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NEW MODES OF THERMAL REACTIONS OF CYCLIC SULFUR YLIDES. SOLVENT UPTAKE AND SPIRO-COMPOUND FORMATION

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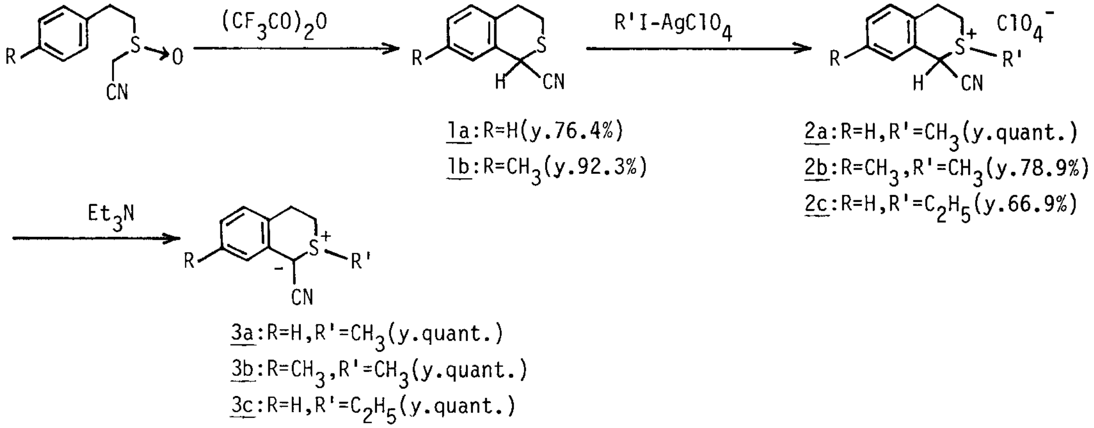
Summary: The thermal reaction of 1-cyano-2-methyl-3,4-dihydro-2-thianaphthalene(3a) in toluene afforded 1-benzyl-1-cyano-2-thiochroman(6a) together with 1-cyano-1-methyl-2-thiochroman(4a), whereas the thermal reaction in ethanol gave the spiro-compound(8a) in 82.7% yield. The structure of the spiro-compounds was established by their spectral data and chemical reactions.

Cyano-stabilized cyclic sulfur ylides underwent thermal [1,2]-[1] and [1,4]rearrangements.[2] In addition, ketenimine formation was also reported as a result of a nitrile group participation in [2,3]sigmatropic rearrangement of cyano-stabilized sulfur ylides.[3] Previously, we reported new [1,4]- and [2,3]rearrangements with the participation of the carbonyl group and ring opening reactions with debenzoylation of the benzoyl-stabilized cyclic sulfur ylides, 2-alkyl(or aryl)-1-benzoyl-3,4-dihydro-2-thianaphthalenes.[4] In connection with these reports, we wish to communicate the novel thermal reactions, solvent uptake, and spiro-compound formation of cyano-stabilized cyclic sulfur ylides, 1-cyano-3,4-dihydro-2-thianaphthalenes(3a-c).

The ylides 3a-c were prepared as shown in Scheme I.

Scheme I



1a:R=H(y.76.4%)
1b:R=CH_3(y.92.3%)

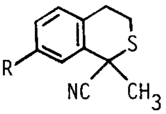
2a:R=H,R'=CH_3(y.quant.)
2b:R=CH_3,R'=CH_3(y.78.9%)
2c:R=H,R'=C_2H_5(y.66.9%)

3a:R=H,R'=CH_3(y.quant.)
3b:R=CH_3,R'=CH_3(y.quant.)
3c:R=H,R'=C_2H_5(y.quant.)

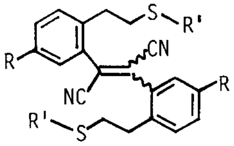
The ylides 3a and 3b were obtained as stable white powders [3a: mp 131-132°(dec.), 3b: mp 154-155°(dec.)]. However the ylide 3c was an unstable oil and gradually decomposed to the dimer 5c at room temperature.

When 2-methyl ylides 3a,b were heated in acetonitrile, dimethylformamide or benzene, Stevens type [1,2]rearranged product 4a,b, 2-thiochroman derivative 1a,b and dimer 5a,b[5] were obtained. The ylide 3c underwent β-elimination to give 1a under the similar conditions. On the contrary, the thermal reaction of the ylides 3a,b in toluene gave the unexpected products, 1-benzyl-1-cyano-2-thiochroman derivatives 6a,b together with 1a,b and 4a,b. The product 6a was identical with an authentic sample prepared by the method of Böhme et al.[6]

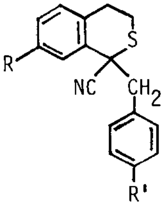
Sulfur ylides are known to undergo Stevens type [1,2]rearrangement, in which a CIDNP enhancement of the NMR signal is observed and the radical coupling products are formed. The [1,2]rearrangement proceeds via radical cage intermediates.[7] However there has been no report on the solvent participation in the rearrangement of sulfur ylides. Therefore, the thermal reactions of 3a with p-substituted toluenes were carried out. The reaction of 3a in p-xylene or p-methoxytoluene afforded 1-(p-substituted benzyl)-1-cyano-2-thiochromans 6c,d, whereas the reaction in p-nitrotoluene did not afford 1-(p-nitrobenzyl)-1-cyano-2-thiochroman. These solvent-uptake products were presumably formed in the following pathway: a methyl radical generated from 3a,b abstracts a hydrogen from toluenes and the benzyl radical thus formed reacts with 1-cyano-2-thiochromanyl radical to yield the products 6a-d.



4a:R=H
4b:R=CH_3



5a:R=H,R'=CH_3
5b:R=CH_3,R'=CH_3
5c:R=H,R'=C_2H_5



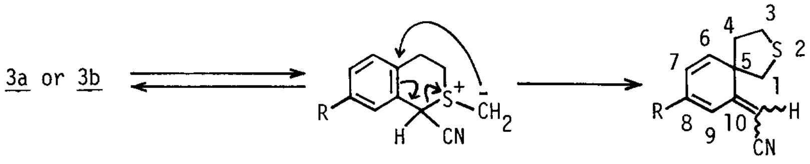
6a:R=H,R'=H
6b:R=CH_3,R'=H
6c:R=H,R'=CH_3
6d:R=H,R'=OCH_3

Table I: Thermal Reactions in Aprotic Solvents

Compd.3	Solvent	Time	Temp.	Products(Yield:%)
a	acetonitrile	60hr	reflux	4a(8.6), 5a(54.2)
a	dimethylformamide	2hr	reflux	4a(39.1), 5a(5.4)
a	benzene	5hr	reflux	1a(11.0), 4a(39.0), 5a(15.4)
b	benzene	4hr	reflux	5b(35.6)
a	toluene	4hr	reflux	1a(4.8), 4a(35.2), 6a(23.2)
b	toluene	4hr	reflux	1b(15*), 4b(39.8), 6b(29*)
c	toluene	3hr	reflux	1a(65.9)
a	p-xylene	2.5hr	reflux	4a(11*), 5a(15.5), 6c(18*)
a	p-methoxytoluene	10min	140-148°	4a(40.3), 5a(9*), 6d(9*)
a	p-nitrotoluene	10min	145-150°	4a(15.5), 5a(24.3)

* Separation of each compounds was so difficult that yields were calculated on the basis of the intensities of methyl groups in the ^1H-NMR spectrum of a mixture.

Scheme II



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8a:R=H

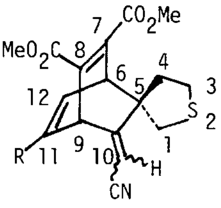
8b:R=CH_3

Table II: Thermal Reaction in Alcohol

Compd.3	Solvent	Time(hr)	Products(Yield:%)
a	ethanol	5	8a(82.7)
a	methanol	2	5a(30.3), 8a(36.0)
b	ethanol	4	8b(58.6)
c	ethanol	3	1a(82.1)

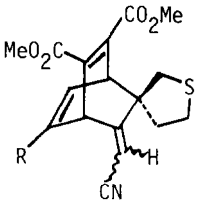
Next, we investigated the thermal reaction of the ylides in protic solvent. Refluxing the ylide 3a in ethanol or methanol afforded the spiro-compound 8a[8]: mp 91-92°; ^{1}H-NMR($CDCl_3$) δ 1.92-1.99(1H,m,4-H), 2.13-2.19(1H,m,4-H), 2.79(1H,d,J=11.2Hz,1-H), 2.96-3.08(3H,m,1-H and 3-H), 5.58(1H,s,10-CH), 6.13-6.14(2H,m,=CH), 6.32-6.36(1H,m,=CH), 6.77(1H,d,J=8Hz,=CH); ^{13}C-NMR($CDCl_3$) δ 29.1(t,4-C), 45.4, 46.0(each t,1-C and 3-C), 53.3(s,5-C), 93.9(d,C-CN), 116.8(s, CN), 121.6, 123.8, 129.4, 138.3(each d, 6-C,7-C,8-C and 9-C), 162.9(s,10-C); IR(KBr) νmax cm^{-1} 2200(CN); MS m/e 189(M^+). The structure of this novel spiro-compound was characterized by ^{13}C-NMR spectrum which exhibited a quaternary carbon at 53.3ppm. The ylide 3b also formed the spiro-compound 8b. The thermal reaction of ylide 3c in ethanol did not yield spiro-compound but eliminated product, 1-cyano-2-thiochroman(1a). The mechanism for the formation of the spiro-compound is shown in Scheme II; the ylide 3a,b isomerizes to methylide 7 in alcohol, and then methylide 7 undergoes [2,3]sigmatropic rearrangement to give spiro-compound 8a,b. This is the first example to form the spiro-compound from the thermal reactions of sulfur ylides. It is very interesting that the reaction proceeds toward the spiro-compound formation even if this process breaks the aromaticity.

Diels-Alder reaction and thermal rearrangement of the spiro-compound were carried out to confirm its structure chemically. Diels-Alder reaction of 8a with dimethyl acetylenedicarboxylate(DMAD) formed a pair of adducts 9a and 10a[9] in 19.6% and 58.5% yields, respectively.



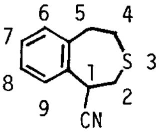
9a:R=H

9b:R=CH_3



10a:R=H

10b:R=CH_3



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8-Methyl derivative 8b reacted similarly with DMAD to give Diels-Alder adducts 9b(mp 87-88°) and 10b(mp 122°). The configration of these compounds was determined by ^{1}H-NMR; signal of a methylene between the spiro-carbon and the sulfur appeared as a singlet in 9 and as a pair of doublets in 10 owing to the anisotropy of an ester group. On the other hand, when a solution of the spiro-compound 8a in benzene was heated at 200° in a sealed tube, 8a underwent thermal isomerization to give 1-cyano-1,2,4,5-tetrahydro-3-benzothiepin 11[9] in 82.3% yield.[10]

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5) The dimers 5a-c are the mixtures of cis- and trans-isomers. Their structures were determined by the MS, ^{1}H- and ^{13}C-NMR spectra, and elemental analysis.
6) H. Böhme and U. Sitorus, Phosphorous and Sulfur, 1, 129(1976).
7) B. M. Trost, L. S. Melvin, Jr., "Sulfur Ylides" Academic Press, N.Y., 1975, Chapter 7; E. Block, "Reactions of Organosulfur Compounds" Academic Press, N.Y., 1978, p.198.
8) This spiro-compound is assumed to be a single isomer judging from its NMR spectra, and the configration of the cyano group cannot be determined by its spectral data.
9) The spectral data of these compounds are as follows: 9a: mp 156-157°; ^{1}H-NMR(CDCl$_3$) δ 1.85 (1H, ddd, J=13.2, 9.2, 7.8Hz, 4-H), 2.14(1H, ddd, J=13.2, 6.5, 3.5Hz, 4-H), 2.96(2H, s, 1-H), 2.98(1H, ddd, J=11.1, 7.8, 3.5Hz, 3-H), 3.08(1H, ddd, J=11.1, 9.2, 6.5Hz, 3-H), 3.82, 3.84(each 3H, s, CO$_2$Me), 4.21(1H, dd, J=5.7, 1.9Hz, 6-H), 5.25(1H, dd, J=5.7, 1.9Hz, 9-H), 5.37(1H, s, 10-CH), 6.60(1H, td, J=5.7, 1.9Hz, 11- or 12-H), 6.63(1H, td, J=5.7, 1.9Hz, 11- or 12-H); IR(KBr) νmax cm^{-1} 2220(CN); MS m/e 331(M$^+$). 10a: mp 156-157°; ^{1}H-NMR(CDCl$_3$) δ 1.85(1H, dt, J=13.2, 7.8Hz, 4-H), 2.00(1H, dt, J=13.2, 5.7Hz, 4-H), 2.60(1H, d, J=11.6Hz, 1-H), 2.94(1H, d, J=11.6Hz, 1-H), 2.95(2H, m, 3-H), 3.83, 3.84(each 3H, s, CO$_2$Me), 4.12(1H, dd, J=5.9, 1.4Hz, 6-H), 5.27 (1H, dd, J=5.9, 1.4Hz, 9-H), 5.45(1H, s, 10-CH), 6.56(1H, ddd, J=6.8, 5.9, 1.4Hz, 11- or 12-H), 6.63(1H, ddd, J=6.8, 5.9, 1.4Hz, 11- or 12-H); IR(KBr) νmax cm^{-1} 2220(CN); MS m/e 331(M$^+$). 11: mp 104.5-106.5°; ^{1}H-NMR(CDCl$_3$) δ 2.70-2.75(2H, m, 4-H), 2.90-3.10(2H, m, 2-H), 3.17-3.30 (1H, m, 5-H), 3.41-3.52(1H, m, 5-H), 4.50(1H, dd, J=7.3, 2.4Hz, 1-H), 7.14-7.44(4H, m, ArH); ^{13}C-NMR(CDCl$_3$) δ 29.3(t, 4-C), 32.9(t, 2-C), 39.4(t, 5-C), 41.3(d, 1-C), 118.9(s, CN), 127.4, 128.4, 128.7, 131.1(each d, 6-C, 7-C, 8-C and 9-C), 134.9, 140.4(each s, 5a-C and 9a-C); IR(KBr) νmax cm^{-1} 2240(CN); MS m/e 189(M$^+$).
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