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SYNTHESIS AND REACTIONS OF YLIDIC THIABENZENES[1)]

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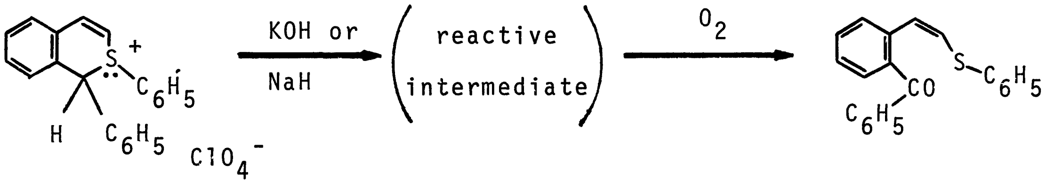
Synthesis and structure of novel ylidic thiabenzenes, 1-cyano- and benzoyl-2-methyl-2-thianaphthalenes (VI and X), are discussed. The reactions of VI with several electrophiles such as dimethyl acetylenedicarboxylate, methyl propiolate, diphenylcyclopropenethione, and diphenylcyclopropene are described together with the mechanisms of the reactions.

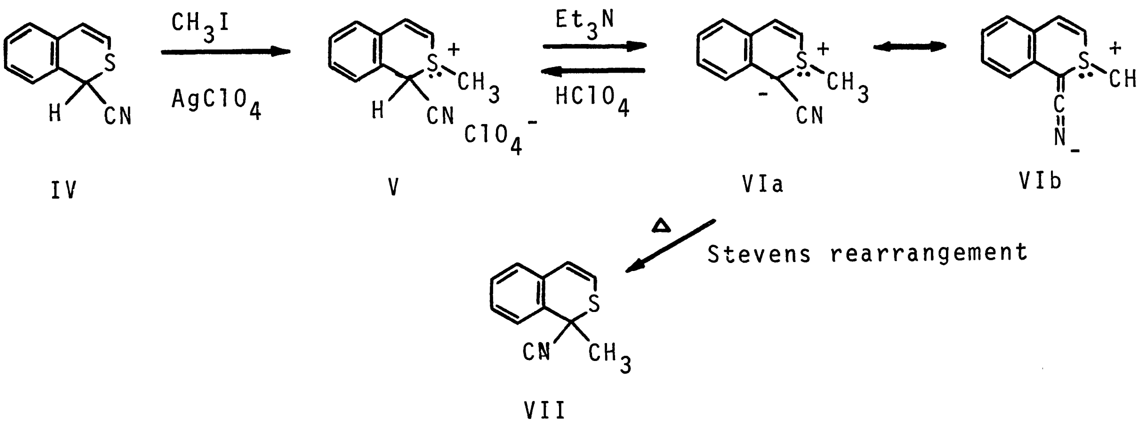
In the previous paper,[2)] we reported that the reactions between 1,2-diphenyl-2-thiochromenium perchlorate (I) and strong bases such as KOH in EtOH and NaH in THF generated an unstable purple intermediate (II), which was readily oxidized with air in the presence of a base-catalyst to form a ring opening product, o-(ω-phenylthiostyryl) phenyl ketone (III).



I II III

In this communication, we wish to report that novel and stable ylidic thiabenzene analogues were successfully synthesized by the reaction between a weak base, such as triethylamine, and cyclic sulfonium salts having strong electron-attracting groups, such as cyano and carbonyl groups, in the place of a phenyl group at 1-position of I. Studies were made also on the reactions of the ylidic thiabenzenes with several electrophiles.

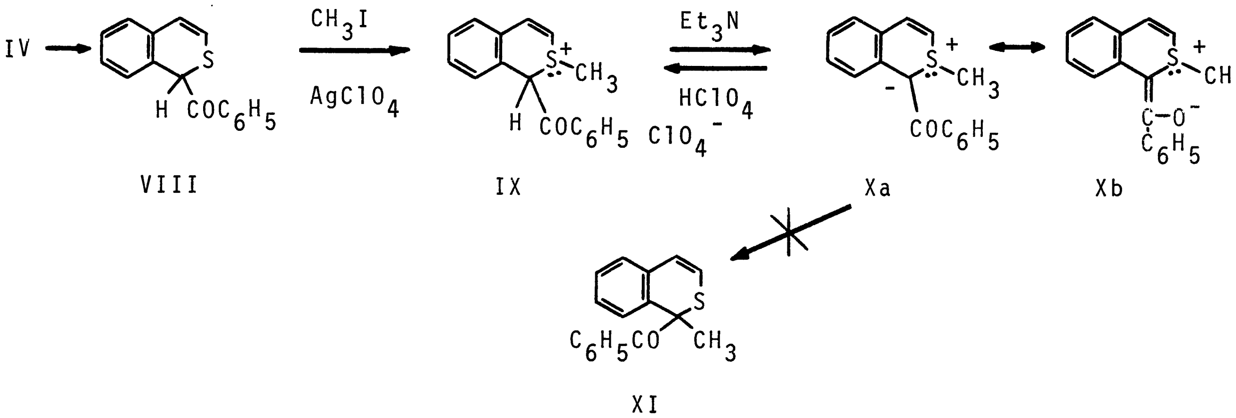
1-Cyano-2-methyl-2-thianaphthalene (VI): The reaction of 2-thianaphthylium perchlorate[3)] and KCN in CH_2Cl_2 at room temperature gave 1-cyano-2-thiochromene (IV), mp 84-85°C, in 55% yield as pale brown needles. Treatment of IV with methyl iodide in the presence of $AgClO_4$ in dichloroethane gave 1-cyano-2-methyl-2-thiochromenium perchlorate (V), mp 178°C (decomp.), in 67% yield as white prisms. V was allowed to react with 2 eq triethylamine in EtOH with cooling for 2 hr to give 1-cyano-2-methyl-2-thianaphthalene (VI), mp 75°C (decomp.), in 93% yield as orange needles from ether: NMR ($CDCl_3$): δ 6.78-7.60 (5H, m, aromatic 4H and $C_{(4)}$-H), 5.83 (1H, d, J=10 Hz, $C_{(3)}$-H), and 2.09 (3H, s, CH_3), IR: ν_{max}^{KBr} 2142 cm^{-1} (CN), UV: λ_{max}^{EtOH} 217 nm (log 3.08), 262 (3.47), and 382 (2.51). VI was quite soluble in benzene, CCl_4, and $CHCl_3$, but soluble in ether only slightly, and very stable at room temperature.



The IR spectrum of VI showed a band at 2142 cm^{-1}, which indicated appreciably strong ionic character of the cyano group, and indicated that resonance form VIb was an important contributor to the over-all electronic structure. The NMR spectrum showed doublet band of the olefinic proton at 3-position of VI at δ 5.83 and indicated a pattern similar to that of vinylsulfonium salts such as V. This band appears in a magnetic field higher than that of olefinic proton in this system. The appearance of the band at such a high magnetic field is attributable to the diamagnetic effects of ylidic carbanion of resonance form VIa through the long-range interaction.[4)]

The physico-chemical data described above suggest that ylide-type bonding predominates in VI. VI was acidified with 70% $HClO_4$ in ether to give V easily, and underwent the Stevens rearrangement on heating in benzene to form 1-cyano-1-methyl-2-thiochromene (VII), bp 130°C/1 mmHg, in 86% yield: NMR ($CDCl_3$): δ 7.10-7.75 (4H, m, aromatic H), 6.92 (1H, d, J=9.5 Hz, $C_{(4)}$-H), 6.44 (1H, d, J=9.5 Hz, $C_{(3)}$-H), and 2.02 (3H, s, CH_3). The photolysis of VI is now being studied.

1-Benzoyl-2-methyl-2-thianaphthalene (X): Treatment of IV with phenylmagnesium bromide in ether followed by the hydrolysis with hydrochloric acid afforded 1-benzoyl-2-thiochromene (VIII), mp 145-146°C, in 46% yield as yellow needles from EtOH. VIII was allowed to react with methyl iodide in the presence of $AgClO_4$ in dichloroethane to give 1-benzoyl-2-methyl-2-thiochromenium perchlorate (IX), mp 158°C, in a quantitative yield as colorless prisms from CH_2Cl_2-ether. The reaction of IX with 2 eq triethylamine in EtOH yielded 1-benzoyl-2-methyl-2-thianaphthalene (X), mp 185°C (decomp.), in a quantitative yield as orange needles from CH_2Cl_2-ether: NMR ($CDCl_3$): δ 6.70-7.70 (10H, m, aromatic 9H and $C_{(4)}$-H), 6.05 (1H, d, J=9.5 Hz, $C_{(3)}$-H), and 2.20 (3H, s, CH_3), IR: ν_{max}^{KBr} 1510 cm^{-1} (CO), UV: λ_{max}^{EtOH} 234 nm (log ε 4.25), 266 (4.24), 301 sh. (3.83), and 405 (3.79). The property of X was different from that of VI to some extent, that is, X was soluble in benzene and ether only slightly but easily soluble in $CHCl_3$ and CH_2Cl_2.



The observation that the carbonyl stretching frequency was 1510 cm^{-1} indicated the delocalization of the carbanion electron of X through the carbonyl group and supported the resonance form Xb as an important contributor to the electronic distribution in X. The NMR spectrum showing the band of the olefinic proton at 3-position of X at δ 6.05 supported the view that resonance form Xa is also an important contributor to the electronic distribution in X, as is the case with VI.

The physico-chemical data described above suggest that X can be also represented by the ylide-type resonance forms Xa and Xb.[4)] X was also converted, like VI, to the corresponding sulfonium salt (IX) by the treatment with 70% $HClO_4$. Refluxing of X in benzene did not give the rearranged product (XI) but formed demethylated compound, 1-benzoyl-2-thiochromene (VIII).

VI and X are novel and remarkably stable crystalline S-alkylthiabenzene analogues, which are quite different from the ylidic thiabenzene 1-oxides prepared by Hortmann's and other groups.[5a-5f)] These are quite unique thiabenzenes because these were isolated in the ylidic form. There have been no reports on the isolation of ylidic thiabenzenes. Therefore, various novel reactivities are expected for these compounds. In this communication, we wish to report only on the reactions of VI with various electrophilic reagents.

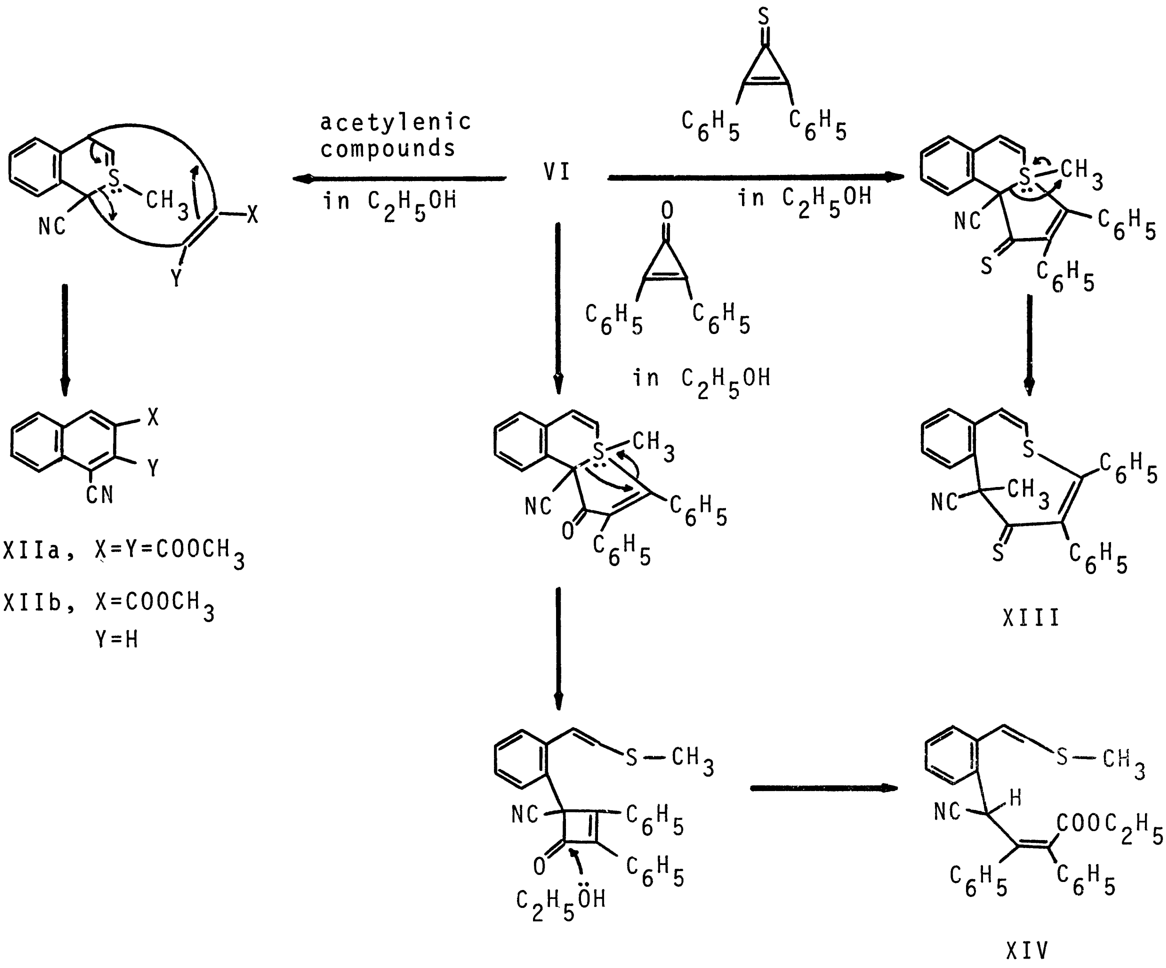
The Reactions of 1-Cyano-2-methyl-2-thianaphthalene (VI) with Various Electrophiles

The reaction of VI with 1 eq dimethyl acetylenedicarboxylate and with 1 eq methyl propiolate in EtOH afforded corresponding naphthalene derivatives XIIa and XIIb, respectively, as a major product: 1-cyano-2,3-bis(methoxycarbonyl)naphthalene (XIIa), mp 133-134°C, as white needles: NMR ($CDCl_3$): δ 8.76 (1H, s, aromatic H), 7.70-8.50 (4H, m, aromatic H), 4.10 (3H, s, $COOCH_3$), and 4.00 (3H, s, $COOCH_3$), IR: ν_{max}^{KBr} 2240 cm^{-1} (CN), 1740 (ester), and 1725 (ester), Mass: m/e 269 (M^+); 1-cyano-3-methoxycarbonylnaphthalene (XIIb), mp 105-106°C, as white needles: NMR ($CDCl_3$): δ 8.83 (1H, d, J=1 Hz, aromatic H), 7.80-8.52 (5H, m, aromatic H), and 4.04 (3H, s, $COOCH_3$), IR: ν_{max}^{KBr} 2220 cm^{-1} (CN) and 1725 (ester), Mass: m/e 211 (M^+). It was assumed that XII was formed by the Diels-Alder reaction of VI with acetylenic compounds.

The treatment of VI with 1 eq diphenylcyclopropenethione in EtOH yielded a ring expansion product (XIII), mp 223-224°C, as a major product as yellow prisms: NMR ($CDCl_3$): δ 7.10-7.70 (13H, m, aromatic H), 7.07 (1H, s, aromatic H), 5.54 (1H, d, J=4 Hz, olefinic H), 4.92 (1H, d, J=4 Hz, olefinic H), and 2.50 (3H, s, CH_3), IR: ν_{max}^{KBr} 2210 cm^{-1} (CN), Mass: m/e 409 (M^+). By the reaction of VI with 1 eq diphenylcyclopropenone in EtOH, an oily product was obtained in 82% yield. The structure of this compound was as shown by XIV by the following data: bp 247°C/0.8 mmHg, NMR

($CDCl_3$): δ 6.50-8.00 (15H, m, aromatic 14H and olefinic H), 6.35 (1H, d, J=11 Hz, olefinic H), 5.70 (1H, s, H-C-CN), 4.30 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 2.34 (3H, s, $S-CH_3$), and 1.29 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), IR: ν_{max}^{KBr} 2220 cm^{-1} (CN) and 1725 ($\Delta^{\alpha,\beta}$-ester), Mass: m/e 440 (M^+).

From the above data, the authors propose the following mechanism for the reactions of VI with the electrophiles. All compounds gave satisfactory elemental analysis.



Studies are being continued on the synthesis of many ylidic thiabenzenes by the reaction with bases of various cyclic sulfonium salts having electron-attracting groups as described above or electron-donating groups in mono-, di-, and tricyclic systems, as well as on the difference of rearrangement of S-substitutents between these two classes of thiabenzenes. The tendency and the limitation of the chemical reactivities of cyclic sulfonium ylides are also being investigated.

REFERENCES AND NOTES

1) This work was presented at the Second Symposium on Organic Sulfur and Phosphorus Compounds, Tokyo, Feb. 15-16, 1974, Abstracts of Papers p. 26.

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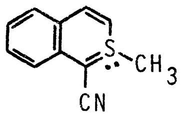
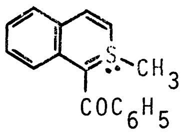
4) The stability of VI and X is hardly attributable to the through-conjugated ylen-like resonance forms VIc and Xc, respectively, because the bands of the protons at C-3 in VI and X were too high to be in an aromatic region in their NMR spectra.



VIc



Xc

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