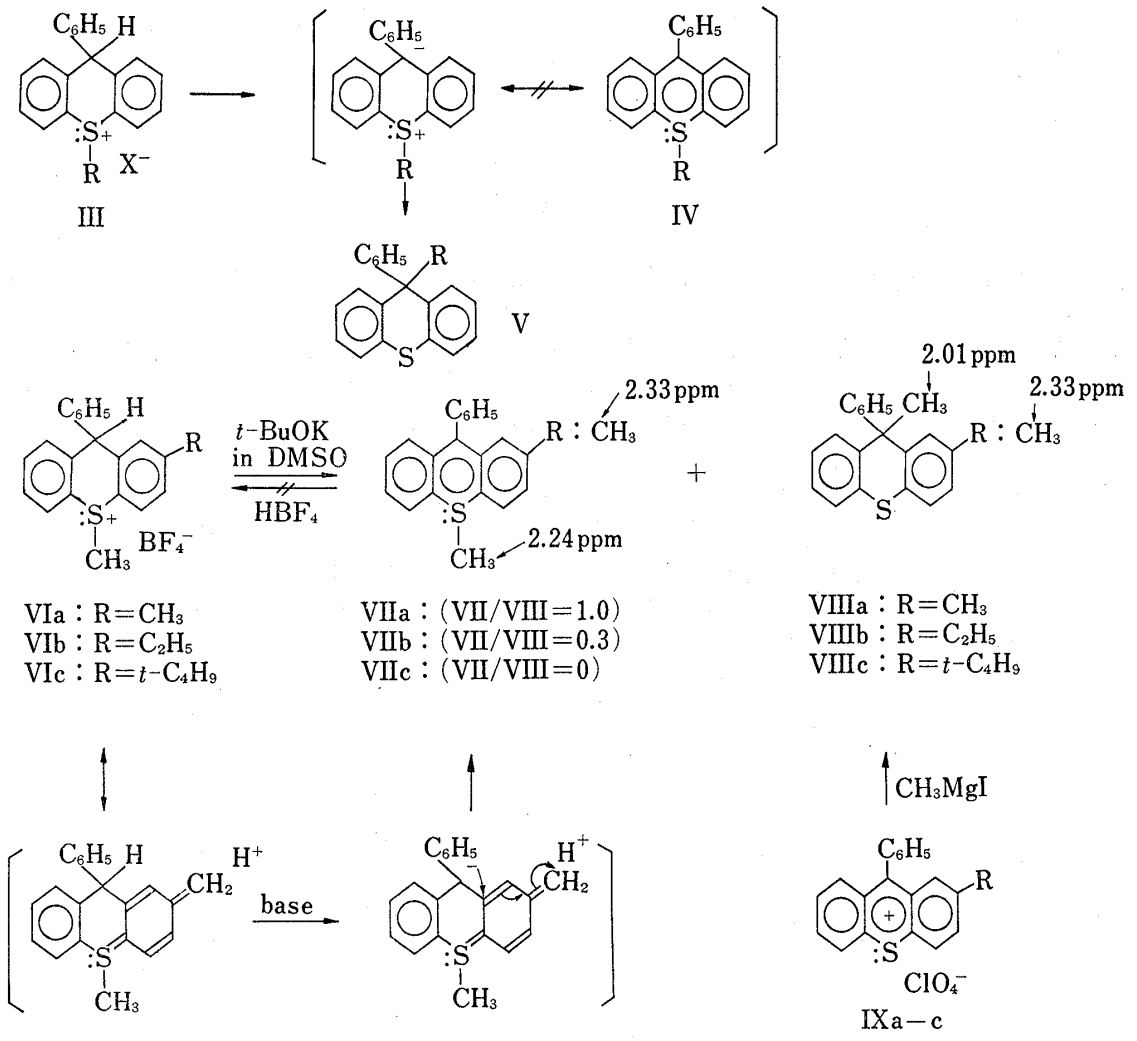


Chart 1

3) A part of this work was presented at the Second Congress of Heterocyclic Chemistry, Nagasaki, Nov. 1969, Abstracts of Papers, p. 242 and also M. Hori, T. Kataoka and H. Shimizu, *Chem. Lett.*, **1974**, 1117.

4) Identical with those authentic samples from IX as shown in Chart 1 using the known method (M. Hori, T. Kataoka, Y. Asahi and E. Mizuta, *Chem. Pharm. Bull.* (Tokyo), **21**, 1692 (1973)).

5) Assumed to be a mixture of VII and VIII with the product ratio as shown in Chart 1 by NMR spectra in $CDCl_3$ with tetramethylsilane as an internal standard.

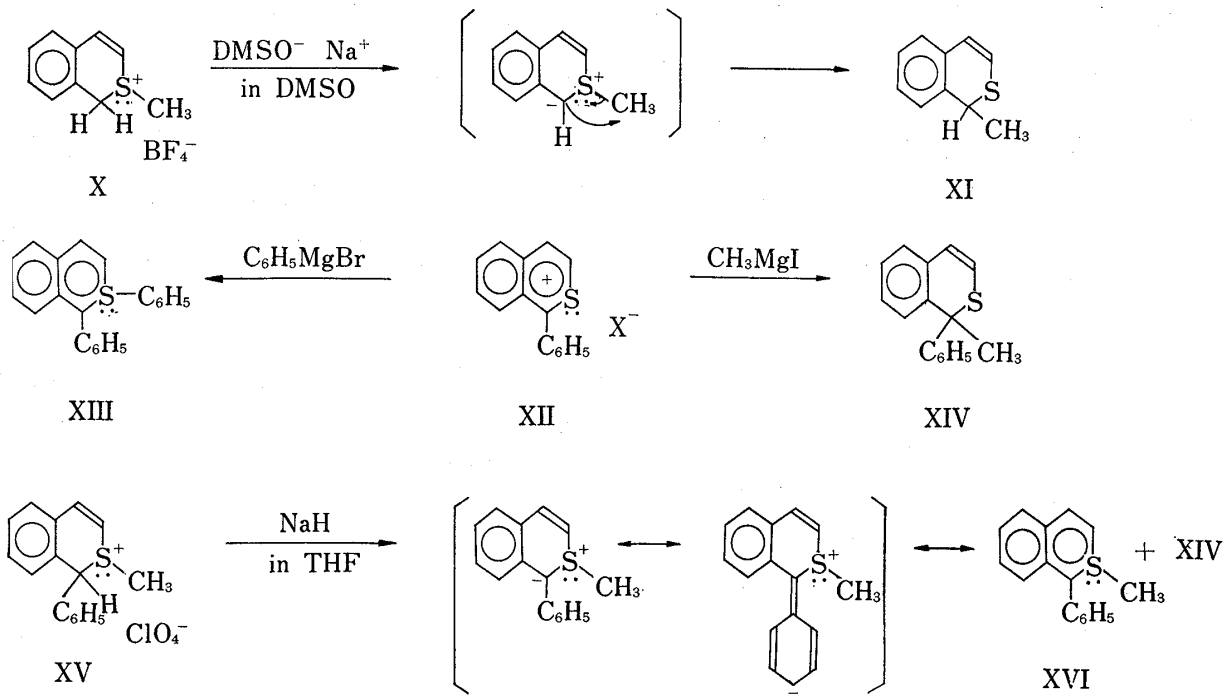
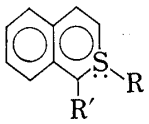


Chart 2

CH_3)) and VIIc (none), respectively. The mixtures were unable to be purified further by means of thin-layer chromatography (TLC) method. The thiabenzene by thiopyran analogue ratios in VII were affected by the variation of the alkyl group at 2-position of VI and in reality, VIIc was not recognized at all in the case of VIc. Reasoning from this data, it is able to assert that in the mechanism of reaction between VI and the base, at least the hyperconjugation effect is concerned.

On the other hand, 2-methyl-2-thiochromenium tetrafluoroborate (X) in bicyclic system also reacted with sodium dimethylsulfinate in DMSO to form a rearranged product, 1-methyl-2-thiochromene (XI, 65%, bp 105° (2 mmHg), NMR ($CDCl_3$) δ: 7.00—7.35 (4H, m, aromatic H), 6.72 (1H, d, J=10 Hz, C_4–H), 6.32 (1H, d,d, J=10, 1.5 Hz, C_3–H), 3.95 (1H, q,d, J=7, 1.5 Hz, C_1–H), 1.48 (3H, d, J=7 Hz, CH_3) as well as III in tricyclic system.



XVII

(R=alkyl or aryl, R′=electron attracting or releasing groups)

Chart 3

However, we reported a finding that the treatment of 1-phenyl-2-thianaphthylium salt (XII) with aromatic Grignard reagent afforded thiabenzene analogue (XIII) while the reaction of XII with alkylmagnesium halide gave only its isomeric compound (XIV).[6] Through the stereo-electronic considerations by the experimental results described above, the synthesis of the objective product, 2-methyl-1-phenyl-2-thianaphthalene (XVI) has been achieved by the reaction of 2-methyl-1-phenyl-2-thiochromenium perchlorate (XV), which has at 1-position aryl group having both properties of steric and electromeric effects, with sodium hydride in tetrahydrofuran under an N_2 stream at room temperature. In this case, the rearranged product (XIV) was also obtained as a minor product (24%). Yield of XVI was 60%

6) Colorless oil, bp 135° (1 mmHg), Mass Spectrum: Calcd. for $C_{16}H_{14}S$: 238. Found: 238 (M^+), 223 (M^+–CH_3). 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). UV λ_{max}^{EtOH} mμ (log ε): 240 (3.89), 322 (3.73) in an ordinary curve (M. Hori, T. Kataoka, H. Shimizu and S. Sugai, *Chem. Pharm. Bull.* (Tokyo), **22**, 2752 (1974).

and XVI showed the following physical constants: yellow powder. mp 55—65° (decomp.). Mass Spectrum: Calcd. for $C_{16}H_{14}S$: 238, Found: 238 (M^+), 223 (M^+–CH_3), 146 (M^+–CH_3, C_6H_5). NMR ($CDCl_3$) δ: 6.90—7.70 (11H, m, aromatic H), 2.30 (3H, broad s, CH_3). UV λ_{max}^{EtOH} mμ (log ε): 244 (4.06), 322 (3.53) in a long tail curve. Compared with the isomeric compound (XIV), the structure of XVI was established by its appearance, mass and NMR spectra, and especially by the ultraviolet (UV) spectrum having a characteristic absorption curve. Incidentally, the NMR spectrum does not show the doublet bands of the proton at C-3 in an olefinic region of the ylidic structure in XVI. All new compounds had satisfactory analytical data to support the assignment.

Further studies on the syntheses and reactivities of compounds (XVII) and also on the application of S-alkylthiabenzenes to the medicinal chemistry are now in progress.

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The Preparation and Chemical Reactions of a Peracid Resin

Recent reports from several laboratories have shown the advantageous application of solid phase synthesis[1] to general organic reactions.[2] Two groups,[3,4] already reported that peracid resins were prepared from cation exchangers and applied to epoxidation of double bonds, however, the peracid resins require some improvements with regard to both stability and reactivity.[5] We now report the preparation of a new peracid resin and its application to some chemical reactions.

A carboxylic acid resin (I) prepared from styrene-divinylbenzene (2%) copolymer[6] was oxidized with 87% hydrogen peroxide and methanesulfonic acid in an ice-bath to yield a peracid resin (II; peracid content, 3.06 mmole/g). The resin (II), when it is stored in a brown-bottle at room temperature, is practically stable.[7]

Oxidation reactions with II were smoothly carried out in dioxane or methanol. Chloroform and dichloromethane, which are usually used in *m*-chloroperbenzoic acid (III) oxidation, are unsuitable, probably because they have little activity of swelling the resin (II). Some results are shown in Table I. The resin (II) has sufficient reactivity for practical purposes.

Compared with the reported results on epoxidation with polypermethacrylic acid (IV),[4] No. 4 and 5 in the table show that the reactivity of II has been considerably improved. When

1) R.B. Merrifield, *J. Amer. Chem. Soc.*, **85**, 2149 (1963).
2) For a review see, C.G. Overberger and K.N. Sannes, *Angew. Chem. internat. Edit.*, **13**, 99 (1974).
3) F. Helfferich and D.B. Luten, *J. Appl. Polymer Sci.*, **8**, 2899 (1964).
4) T. Takagi, *Polymer Letters*, **5**, 1031 (1967).
5) The half-life time of peracid resins prepared from bifunctional cation exchangers is only 2 days.[3] Polypermethacrylic acid (IV) can be stored at 0—5° for 2 months without substantial loss of its oxidation capacity, however, at 25° 20% of active oxygen was lost after 60 hr.[4]
6) R.L. Letsinger, M.J. Kornet and V. Manadevan, *J. Amer. Chem. Soc.*, **86**, 5163 (1964).
7) Decomposition of peracid after 2 months storage was less than 1.5%.