Preparation and Thermal Ring Opening of 1-(Methylthio)cyclopropenes

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The reaction of (methylthio)diphenyl- and methyl(methylthio)phenylcyclopropenium salts with Grignard reagents (methyl, 1-methylethyl, and phenyl) yielded 1-(methylthio)cyclopropenes as major products together with isomeric 3-methylthio-1-cyclopropenes in moderate total yields. Phenyllithium also reacted similarly with the salt to afford cyclopropenes in lower yields. Thermal ring opening of 1-(methylthio)cyclopropenes took place readily at room temperature or on heating at around 80 °C to give indene and/or butadiene derivatives in good yields. Product analysis of the reaction in methanol as well as kinetic studies of one of 1-(methylthio)cyclopropenes gave strong evidence for the intermediacy of vinylcarbene in the ring opening of cyclopropene.

Cyclopropenes have long intrigued chemists because of their strained structure. Indeed, extensive as well as intensive studies on preparation of new cyclopropenes,[2-5] photochemical and thermal ring opening,[6-14] and synthetic utilization of cyclopropenes[15-19] have been of continuing interest.

In continuation of our studies on the reactions of mono(alkylthio)cyclopropenium salts,[20] we found an easy route for the preparation and facile ring-opening reaction of 1-(alkylthio)cyclopropenes (**2**). In this paper we report full details of the results.

The reaction of tris(alkylthio)cyclopropenium salts with nucleophiles have been reported to yield substitution products (cyclopropenes or ring-opened products) proceeding through an addition-elimination mechanism.[19]

1-Sulfinyl- and 1-sulfonylcyclopropenes are obtained by the photolysis of the corresponding 3*H*-pyrazoles at −30 °C.[21,22] In contrast, there is no report describing any 1-alkylthiocyclopropene as a stable compound.[23,24]

Table 1. The Reaction of **1a** with PhMgBr or PhLi

Reactant /mol[a]	Reaction conditions[b] Solvent	Additive[c]	Products(Yield/%) **2a**	**3a**
PhMgBr (3)	Ether		64	23
(5)	Ether		72	5
(5)	Ether	c	69	4
(5)	THF		64	5
(5)	THF	c	55	14
PhLi (5)	Ether		39	15
(5)	Ether	c	26	11
(5)	THF		14	9
(5)	THF	c	17	0
(5)	THF[d]		0	0

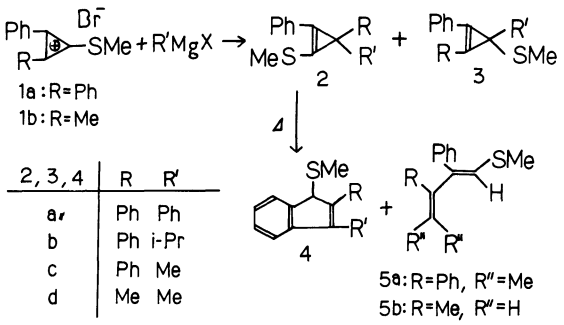
a) Moles of the reactant to one mole of **1a**. b) Reaction at room temperature otherwise noted. c) *N,N,N',N'*-Tetramethylethylenediamine (TMED, 5 mol) was added. d) At −50°C.

To a suspension of 1-methylthio-2,3-diphenylcyclopropenium bromide (**1a**)[20] in dry benzene was added phenylmagnesium bromide (3 times excess) in one portion, and the mixture was stirred giving a clean solution. After 5 min the resulting solution was quenched with ice water and the organic layer was separated. ^{1}H NMR spectroscopic analyses revealed that the crude product was a mixture of two isomeric cyclopropenes **2a** and **3a**. The major component was separated by column chromatography and confirmed to be 1-methylthio-2,3,3-triphenylcyclopropene (**2a**) on the basis of IR, ^{1}H and ^{13}C NMR, and mass spectral data. The other isomer **3a** decomposed upon attempted chromatographic separation. All attempts to improve yields or to change product ratios of **2a** and **3a** were unsuccessful as shown in Table 1. The use of phenyllithium gave large amounts of unidentified byproducts. The reaction of trisubstituted cyclopropenium salts with Grignard reagents provides a general route for the preparation of cyclopropenes.[6,9,12,14] This is indeed the case for **1a**. The reaction of **1a** with Grignard reagent in ether or THF produced 1-(alkylthio)cyclopropenes, though no change in product ratio was observed on addition of tetramethylethylenediamine (TMED).[25]

Similar treatment of **1a** and **1b** with other Grignard reagents, R'MgX, gave the corresponding cyclopropenes **2** in good yields together with isomeric cyclopropenes **3** (Table 2). Cyclopropene **3a**, which

Table 2. The Reaction of **1a** and **1b** with Grignard Reagents

1	Reactants R'MgX	Products(Yield/%)	
1a	PhMgBr	**2a**(64)	**3a**(23)
1a	*i*-PrMgBr	**2b**(90)	**3b**(0)
1a	MeMgI	**2c**(83)	**3c**(12)
1b	MeMgI	**2d**(96)	**3d**(0)
1b	PhMgBr	**2a**(82)	



Scheme 1.

could not be purified by chromatography, was independently prepared from triphenylcyclopropenium perchlorate and methanethiol in the presence of triethylamine.

An examination of the distribution of the products **2** and **3** suggests that Grignard reagents preferentially attack the carbon atom unsubstituted by sulfur, this regioselectivity being attributed to the strong electron-releasing properties of methylthio group and steric repulsion between the substituents (MeS and/or Ph) of **1** and Grignard reagents.

Tetraphenylcyclopropene rearranges at temperatures as high as 235—240 °C to give triphenylindene,[26] whereas the ring opening reaction of 1-(methylthio)-cyclopropenes **2a—d** took place easily at room temperature or on heating at 80 °C, producing indene **4** and/or butadiene derivatives **5** in good yields as shown in Table 3, although 3-(methylthio)-1,2,3-triphenylcycloprop-1-ene (**3a**) was stable even at 200 °C. The structures of the products **4a—c** and **5a,b** was confirmed on the basis of their spectroscopic studies.

Theoretical calculations suggest that the ring opening of cyclopropene proceeds directly to a diradical planar intermediate.[27,28] To explain the photolysis products of cyclopropene, a diradical and/or vinylcarbene has been postulated.[6,9,10–14,29] Few studies have been performed as to the mechanistic aspects of thermal ring opening of cyclopropenes.[30]

The relatively stable cyclopropene **2b** was subjected to precise studies for the ring-opening reaction. Thermolysis of **2b** in benzene gave indene **4b** and butadiene **5a** in a 1:1 ratio (Table 3), whereas thermolysis of **2b** in boiling methanol afforded methyl ether **6E** and **6Z** in 51% yield along with **4b** and **5a** in 43% yield. Addition of triethylamine or sodium hydroxide to the methanol solution increased the total yield of **6E** and **6Z** to a maximum of 82%. The structure of **6E** and **6Z** was confirmed by ^{1}H NMR data as well as by conversion to aldehydes **7E** and **7Z** on treatment with mercury(II) acetate in acetic acid. The stereochemistry of **6** and **7** was assigned on the assumption that the protons of a group R cis to the phenyl are shielded and appear at higher field than those of the group R trans to the phenyl.[31] The ratios of **6E** and **6Z**, and **7E** and **7Z** were determined to be 7:3 and 2:1, respectively, by ^{1}H NMR analysis, though separation of mixtures of E and Z by chromatography was unsuccessful.

Table 3. Thermolysis of **2a—d** and **3a** in Benzene

Reactant	Reaction conditions		Product(Yield/%)
	Temp/°C	Time/h	
2a	25	3	**4a**(95)
2b	80	30	**4b**(46), **5a**(44)
2c	80	2	**4c**(87)
2d	80	4	**5b**(82)
3c	200	100	Recovery

Table 4. Rate Constants for the Thermolysis of **2b**

Solvent (ε)	Temp/°C	$10^5 k_1$ s^{-1}
PhCl (5.61)	65.3	3.45±0.15
Pyridine (12.3)	65.3	2.66±0.16
PhCN (25.2)	65.3	2.77±0.13
CD_3OD (32.6)	60.2	2.69±0.10
	65.3	4.57±0.19, 4.41±0.23[a] 4.60±0.25[b]
	69.8	7.37±0.43
	75.0	11.8 ±0.43
$PhNO_2$ (34.6)	65.3	2.67±0.17
$MeNO_2$ (38.6)	65.3	3.01±0.17

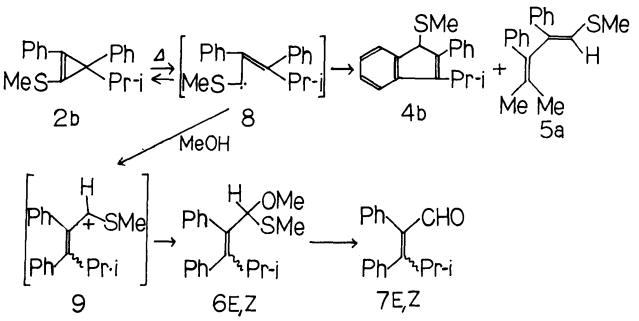
To a solution of **2b** (0.09—0.13 mol dm^{-3}) NaOD was added at a) 0.07 and b) 0.14 mol dm^{-3}.

We have performed a kinetic experiment in order to help clarify a reasonable mechanism for the ring opening of **2**. The rate was followed at suitable time intervals by analyzing the ^{1}H NMR spectra of the methylthio group of **2b** by using methyl phenyl sulfide or dimethyl sulfone internal standard. The disappearance of **2b** gave a good first-order rate constant k_1. The change of the solvent from chlorobenzene to nitromethane (ε 5.6—38.6) did not affect significantly the reaction rate (Table 4).

With regard to formation of the methyl ether, the kinetic experiment ruled out a mechanism involving a nucleophilic attack of alkoxide onto the cyclopropene ring of **2b** to give **6E** and **6Z**, since addition of sodium hydroxide to the methanol solution had no effect on the rate constants.

Tetraphenylcyclopropene has been reported to rearrange to indene with the activation energy of 167 kJ mol^{-1},[26] while the rearrangement of **2b** requires 98.6 kJ mol^{-1}.

These results indicate a sequence involving ring opening of **2b** to give a more stable vinylcarbene, stabilized by the adjacent alkylthio group,[32] followed by intramolecular hydrogen abstraction to afford **4b**



Scheme 2.

and/or **5a**. In contrast to tetraphenylcyclopropene[26] and **3a**, the introduction of alkylthio groups on carbon-1 of the cyclopropene ring made the ring opening easier. The fact that the addtion of a base to the methanolic solution of **2b** increased the yields of methyl ethers **6E** and **6Z** might be attributable to the high reactivity of methoxide with the protonated vinylcarbene (the alkylthiocarbonium ion **9**).

Laser flash photolysis technique has provided insight on the chemistry of the carbene intermediate.[33-35] Carbene reacts with alcohols to give either C–H or O–H insertion products depending on its multiplicity.[33-35] Singlet ground state carbenes yield ethers by the reaction with alcohols.[33,34a,b,36]

It has been clarified that protonation and ylide formation mechanisms are possible for the ether generation depending on the structure of carbene.[37]

Products analyses of photochemical ring opening of 5-(alkylthio)pyrazoline[23,24] and thermal ring opening of 1-sulfinyl- and 1-sulfonylcyclopropenes[21,22] have revealed the intermediacy of thio-, sulfinyl-, and sulfonylvinylcarbenes. Furthermore, an alkoxcarbene intermediate, e.g., an oxygen analogue of **8**, has been postulated and trapped by methanol or ethanol in the photochemical reaction of nortricyclanone and related compounds.[38]

Sulfur-substituted carbenes are known to serve either as a nucleophle or an electrophile, depending on the substituent and reaction conditions.[37] We feel, though not well-founded, that **8** is protonated prior to nucleophilic attack by methanol or methoxide ion since the electron-releasing property of the methylthio group would stabilize a carbonium ion intermediate **9** as revealed in the facile ring-opening reaction of **1a** with cyclic and acyclic 1,3-diketones.[20]

In summary, an appropriate substitution of cyclopropenes with an alkylthio group permits thermally facile ring opening leading to indene and/or butadiene derivatives in good yields.

Experimental

1) General. Melting points were uncorrected. The ^{13}C FT NMR spectra were recorded either on a JEOL JNM FX-60 spectrometer (15.04 MHz) or JEOL JNM FX-90Q (22.49 MHz) and ^1H NMR spectra on a Hitachi-Perkin Elmer R-24 (60 MHz). The IR spectra were recorded on a JASCO A-3 spectrometer.

2) Preparation of (Methylthio)cyclopropenium Salts. (Methylthio)cyclopropenium salts **1** and triphenylcyclopropenium salt were prepared as previously described.[20]

3) The Reaction of Cyclopropenium Salts 1 with Grignard Reagents to Give Cyclopropenes 2 and 3. General Procedure. To a cooled suspension of **1** (3 mmol) in benzene (20 ml) was added a Grignard reagent (9 mmol or 15 mmol in ether or in THF 15 ml prepared before hand and TMED was added in some runs) for 5 min with stirring. The mixture was stirred for additional 5 min to give a clean solution. Crushed ice (30 g) was added to the solution portionwise, and the organic layer was separated and dried over sodium carbonate. The ^1H NMR and IR spectroscopic studies indicated that the crude product was a mixture of two isomeric cyclopropenes. The yields of the respective products were estimated by ^1H NMR integration using dimethyl sulfone as an inner standard and the results are shown in Table 1.

The reaction of **1a** with phenylmagnesium bromide yielded a mixture of cyclopropenes. The major product was isolated by chromatography over silica gel and identified to be 1-methylthio-1,2,3-triphenyl-1-cyclopropene (**2a**). Oil; IR(neat) 1790 cm^{-1}; ^1H NMR($CDCl_3$) δ=2.44 (3H, s, MeS) and 6.9—7.6 (15H, m, 3 Ph). **2a** was thermally unstable even at room temperature to yield **4a** (see the next section). The minor product was not isolated, but its IR and ^1H NMR spectrum indicated the presence of 3-methylthio-1,2,3-triphenylcycloprop-1-ene (**3a**) in the crude reaction product.

Independent preparation of **3a** was undertaken. A suspension of triphenylcyclopropenium perchlorate (1 mmol)in a mixture of methanethiol (3 mmol), triethylamine (2 mmol) and dry benzene (20 ml) was stirred at room temperature for 3 h. After the separation of the precipitate, the benzene solution was condensed and the residue was crystallized from hexane to yield colorless crystals of **3a** in a 67% yield. **3a**: Mp 121.5—122.5 °C; IR (KBr) 1820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.95 (3H, s, MeS) and 7.0—7.9 (15H, m, 3 Ph); MS (*m/z*) 314 (M^+). Found: C, 83.45; H, 5.77%. Calcd for $C_{22}H_{18}S$: 84.03; H, 5.77%.

The reaction of **1a** with 1-methylethylmagnesium bromide yielded 3-(1-methylethyl)-2-methylthio-1,3-diphenylcyclopropene (**2h**): Oil; IR (neat) 1780 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 and 0.92 (6H, d, *J*=7 Hz, 2Me), 2.48 (3H, s, MeS), 2.87 (1H, sept, *J*=7 Hz $Me_2C\underline{H}$), and 7.0—7.7 (10H, m, 2Ph); ^{13}C NMR ($CDCl_3$) δ=17.2 (q, MeS), 21.1 and 21.4 (q, $\underline{Me}_2CH$), 30.8 (d, $Me_2\underline{C}H$), 43.7 (s, C_3), 115.3 (s), 117.2 (s), 125.4 (d), 127.0 (d), 127.2 (d), 127.8 (d), 128.0 (d), 128.6 (d), 129.2 (s), and 145.8 (s); MS (*m/z*) 280 (M^+). Found: C, 80.54; H, 7.02%. Calcd for $C_{19}H_{20}S$: C, 81.38; H, 7.19%.

The reaction of **1a** with methylmagnesium iodide yielded two cyclopropenes. The major product was isolated over silica-gel chromatography and was found to be 3-methyl-2-methylthio-1,3-diphenylcyclopropene (**2c**): Oil; IR (neat) 1780 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.71 (3H, s, C_3-Me), 2.39 (3H, s, MeS), and 6.9—7.6 (10H, m, 2Ph); ^{13}C NMR ($CDCl_3$) δ=16.5 (q, C_3-$\underline{Me}$), 22.1 (q, MeS), 31.9 (s, C_3), 116.0 (s), 117.6 (s), 125.3 (d), 125.9 (s), 126.1 (d), 127.2 (d), 127.8 (d), 128.0 (d), and 146.8 (s); MS (*m/z*) 252 (M^+). Found: C, 80.62; H, 6.31%.

Calcd for $C_{17}H_{16}S$: C, 80.90; H, 6.38%.

The minor product was not isolated(decomposed during chromatography), but found to be 3-methyl-3-methylthio-1,2-diphenylcyclopropene (**3c**): IR (neat) 1810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.42 (3H, s, Me), 2.07 (3H, s, MeS).

The reaction of 1-methyl-2-methylthio-3-phenylcyclopropenium bromide (**1b**) with methylmagnesium iodide yielded 3,3-dimethyl-1-methylthio-2-phenylcyclopropene (**2d**) as a major product. **2d**: Oil; IR (neat) 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.39 (6H, s, 2Me), 2.54 (3H, s, MeS), and 7.1—7.5 (5H, m, Ph); MS (*m/z*) 190 (M^+). Found: C, 75.31; H, 7.42%. Calcd for $C_{12}H_{14}S$: C, 75.73; H, 7.41%.

4) Thermolysis of 2 and 3a. A solution of **2** or **3a** in benzene was heated at appropriate temperature. The reaction was checked by means of TLC (silica gel, $CHCl_3$–petroleum ether, 1:4) at suitable time intervals. After the reaction, the mixture was either chromatographed over silica gel or recrystallized from an appropriate solvent.

Upon heating at 80 °C or on standing at room temperature **2a** gave 1-methylthio-2,3-diphenylindede (**4a**): Mp 158 °C (2-propanol); ^1H NMR ($CDCl_3$) δ=1.41 (3H, s, MeS), 4.82 (1H, s, 1-CH), and 7.0—8.1 (14H, m, Arom); ^{13}C NMR ($CDCl_3$) δ=9.1 (q, MeS), 52.0 (d, C_1) , 120.3 (d), 124.1 (d), 126.0 (d), 127.2 (d), 127.5 (d), 127.6 (d), 127.9 (d), 128.6 (d), 129.4 (d), 134.6 (s), 134.9 (s), 140.7 (s), 142.0 (s), 144.1 (s), and 144.7 (s); MS (*m/z*) 314 (M^+). Found: C, 84.14; H, 5.84%. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77%.

Upon heating **2b** yielded 3-(1-methylethyl)-1-methylthio-2-phenylindede **4b** and 4-methyl-1-methylthio-2,3-diphenyl-1,3-pentadiene (**5a**). **4b**: Mp 108—109 °C (2-propanol); ^1H NMR ($CDCl_3$) δ=1.30 (3H, d, *J*=7 Hz, Me CH), 1.39 (3H, s, MeS), 1.46 (3H, d, *J*=7 Hz, MeCH), 3.32 (1H, m, Me_2CH), 4.69 (1H, s, C_1H), and 7.2—7.9 (10H, m, 2 Ph); MS (*m/z*) 280 (M^+). Found: C, 81.11; H, 7.16%. Calcd for $C_{19}H_{20}S$: C, 81.38; H, 7.19%.

5a: Mp 103—104 °C (2-propanol); ^1H NMR ($CDCl_3$) δ=1.71 (3H, s, CH_3), 1.84 (3H, s, CH_3), 2.25 (3H, s, MeS), 6.06 (1H, s, C_1–H), and 7.0—7.5 (10H, m, 2 Ph); MS (*m/z*) 280 (M^+). Found: C, 80.86; 7.09%. Calcd for $C_{19}H_{20}S$: C, 81.38; H, 7.19%.

Upon heating at 80 °C for 2 h **2c** yielded **4c** in 87% yield. 3-Methyl-1-methylthio-2-phenylindene (**4c**): Mp 89—91 °C (MeOH); ^1H NMR ($CDCl_3$) δ=1.30 (3H, s, MeS), 2.23 (3H, d, *J*=2 Hz. 3-Me), 4.72 (1H, q, *J*=2 Hz, 1-CH), and 6.9—7.8 (9H, m, Arom); ^{13}C NMR ($CDCl_3$) δ=9.2 (q, MeS), 11.8 (q, 3-Me), 52.0 (d, 1-CH), 119.0 (d), 123.7 (d), 125.8 (d), 127.1 (d), 127.5 (d), 128.2 (d), 129.1 (d), 135.5 (s), 135.9 (s), 141.4 (s), 143.9 (s), and 145.6 (s); MS (*m/z*) 252 (M^+). Found: C, 80.73; 6.43%. Calcd for $C_{17}H_{16}S$: C, 80.90; H, 6.38%.

On heating **2d** gave 3-methyl-1-methylthio-2-phenyl-1,3-butadiene (**5b**): Mp 41 °C (hexane); ^1H NMR ($CDCl_3$) δ=1.93 (3H, bs, CH_3), 2.16 (3H, s, MeS), 4.43 (1H, bs, CH), 4.80 (1H, bs, CH), 6.20 (1H, bs, CH), and 6.9—7.6 (5H, m, Ph); MS (*m/z*) 190 (M^+). Found: C, 75.51; H, 7.43%. Calcd for $C_{12}H_{14}S$: C, 75.73; H, 7.41%.

5) Thermolysis of 2b in Methanol. A solution of **2b** (200 mg) in methanol (10 ml) was heated at reflux and the reaction was monitored by means of TLC (silica gel, chloroform–petroleum ether, 1:4). After the reaction (24 h) the mixture was condensed and chromatographed over silica gel to give two mixtures. The former elution was a mixture of **4b** and **5a** in 43% yield, products from thermolysis of **2b**, and the latter was a mixture of (*E*)- and (*Z*)-1-methoxy-4-methyl-1-methylthio-2,3-diphenyl-2-pentenes (**6E**) and (**6Z**). Although the separation of the two methyl ethers by chromatography was unsuccessful, ^1H NMR spectra of the mixture showed two groups of signals corresponding to **6E** and **6Z** in a ratio of 3:7. **6E**: ^1H NMR ($CDCl_3$) δ=0.98 and 1.00 (6H, d, *J*=7 Hz, Me_2CH), 2.13 (3H, s, MeS), 2.5—3.2 (1H, m, Me_2CH), 3.46 (3H, s, MeO), 5.29 (1H, s, CH), and 6.6—7.6 (10H, m, 2Ph). **6Z**: δ=0.78 (6H, d, *J*=7 Hz, Me_2), 1.75 (3H, s, MeS), 2.5—3.2 (1H, m, Me_2CH), 3.16 (3H, s, MeO), 4.56 (1H, s, CH), and 6.6—7.6 (10H, m, 2 Ph). MS (*m/z*) 312 (M^+). Found: C, 76.75; H, 7.78%. Calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.74%.

Desulfurization of a mixture of **6E** and **6Z** with mercury(II) acetate in aqueous chloroform (bilayers reaction) gave a mixture of two aldehydes (*E*)- and (*Z*)-4-methyl-2,3-diphenyl-2-pentenal (**7E** and **7Z**) in a 58% yield. ^1H NMR spectrum of the mixture ($CDCl_3$) showed two sets of signals: δ=1.05 (6H, d, *J*=7 Hz, Me_2), 3.83 (1H, sept, *J*=7 Hz, Me_2CH), and 10.18 (1H, s, CHO), and 0.85 (6H, d, *J*=7 Hz, Me_2), 2.72 (1H, sept, *J*=7 Hz, Me_2CH), and 9.13 (1H, s, CHO) corresponding to **7E** and **7Z** (2:1) together with 6.4—7.5 (m, Ph); MS (*m/z*) 222 (M^+). Found: C, 86.94; H, 7.28%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25.

Addition of triethylamine (1 ml) or sodium hydroxide (0.3 g) to a solution of **2b** (0.2 g) in methanol (10 ml) increased the yield of the methyl ether **6** to 82% and no **4b** and **5a** were isolated.

5) Kinetic Experiment of Thermolysis of 2b. A solution of **2b** (0.09—0.13 M (1 mol dm^{-3})) and methyl phenyl sulfide or dimethyl sulfone as an inner standard in an appropriate solvent was sealed in an NMR sample tube and was kept stand in a thermostated bath (±0.1 °C); the rate was followed at suitable time intervals (at least 10 times) by analyzing the ^1H NMR spectra of the methyl groups of **2b** and the internal standard by the peak-height method averaging 5 measurements. The results are summarized in Table 4.

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