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NOVEL RING-CLOSING REACTIONS IN THERMOLYSES OF 2-METHYLENE-1,3,4-THIADIAZOLINE DERIVATIVES

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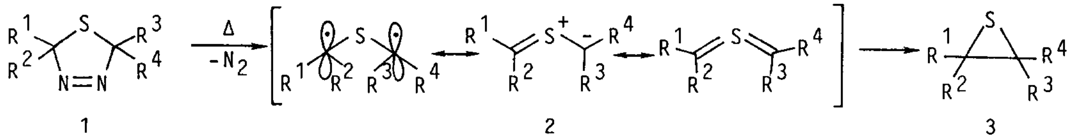
Abstract: Thermal decomposition of 2-methylene-1,3,4-thiadiazoline derivatives produced allene episulfide, benzothiophene, and divinyl sulfide derivatives via 1,3- and 1,5-diradical or thioxyallyl intermediate.

Thermal decomposition of 1,3,4-thiadiazolines(1) involves loss of nitrogen to give a thiocarbonyl ylide(2),[1] which may be described in terms of 1,3-dipole, biradical, or "tetravalent sulfur" resonance structure. The chief reactions of thiocarbonyl ylide(2) are ring closures which are used for the preparation of thiiranes(3)[1a-c,2] and formation of cycloadducts with suitable dipolarophiles.[1c,3] In view of the fascinating chemistry associated with hetero atom analogous tautomeric system of methylenecyclopropane, several attempts to prepare the analogous sulfur system[2a,4] were reported but only two allene episulfides, tetra(trifuluoromethyl)(5: R=R'=CF_3)[2a] and tetramethyl(5: R=R'=Me)[4a] derivatives have been synthesized. Thermal decomposition of 4 may be one of a good approach to produce allene episulfides. One example known of allene epiulfide formation on thermolysis of 2-methylene-1,3,4-thiadiazoline derivative(4: R=R'=CF_3), tetra(trifluoromethyl) substituted allene episulfide (5: R=R'=CF_3)[2a] was reported. Now we report nature of intermediates in thermal decomposition of some 2-methylene-1,3,4-thiadiazolines.

2-Methylene-1,3,4-thiadiazoline(4b) was synthesized by cyclic addition of 1-diazoalkene[5] with thiobenzophenone, and 4a and 4c were of diazo compounds with diphenylthioketene, respectively.[6] The results of thermolyses of 4 are shown in Table 1.

Thiadiazoline(4a) was decomposed to give products 5a and 7a in 10% and 75%, respectively. However, tetraphenylallene episulfide(5a) was not purified



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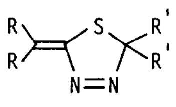

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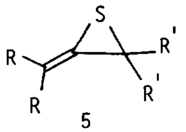

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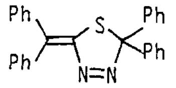
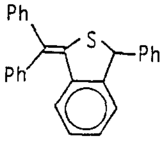
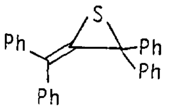
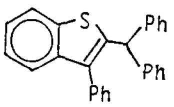
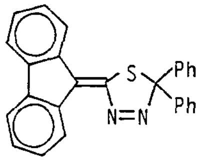
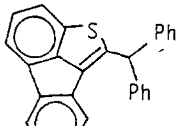
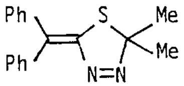
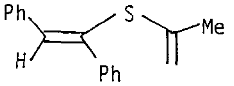
Table 1 Thermal Decomposition of 2-Methylidene-1,3,4-thiadiazoline Derivatives[7]

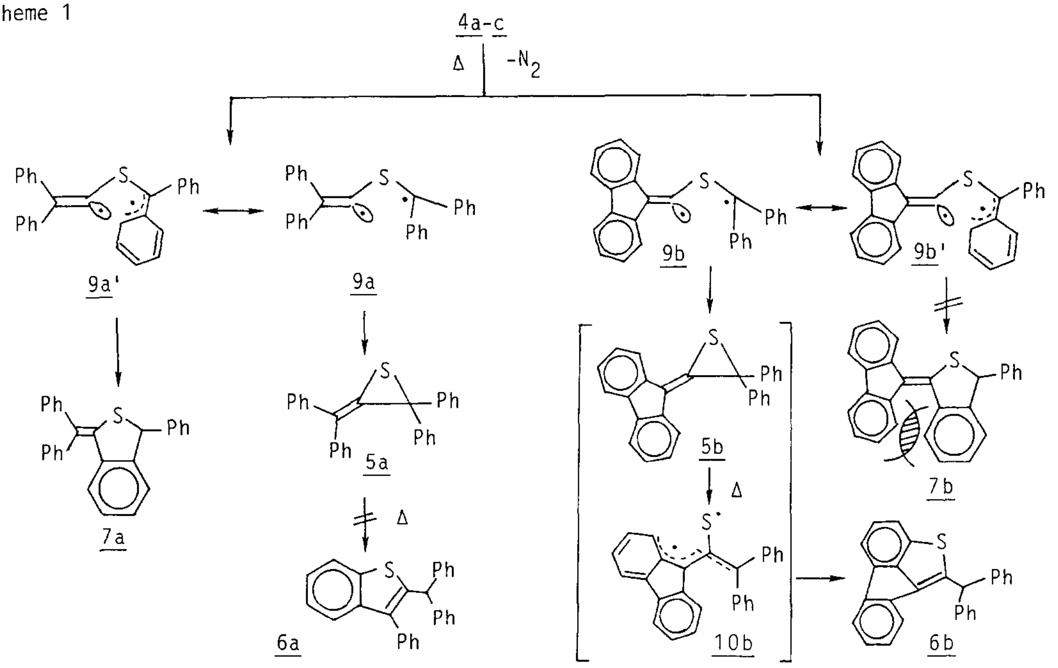
Substrate	Reaction Condition	Products (yields)
 4a	xylene reflux / 40 min	 7a(75%)[a]  5a(10%)[b]  6a[b]
 4b	xylene reflux / 3 hr	 6b(quant.)[a]
 4c	diglyme reflux / 45 min	 8(90%)[c]

a: Spectral data of products(7a and 6b) are shown in Ref.9. b: Tetraphenylallene episulfide (5a) was quantitatively isomerized to 6a when 5a was purified. See Ref.8. c: Spectral data of 8 are shown in Ref.11.

since the isomerization of 5a to 6a easily occurred quantitatively on silica gel or in HPLC.[8] Obviously, the major product was formed by the recombination of vinyl radical with phenyl group through 1,5-diradical(9a'), and the compound 5a was formed by direct cyclization of 1,3-diradical(9a)[10] as shown in Scheme 1. These results suggest that the five-membered cyclic transition state is more likely to occur than the recombination of 1,3-diradical. Similarly, decomposition of 4b gave 6b quantitatively. Expected compounds 5b and 7b were not observed in the reaction mixture. No similar ambiguity exists for 6b, which could readily be identified through an examination of its spectra. Compound 6b owes its formation to allene episulfide(5b). Decomposition of 5b leads to a thioxyallyl diradical(10b) that can give 6b by intramolecular recombination of sulfur radical with the planar fluorenyl ring. The relative difficulty in forming 7b and concomitant increase in apparent 6b formation may reflect an increased steric repulsion between a proton at peri-position of fluorenyl group and one at ortho-position of phenyl group from examination of molecular models. Thiadiazoline(4c) gave only the vinyl sulfide(8) produced through intramolecular hydrogen abstraction from methyl group.[11]

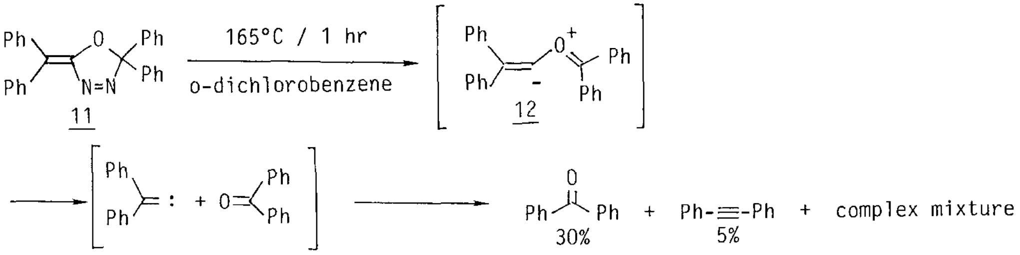
The formation of 6b led us to attempt the isolation of allene episulfide (5b). When the decomposition of 4b was carried out in the presence of p-nitrobenzaldehyde which is known to react with allene episulfide,[12] however corresponding cyclic adduct(1,3-oxathiolane derivative) could not be isolated, probably because the fast ring opening of 5b produced the biradical thioxyallyl(10b).[12b]

Scheme 1



In thermolysis of analogous oxygen system(11) benzophenone and diphenylacetylene were obtained as identified products(Scheme 2). The decomposition of carbonyl ylide(12), the suspected intermediate to vinylidene carbene might be more efficient than ring-closing to oxirane.[13]

Scheme 2



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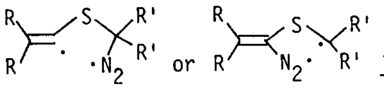
7) A solution of 4a-c(1 mmol) in 15-20 ml of dry solvent was refluxed under N_2 atmosphere and the products were purified by SiO_2 column chromatography and/or HPLC.

8) Acid-catalized isomerization of allene episulfides is now under investigation and will be reported elsewhere. 6a: ^{1}H-NMR(CDCl$_3$)δ 6.12(s,1H), 6.68-7.83(m,9H), 7.20(br.s,10H); ^{13}C-NMR(CDCl$_3$)δ 143.5(s), 138.0(s), 136.0(s), 134.7(s), 134.5(s), 130.1(s), 128.9(d), 128.8(d), 128.7(d), 128.5(d), 128.2(d), 127.1(d), 126.9(d), 124.1(d), 123.1(d), 121.1(d), 120.6(d), 50.4(d).

9) 6b: mp.160.5-162.5°C(decomp. yellow-green crystals) ^{1}H-NMR(CCl$_4$)δ 5.90 (s,1H), 6.97-8.03(m,17H); ^{13}C-NMR(CDCl$_3$)δ 147.1(s), 140.5(s), 137.1(s), 134.6(s), 134.4(s), 133.5(s), 132.0(s), 129.0(d), 128.8(d), 127.8(d), 127.4(d), 127.1(d), 125.1(d), 124.0(d), 123.2(d), 121.3(d), 120.3(d), 120.0(d), 47.1(d). Elemental Anal. Calcd for $C_{27}H_{20}S$. C: 86.59; H:4.84. Found: C:86.48; H:4.88. 7a: mp.176.5-178.0°C(light yellow needles) ^{1}H-NMR(CDCl$_3$)δ 5.71(s,1H), 6.48-7.13(m,6H), 7.21(s,5H), 7.29(br.s,8H); ^{13}C-NMR(CDCl$_3$)δ 147.1(s), 143.9(s), 142.4(s), 142.0(s), 138.7(s), 138.4(s), 131.9(s), 130.1(d), 128.9(d), 128.6(d), 128.3(d), 128.2(d), 127.7(d), 127.5 (d), 127.4(d), 127.3(d), 126.4(d), 125.9(d), 125.2(d), 55.5(d). Elemental Anal. Calcd for $C_{27}H_{20}S$. C:86.13; H:5.35. Found: C:86.14; H:5.42.

10) Another intermediate such as a diazenyl diradical (13) can not be ruled out.



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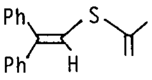
11) Although the high yield of the product is in accord with the proposed structure, and the spectra are reasonable for 8, there is a problem in differentiating 8 from 8' in which the positions of the hydrogen and phenyl group are interchanged. Detailed reaction mechanism is under investigation. 8: colorless oil. ^{1}H-NMR(CDCl$_3$)δ 2.00-2.13(m,3H), 5.10-5.33(m,2H), 7.01(s, 1H), 7.45(s,5H), 7.55(s,5H); ^{13}C-NMR(CDCl$_3$)δ 141.8(s), 141.5(s), 140.2(s), 139.1(s), 132.3(s), 129.7(d), 128.7(d), 128.2(d), 127.7(d), 127.2(d), 121.3(d), 110.0 (t), 23.5(q). Elemental Anal. Calcd for $C_{17}H_{16}S$. C:80.90; H:6.39. Found: C:80.70; H:6.32.



8'

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