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Polar Cycloaddition of Monocyclic 1,2-Thiazinylium Salt and Transformation of the Cycloadducts to 1,2-Azathiabenzenes

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Abstract: *Deprotonation of the cycloadducts, which were newly obtained from polar cycloaddition of monocyclic 1,2-thiazinylium salt with 1,3-butadienes, with a strong base provided 1,2-azathiabenzenes having sulfur at a bridgehead position.*

Key words: polar cycloaddition, 1,2-thiazinylium salt, 1,2-azathiabenzene

In our earlier work, we found novel polar cycloaddition of the C=S$^+$ bond of thiopyrylium salts with various 1,3-butadienes.[1] Recently, we also reported interesting polar cycloadditions of the N=S$^+$ bond of benzo-fused 1,2-thiazinylium salt with several 1,3-butadienes.[2] These polar cycloaddition products afforded new sulfur-containing heterocyclic compounds through various ring transformations.

We next turned our attention to the polar cycloaddition of monocyclic 1,2-thiazinylium salt **I** having no condensed-benzene ring. The salt **I** has two possible different active bonds (C=S$^+$ and N=S$^+$ bonds) for the cycloaddition, apparent from the resonance cannonical structures IA and IB as depicted below without any destruction of the benzenoid necessary for the benzene-condensed 1,2-thiazinylium salt. In this communication, we report the synthesis and cycloaddition of 4,5-diphenyl-1,2-thiazinylium salt **5** with 1,3-dienes and, further, isolation of azathiabenzene derivatives derived from the cycloadducts obtained by treatment with some bases.

IA **IB**

The salt **5** was prepared by the route depicted in Scheme 1. N-Sulfunyl trichloroethoxycarbonylurethan (**1**) generated by the method reported by Wald *et al.*,[3] was allowed to react with 2,3-diphenyl-1,3-butadiene to give N-substituted dihydro-1,2-thiazine 1-oxide **2**[4] in 78% yield. Reductive removal of a *tert*-butoxycarbonyl group of the compound **2** with zinc in refluxing *tert*-BuOH afforded a thiazine sulfoxide **3** in 93% yield. The sulfoxide **3** was then submitted to Pummerer reaction with trifluoroacetic anhydride in dichloromethne at

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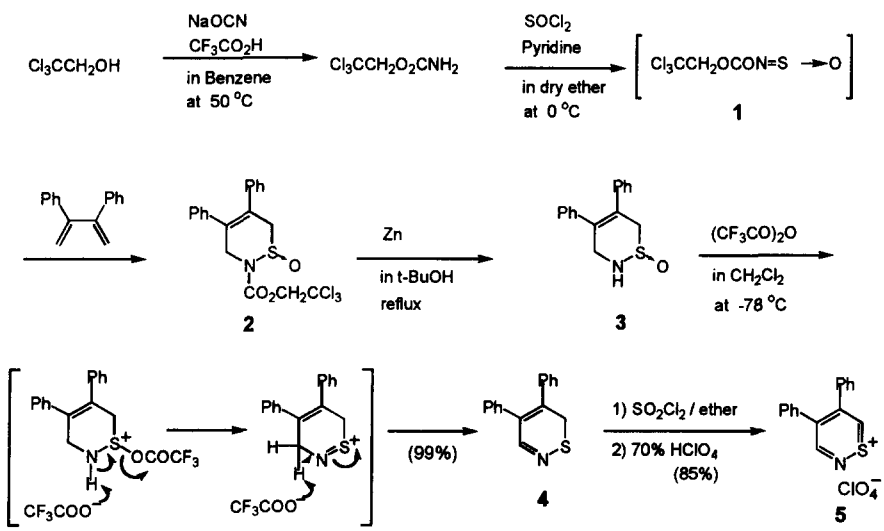
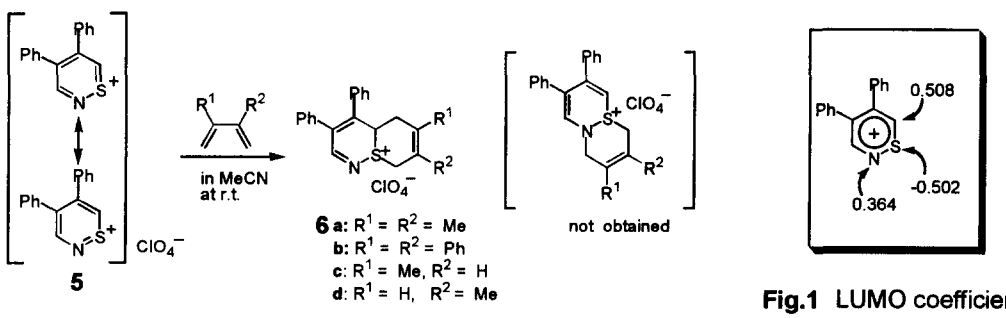
-78 °C to yield 4,5-diphenyl-5*H*-1,2-thiazine (**4**) , mp 140-142 °C in 99% yield. Treatment of thiazine **4** with sulfuryl chloride, followed by addition of 70% perchloric acid gave our target compound, 4,5-diphenyl-1,2-



Scheme 1

thiazinylium perchlorate (**5**) as yellow needles, mp 147-150 °C in 85% yield. Thus, addition of 2,3-dimethyl-1,3-butadienes to the salt **5** in acetonitrile at room temperature resulted in the formation of the product **6a** cycloadded across the C=S$^+$ bond in 99% yield, but no cycloadduct across the N=S$^+$ bond was obtained. The structural elucidation of the cycloadduct **6a** was achieved mainly on the basis of NMR spectral data, showing a typical tertiary hydrogen signal as a double of doublet coupled with adjacent methylene hydrogens



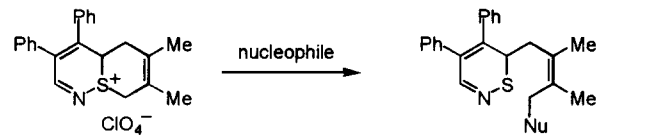
Scheme 2

Fig.1 LUMO coefficients

(J=8 and 6 Hz) at δ 5.35 in the ^{1}H-NMR spectrum and a tertiary carbon atom at δ 43.2 (d) in the ^{13}C-NMR spectrum. Similarly, other 1,3-butadienes, 2,3-diphenyl-1,3-butadiene and isoprene also afforded the corresponding cycloadducts **6b** and **6c** in 99% and 82% yields, respectively. A small amount of regioisomer **6d** (2%) was obtained from the cycloaddition with isoprene. The above complete regiospecificity of the cycloaddition across only the C=S$^+$ bond would be rationalized in terms of Frontier Molecular Orbital

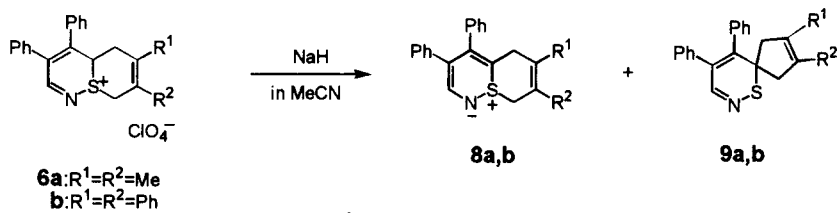
coefficients in the salt **5**. The above cycloaddition would be considered to be $LUMO_{salt}$-$HOMO_{diene}$ interacted reaction. MOPAC 93 PM3 calculation of 1,2-thiazinylium salt **5** showed the values of LUMO coefficients for C(6), S and N are 0.508, -0.502 and 0.364, respectively, as shown in Figure 1[5]. These values strongly suggest the preference of the reaction site of the $C=S^+$ bond.

We next investigated the chemical transformation of the cycloadduct **6** by the reaction with some nucleophiles and bases. Nucleophiles such as alcohols and primary amine reacted with the cycloadduct **6a** to cleave regiospecifically the sulfur-carbon bond , thus affording ring-opened products **7** in good yields as shown in Scheme 3.



Scheme 3

On the other hand, deprotonation of the cycloadduct **6a** with sodium hydride in acetonitrile at 0 °C afforded cyclic sulfilimine **8a** (57%), the so-called 1,2- azathiabenzene derivative as pale yellow crystals together with a

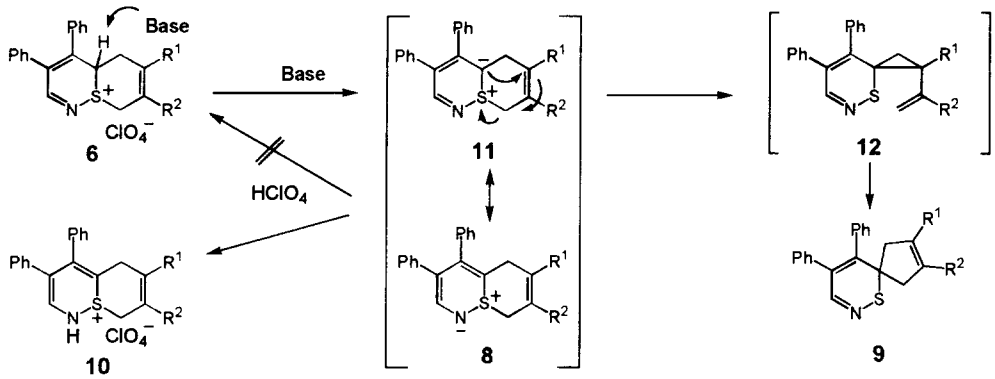


Scheme 4

spiro compound **9a** (10%) (Scheme 4). Another similar 1,2-azathiabenzene **8b** was obtained in 50% yield along with a spiro compound **9b** (27%) by treatment of the cycloadduct **6b** with sodium hydride in acetonitrile at 0 °C. The structures of **8a, b** and **9a, b** were determined by combination of their elementary analysis, mass and other spectral data. In addition, especially, the structure of the 1,2-azathiabenzene **8** was also confirmed by chemical evidence as shown in Scheme 5: protonation of **8a** (R^1=R^2=Me) with 70% perchloric acid yielded the corresponding cyclic amino sulfonium salt **10a** in 87% yield, but not the starting sulfonium compound **6a**, suggesting predominance of sulfilimine structure **8a** rather than cyclic sufonium ylide structure **11a**. The compound **8** could be recognized as the first example of 1,2-azathiabenzene having sulfur at a bridgehead position.

A proposed mechanism for the formation of **8** and **9** also is shown in Scheme 5. The most acidic proton adjacent to sulfur in **6** is deprotonated with a base to give the sulfonium ylide intermediate **11**, which resonates with 1,2-azathiabenzene **8** as a more highly contributed resonance form. Some of the intermediate **11** is

subsequently degraded *via* a 2,3-sigmatropic rearrangement into the vinylcyclopropane intermediate **12**.[6] The intermediate **12** would undergo rearrangement to furnish the spiro compound **9**.



Scheme 5

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2. H. Shimizu, T. Hatano, T. Matsuda and T. Iwamura, *Tetrahedron Lett.*, **1999**, *40*, 95.
3. L. Wald and W. Wucherpfennig, *Ann. Chem.*, **1971**, *746*, 28.
4. Satisfactory analytical data were obtained for all new compounds. Data for the selected compounds. **5**: yellow needles (CH_2Cl_2-ether), mp. 147-150 °C (dec.). IR(KBr) cm^{-1}: 1094 (ClO_4^-). ^{1}H-NMR ($CDCl_3$) δ : 7.34-7.59(10H, m, ArH), 10.25(1H, d, J=1.5Hz, CH), 10.97(1H, d, J=1.5Hz, CH). ^{13}C-NMR($CDCl_3$) δ : 128.4(d), 128.5(d), 129.7(d), 130.0(d), 131.1(d), 133.3(s), 133.5(s), 149.2(s), 151.5(s), 164.4(s), 174.3(s). **6a**: yellow needles(CH_2Cl_2-ether), mp. 134-136 °C(dec.). IR(KBr) cm^{-1}: 1091(ClO_4^-). ^{1}H-NMR ($CDCl_3$) δ : 1.86(3H, s, CH_3), 1.93(3H, s, CH_3), 2.41(1H, dd, J=8, 6Hz, C*H*H), 2.42(1H, dd, J=8, 6Hz, CH*H*), 4.21(1H, d, J=15Hz, SC*H*H), 4.50(1H, d, J=15Hz, SCH*H*), 5.35(1H, dd, J=8, 6Hz, CH), 7.07-7.32(10H, m, ArH), 8.49(1H, s, N=CH). ^{13}C-NMR ($CDCl_3$) δ : 20.3(q), 20.8(q), 31.9(t), 43.2(d), 44.8(t), 120.6(s), 128.8(d), 129.0(d), 129.15(d), 129.19(d), 129.7(d), 130.4(d), 130.6(s), 132.3(s), 134.1(s), 134.2(s), 143.3(s), 169.8(d). **6b**: yellow needles (CH_2Cl_2-ether), mp. 108-112°C(dec.). IR(KBr) cm^{-1}: 1095(ClO_4^-). ^{1}H-NMR ($CDCl_3$) δ : 2.91(1H, dd, J=15, 7Hz, C*H*H), 3.07(1H, dd, J=15, 5Hz, CH*H*), 4.78(1H, d, J=15Hz, SC*H*H), 4.90(1H, d, J=15Hz, SCH*H*), 5.87(1H, dd, J=7, 5Hz, CH), 6.71(2H, m, ArH), 6.90(2H, m, ArH), 6.98(2H, m, ArH), 7.10(2H, m, ArH), 7.17-7.20(8H, m, ArH), 7.26-7.27(4H, m, ArH), 8.50(1H, s, N=CH). ^{13}C-NMR ($CDCl_3$) δ : 34.8(t), 46.3(d), 48.6(t), 128.0(d), 128.1(d), 128.5(d), 128.53(d), 128.6(d), 128.8(d), 128.88(d), 128.93(d), 129.0(d), 129.1(d), 129.3(s), 130.0(d, 130.2(s), 134.1(s), 134.8(s), 140.0(s), 140.2(s), 142.3(s), 147.4(s), 169.0(d). **6c**: yellow needles (CH_2Cl_2-ether), mp. 109-111 °C(dec.), IR(KBr) cm^{-1}: 1094(ClO_4^-). ^{1}H-NMR ($CDCl_3$) δ : 1.85(3H, s, CH_3), 2.36(1H, dd, J=17, 6Hz, C*H*H), 2.44(1H, dd, J=17, 8Hz, CH*H*), 4.32(1H, d, J=17, 6Hz, SC*H*H), 4.69(1H, d, J=17Hz, SCH*H*), 5.16(1H, dd, J=8, 6Hz, CH), 5.73(1H, brs, CH=), 7.15-7.18(2H, m, ArH), 7.25-7.33(8H, m, ArH), 8.67(1H, s, N=CH). ^{13}C-NMR ($CDCl_3$) δ : 24.9(q), 28.2(t), 38.8(t), 41.9(d), 111.6(d), 128.8(d), 129.0(d), 129.2(d), 129.3(d), 129.9(d), 130.7(d), 131.9(s), 133.4(s), 133.7(s), 138.5(s), 144.5(s), 171.4(d). **6d**: ^{1}H-NMR ($CDCl_3$) δ : 1.96(3H, s, CH_3), 2.30-2.47(2H, m, CH_2), 4.17(1H, d, J=7Hz, SC*H*H), 4.69(1H, d, J=7Hz, SCH*H*), 5.09(1H, t, J=6Hz, CH), 5.92(1H, brs, =CH). **8a**: yellow crystals (CH_2Cl_2-hexane), mp. 140-142 °C(dec.). MS m/z: 331(M^+). ^{1}H-NMR ($CDCl_3$) δ : 1.68(3H, s, Me), 1.81(1H, d, J=17Hz, C*H*H), 1.84(3H, s, Me), 2.74(1H, d, J=17Hz, CH*H*), 3.02(1H, d, J=17Hz, SC*H*H), 3.92(1H, d, J=17Hz, SCH*H*), 7.24-7.36(8H, m, ArH), 7.39-7.41(2H, m, ArH), 8.39(1H, s, NCH=). ^{13}C-NMR ($CDCl_3$) δ : 19.5(q), 20.2(q), 32.3(t), 37.5(t), 84.2(s), 122.8(s), 125.4(s), 128.1(d), 128.2(d), 128.3(d), 128.57(d), 128.6(d), 128.7(d), 132.2(s), 133.7(s), 136.8(s), 161.1(s), 164.5(d). **8b**: yellow crystals ($CHCl_3$-ether). mp. 154-156 °C(dec.). MS m/z: 455(M^+). ^{1}H-NMR ($CDCl_3$) δ : 2.41(1H, d, J=17.6Hz, C*H*H), 3.12(1H, d, J=17.6Hz, CH*H*), 3.62(1H, d, J=17.1Hz, SC*H*H), 4.29(1H, d, J=17.1Hz, SCH*H*), 6.98-7.13(10H, m, ArH), 7.25-7.42(10H, m, ArH), 8.52(1H, s, NCH=). ^{13}C-NMR ($CDCl_3$) δ : 32.7(t), 38.2(t), 84.5(s), 126.3(d), 126.4(d), 127.8(d), 127.9(d), 128.2(d), 128.3(d), 128.5(d), 128.7(d), 128.8(d), 129.3(d), 129.4(s), 132.4(s), 133.7(s), 134.7(s), 137.1(s), 142.0(s), 142.7(s), 161.1(s), 165.0(d).
5. The MO calculation of 4,5-diphenyl-1,2-thiazinylium cation was performed with the PM3 hamiltonian by "WinMOPAC v2.0 (Fujitsu Ltd.) for the Windows 95 (Microsoft Inc.)", which is based on the MOPAC97 of Dr. J.J.P. Stewart and Fujitsu Ltd., Tokyo, Japan.
6. The similar vinylcyclopropane intermediates were detected or isolated from deprotonation of the cycloaddition products of 1- or 2-thianaphthylium salts with 1,3-butadiene, respectively, and further, the vinylcyclopropanes rearranged to afford the corresponding spiro compounds even at 0 °C or on heating, respectively.[1b, 1c]