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Generation of Nonstabilized Thiazolium and 2-Methylthiazolium Methylides

Otohiko TSUGE,* Shuji KANEMASA, and Satoru KURAOKA
Research Institute of Industrial Science, and Department of Molecular Science and Technology, Interdisciplinary Graduate School of Engineering Science, Kyushu University, Kasugakoen, Kasuga 816
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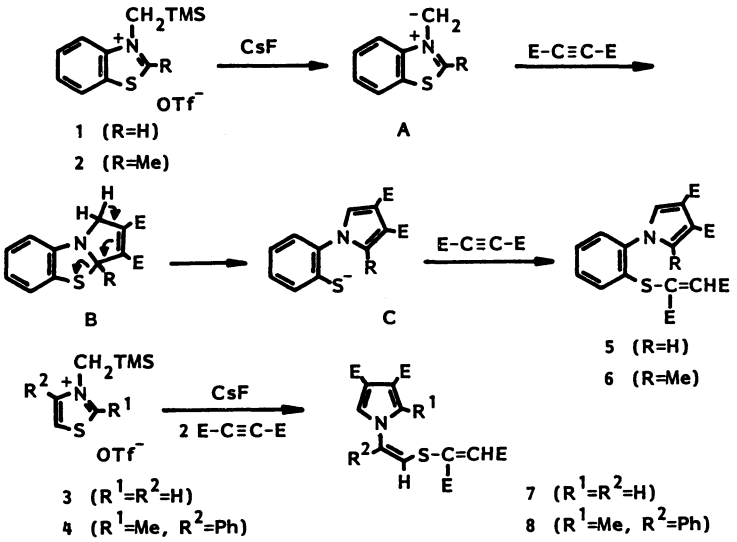
Desilylation of 3-(trimethylsilylmethyl)thiazolium triflates including 2-methyl derivatives with CsF generates the corresponding thiazolium methylides which are trapped with acetylenic and olefinic dipolarophiles. This paper presents the first example for the generation of nonstabilized thiazolium methylides including 2-methyl derivatives.

Thiazolium salts are versatile reagents in the filed of heterocyclic synthesis as their deprotonation leads to two sorts of reactive species. The deprotonation at the α-position of a highly acidic alkyl moiety on the nitrogen generates thiazolium methylides as 1,3-dipoles[1] and at the 2-alkyl substituent 2-methylenethiazolines as nucleophilic ketene acetals.[2] As shown with an example of 2-methyl-3-phenacylbenzothiazolium bromide,[3] however, even in the case of 2-methylthiazolium salts bearing a highly acidic alkyl moiety such as a phenacyl group on the nitrogen, the deprotonation occurs at the 2-methyl group leading to 2-methylenethiazolines. Thus, thiazolium methylides having 2-methyl group have not been reported up to date. In addition, nonstabilized methylides in thiazolium series, which carry no stabilizing substituents on the ylide carbon, have not been investigated, although increasing interest is recently being shown in nonstabilized nitrogen ylides.[4]

We have recently demonstrated that pyridinium triflates having a trimethylsilylmethyl group on the nitrogen generate nonstabilized pyridinium methylides when desilylated with a silylophile.[5] This method will be effectively applied to the generation of nonstabilized thiazolium methylides.

In the present paper we wish to report the generation of nonstabilized thiazolium methylides including 2-methyl derivatives from 3-(trimethylsilylmethyl)-thiazolium triflates.

When 3-(trimethylsilylmethyl)benzothiazolium triflate (**1**) and its 2-methyl derivative **2**, which were easily prepared from the corresponding thiazole and trimethylsilylmethyl triflate, were allowed to react with dimethyl acetylenedicarboxylate (DMAD, 2 equivalents) in the presence of cesium fluoride (1 equivalent) under reflux in 1,2-dimethoxyethane (DME) for 24 h, oily products **5** and **6** were obtained in 69 and 88% yields, respectively. On the basis of spectral data, the products **5** and **6**, in which two molecules of DMAD were incorporated, were assigned as a mixture of *N*-arylpyrrole compounds whose alkenylthio moieties on the phenyl group are in *E* and *Z* configurations. The NMR spectra were helpful for the structural determination since those



Scheme 1.

for the aryl moieties on the nitrogen were readily assigned by comparison with those of a model compound, a mixture of dimethyl phenylthiofumarate and -maleate obtainable from thiophenol and DMAD.[6]

As shown in Scheme 1, the formation of **5** and **6** strongly supports the intervention of a nonstabilized benzothiazolium methylide **A**. The methylide **A** is generated by the desilylation of the triflate **1** or **2**, and then **A** adds to DMAD forming a [3+2] cycloadduct **B**. The proton elimination in **B** opens the thiazoline ring to yield an anionic intermediate **C**, which is trapped with the second molecule of DMAD to give the final product **5** or **6**. The process from **B** to **C** is closely similar to that of rearrangement of intermediary [3+2] cycloadducts formed from stabilized thiazolium[1a,c] and imidazolium methylides[1a] and DMAD.

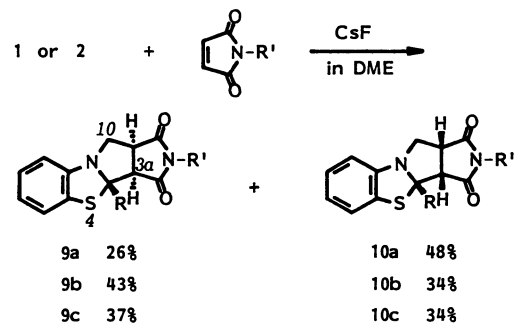
Even when an equivalent of DMAD was used in the above reaction a 1:1 adduct was not formed but instead **5** and **6** were obtained in low yields.

Under the same reaction conditions, the reaction of 3-(trimethylsilylmethyl)thiazolium triflate (**3**) and its 2-methyl-4-phenyl derivative **4** with DMAD in the presence of cesium fluoride proceeded through the same course to give the *N*-alkenylpyrroles **7** and **8** in 33 and 36% yields, respectively. In the compounds **7** and **8** the alkenylthio moieties originated from the second addition of DMAD are in *E* and *Z* forms.

Although stabilized thiazolium methylides reacted with DMAD to give rearranged products,[1a,c] they gave stable [3+2] cycloadducts in the reactions with olefinc dipolarophiles.[1d,f,h] Thus, we investigated the reaction with cyclic olefins, maleimides, in order to obtain the direct evidence for the generation of a nonstabilized thiazolium methylide through isolation of a [3+2] cycloadduct.

In fact, a nonstabilized thiazolium methylide such as **A** in the reaction with a maleimide was trapped as an isolabe [3+2] cycloadduct.

The reaction of the triflate **1** with *N*-(*p*-tolyl)maleimide or *N*-methylmaleimide (1 equivalent) in the presence of cesium fluoride (1 equivalent) in DME at room temperature for 24 h afforded a mixture of the corresponding *exo*-**9a** or **9b** and *endo*-cycloadduct **10a** or **10b**, together with recovery of the maleimide.



Scheme 2.

Under the same conditions, the triflate **2** reacted with *N*-(*p*-tolyl)maleimide in the presence of cesium fluoride to give a mixture of the *exo*- **9c** and *endo*-cycloadduct **10c** (Scheme 2). Owing to polymerization of the imide, however, [3+2] cycloadducts were not obtained in the reactions of triflates **3** and **4** under the same reaction conditions.

Structural elucidation of cycloadducts **9** and **10** was accomplished on the basis of spectral data. In the ^{1}H NMR spectra the 3a-H and 3b-H or 3b-Me in *exo*-cycloadducts **9** appeared downfield of those in *endo*-cycloadducts **10** owing to the anisotropy of 4-sulfur atom and 3-carbonyl group, respectively.

It should be emphasized that these cycloadducts are stable enough to be isolated,[7] and that these nonstereoselective cycloadditions are in contrast with the highly *endo*-selective cycloadditions of stabilized thiazolium methylides.[1d,f-h]

The present results provide the first example for the generation of nonstabilized thiazolium methylides as well as 2-methylthiazolium methylides.[8]

Experimental

General. IR spectra were obtained on a JASCO A-702 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-40 or a JEOL FX-100 instrument, and ^{13}C NMR spectra were measured on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. Mass spectra were taken with a JEOL JMS-01SG-2 spectrometer at 75 eV ionization energy. Elemental analyses were performed on a Hitachi O26 CHN micro analyzer. All reactions were carried out under dry nitrogen.

Materials. Trimethylsilylmethyl triflate was prepared according to the reported method.[9] The following reagents were commercially available: benzothiazole, 2-methylbenzothiazole, thiazole, 2-methyl-4-phenylthiazole, dimethyl acetylenedicarboxylate and *N*-(*p*-tolyl)maleimide, and *N*-methylmaleimide.

General Procedure for the Preparation of Thiazolium Triflate. A solution of a thiazole (12.7 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a solution of trimethylsilylmethyl triflate (3.0 g, 12.7 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature with stirring. After the mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo to leave pure thiazolium triflate in good yield.

3-(Trimethylsilylmethyl)benzothiazolium Triflate (1): yield 100%; mp 110—111 °C; colorless needles; IR (KBr) 1250, 1150, 1030, 850 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=0.07 (s, 9H, $(CH_3)_3Si$), 4.64 (s, 2H, CH_2), 7.75—7.98 (m, 2H, 5- and 6-**H**), 8.34—8.54 (m, 2H, 4- and 7-**H**), 10.33 (s, 1H, 2-**H**); MS *m/z* 222 (M^+), 135 (M^+-CH_2TMS, base peak). Found:

C, 38.66; H, 4.48; N, 4.06%. Calcd for $C_{12}H_{16}NO_3S_2SiF_3$: C, 38.80; H, 4.34; N, 3.77%.

2-Methyl-3-(trimethylsilylmethyl)benzothiazolium Triflate (2): yield 100%; mp 119—120 °C; colorless prisms; IR (KBr) 1250, 1150, 1025, 850 cm^{-1}; ^1H NMR (DMSO-d_6) δ=0.13 (s, 9H, $(CH_3)_3Si$), 3.31 (s, 3H, 2-CH_3), 4.53 (s, 2H, CH_2), 7.68—7.95 (m, 2H, 5- and 6-**H**), 8.24—8.45 (m, 2H, 4- and 7-**H**); MS *m/z* 236 (M^+, base peak). Found: C, 40.29; H, 4.68; N, 3.84%. Calcd for $C_{13}H_{18}NO_3S_2SiF_3$: C, 40.50; H, 4.71; N, 3.63%.

3-(Trimethylsilylmethyl)thiazolium Triflate (3): yield 94%; mp 119—120 °C; colorless prisms; IR (KBr) 1250, 1140; 1020, 845 cm^{-1}; ^1H NMR (DMSO-d_6) δ=0.08 (s, 9H, $(CH_3)_3Si$), 4.19 (s, 2H, CH_2), 8.34 (t, 2H, J=1.0 Hz, 4- and 5-**H**), 9.92 (t, 1H, J=1.0 Hz, 2-**H**); MS *m/z* 172 (M^+, base peak). Found: C, 29.94; H, 4.35; N, 4.63%. Calcd for $C_8H_{14}NO_3S_2SiF_3$: C, 29.90; H, 4.39; N, 4.36%.

2-Methyl-4-phenyl-3-(trimethylsilylmethyl)thiazolium Triflate (4): Yield 83%; mp 130—132 °C; pale yellow prisms; IR (KBr) 1250, 1145, 1025, 850 cm^{-1}; ^1H NMR (DMSO-d_6) δ=—0.14 (s, 9H, $(CH_3)_3Si$), 2.95 (s, 3H, 2-CH_3), 4.23 (s, 2H, CH_2), 7.69 (s. 5H, Ar**H**), 8.18 (s, 1H, 5-**H**); MS *m/z* 262 (M^+), 135 (base peak). Found: C, 43.51; H, 4.70; N, 3.65%. Calcd for $C_{15}H_{20}NO_3S_2SiF_3$: C, 43.78; H, 4.90; N, 3.40%.

Reaction of Triflate 1 with DMAD in the Presence of Cesium Fluoride. A mixture of **1** (371 mg, 1 mmol), DMAD (284 mg, 2 mmol) and CsF (152 mg, 1 mmol) in dry DME (3 mL) was refluxed for 24 h. To the reaction mixture was added water (30 mL), and the resultant mixture was extracted with $CHCl_3$ (50 mL×2). The $CHCl_3$ extract was dried over $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on silica gel using $CHCl_3$–Et_2O (9/1) as an eluent to give 300 mg (69%) of a mixture of *E* and *Z* forms of *N*-arylpyrrole **5** as brownish yellow viscous oil, which was thermally unstable: IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.48, 3.75 (each s, 3H×5/6, OCH_3 in *Z* form), 3.58, 3.68 (each s, 3H×1/6, OCH_3 in *E* form), 3.83 (s, 6H×5/6, OCH_3 in *Z* form), 3.85 (s, 6H×1/6, OCH_3 in *E* form), 5.75 (s, 1H×1/6, =C**H** in *E* form), 6.55 (s, 1H×5/6, =C**H** in *Z* form), 7.34—7.50 (m, 6H, Ar**H** and α-**H** of pyrrole ring); ^{13}C NMR ($CDCl_3$) of *Z* form δ=51.49, 52.02, 52.96 (each q), 116.48 (s, β-**C** of pyrrole ring), 123.17 (d, =**C**H), 127.28 (s), 129.40 (d, α-**C** of pyrrole ring), 129.75, 130.22, 134.68 (each d), 140.37 (s), 145.72 (s, =**C**^{S–}), 163.56, 163.85, 164.86 (each s, **C**=O); HRMS *m/z* 433.0841 ($C_{20}H_{19}NO_8S$ requires 433.0830).

Similarly, triflates **2—4** reacted with DMAD (2 equivalents) under the influence of CsF (1 equivalent) in dry DME under reflux for 24 h to give a mixture of *E* and *Z* forms of the corresponding pyrrole compounds **6—8**, respectively.

6: Yield 88%; red-colored viscous oil; IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.15 (s, 3H×1/11, C-CH_3 in *E* form), 2.20 (s, 3H×10/11, C-CH_3 in *Z* form), 3.48, 3.61, 3.68, 3.72 (each s, 3H×1/11, OCH_3 in *E* form), 3.52, 3.76, 3.80, 3.85 (each s, 3H×10/11, OCH_3 in *Z* form), 5.79 (s, 1H×1/11, =C**H** in *E* form), 6.65 (s, 1H×10/11, =C**H** in *Z* form), 7.17—7.50 (m, 5H, Ar**H**); MS *m/z* 447 (M^+), 356 (base peak). Found: C, 56.48; H, 4.85; N, 2.91%. Calcd for $C_{21}H_{21}NO_8S$: C, 56.37; H, 4.73; N, 3.13%.

7: Yield 33%; brownish yellow viscous oil; IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.75 (s, 3H×2/5, OCH_3 in *Z* form), 3.79 (s, 3H×3/5, OCH_3 in *E* form), 3.83 (s, 6H, OCH_3 in *E* and *Z* forms), 3.85 (s, 3H×3/5, OCH_3 in *E* form), 3.89 (s, 3H×2/5, OCH_3 in *Z* form), 5.95 (d, 1H×3/5, J=3.8 Hz, =C^{S–}**H** in *E* form), 6.04 (s, 1H×3/5, =C**H**E in *E* form), 6.05 (d, 1H×3/5, J=3.8 Hz, =C^{N<}**H** in *E* form), 6.69 (s, 1H×2/5, =C**H**E in *Z* form), 6.79 (d, 1H×2/5, J=8.6 Hz, =C^{S–}**H** in *Z* form) 6.95 (d, 1H×2/5, J=8.6 Hz, =C^{N<}**H** in *Z* form), 7.55 (s, 2H×2/5, α-**H** of pyrrole ring in *Z* form), 7.59 (s, 2H×3/5, α-H of pyrrole ring in *E* form); ^{13}C NMR ($CDCl_3$) of a mixture of *E* and *Z* forms δ=51.65, 52.19, 53.36, 53.51 (each q), 106.72, 111.54 (each d, =**C**HE), 116.81, 117.20 (each s, β-**C** of pyrrole ring), 117.23, 123.72 (each d, =**C**^{N<}**H**), 126.80, 129.52 (each d, =**C**^{S–}**H**), 127.87, 128.01 (each d, α-**C** of pyrrole ring), 143.31, 144.68 (each s, =**C**^{S–}**H**), 163.15, 163.29, 163.63, 163.83, 164.76 (each s, **C**=O); MS *m/z* 383 (M^+), 292 (base peak). Found: C, 49.88; H, 4.48; N, 3.79%. Calcd for $C_{16}H_{17}NO_8S$: C, 50.12; H, 4.47; N, 3.65%.

8: Yield 36%; brownish yellow viscous oil; IR (neat) 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.16 (s, 3H×8/9, C-CH_3 in *E* form), 2.21 (s, 3H×1/9, C-CH_3 in *Z* form), 3.74 (s, 3H×8/9, OCH_3 in *E* form), 3.76 (s, 3H×1/9, OCH_3 in *Z* form), 3.81 (s, 3H, OCH_3 in *E* and *Z* forms), 3.86 (s, 3H×8/9, OCH_3 in *E* form), 3.89 (s, 3H×1/9, OCH_3 in *Z* form), 3.91 (s, 3H, OCH_3 in *E* and *Z* forms), 6.05 (s, 1H×8/9, =C**H**E in *E* form), 6.74 (s, 1H×1/9, =C**H**E in *Z* form), 7.00—7.37 (m, 7H, Ar**H** and α-**H** of pyrrole ring); MS *m/z* 473 (M^+), 382 (base peak). Found: C, 58.34; H, 4.99; N, 3.08%. Calcd for $C_{23}H_{23}NO_8S$: C, 58.34; H, 4.86; N, 2.96%.

Reaction of Triflate 1 with Maleimide in the Presence of Cesium Fluoride. A mixture of **1** (742 mg, 2 mmol), *N*-(*p*-tolyl)maleimide (374 mg, 2 mmol) and CsF (304 mg, 2 mmol) in dry DME (6 mL) was stirred at room temperature for 24 h. To the reaction mixture was added water (30 mL), and the resultant mixture was extracted with $CHCl_3$ (50 mL×2). The extract was dried over $MgSO_4$ and concentrated *in vacuo* to leave a residue. The residue was chromatographed on silica gel to give 177 mg (26%) of the *exo*-cycloadduct **9a** (from $CHCl_3$ elution) and 323 mg (48%) of the *endo*-cycloadduct **10a** (from $CHCl_3$–Et_2O (9/1) elution), together with recovery of 90 mg (24%) of the maleimide (from $CHCl_3$ elution).

9a: Pale yellow prisms; mp 153—154 °C; IR (KBr) 1765, 1695 cm^{-1}; ^1H NMR (benzene-d_6) δ=1.99 (s, 3H, CH_3), 2.66 (ddd, 1H, J=8.7, 8.0, 3.9 Hz, 10a-**H**), 3.03 (dd, 1H, J=8.7, 2.7 Hz, 3a-**H**), 3.13 (dd, 1H, J=10.1, 8.0 Hz, 10-**H**), 3.38 (dd, 1H, J=10.1, 3.9 Hz, 10-**H**), 5.52 (d, 1H, J=2.7 Hz, 3b-**H**), 6.44—7.23 (m, 8H, Ar**H**); MS *m/z* 336 (M^+), 150 (base peak). Found: C, 68.12; H, 4.75; N, 8.17%. Calcd for $C_{19}H_{16}N_2O_2S$: C, 67.84; H, 4.79; N, 8.33%.

10a: Colorless solid; mp 69—71 °C;[10] IR (KBr) 1770, 1690 cm^{-1}; ^1H NMR (benzene-d_6) δ=1.94 (s, 3H, CH_3), 2.44 (t, 1H, J=7.8 Hz, 10a-**H**), 2.61 (t, 1H, J=7.8 Hz, 3a-**H**), 2.67 (dd, 1H, J=12.0, 7.8 Hz, 3b-**H**), 6.38—7.50 (m, 8H, Ar**H**); MS *m/z* 336 (M^+), 107 (base peak).

Similarly, **1** reacted with *N*-methylmaleimide (1 equivalent) in the presence of CsF (1 equivalent) in dry DME at

room temperature for 24 h to give the *exo*-cycloadduct **9b** and *endo*-cycloadduct **10b** in 43 and 34% yields respectively, besides recovery of the maleimide (20%).

9b: Colorless needles; mp 134—135 °C; IR (KBr) 1775, 1700 cm^{-1}; ^1H NMR (benzene-d_6) δ=2.47 (s, 3H, NCH_3), 2.52 (dt, 1H, J=3.9, 7.8 Hz, 10a-**H**), 2.92 (dd, 1H, J=7.8, 2.6 Hz, 3a-**H**), 3.08 (dd, 1H, J=10.5, 7.8 Hz, 10-**H**), 3.28 (dd, 1H, J=10.5, 5.3 Hz, 10-**H**), 5.43 (d, 1H, J=2.6 Hz, 3b-**H**) 6.45—6.94 (m, 4H, Ar**H**); MS m/z 260 (M^+), 150 (base peak). Found: C, 59.80; H, 4.61; N, 10.63%. Calcd for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65; N, 10.76%.

10b: Colorless solid; mp 116—120 °C;[10] IR (KBr) 1775, 1700 cm^{-1}; ^1H NMR (benzene-d_6) δ=2.25 (s, 3H, NCH_3), 2.32—2.62 (m, 3H, 3a-**H**, 10-**H**, and 10a-**H**), 3.87 (dd, 1H, J=12.7, 1.2 Hz, 10-**H**), 4.70 (d, 1H, J=7.7 Hz, 3b-**H**), 6.32—6.95 (m, 4H, Ar**H**); MS m/z 260 (M^+), 150 (base peak).

Reaction of Triflate **2** *with* N-*(p-Tolyl)maleimide in the Presence of Cesium Fluoride.* After the reaction of **2** (1.155 g, 3 mmol) with the maleimide (561 mg, 3 mmol) in the presence of CsF (456 mg, 3 mmol) in dry DME (9 mL) was performed at room temperature for 24 h, purification of the reaction mixture by chromatography (SiO_2) afforded the *exo*-cycloadduct **9c** (385 mg, 37%) and *endo*-cycloadduct **10c** (361 mg, 34%), together with recovery of the maleimide (60 mg, 11%).

9c: Colorless prisms; mp 140—141 °C; IR (KBr) 1770, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.76 (s, 3H, 3b-CH_3), 2.39 (s, 3H, CH_3), 3.41 (dd, 1H, J=9.4, 7.9 Hz, 10-**H**), 3.64 (ddd, 1H, J=8.7, 7.9, 1.9 Hz, 10a-**H**), 3.87 (dd, 1H, J=7.9, 1.9 Hz, 10-**H**), 3.89 (d, 1H, J=8.7 Hz, 3a-**H**), 8.00—8.33 (m, 8H, Ar**H**); MS m/z 350 (M^+), 163 (base peak). Found: C, 68.30; H, 5.21; N, 7.81%. Calcd for $C_{20}H_{18}N_2O_2S$: C, 68.53; H, 5.18; N, 8.00%.

10c: Colorless solid; mp 67—70 °C;[10] IR (KBr) 1770, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.88 (s, 3H, 3b-CH_3), 2.29 (s, 3H, CH_3), 3.31—3.76 (m, 3H, 3a-**H**, 10-**H**, and 10a-**H**), 4.25 (d, 1H, J=10.7 Hz, 10-**H**), 6.49—7.17 (m, 8H, Ar**H**); MS m/z 350 (M^+), 163 (base peak).

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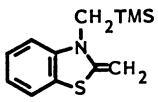
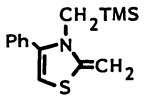
6) The reaction of thiophenol with DMAD (1 equivalent) in the presence of catalytic amount of NaOMe in refluxing THF for 20 h gave a mixture of dimethyl phenylthiofumarate and -maleate (1/1) in 93% yield: yellow viscous oil; ^1H NMR ($CDCl_3$) δ=3.32, 3.64, 3.70, 3.77 (each s, 3H×1/2, OCH_3), 5.48, 6.38 (each s, 1H×1/2, =**CH**), 7.24—7.60 (m, 5H, Ar**H**); ^{13}C NMR ($CDCl_3$) δ=51.61, 52.43, 52.66 (each q), 113.90, 118.77 (each d, =**CH**), 149.71, 151.18 (each s, $OC(-S)=C$), 163.69, 164.39, 164.92, 165.09 (each s, **C**=O).

7) The cycloadducts between nonstabilized pyridinium methylides and olefinic dipolarophiles are too labile to be isolated (see Ref. 5).

8) When treated with triethylamine (1 equivalent) in DME at room temperature, the triflates **2** and **4** generated the corresponding 2-methylenethiazolines **D** and **E** which were trapped as benzoylated products, respectively.



D



E

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10) Purification of *endo*-cycloadducts, **10a—10c**, was difficult owing to their thermal instability.