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NATURE OF THIOXYALLYL INTERMEDIATE IN THE DECOMPOSITION OF ALLENE EPISULFIDE AND PYRAZOLINE-4-THIONE

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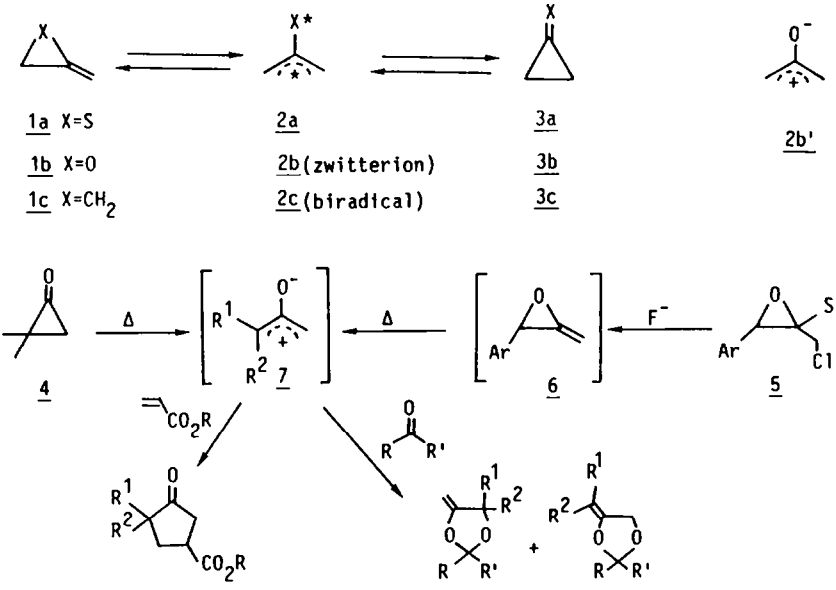
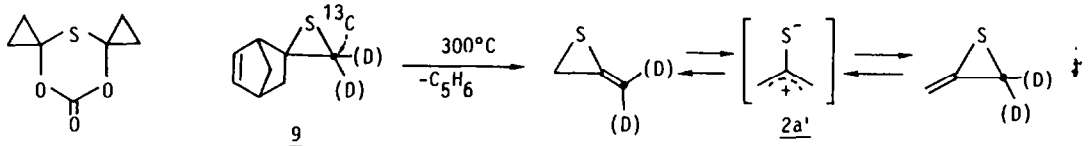
Abstract: Thermolysis of tetramethylallene episulfide(10) gave 2,4-dimethyl-3-mercaptopenta-1,3-diene(12) via thioxyallyl intermediate(13) by unimolecular C-S bond cleavage. 3,3,5,5-Tetramethylpyrazoline-4-thione(11) also gave 12 probably via the same intermediate(13), which has a biradical character.

Introduction

Tautomeric systems of methylenecyclopropane and its hetero atom analogue have attracted much attention and are still a field of current interest in the latter systems. Numerous examples of analogous oxygen system are well documented for allene oxide(1b)[1] and cyclopropanone (3b),[2] including oxyallyl intermediate(2b).[2,3] Formation of zwitterionic oxyallyl(2b') as intermediate in the reaction of cyclopropanone or allene oxide has been demonstrated by trapping the zwitterion with various reagents.[4,5]



Comparatively little is documented concerning the tautomeric reaction of analogous sulfur system, clearly because cyclopropanethione(3a) is unknown. De Boer et al.[6] suggested that in pyrolysis of carbonate(8) the formation of thermodynamically stable allene episulfide(1a) is proceeded via cyclopropanethione(3a). Block[7] proposed that a thioxyallyl ion(2a') like oxygen analogue could be formed by the pyrolysis of spiro thiirane(9). Saalfrank et al.[8] postulated the intermediacy of 2a' in the reaction of elemental sulfur with substituted allene obtained from an oxaphosphetane, but no evidence for a presence of allene episulfide and cyclopropanethione was presented. Acid catalyzed reaction of allene episulfide(10) has been recently investigated to give thiaheterocycles via thioxyallyl ion.[9] The evidence for such an intermediate was also observed by spectroscopic studies of 10 in super acid.[10]



8 9 2a'

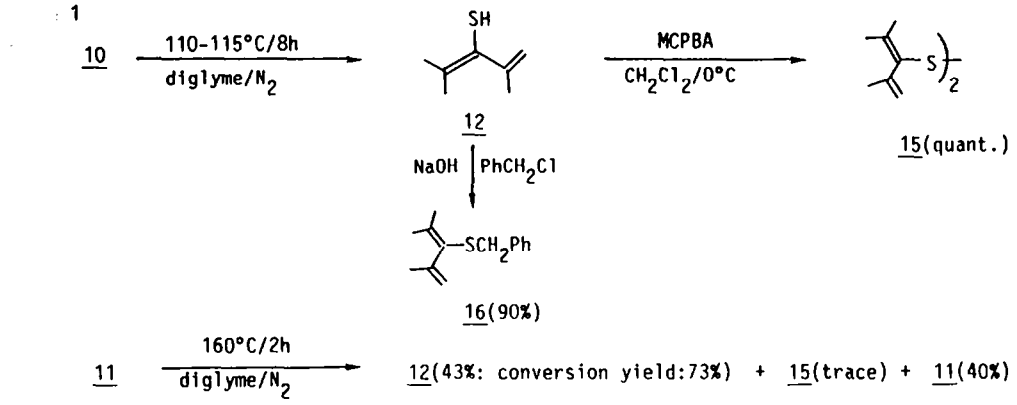
10 11

We now report that the thermal decomposition of tetramethylallene episulfide (10)[11] gives the identical product with those from 3,3,5,5-tetramethyl-Δ^1-pyrazoline-4-thione(11)[12] with attention to the effect of certain reaction variables.

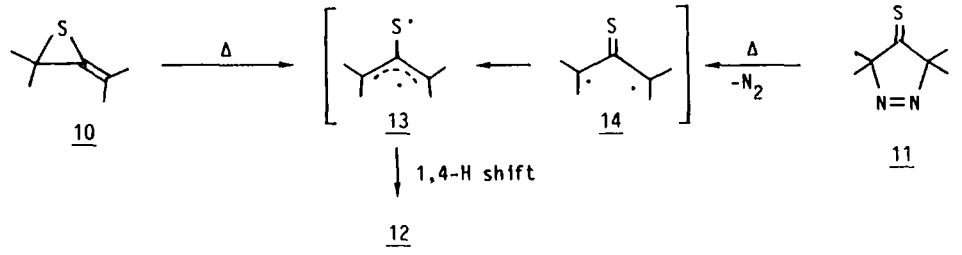
Results and Discussion

Thermolysis of tetramethylallene episulfide(10) in diglyme at 110-115°C under N_2 atmosphere for 8 h gave a brown oil with thiol smell . Chromatographic purification afforded a colorless thermally stable 2,4-dimethyl-3-mercaptopenta-1,3-diene(12) as a sole product in 69% yield which was identified by spectroscopic and analytical data. Formation of 12 can be accounted for by the initial C-S bond cleavage to produce thioxyallyl intermediate(13) followed by intramolecular 1,4-hydrogen shift. Similar observations were reported for an oxyallyl intermediate in thermal decomposition of 2,2-dimethylcyclopropanone producing α,β-enone.[13] Oxidation of compound 12 by mCPBA easily gave the corresponding disulfide(15) and the reaction with benzyl chloride in the presence of base(NaOH) yielded the corresponding benzyl vinyl sulfide(16).

Thermal denitrogenation and recombination of pyrazoline-4-thione(11) seems to be a convenient route for synthesis of cyclopropanethione(3a). When thermolysis of 11 was carried out in refluxing diglyme(162°C) under N_2 atmosphere for 2 h, 12(43%, conversion yield: 73%) and a trace of disulfide(15) were obtained with 40% of recovered 11, but not cyclopropanethione. It is attractive to speculate that the thioxyallyl might be involved via 14 in thermolysis of 11 . Intermediate (13) may be more stable than 14 which is agreed with the result of MCSCF studies of thioxyallyl intermediate we reported.[14] Similar processes have been reported in thermolysis of 3,3,5,5-tetramethylpyrazoline-4-one.[15]



Scheme 2



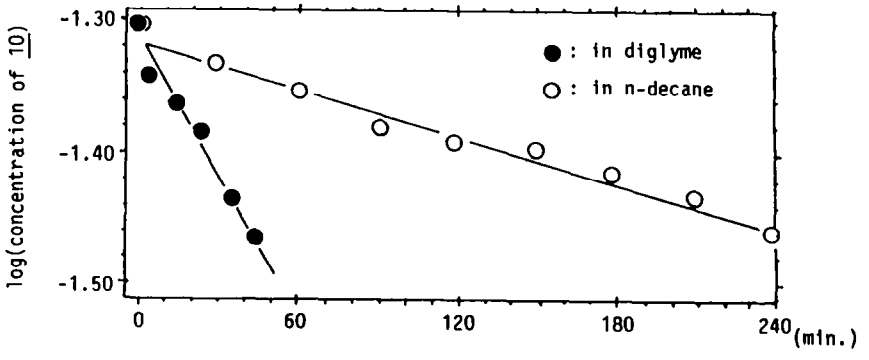
This result was different from that of photolysis of 11 at 5°C which gives only 10 in good yield and no cyclopropnethione and 12 are detected.[15a]

The major question remained is the nature of thioxyallyl intermediate. We now attempted to characterize it by kinetic studies and trapping reactions.

The rate of thermal decomposition of 10 in liquid phase was measured by GLC. The relationship between the concentration of 10 and reaction time at 130°C is given in Fig.1. First-order rate constants(k) are shown in Table 1 along with activation parameters.

The rate constant(k) in diglyme is 6 times greater than the value in n-decane and the activation energy is decreased in the polar solvent. Such

Fig.1 First-order Relationship of Logarithm(concentration of 10) vs. Reaction Time of The Thermolysis of 10 at 130°C.*



*: Decrease of concentration of 10 was measured by GLC using the 0.05M solution where about 15% of 10 was comsumed.

Table 1 Rate Constants and Activation Parameters for The Thermolysis of 10 in Diglyme and n-Decane.

	Temperature(°C)	Rata Constant k (s^{-1})	Activation Parameters
in diglyme	113.0	2.51×10^{-5}	Ea= 26.5 $kcalmol^{-1}$
	130.0	1.29×10^{-4}	$\Delta H^{\neq}$= 26.2 $kcalmol^{-1}$
	150.0	5.52×10^{-4}	$\Delta S^{\neq}$= -12.1 e.u.
in n-decane	112.0	3.14×10^{-6}	Ea= 29.7 $kcalmol^{-1}$
	130.0	2.19×10^{-5}	$\Delta H^{\neq}$= 35.9 $kcalmol^{-1}$
	150.0	1.23×10^{-4}	$\Delta S^{\neq}$= 8.8 e.u.

solvent effect may arise from the dipole moment of C-S bond in thioxyallyl intermediate. But other possibilities abound.

Furthermore, thermolysis of 10 or 11 was carried out in the presence of carbonyl compounds in order to characterize thioxyallyl(13) intermediate. Heating 10 with 10 equiv. of benzaldehyde in diglyme at 110-115°C under N_2 atmosphere for 8 h gave 1,3-oxathiolane derivative(17b) in 40% yield with 20% of mercaptopentadiene(12). Results are summarized in Table 2 for other carbonyl compounds. Disulfide(15) and dimer (20)[16] were also obtained as by-products in less than 10% total yield except run 1 and 4. In the reaction with electrophiles such as p-nitrobenzaldehyde and diphenylketene(runs 1 and 4), oxathiolanes (17a and 18) were obtained in high yields without 12 in short reaction time. With other carbonyl compounds(runs 2,3 and 5), 12 was obtained with decreasing the yields of cyclic adducts(17b, 17c and 19).

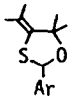
Thermal reaction of 11 were also carried out in the presence of 10 equiv. of aldehydes and results are summarized in Table 3. It is surprising to find that unlike the reaction of 10 with aldehydes, mercaptopentadiene(12) was obtained as main product, but no oxathiolanes.

Table 2 Thermolysis of Tetramethylallene Episulfide(10) with Carbonyl Compounds in Diglyme(110-115°C).

Run	Carbonyl Compounds		Reaction Time(h)	Addition Product(%)		12(%)[a]	Others[b,c]
1		X=NO_2	0.25	17a	70	0	—
2	X-⟨⟩-CHO	X=H	8.0	17b	40	20	15,20(trace)
3		X=CH_3	10.0	17c	7	65	15(5%)
4	Ph, Ph>C=C=O		1.0	18	86	0	—
5	PhCH=CHCPh (O)		11.0	19	15	75	15,20(trace)

a: GLC yield. b; By-product, 15 and 20 were obtained in less than 10% total yield.
c: The structure of dimer 20 is shown in Ref.16.

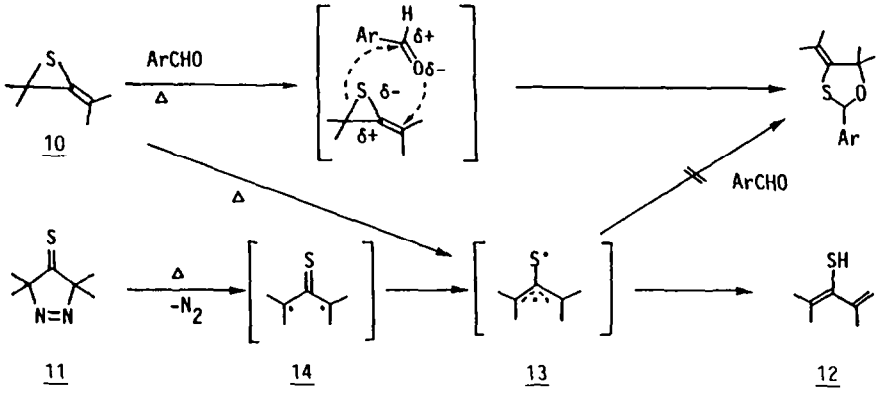
Table 3 Thermolysis of Pyrazolin-4-thione(11) with Carbonyl Compounds in Diglyme(160°C,2h).

Carbonyl Compounds	product(%)				
	 12	 15			 11
benzaldehyde	27(60)[a,b]	trace	5(10)[b,c]	0	55[a]
p-nitrobenzaldehyde	16(33)[a,b]	10(21)[b,c]	5(10)[b,c]	0	52[a]

a: GLC yields. b: Values in parentheses are conversion yields. c: Isolated yields.

These results suggest that thioxyallyl intermediate is difficult to react with aldehydes, and their reactivities are different from oxyallyl having ionic character.[17] Apparently, the formation of cyclic adducts proceeds in a different pathway from thioxyallyl intermediate(13), and can be accounted for by the mechanisms outlined in scheme 3. Although the ring opening to thioxyallyl(13) is much slow, initial attack of sulfur on carbonyl carbon followed by oxygen attack on olefin carbon of episulfide would give the oxathiolane derivatives. Nevertheless, two competing reactions, cyclization with carbonyl compounds and thermal C-S bond cleavage step were observed, when thermolysis of 10 was carried out in the presence of carbonyl compounds having electron-donating group. Alternatively thioxyallyl intermediate(13) seems to have a biradical character in contrast with the zwitterionic character of oxyallyl intermediate.

Scheme 3



Conclusion

Thioxyallyl intermediate(13) having a biradical character with some ionic nature was truely produced in thermal C-S bond cleavage of allene episulfide(10) and thermal denitrogenation of pyrazoline-4-thione(11). Formation of oxathiolanes was observed in thermal reaction of 10 with carbonyl compounds by concerted ionic reaction pathways, but not through thioxyallyl intermediate. Thioxyallyl intermediate afforded only mercaptopentadiene(12) via intramolecular 1,4-hydrogen shift.

Experimental section

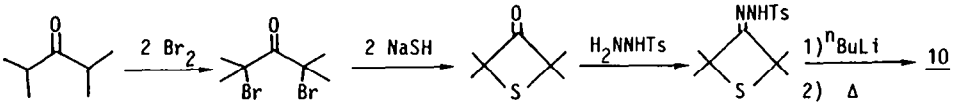
General procedure

^{1}H-NMR spectra were recorded at 60 MHz with a Varian EM-360A spectrometer; chemical shift(δ) are in parts per million downfield from internal tetramethylsilane. ^{13}C-NMR spectra were recorded on a JEOL FX-100 spectrometer. IR spectra were obtained on a Hitachi 260-50 infrared spectrometer. Mass spectra were obtained by a Hitachi RMU-6M mass spectrometer. Analytical determinations by gas-liquid chromatography(GLC) were performed on a Hitachi Model-163 with a thermal conductive detector, using glass column(3mm x 1m, 3% Silicon OV-1 oil on Celite 545). Column chromatography was performed by use of Merck Kieselgel 60(70-230 mesh).

Synthesis of Tetramethylallene Episulfide(10)

Tetramethylallene episulfide(10) was prepared according to Scheme 4.[11]

Scheme 4



2,4-Dibromo-2,4-dimethyl-3-pentanone

To a solution of 2,4-dimethyl-3-pentanone(228g, 2.0mol) in 500ml of carbon tetrachloride was added dropwise bromine(756g, 4.2mol) in 1l of carbon tetrachloride. After the addition was completed, the reaction mixture was warmed at 50°C overnight. Then the reaction mixture was cooled to room temperature and was stirred with aqueous sodium thiosulfate. The solution was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was distilled under reduced pressure to give 2,4-dibromo-2,4-dimethyl-3-pentanone(442g, 81%). bp 92-94°C/18mmHg

2,2,4,4-Tetramethyl-3-thietanone

A solution of sodium(50.3g, 2.2mol) in 1.3l of methanol was saturated with hydrogen sulfide. 2,4-Dibromo-2,4-dimethyl-3-pentanone(320g, 1.18mol) was added dropwise with stirring and continuously passed with hydrogen sulfide. During the reaction, the temperature was kept below 20°C. The reaction mixture was left at room temperature under hydrogen sulfide atmosphere overnight, then it was poured into a large excess of water, and extracted with ether. After ethereal extract was dried over anhydrous sodium sulfate, the solvent was evaporated under reduced pressure. The residue was filtered to give 2,2,4,4-tetramethyl-3-thietanone (115g, 67%). It was used for next reaction without further purification.

Tosyl Hydrazone of 2,2,4,4-Tetramethyl-3-thietanone

To a mixture of 2,2,4,4-tetramethyl-3-thietanone(115g, 0.8mol) and toluenesulfonyl hydrazide(220g, 1.19mol) was added with catalytic amount of p-toluenesulfonic acid and was stirred under reflux. After 4 days, the reaction mixture was cooled to room temperature and was filtered to give tosyl hydrazone of 2,2,4,4-tetramethyl-3-thietanone(78g, 38%).

Tetramethylallene Episulfide(10)

To a solution of tosyl hydrazone of 2,2,4,4-tetramethyl-3-thietanone(576mg, 2mmol) in 60ml of dry THF was added n-butyllithium(2mmol) at -78°C. The reaction mixture was warmed to room temperature and was transferred to round bottomed flask, and then THF was removed under reduced pressure. The flask was fitted with a cold trap(liq. nitrogen) and was carefully heated at 130-150°C under 10^{-3} Torr by use of a vacuum line. The allene episulfide 10 was collected as almost pure oil in a cold trap and was purified by trap to trap distillation (149mg, 58%). ^{1}H-NMR($CDCl_3$)δ 1.85(bs,6H), 1.70(s,6H); ^{13}C-NMR($CDCl_3$)δ 130.9, 114.2, 46.2, 28.1, 21.1, 21.0; IR(cm^{-1}, $CDCl_3$) 1738w.

Synthesis of 3,3,5,5-Tetramethylpyrazoline-4-thione(11)

Pyrazoline-4-thione(11) was produced as highly volatile red crystals by the method of R. J. Bushby.[12]

Thermolysis of Tetramethylallene Episulfide(10) in Diglyme

A solution of 10(256mg, 2mmol) in 10ml of dry diglyme was heated at 110-115°C for 6 h under N_2 atmosphere. The reaction mixture was poured into water and extracted with hexane. The hexane solution was dried and evaporated without heating. The residue oil was purified by GLC. GLC yield was 69%. ^{1}H-NMR (CCl_4)δ 1.73 (s,3H), 1.80(s,3H), 1.92(s,3H), 2.32(s,1H), 4.80(m,1H), 4.92(m,1H); ^{13}C-NMR($CDCl_3$)δ 146.6, 128.1, 123.9, 114.0, 22.0, 21.6; Mass m/e 128 (M^+).

Thermolysis of 11 in Diglyme

A solution of 11(312mg, 2mmol) in 10ml of dry diglyme was refluxed for 2 h. The products were detected by GLC and isolated. Retention time of GLC and spectroscopic data of the products were identical with those of 12 and 15.

Reaction of 12 with mCPBA and Benzyl Chloride

Mercaptopentadiene(12) was easily oxidized by equimolar amount of mCPBA in CH_2Cl_2 at 0 C to give disulfide(15) quantitatively as a colorless oil. ^{1}H-NMR ($CDCl_3$)δ 1.78(s,3H), 1.83(s,3H), 1.95(s,3H), 4.75(m,1H),5.13(m,1H); ^{13}C-NMR ($CDCl_3$)δ 142.3, 136.1, 133.3, 116.6, 23.0, 22.3, 22.2; Mass m/e 254 (M^+),

Elemental Anal. Calcd for $C_{14}H_{22}S_2$. C:66.08; H:8.71. Found: C:66.15; H:8.72.

Mercaptopentadiene(12) was reacted with equimolar amount of benzyl chloride under NaOH/MeOH condition. Benzyl vinyl sulfide(16) was given in 90% yield. ^{1}H-NMR(CCl_4)δ 1.77(s,3H), 1.90(s,3H), 3.63(s,2H), 4.67(m,1H), 5.10(m,1H), 7,27(s,5H); ^{13}C-NMR($CDCl_3$)δ 142.8, 139.0, 135.3, 130.2, 128.8, 128.2, 126.6, 115.7, 37.3, 22.3, 21.8; Elemental Anal. Calcd for $C_{14}H_{18}S$. C:77.00; H:8.30. Found: C:76.55; H:8.28.

Kinetic Study of Thermolysis of 10 in Liquid Phase

Kinetic runs were underwent by use of 0.05M solution of 10 in diglyme or n-decane. The solution was heated at 112°C, 130°C and 150°C under N_2 atmosphere. For each interval, a constant volume of the solution was withdrawn and was subjected to GLC analysis using n-octane as an internal standard, till ca.15% of 10 was consumed.

In diglyme, first-order rate constant(k) at 130°C and activation energy(Ea) were caluculated to be $1.29\times10^{-4}s^{-1}$ and $26.5kcalmol^{-1}$ from equations (1) and (2), respectively.

$$\log C = -1.31 - 5.59\times10^{-5}t \quad \text{--------(1)}$$

$$\log k = 10.452 - 5800.3T \quad \text{---------(2)}$$

In n-decane, first-order rate constant(k) at 130°C was $2.19\times10^{-5}s^{-1}$(equation (3)) and Ea=29.7kcalmol^{-1}(equation(4)).

$$\log C = -1.31 - 19.60\times10^{-6}t \quad \text{------(3)}$$

$$\log k = 11.910 - 6694.9T \quad \text{---------(4)}$$

Thermolysis of 10 in the Presence of Carbonyl Compounds

General procedure

The mixture of 10(1mmol) and benzaldehyde(10mmol) dissolved in dry diglyme (5ml) was heated for 8 h at 110-115°C under N_2 atmosphere. Removal of excess benzaldehyde and diglyme under reduced pressure gave the crude adduct(17b) which was purified by the silica gel chromatography(eluent: hexane:ether=10:1). Spectral data of adducts: 17b ^{1}H-NMR($CDCl_3$)δ1.53(s,3H), 1.70(s,3H), 1.80(s,3H), 1.87(s,3H), 6.18(s,1H), 7.23-7.33(m,5H); ^{13}C-NMR($CDCl_3$)δ 138.9, 137.8, 128.8, 126.9, 117.3, 86.0, 82.0, 27.8, 26.9, 24.6, 20.4; Mass m/e 234 (M^+); Elemental Anal. Calcd for $C_{14}H_{18}OS$. C:71.75; H:7.74. Found: C:71.53; H:7.80. 17a mp. 81.5-83.0°C(yellowish crystals) ^{1}H-NMR(CCl_4)δ1.54(s,3H), 1.71(s,3H), 1.77(s,3H), 1.84(s,3H), 6.30(s,1H), 8.04(AB,J_{AB}=9.0Hz,$\Delta\nu_{AB}$=33.0Hz,4H); ^{13}C-NMR($CDCl_3$)δ 148.0, 145.4, 137.9, 127.5, 123.9, 118.2, 86.8, 80.6, 27.7, 27.0, 24.7, 20.4; Elemental Anal. Calcd for $C_{14}H_{17}NO_3S$. C:60.19; H:6.13; N:5.01. Found: C:60.23; H:6.17; N:4.95. 17c ^{1}H-NMR(CCl_4)δ1.25(s,3H), 1.73(s,3H), 1.82(s,3H), 1.90 (s,3H), 2.33(s,3H), 4.75(s,1H), 7.17(AB,J_{AB}=6.6Hz,$\Delta\nu_{AB}$=24.9Hz,4H). 18 mp. 109-110°C(white crystal) ^{1}H-NMR(CCl_4)δ1.69(s,3H), 1.71(s,6H), 1.84(s,3H), 7.18-7.47(m,10H); ^{13}C-NMR($CDCl_3$)δ 141.5, 139.3, 133.7, 131.0, 128.5, 127.8, 126.9, 125.1, 118.4, 110.3, 90.3, 27.1, 26.1, 20.4; IR(cm^{-1},KBr) 2975, 1600, 1590, 1490; Mass m/e 322 (M^+); Elemental Anal. Calcd for $C_{21}H_{22}OS$. C:78.21; H:6.89. Found: C:77.96; H:6.87. 19 mp. 122-123°C(white crystals) ^{1}H-NMR(CCl_4)δ1.22 (s,3H), 1.36(s,3H), 1.76(s,3H), 1.88(s,3H), 4.25(d,J=12Hz,1H), 4.95(d,J=12Hz,1H), 7.17-7.88(m,10H); ^{13}C-NMR($CDCl_3$)δ 199.1, 139.5, 139.0, 138.4, 132.9, 128.5, 128.1, 127.6, 118.4, 68.4, 50.4, 49.5, 28.3, 26.2, 22.4, 20.1; Mass m/e 366 (M^+); Elemental Anal. Calcd for $C_{22}H_{22}OS$. C:78.52; H:7.18. Found: C:78.31; 7.31.

Thermolysis of 11 in the Presence of Aldehydes

The mixture of 11(2mmol) and p-nitrobenzaldehyde(20mmol) in dry diglyme(10ml) was refluxed for 2 h under N_2 atmosphere. Yields of 11 and 12 were measured by GLC. The reaction mixture was distilled under reduced pressure to remove diglyme, 11 and 12. The residue was purified by SiO_2 column chromatography to give 15 and pyrazoline-4-one.

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16) The structure of dimer(20) is as follows.

20

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