

Stable Sulfur Ylides. XII.¹⁾ Reaction of 3-Alkyl(aryl)thio-silyloxydienes Derived from Stable Sulfur Ylides with Aromatic Aldehydes. Synthesis and Structure of Thiolanium Ylides

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The Lewis acid-catalyzed cyclocondensation of methylthio (or phenylthio)-silyloxydienes (**2**), easily derived from stable sulfur ylides (**1**), with several aromatic aldehydes (**3**) was investigated. Namely, in the case of boron trifluoride normal reaction products, 2,3-dihydro-4-pyrones (**4**), were obtained in good yields. Novel reaction products, thiolanium ylides (**6** and **7**), were obtained in the presence of titanium(IV) chloride. The structures of **6g** was established by X-ray crystallography.

Keywords methylthio-silyloxydiene; thiolanium ylide; 2,3-dihydro-4-pyrone; titanium(IV) chloride; X-ray crystallography; Lewis acid; boron trifluoride; aromatic aldehyde

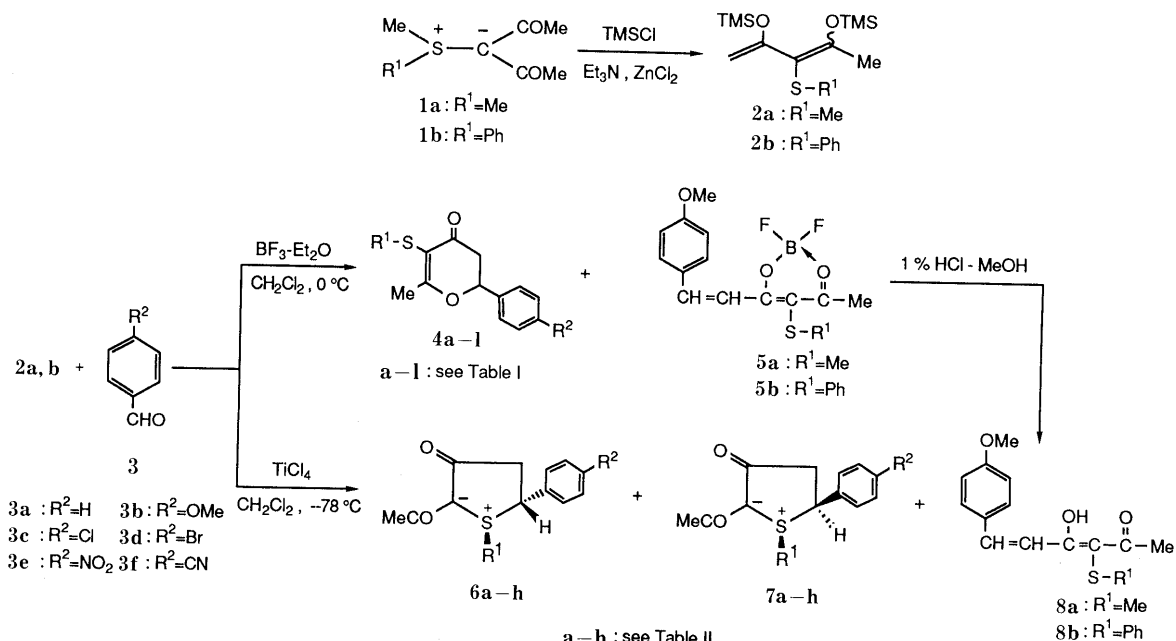
A number of dienes,²⁾ possessing a trimethylsilyloxy or methoxy group as an electron-donating group, have been prepared and widely applied to the syntheses of carbocyclic and heterocyclic compounds.³⁾ Danishefsky *et al.*⁴⁾ have reported that the reaction of silyloxydienes with aldehydes afforded 2,3-dihydro-4-pyrones using Lewis acids such as boron trifluoride and zinc chloride. Previously, we reported¹⁾ the preparation of 2,4-bis(trimethylsilyloxy)-3-methylthio (or 3-phenylthio)-1,3-pentadiene (**2a** or **2b**) by the reaction of dimethylsulfonium (or methylphenylsulfonium) diacetylmethylide (**1a** or **1b**) with chlorotrimethylsilane in quantitative yield. In this paper, we report that the reactions of silyloxydienes (**2**) with aromatic aldehydes (**3**) in the presence of several Lewis acids gave 2,3-dihydro-4-pyrone derivatives (**4**) or thiolanium ylides (**6** and **7**), and that the reaction products were affected by the Lewis acid used.

2,3-Dihydro-4-pyrones The reaction of **2a** with benzaldehyde (**3a**) in the presence of boron trifluoride gave 6-methyl-5-methylthio-2-phenyl-2,3-dihydro-4-pyrone (**4a**) in 92% yield. Similarly, 5-methylthio- (and 5-phenylthio)-4-pyrone derivatives (**4b**—**4i**) were obtained in 62—98% yields as shown in Table I. Other Lewis acids such as SnCl₄,

AlCl₃, and ZnCl₂ were examined in this reaction, and 2,3-dihydro-4-pyrones (**4a** and **4g**) were obtained in all cases. The yields were reduced, however in comparison with those obtained with boron trifluoride. In the case of the reactions of **2a** and **2b** with *p*-anisaldehyde (**3b**), styrene derivatives (**5a** and **5b**) co-ordinated with boron difluoride were isolated as by-products. The structures of **5a** and **5b** were established by elemental analyses and spectral data. These products were easily hydrolyzed to **8a** and **8b**.

Thiolanium Ylides In 1974 Mukaiyama *et al.*⁵⁾ reported that titanium (IV) chloride was a very useful catalyst for the reactions of silylenolethers with carbonyl compounds, and numerous useful compounds^{2a, b, 3c)} were prepared. Chan *et al.*^{3j, 6)} have reported the application of titanium(IV) chloride to the reaction of silyloxydienes, derived from 1,3-dicarbonyl compounds, with several dienophiles.

Therefore, we examined the reaction of **2a** with benzaldehyde (**3a**) in the presence of titanium(IV) chloride, and two products, **6a** (mp 168—170 °C) and **7a** (mp 155—157 °C), were isolated by silica gel column chromatography (Table II). The products (**6a** and **7a**) were found to have the same molecular formula of C₁₃H₁₄O₂S, corresponding to



a—h : see Table II
Chart 1

TABLE I. Reaction of **2** with **3** in the Presence of $\text{BF}_3\text{-Et}_2\text{O}$

Diene 2	Aldehyde 3	Products ^{a)} (Yield %)			
		R ¹	R ²	4	
2a	3a	Me	H	4a	(92)
2a	3b	Me	OMe	4b	(78)
2a	3c	Me	Cl	4c	(48)
2a	3d	Me	Br	4d	(96)
2a	3e	Me	NO ₂	4e	(94)
2a	3f	Me	CN	4f	(98)
2b	3a	Ph	H	4g	(69)
2b	3b	Ph	OMe	4h	(62)
2b	3c	Ph	Cl	4i	(75)
2b	3d	Ph	Br	4j	(89)
2b	3e	Ph	NO ₂	4k	(98)
2b	3f	Ph	CN	4l	(72)

a) In the case of **3b**, a styrene derivative (**5a** or **5b**) was obtained as a by-product (refer to Experimental).

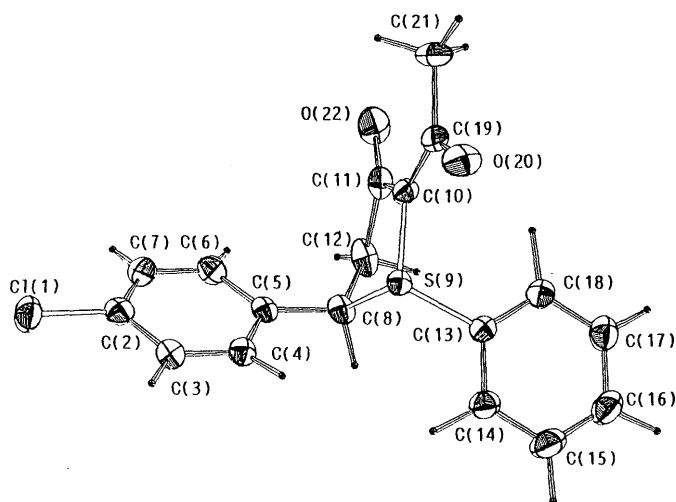
TABLE II. Reaction of **2** with **3** in the Presence of TiCl_4

Diene 2	Aldehyde 3	Products ^{a)} (Yield %)			
		R ¹	R ²	6	7
2a	3a	Me	H	6a (30)	7a (29)
2a	3b	Me	OMe	6b (33)	7b (21)
2a	3c	Me	Cl	6c (30)	7c (25)
2a	3d	Me	Br	6d (22)	7d (19)
2b	3a	Ph	H	6e (48)	7e —
2b	3b	Ph	OMe	6f (12)	7f —
2b	3c	Ph	Cl	6g (19)	7g (31)
2b	3d	Ph	Br	6h (10)	7h (30)

a) In the case of **3b**, a styrene derivative (**8a** or **8b**) was isolated (refer to Experimental).

that of the 2,3-dihydro-4-pyrone (**4a**). However, the infrared (IR) spectra of **6a** and **7a** showed no typical carbonyl absorption bands at $1650\text{--}1750\text{ cm}^{-1}$, and the ultraviolet (UV) spectra showed absorption maxima at near 230 and 280 nm, whereas 2,3-dihydro-4-pyrones showed the carbonyl absorption at $1660\text{--}1680\text{ cm}^{-1}$ and an absorption maximum at $250\text{--}260\text{ nm}$ (Tables VI and VIII). In the carbon-13 and proton correlation spectroscopy ($^{13}\text{C}\text{--}^1\text{H}$ COSY) of **6a** and **6b**, the signals of two methyl carbons (S-CH_3 and CO-CH_3), $-\text{CH}_2\text{CH}-$, quaternary carbon, and two carbonyl carbons could be identified excluding the phenyl group.

From the above-mentioned spectral data, **6a** and **7a** were presumed to be stereoisomers of thiolanium ylides. The stereochemistry of **6a** and **7a** was shown to be *trans* and *cis*, respectively, by nuclear Overhauser effect difference spectra (NOEDIF) (refer to Experimental). Similarly, thiolanium ylides (**6b**—**h** and **7b**—**h**) were obtained by the reactions of **2a** and **2b** with *p*-anisaldehyde (**3b**), *p*-chlorobenzaldehyde (**3c**), and *p*-bromobenzaldehyde (**3d**). There have been several reports⁷⁾ on the syntheses of endocyclic sulfur ylides, but this is a new synthesis of thiolanium ylide starting from a sulfur-substituted silyloxydiene. In the case of reaction of *p*-anisaldehyde (**3b**), a styrene derivative (**8a** or **8b**) was obtained as another product.

Fig. 1. Perspective View of **6g** and the Atomic NumberingTABLE III. Final Atomic Coordinates ($\times 10^5$) for **6g** with Standard Deviations in Parentheses and Equivalent Isotropic Factors

Atom	x	y	z	B
Cl(1)	1329 (16)	82026 (18)	67521 (23)	5.4 (1)
S(9)	61830 (13)	59120 (13)	85809 (15)	2.8 (1)
O(20)	63584 (51)	72603 (42)	115940 (45)	5.4 (1)
O(22)	71232 (48)	92141 (47)	68440 (60)	5.8 (1)
C(2)	18315 (56)	76324 (58)	66206 (66)	3.7 (1)
C(3)	22969 (56)	63991 (58)	73758 (66)	3.6 (1)
C(4)	36470 (55)	59442 (57)	72573 (63)	3.4 (1)
C(5)	45500 (52)	66552 (55)	64398 (58)	3.1 (1)
C(6)	40586 (58)	78637 (59)	56913 (69)	3.8 (1)
C(7)	27070 (62)	83259 (59)	57900 (74)	4.2 (1)
C(8)	60214 (56)	60978 (59)	63442 (60)	3.5 (1)
C(10)	65910 (54)	75011 (51)	87060 (63)	3.2 (1)
C(11)	69027 (56)	80654 (60)	71044 (72)	3.8 (1)
C(12)	69650 (59)	69757 (71)	56653 (66)	4.5 (1)
C(13)	76673 (54)	44978 (52)	83062 (59)	3.1 (1)
C(14)	74686 (64)	31528 (59)	81618 (73)	4.2 (1)
C(15)	85650 (73)	20163 (63)	79788 (87)	5.3 (1)
C(16)	98189 (70)	22181 (65)	79426 (85)	5.3 (1)
C(17)	99838 (64)	35604 (69)	81135 (78)	4.8 (1)
C(18)	88963 (58)	47216 (57)	82794 (68)	3.7 (1)
C(19)	65380 (60)	80032 (57)	104093 (73)	4.0 (1)
C(21)	67270 (83)	94787 (64)	106878 (96)	6.1 (1)

The absolute structures of **6** were established to *trans* thiolanium ylides in comparison with **6g**, which was confirmed to be *trans*-2-acetyl-5-(4-chlorophenyl)-3-oxo-1-phenylthiolane-2-ylide with the help of X-ray crystallographic analysis as shown in Fig. 1. The proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra of **7** exhibited at δ 2.10—2.13 and δ 5.01—5.05 due to S-CH_3 and CH signals, and these chemical shifts were abnormal compared with those of **6**. This phenomenon could be explained in terms of the magnetic anisotropic effect of the phenyl group, the free rotation of which was inhibited by steric hindrance. Therefore, the S-CH_3 group existed over the plane of the phenyl group and the CH group was in the same plane.

The reaction pathways for the formation of ylides (**6** and **7**) and the styrene derivative (**8**) are postulated to be as shown in Chart 2. Initially, the aldehyde-titanium chloride complex (**3-Ti**) reacts with the diene (**2**) to give an intermediate (**I**). The ylides would be formed *via* path a: the

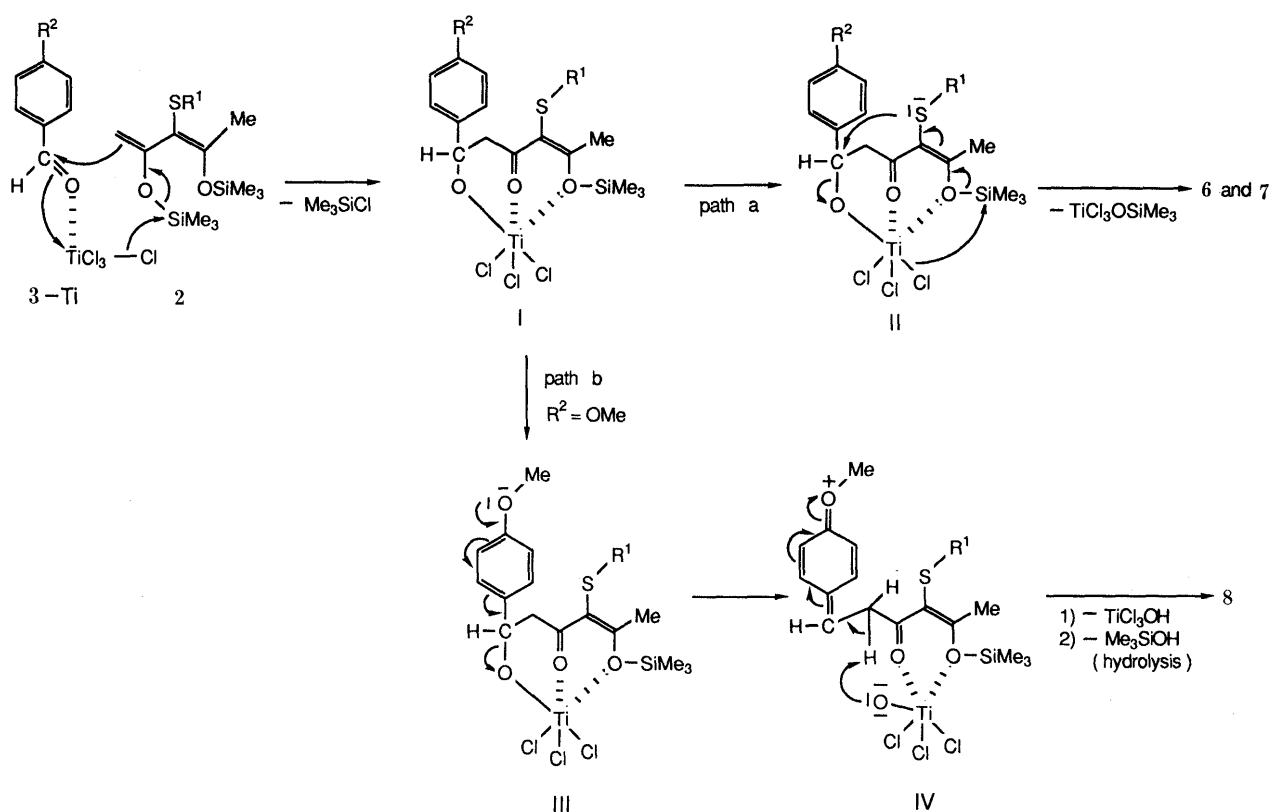


Chart 2

TABLE IV. Bond Lengths (Å) for **6g** with Standard Deviations in Parentheses

Bond	Distance	Bond	Distance
Cl(1)-C(2)	1.730 (6)	C(6)-C(7)	1.378 (9)
S(9)-C(8)	1.871 (6)	C(8)-C(12)	1.493 (9)
S(9)-C(10)	1.726 (6)	C(10)-C(11)	1.425 (8)
S(9)-C(13)	1.797 (6)	C(10)-C(19)	1.443 (9)
O(20)-C(19)	1.226 (8)	C(11)-C(12)	1.546 (9)
O(22)-C(11)	1.220 (8)	C(13)-C(14)	1.395 (9)
C(2)-C(3)	1.404 (8)	C(13)-C(18)	1.369 (8)
C(2)-C(7)	1.346 (9)	C(14)-C(15)	1.38 (1)
C(3)-C(4)	1.373 (8)	C(15)-C(16)	1.38 (1)
C(4)-C(5)	1.375 (8)	C(16)-C(17)	1.38 (1)
C(5)-C(6)	1.389 (8)	C(17)-C(18)	1.392 (9)
C(5)-C(8)	1.507 (8)	C(19)-C(21)	1.53 (1)

TABLE V. Bond Angles (°) for **6g** with Standard Deviations in Parentheses

C(8)-S(9)-C(10)	92.7 (3)	S(9)-C(10)-C(19)	114.0 (4)
C(8)-S(9)-C(13)	102.0 (3)	C(11)-C(10)-C(19)	132.6 (5)
C(10)-S(9)-C(13)	109.6 (3)	O(22)-C(11)-C(10)	126.8 (6)
Cl(1)-C(2)-C(3)	118.5 (5)	O(22)-C(11)-C(12)	123.5 (6)
Cl(1)-C(2)-C(7)	121.6 (5)	C(10)-C(11)-C(12)	109.7 (5)
C(3)-C(2)-C(7)	119.8 (5)	C(8)-C(12)-C(11)	108.6 (5)
C(2)-C(3)-C(4)	118.3 (5)	S(9)-C(13)-C(14)	115.0 (5)
C(3)-C(4)-C(5)	122.5 (5)	S(9)-C(13)-C(18)	122.5 (5)
C(4)-C(5)-C(6)	117.8 (5)	C(14)-C(13)-C(18)	122.4 (6)
C(4)-C(5)-C(8)	120.0 (5)	C(13)-C(14)-C(15)	118.0 (6)
C(6)-C(5)-C(8)	122.3 (5)	C(14)-C(15)-C(16)	120.5 (7)
C(5)-C(6)-C(7)	120.4 (6)	C(15)-C(16)-C(17)	120.3 (7)
C(2)-C(7)-C(6)	121.2 (6)	C(16)-C(17)-C(18)	120.2 (6)
S(9)-C(8)-C(5)	106.7 (4)	C(13)-C(18)-C(17)	118.6 (6)
S(9)-C(8)-C(12)	102.9 (4)	O(20)-C(19)-C(10)	120.7 (6)
C(5)-C(8)-C(12)	119.3 (5)	O(20)-C(19)-C(21)	121.2 (6)
S(9)-C(10)-C(11)	113.4 (4)	C(10)-C(19)-C(21)	118.2 (6)

sulfur atom is sufficiently close to the aldehyde carbon atom for ring closure by coordination of the titanium atom with the oxygen atoms (II). When the aldehydes possess an electron-withdrawing or no substituent, path a is predominant because the ylides are obtained almost exclusively. In the case of *p*-anisaldehyde, which possesses an electron-donating substituent, two competitive routes (paths a and b) must be considered. The styrene derivative would be formed as follows: the bond fission of the aldehyde C-O bond would be affected by electron-release from the MeO-group of the aldehyde (III), and the resulting TiO^- moiety would abstract the hydrogen atom (IV) and then be hydrolyzed to give the styrene compound (8).

X-Ray Crystallography of **6g** A perspective view, final atomic coordinates, bond lengths, and bond angles of **6g** determined by X-ray crystallography are shown in Fig. 1 and Tables III, IV, and V, respectively. No abnormal bond

lengths or angles were found in the structure except C(8)-S(9). The arrangement around the sulfur atom is pyramidal in form and the carbon atom of C(10) is planar. The bond distances of connecting with the ylide carbon (10), C(10)-S(9) (1.726 Å), C(10)-C(11) (1.425 Å), and C(10)-C(19) (1.443 Å), are nearly identical with those of dimethylsulfonium dicyanomethylide⁸⁾ and correspond to the mean value of single and double bonds of C-S and C-C, respectively. The C(19)-O(20) and C(11)-O(22) distances in the ylide are 1.226 and 1.220 Å, respectively, which appear to be somewhat longer than the typical C=O distance of 1.20 Å. Therefore, the unshared electrons on the ylide carbon must be delocalized into the 3d-orbitals of the sulfur atom and the π -orbitals of the vicinal carbonyl groups. The C(13)-

S(9) distance, 1.797 Å, agrees well with the carbon–sulfur single bond distance (1.809 Å) found in dimethyl sulfide.⁹⁾ However, the C(8)–S(9) distance is longer than the mean S–C single bond distance by about 0.07 Å.¹⁰⁾

Experimental

All melting points were measured with a Yanaco micro melting point apparatus, and are uncorrected. IR spectra were measured with a JASCO IR-810 spectrophotometer. UV spectra were recorded in ethanol on a Hitachi 323 spectrophotometer. ¹H-NMR spectral measurements were carried out with a JEOL JNM FX-90Q Fourier-transform spectrometer (90 MHz). NOEDIF, ¹³C–¹H COSY, and ¹¹B-NMR were carried out with a JEOL JNM GX-400 Fourier-transform spectrometer (100 MHz for ¹³C and 128 MHz for ¹¹B). Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) as an internal and BBr₃ as an external standard. Mass spectra (MS) were taken with a JEOL JMS-DX-303 spectrometer and a JEOL JMA-DA-5000 data processor by the electron impact (EI)

ionization method.

Typical Procedure for 2,3-Dihydro-4-pyrone Derivatives (4) The following procedure for the preparation of 6-methyl-5-methylthio-2-phenyl-2,3-dihydro-4-pyrone (**4a**) is representative. Boron trifluoride (0.62 ml, 5 mmol) was added to a mixture of silyloxydiene (**2a**: 1.453 g, 5 mmol) and benzaldehyde (**3a**: 0.531 g, 5 mmol) in dry CH₂Cl₂ (10 ml) under argon at 0 °C. The resulting yellow solution was stirred at 0 °C for 3 h. The reaction mixture was poured into 3% NaHCO₃ and extracted with CHCl₃ (3 times). The combined extract was dried over MgSO₄ and concentrated to give an yellowish syrup (1.314 g). The syrup was column-chromatographed (eluent CHCl₃) to give **4a** (6-methyl-5-methylthio-2-phenyl-2,3-dihydro-4-pyrone, 1.076 g, 92%). Other 2,3-dihydro-4-pyrones (**4b**–**1**) were prepared from **2a**, **b** and **3a**–**f** in the same way as **4a**, respectively (Table I).

In the case of the reaction of **2a**, **b** with **3b**, **5a** and **5b** were obtained from the earlier fractions of column chromatography, and **5a** and **5b** were hydrolyzed to **8a** and **8b** in 95% yields by treatment with 1% HCl–MeOH at room temperature for 5 min.

Difluoro[6-(4-methoxyphenyl)-3-methylthio-5-hexene-2,4-dionato-

TABLE VI. Physical Properties and Spectral Data for 4

No.	mp, °C (Solvent) ^{a)}	Formula	Anal. Calcd (Found)				MS, <i>m/z</i> (Relative intensity)	IR (KBr) cm ⁻¹	UV λ _{max} ^{EtOH} nm (log ε)
			C	H	S	Others			
4a	47–50 (A)	C ₁₃ H ₁₄ O ₂ S	66.64 (66.57)	6.02 6.03	13.68 13.82)		234 (M ⁺ , 30) 88 (100) 43 (100)	1660 (C=O) 1560 (C=O)	262 (3.81)
4b	69–70 (A)	C ₁₄ H ₁₆ O ₃ S	63.61 (63.55)	6.10 6.11	12.13 12.18)		264 (M ⁺ , 42) 134 (100)	1660 (C=O) 1550 (C=O)	228 (4.12) 262 (3.89) 281 (3.75)
4c	177–178 (B)	C ₁₃ H ₁₃ ClO ₂ S	58.10 (57.98)	4.88 4.79	11.93 11.77)	Cl, 13.19 (13.28)	270 (M ⁺ , 27) 268 (M ⁺ , 70) 130 (66) 88 (100)	1660 (C=O) 1560 (C=O)	222 (4.16) 262 (3.82)
4d	88–90 (B)	C ₁₃ H ₁₃ BrO ₂ S	49.85 (49.80)	4.18 4.18	10.24 10.18)	Br, 25.51 (25.43)	314 (M ⁺ , 9) 312 (M ⁺ , 7) 184 (9) 88 (23) 43 (100)	1660 (C=O) 1560 (C=O)	230 (4.14) 261 (3.80)
4e	133–136 (B)	C ₁₃ H ₁₃ NO ₄ S	55.90 (56.03)	4.69 4.69	11.48 11.41)	N, 5.01 (4.95)	279 (M ⁺ , 15) 130 (16) 88 (34) 43 (100)	1660 (C=O) 1560 (C=O) 1520 (NO ₂) 1340 (NO ₂)	263 (4.25)
4f	140–143 (B)	C ₁₄ H ₁₃ NO ₂ S	64.84 (64.80)	5.05 5.14	12.36 12.22)	N, 5.40 (5.36)	259 (M ⁺ , 43) 130 (40) 88 (67) 43 (100)	2920 (CH ₃) 2230 (CN) 1660 (C=O) 1560 (C=O)	234 (4.35) 264 (3.85) 280 (3.69) 300 (3.47)
4g	100–103 (C)	C ₁₉ H ₁₈ O ₃ S	69.91 (69.78)	5.56 5.58	9.82 9.92)		326 (M ⁺ , 13) 134 (100)	1660 (C=O) 1540 (C=O)	228 (4.24) 251 (4.27)
4h	90–91 (A)	C ₁₈ H ₁₆ O ₂ S	72.95 (72.87)	5.44 5.54	10.82 10.77)		296 (M ⁺ , 30) 192 (50) 150 (62) 43 (100)	1680 (C=O) 1560 (C=O)	252 (4.20)
4i	119–121 (B)	C ₁₈ H ₁₅ ClO ₂ S	65.35 (65.33)	4.57 4.62	9.69 10.21)	Cl, 10.72 (10.80)	332 (M ⁺ , 17) 330 (M ⁺ , 44) 192 (49) 150 (62) 43 (100)	1660 (C=O) 1540 (C=O)	220 (3.68) 250 (3.62)
4j	99–100 (B)	C ₁₈ H ₁₅ BrO ₂ S	57.61 (57.07)	4.03 4.11	8.54 8.47)	Br, 21.29 (21.14)	376 (M ⁺ , 26) 374 (M ⁺ , 26) 192 (46) 150 (55) 43 (100)	1660 (C=O) 1540 (C=O)	231 (3.94) 251 (3.89)
4k	137–140 (B)	C ₁₈ H ₁₅ NO ₄ S	63.33 (63.17)	4.43 4.51	9.39 9.37)	N, 4.10 (4.03)	341 (M ⁺ , 11) 192 (12) 78 (100) 43 (99)	1670 (C=O) 1540 (C=O) 1520 (NO ₂) 1340 (NO ₂)	254 (4.37)
4l	145–147 (B)	C ₁₉ H ₁₅ NO ₂ S	71.01 (70.67)	4.70 4.84	9.98 9.82)	N, 4.36 (4.31)	321 (M ⁺ , 13) 192 (15) 78 (31) 43 (100)	2230 (CN) 1670 (C=O) 1550 (C=O)	237 (4.44) 252 (4.21) 280 (3.81)

a) (A) ether–*n*-hexane, (B) benzene–*n*-hexane, (C) ether.

O,O']boron (**5a**): 21%. mp 156–157 °C (*n*-hexane/benzene as orange needles). *Anal.* Calcd for $C_{14}H_{15}BF_2O_3S$: C, 53.87; H, 4.84; S, 10.27. Found: C, 53.79; H, 4.90; S, 10.50. IR (KBr): 1590 (C=O) cm^{-1} , UV λ_{max}^{EtOH} nm (log ϵ): 244 (3.88), 371 (4.48). MS m/z : 312 (M^+), 161 (base). 1H -NMR (90 MHz, $CDCl_3$) δ : 2.22 (3H, s, S-CH₃), 2.66 (3H, s, CO-CH₃), 3.89 (3H,

s, O-CH₃), 6.96 (2H, d, J =8.8 Hz, phenyl), 7.65 (1H, d, J =15.5 Hz, CH=CH), 7.67 (2H, d, J =8.8 Hz, phenyl), 8.16 (1H, d, J =15.5 Hz, CH=CH). ^{11}B -NMR ($CDCl_3$) δ : -16.70.

Difluoro[6-(4-methoxyphenyl)-3-phenylthio-5-hexene-2,4-dionato-*O,O'*]boron (**5b**): 36%. mp 115–117 °C (*n*-hexane/benzene as orange

TABLE VII. 1H -NMR Data for **4** in $CDCl_3$ (90 MHz)

No.	C-CH ₃	CH ₂	CH	S-CH ₃	S-C ₆ H ₅	C-C ₆ H ₅
4a	2.44, s	2.77, dd J =5.4, 16.6	2.88, dd J =12.3, 16.6	5.40, dd J =5.4, 12.3	2.21, s	7.40, s
4b	2.42, s	2.73, dd J =4.6, 16.6	2.97, dd J =12.9, 16.7	5.34, dd J =4.6, 12.9	2.20, s	6.93, d J =8.7 7.32, d J =8.7
4c	2.44, s	2.75, dd J =5.8, 16.8	2.88, dd J =11.7, 16.8	5.40, dd J =5.8, 11.7	2.20, s	7.35–7.50, m
4d	2.44, s	2.77, dd J =6.0, 16.7	2.82, dd J =11.7, 16.7	5.38, dd J =6.0, 11.7	2.20, s	7.26, d J =8.5 7.55, d J =8.5
4e	2.48, s	2.84, dd J =7.9, 16.8	2.84, dd J =11.7, 16.7	5.36, dd J =7.9, 9.6	2.21, s	7.59, d J =8.9 8.29, d J =8.9
4f	2.46, s	2.81, dd J =7.5, 16.5	2.82, dd J =9.9, 16.5	5.54, dd J =7.5, 9.9	2.21, s	7.52, d J =8.4 7.71, d J =8.4
4g	2.42, s	2.88, dd J =5.3, 16.7	2.99, dd J =11.7, 16.7	5.54, dd J =5.3, 11.7	—	7.00–7.30, m 7.42, s
4h	2.40, s	2.85, dd J =4.7, 16.7	3.08, dd J =12.2, 16.7	5.49, dd J =4.7, 12.2	—	7.00–7.25, m 6.94, d J =8.7 7.36, d J =8.7
4i	2.43, s	2.86, dd J =6.0, 16.7	2.94, dd J =11.1, 16.7	5.52, dd J =6.0, 11.7	—	6.99–7.52, m 7.39, s
4j	2.44, s	2.90, dd J =5.9, 16.8	2.95, dd J =11.0, 16.8	5.50, dd J =5.9, 11.0	—	6.85–7.40, m 7.29, d J =8.4 7.57, d J =8.4
4k	2.48, s	2.93, dd J =7.7, 16.5	2.93, dd J =9.7, 16.5	5.66, dd J =7.7, 9.7	—	7.00–7.42, m 7.29, d J =8.8 8.30, d J =8.8
4l	2.47, s	2.93, dd J =7.5, 16.5	2.94, dd J =9.6, 16.5	5.60, dd J =7.5, 9.6	—	7.00–7.35, m 7.55, d J =8.3 7.73, d J =8.3

TABLE VIII. Physical Properties and Spectral Data for **6** and **7**

No.	mp, °C (Solvent) ^a	Formula	<i>Anal.</i> Calcd (Found)				MS, m/z (Relative intensity)	IR (KBr) cm^{-1}	UV λ_{max}^{EtOH} nm (log ϵ)
			C	H	S	Others			
6a	168–170 (dec.) (B)	$C_{13}H_{14}O_2S$	66.64 (66.43)	6.02 6.03	13.68 13.55)		234 (M^+ , 53) 130 (61) 83 (93) 43 (100)	1660 (C=O) 1570 (C=O) 1380 (Ac)	220 (4.09) 228 (4.01) 283 (4.15)
6b	169–170 (dec.) (A)	$C_{14}H_{16}O_3S$	63.61 (63.29)	6.10 6.21	12.13 11.84)		264 (M^+ , 33) 161 (17) 134 (100) 43 (54)	1610 (C=O) 1560 (C=O) 1390 (Ac)	241 (4.15) 280 (4.16)
6c	185–187 (dec.) (B)	$C_{13}H_{13}ClO_2S$	58.10 (58.05)	4.88 4.87	11.93 11.82)	Cl, 13.19 (13.07)	270 (M^+ , 16) 268 (M^+ , 37) 130 (58) 88 (10)	1610 (C=O) 1580 (C=O) 1390 (Ac)	228 (4.27) 282 (4.14)
6d	184–187 (dec.) (B)	$C_{13}H_{13}BrO_2S$	49.85 (49.91)	4.18 4.22	10.24 10.11)	Br, 25.51 (25.23)	314 (M^+ , 30) 312 (M^+ , 29) 130 (60) 88 (65) 43 (100)	1600 (C=O) 1560 (C=O) 1390 (Ac)	233 (4.29) 281 (4.13)
6e	170–180 (dec.) (C)	$C_{18}H_{16}O_2S$	72.95 (72.81)	5.44 5.54	10.81 10.86)		296 (M^+ , 58) 192 (30) 150 (35)	1620 (C=O) 1560 (C=O) 1380 (Ac)	231 (4.02) 275 (3.83)
6f	133–136 (dec.) (B)	$C_{19}H_{18}O_3S$	69.91 (69.96)	5.56 5.38	9.82 9.56)		326 (M^+ , 35) 192 (20) 150 (30) 43 (100)	1610 (C=O) 1560 (C=O) 1390 (Ac)	230 (4.25) 280 (3.78)
6g	165–166 (dec.) (B)	$C_{18}H_{15}ClO_2S$	65.35 (65.34)	4.57 4.64	9.69 9.64)	Cl, 10.72 (10.58)	332 (M^+ , 20) 330 (M^+ , 49) 192 (59) 150 (72) 138 (100)	1640 (C=O) 1580 (C=O) 1390 (Ac)	239 (4.44) 275 (4.17)
6h	174–176 (dec.) (B)	$C_{18}H_{15}BrO_2S$	57.61 (57.48)	4.03 4.12	8.54 8.42)	Br, 21.29 (21.18)	376 (M^+ , 29) 374 (M^+ , 27) 192 (42)	1610 (C=O) 1580 (C=O) 1390 (Ac)	241 (4.46) 275 (4.15)

TABLE VIII. (continued)

No.	mp, °C (Solvent) ^{a)}	Formula	Anal. Calcd (Found)				MS, <i>m/z</i> (Relative intensity)	IR (KBr) cm ⁻¹	UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ)
			C	H	S	Others			
7a	155—157 (dec.) (D)	C ₁₃ H ₁₄ O ₂ S	66.64 (66.62)	6.02 6.01	13.68 13.59		234 (M ⁺ , 44) 130 (55) 88 (91) 43 (100)	1620 (C=O) 1560 (C=O) 1390 (Ac)	222 (4.16) 280 (4.16)
7b	180—182 (dec.) (D)	C ₁₄ H ₁₆ O ₃ S	63.61 (63.53)	6.10 6.10	12.13 12.20		264 (M ⁺ , 14) 134 (37) 43 (100)	1610 (C=O) 1560 (C=O) 1390 (Ac)	240 (4.26) 279 (4.21)
7c	207—208 (dec.) (B)	C ₁₃ H ₁₃ ClO ₂ S	58.10 (57.93)	4.88 4.89	11.93 11.87	Cl, 13.19 (13.01)	270 (M ⁺ , 15) 268 (M ⁺ , 37) 138 (51) 130 (59) 88 (100)	1620 (C=O) 1570 (C=O) 1400 (Ac)	230 (4.36) 279 (4.18)
7d	199—203 (dec.) (B)	C ₁₃ H ₁₃ BrO ₂ S	49.85 (49.83)	4.18 4.23	10.24 9.94	Br, 25.51 (25.32)	314 (M ⁺ , 31) 312 (M ⁺ , 30) 182 (27) 130 (58) 43 (100)	1610 (C=O) 1560 (C=O) 1390 (Ac)	234 (4.35) 279 (4.16)
7g	166—167 (dec.) (B)	C ₁₈ H ₁₅ ClO ₂ S	65.35 (65.11)	4.57 4.66	9.69 9.51	Cl, 10.72 (10.58)	332 (M ⁺ , 24) 330 (M ⁺ , 57) 192 (68) 150 (100) 138 (30)	1640 (C=O) 1560 (C=O) 1380 (Ac)	233 (4.39) 276 (4.14)
7h	174—175 (dec.) (B)	C ₁₈ H ₁₅ BrO ₂ S	57.61 (57.40)	4.03 4.13	8.54 8.47	Br, 21.29 (21.28)	376 (M ⁺ , 29) 374 (M ⁺ , 25) 192 (43) 184 (100) 43 (100)	1610 (C=O) 1580 (C=O) 1390 (Ac)	232 (4.39) 275 (4.15)

a) (A) ethyl acetate-ether, (B) ethyl acetate, (C) benzene-*n*-hexane, (D) ethyl acetate-*n*-hexane, (E) methanol, (F) ether-*n*-hexane.

TABLE IX. ¹H-NMR Data for 6 and 7 in CDCl₃ (90 MHz)

No.	CO-CH ₃	CH ₂	CH	S-CH ₃	S-C ₆ H ₅	C-C ₆ H ₅
6a	2.47, s	3.02, dd <i>J</i> =3.3, 17.2	3.50, dd <i>J</i> =8.6, 17.2	4.43, dd <i>J</i> =3.3, 8.6	2.81, s	7.38, s
6b	2.46, s	3.00, dd <i>J</i> =3.3, 17.2	3.47, dd <i>J</i> =8.6, 17.2	4.40, dd <i>J</i> =3.3, 8.6	2.79, s	6.91, d <i>J</i> =8.7 7.27, d <i>J</i> =8.7
6c	2.46, s	2.94, dd <i>J</i> =3.0, 17.2	3.50, dd <i>J</i> =8.6, 17.2	4.38, dd <i>J</i> =3.0, 8.6	2.81, s	7.22—7.45, m
6d	2.46, s	2.97, dd <i>J</i> =2.8, 17.2	3.50, dd <i>J</i> =8.5, 17.2	4.38, dd <i>J</i> =2.8, 8.5	2.82, s	7.23, d <i>J</i> =8.6 7.54, d <i>J</i> =8.6
6e	2.58, s	2.86, dd <i>J</i> =2.3, 16.6	3.26, dd <i>J</i> =8.3, 16.6	4.38, dd <i>J</i> =2.3, 8.3	—	6.85—7.57, m
6f	2.59, s	3.01, dd <i>J</i> =3.1, 16.9	3.52, dd <i>J</i> =8.6, 16.9	4.39, dd <i>J</i> =3.1, 8.6	—	6.89—7.67, m
6g	2.56, s	2.90, dd <i>J</i> =2.3, 16.6	3.34, dd <i>J</i> =8.3, 17.0	4.38, dd <i>J</i> =2.3, 8.3	7.62, s	7.38, s 7.39, s
6h	2.58, s	2.89, dd <i>J</i> =2.2, 17.0	3.33, dd <i>J</i> =8.3, 17.0	4.37, dd <i>J</i> =2.2, 8.3	7.62, s	7.28, d <i>J</i> =8.4 7.57, d <i>J</i> =8.4
7a	2.45, s	3.00, dd <i>J</i> =7.4, 16.6	3.48, dd <i>J</i> =12.3, 16.6	5.05, dd <i>J</i> =7.5, 12.3	2.11, s	7.46, br s
7b	2.45, s	2.97, dd <i>J</i> =7.5, 16.6	3.42, dd <i>J</i> =12.2, 16.6	5.05, dd <i>J</i> =7.5, 12.2	2.10, s	7.00, d <i>J</i> =8.9 7.32, d <i>J</i> =8.9
7c	2.45, s	3.00, dd <i>J</i> =7.5, 16.4	3.41, dd <i>J</i> =12.1, 16.4	5.03, dd <i>J</i> =7.5, 12.1	2.13, s	7.24—7.55, m
7d	2.45, s	3.00, dd <i>J</i> =7.6, 16.3	3.41, dd <i>J</i> =12.2, 16.3	5.01, dd <i>J</i> =7.6, 12.2	2.13, s	7.29, d <i>J</i> =8.4 7.64, d <i>J</i> =8.4
7g	2.58, s	2.86, dd <i>J</i> =7.7, 16.6	3.17, dd <i>J</i> =12.2, 16.6	5.14, dd <i>J</i> =7.7, 12.2	—	6.78—7.60, m
7h	2.58, s	2.86, dd <i>J</i> =7.4, 16.6	3.18, dd <i>J</i> =12.2, 16.6	5.11, dd <i>J</i> =7.4, 12.2	7.25—7.62, m	6.76, d <i>J</i> =8.4 7.05, d <i>J</i> =8.4

needles). Anal. Calcd for C₁₉H₁₇BF₂O₃S: C, 60.98; H, 4.56; S, 8.57. Found: C, 61.01; H, 4.66; S, 8.62. IR (KBr): 1590 (C=O) cm⁻¹. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 246 (4.27), 371 (4.51). MS *m/z*: 374 (M⁺), 161 (base). ¹H-NMR (90 MHz, CDCl₃) δ : 2.54 (3H, s, CO-CH₃), 3.86 (3H, s, O-CH₃), 6.91 (2H,

d, *J*=8.7 Hz, phenyl), 7.00—7.39 (5H, m, S-phenyl), 7.46 (1H, d, *J*=15.4 Hz, CH=CH), 7.58 (2H, d, *J*=8.7 Hz, phenyl), 8.20 (1H, d, *J*=15.4 Hz, CH=CH). ¹¹B-NMR (CDCl₃) δ : -16.55.

Typical Procedure for Thiolanium Ylides (6 and 7) The following pro-

cedure for the preparation of thiolanium ylides (**6a** and **7a**) is representative. Titanium(IV) chloride (0.55 ml, 5 mmol) was added to a mixture of silyloxydiene (**2a**; 1.453 g, 5 mmol) and benzaldehyde (**3a**; 0.531 g, 5 mmol) in dry CH_2Cl_2 (10 ml) under argon at -78°C . The resulting dark brown solution was stirred at -78°C for 3 h, then allowed to warm to room temperature and stirred overnight. The reaction mixture was neutralized with 3% NaHCO_3 and the whole was extracted with CHCl_3 (3 times). The combined extract was dried over MgSO_4 and the solvent was evaporated to give a yellowish syrup (0.785 g). The syrup was column-chromatographed on a silica gel column (eluent 0.5% MeOH in CHCl_3) to give thiolanium ylide (**6a**; the former fractions, 0.351 g, 30% and **7a**; the later fractions, 0.339 g, 29%). Other thiolanium ylides (**6b–h** and **7b–h**) were prepared from **2a**, **b** and **3b–d** in the same way as **6a** and **7a**, respectively (Table II). In the case of the reaction of **2** with **3b**, **8a** and **8b** were obtained from the earlier fractions of column chromatography.

trans-2-Acetyl-3-oxo-5-phenyl-1-methylthiolane-2-ylide (**6a**): NOEDIF: 2.81→3.50 (0.6%), 4.43 (2.7%); 3.02→3.50 (25.2%); 3.50→3.02 (25.9%), 4.43 (10.1%); 4.43→2.81 (4.2%), 3.50 (5.5%). ^{13}C -NMR (100 MHz, CDCl_3 , C–H COSY) δ : 26.54 (CO– CH_3), 30.40 (S– CH_3), 43.59 (CH_2), 52.54 (CH), 92.13 (C-2), 127.31, 129.61, 129.72 and 135.83 (phenyl), 185.54 (C=O(3)), 190.40 (CH_3 –C=O).

cis-2-Acetyl-3-oxo-5-phenyl-1-methylthiolane-2-ylide (**7a**): NOEDIF: 2.11→3.00 (0.2%), 3.48 (0.9%), 5.05 (0.1%); 3.00→3.48 (24.5%), 5.05 (9.6%); 3.48→3.00 (26.1%); 5.05→3.00 (5.2%). ^{13}C -NMR (100 MHz, CDCl_3 , C–H COSY) δ : 23.20 (S– CH_3), 26.78 (CO– CH_3), 39.08 (CH_2), 49.90 (CH), 94.77 (C-2), 128.28, 129.92, 130.19 and 130.38 (phenyl), 185.26 (C=O(3)), 190.28 (CH_3 –C=O).

6-(4-Methoxyphenyl)-3-methylthio-5-hexene-2,4-dione (**8a**): 23%. mp 84 – 86°C (methanol). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_5\text{S}$: C, 63.61; H, 6.10; S, 12.13. Found: C, 63.5; H, 6.09; S, 12.04. IR (KBr): 1600 (C=O) cm^{-1} . UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 241 (3.92), 316 (3.89), 366 (4.48). MS m/z : 326 (M^+), 134 (base). ^1H -NMR (90 MHz, CDCl_3) δ : 2.18 (3H, s, S– CH_3), 2.53 (3H, s, CO– CH_3), 3.85 (3H, s, O– CH_3), 6.93 and 7.60 (each 2H, d, $J=9.0$ Hz, phenyl), 7.64 and 7.67 (each 1H, d, $J=16.6$ Hz, CH=CH), 17.07 (1H, s, enol).

6-(4-Methoxyphenyl)-3-phenylthio-5-hexene-2,4-dione (**8b**): 51%. mp 83 – 84°C (*n*-hexane/ether). Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_5\text{S}$: C, 69.91; H, 5.56; S, 9.82. Found: C, 69.92; H, 5.65; S, 9.60. IR (KBr): 1600 (C=O) cm^{-1} . UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 246 (3.96), 370 (4.21). MS m/z : 326 (M^+), 134 (base). ^1H -NMR (90 MHz, CDCl_3) δ : 2.37 (3H, s, CO– CH_3), 3.81 (3H, s, O– CH_3), 6.86 (2H, d, $J=9.0$ Hz, phenyl), 7.00–7.42 (5H, m, S-phenyl), 7.44 (1H, d, $J=15.9$ Hz, CH=CH), 7.48 (2H, d, $J=9.0$ Hz, phenyl), 7.70 (1H, d, $J=15.9$ Hz, CH=CH), 17.29 (1H, s, enol).

X-Ray Analysis of 6g A single crystal of **6g** was obtained from *n*-hexane/ethyl acetate by vapor diffusion technique. A single crystal, with dimensions of approximately $0.1 \times 0.3 \times 0.5 \text{ mm}^3$ was used for X-ray diffraction data collection. The intensity data were collected on a Rigaku AFC-5 diffractometer with monochromated CuK_α radiation ($\lambda = 1.54178 \text{ \AA}$) using the $\omega = 2\theta$ scan method at an ω scan speed of $4^\circ/\text{min}$. The structure was solved by the direct method using the MULTAN program¹¹⁾ and was refined by the full-matrix least-squares method, minimizing the function

$$\sum_w (|F_o| - |F_c|)^2 \quad \text{with } w = 1/\sigma^2.$$

Crystal Data: **6g**; $\text{C}_{18}\text{H}_{15}\text{ClO}_2\text{S}$; $M_r = 330.838$; trichlinic; $P\bar{1}$; $a = 10.607$, $b = 9.833$, $c = 8.115 (\text{\AA})$; $Z = 2$; $D_{\text{obsd}} = 1.278$, $D_{\text{calcd}} = 1.280 \text{ g/cm}^3$; volume = $796.12 (\text{\AA}^3)$; R value = 0.0656.

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References and Notes

- 1) Part XI: S. Furukawa, J. Igarashi, K. Shima, M. Watanabe, and T. Kinoshita, *Chem. Pharm. Bull.*, **38**, 5 (1990).
- 2) a) J. K. Rasmussen, *Synthesis*, **1977**, 91; b) M. Petrizilka and J. I. Grayson, *ibid.*, **1981**, 753; c) S. M. Weinreb and R. R. Staib, *Tetrahedron*, **38**, 3087 (1982).
- 3) a) T. Ibuki, Y. Mori, and Y. Inubushi, *Chem. Pharm. Bull.*, **26**, 2442 (1978); b) D. W. Cameron, G. I. Feutrell, and P. G. McKey, *Tetrahedron Lett.*, **22**, 701 (1981); c) P. Brownbridge, *Synthesis*, **1983**, 1 and 85; d) P. J. Proteau and P. B. Hopkins, *J. Org. Chem.*, **50**, 141 (1985); e) J. P. Vacca, *Tetrahedron Lett.*, **26**, 1277 (1985); f) M. P. Johnson and C. J. Moody, *J. Chem. Soc., Perkin Trans. I*, **1985**, 71; g) B. Simoneau, J. Savard, and P. Brassard, *J. Org. Chem.*, **50**, 5434 (1985); h) T. H. Chan and D. Stössel, *ibid.*, **51**, 2423 (1986); i) T. H. Chan and C. V. C. Prasad, *ibid.*, **51**, 3012 (1986); j) T. H. Chan and P. Brownbridge, *Tetrahedron*, **37**, Suppl. I, 387 (1981).
- 4) a) S. Danishefsky, J. F. Kerwin, and S. Kobayashi, *J. Am. Chem. Soc.*, **104**, 358 (1982); b) S. Danishefsky, N. Kato, D. Askin, and J. F. Kerwin, *ibid.*, **104**, 360 (1982).
- 5) T. Mukaiyama, K. Banno, and K. Narasaka, *J. Am. Chem. Soc.*, **96**, 7503 (1974).
- 6) a) P. Brownbridge and T. H. Chan, *Tetrahedron Lett.*, **1979**, 4437; b) T. H. Chan and T. Chaly, *ibid.*, **23**, 2935 (1982); c) H. M. Wallace and T. H. Chan, *Tetrahedron*, **39**, 847 (1983); d) P. Brownbridge, T. H. Chan, M. A. Brook, and G. J. Kang, *Can. J. Chem.*, **61**, 688 (1983).
- 7) C. R. Johnson and L. J. Pepoy, *J. Org. Chem.*, **37**, 671 (1972); C. Kissel, R. J. Holland, and M. C. Caserio, *ibid.*, **37**, 2720 (1972).
- 8) A. T. Christensen and W. G. Witmore, *Acta Crystallogr., Sect. B*, **25**, 73 (1969).
- 9) W. Maier, *Angew. Chem.*, **73**, 120 (1961).
- 10) We can not discuss this point as yet, since we have not yet obtained satisfactory X-ray data for the *cis*-form (compound **7**). We discuss it elsewhere.
- 11) P. Main, S. E. Hull, L. Lessinger, G. German, J.-P. Declercq, and M. M. Woolson, MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, University of York, England and Louvain-Laveuva, Belgium, 1978.