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단 신

t-부틸 트리메틸실릴 티오케톤과 디아조메탄의 고리화 첨가반응

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Cycloaddition Reactions of *t*-Butyl Trimethylsilyl Thioketone with Diazomethanes

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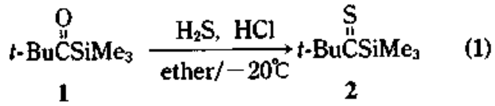
The chemistry of aromatic thioacylsilanes has been extensively studied[1]. However, aliphatic thioacylsilanes were not explored, in spite of their high theoretical interest and synthetic potential. Recently, we[2] and Bonini[3] have reported the preparation and some chemical behaviors of a surprisingly stable aliphatic thioacylsilane, *t*-butyl trimethylsilyl thioketone (2) (Eq. 1).



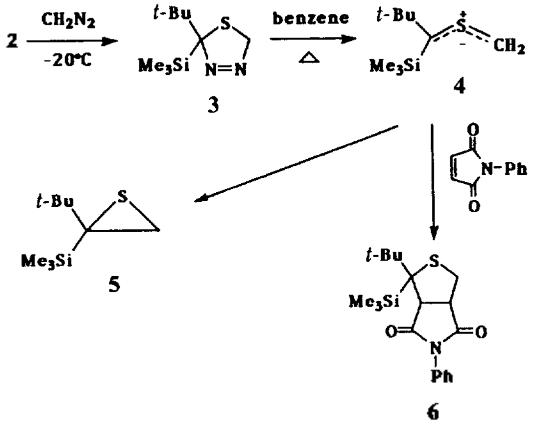
$$t\text{-Bu}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{SiMe}_3 \xrightarrow[\text{ether}/-20℃]{\text{H}_2\text{S, HCl}} t\text{-Bu}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{SiMe}_3 \qquad (1)$$

1　　　2

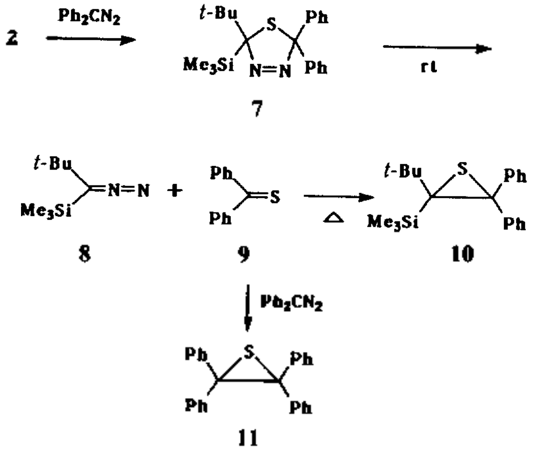
In this report, we describe the reaction of **2** with diazomethanes. When an ethereal solution of diazomethane was added to t-butyl trimethylsilyl thioketone (**2**) in ether at −20℃, the blue color of **2** rapidly disappeared. After chromatography on silica gel (hexane:ether=8:1), 2-*t*-butyl-2-trimethylsilyl-1,3,4-thiadiazoline (**3**) was isolated in 77% yield. The chemical shift (δ 5.60) of the methylene protons of **3** is consistent with the reported values of 1,3,4-thiadiazoline ring system[4].

Thiadiazoline **3** was very stable and could be stored for a few weeks in a refrigerator (−10℃) without appreciable decomposition. However, when benzene solution of **3** was heated to 70℃, thiirane **5** was obtained in 80% yield. Thiocarbonyl ylide **4** was speculated to be the intermediate. The sequential formation of **4** and **5** was confirmed by observing cycloaddition product **6** (45% yield) from the reaction of **3** with *N*-phenylmaleimide in refluxing benzene (*Scheme* 1).

When **2** was treated with one equivalent of diphenyldiazomethane in benzene at room temperature, the initial red color of diphenyldiazomethane disappeared rapidly and the solution turned blue. After 10 minutes the reaction mixture was chromatographed on silica gel (hexane:ether=8:1), to give thiobenzophenone (**9**, 88%) and a small amount of tetraphenylthiirane (**11**). At this stage,



Scheme 1



Scheme 2

thiirane **10** was obtained only in 3% yield. The infrared spectrum of the reaction mixture showed the N-N stretching vibration at 2031 cm^{-1}, which indicates the presence of α-silyldiazoalkane[5]. After **2** was allowed to react with 2.1 equivalents of diphenyldiazomethane in ether, and all the volatile components were vacuum distilled into a cold trap in dry ice-acetone bath. Redistillation of the yellow distillate gave pure **8** (44%). Tetraphenylthiirane (**11**) was obtained in 86% yield from the nonvolatile residue by column chromatography (*Scheme* 2). This result suggests that the adduct **7** is indeed formed, and that the rate of the cleavage of **7** to **8** and **9** is faster than the extrusion of nitrogen from **7** to give thiirane **10**.

When less than one equivalent of diphenyldiazomethane was allowed to react with **2** in ether at −78℃, and warmed to room temperature, **11** was not formed. This indicates that cycloaddition reaction leading to **7** is not reversible. Similar cleavage reaction was suggested on the pyrolysis of *trans*-2,5-di-*t*-butyl-2,5-dimethyl-1,3,4-thiadiazoline, but was reported hardly reproducible. Besides thiirane was not produced either[8,9].

When **2** was treated with one equivalent of diphenyldiazomethane in benzene at room temperature for 10 minutes, and then heated to reflux for 6 hours, thiirane **10** was formed in 77% yield.

The thermal stabilities and cleavage patterns of 1,3,4-thiadiazoline **3** and **7** were found to be very different. As was proposed previously[10] and confirmed in the reaction of **2** and diazomethane in *Scheme* 1, **3** lost nitrogen to give thiocarbonyl ylide which was cyclized to thiirane **5**, or trapped by N-phenylmaleimide. On the contrary, **7** cleaved to **8** and **9** without nitrogen extrusion at room temperature. When the reaction of **2** with diphenyldiazomethane was performed in the presence of N-phenylmaleimide, no cycloaddition product like **6** was obtained. Thus the formation of the thiirane **10** from the reaction of **2** and diphenyldiazomethane in refluxing benzene may be explained by the reaction between thiobenzophenone (**9**) and *t*-butyl(trimethylsilyl)carbene which is suspected to be generated from the diazo compound **8**. However, no adducts were obtained when the reaction of **8** with cyclohexene or with alcohols in the presence of cuprous chloride were attempted.

In conclusion, it is interesting to note the dramatically different behavior with diazomethane and with diphenyldiazomethane in the reactions with **2**, though a consistent explanation for this remarkable difference is lacking at the present time[11].

EXPERIMENTAL

^{1}H-NMR spectra were recorded on a Varian EM-360A (60 MHz) or JEOL JSX 270 (270 MHz) spectrometer using tetramethylsilane as an internal standard. ^{13}C-NMR spectra were recorded on a JEOL JSX 270 (68 MHz) spectrometer with $CDCl_3$ as solvent and internal standard. Infrared spectra were recorded on a Mattson Polaris Icon FTIR spectrometer as neat films on potassium bromide plates. Mass spectra were performed on a JEOL JMS-DX 300 spectrometer. Diazomethane[12] and diphenyldiazomethane[13] were prepared according to literature methods.

2-*t*-Butyl-2-trimethylsilyl-1,3,4-thiadiazoline (3). To a cold (−20℃), stirred solution of the thioacylsilane **2** (194 mg, 1.11 mmol) in ether (5 m*l*), the etheral solution of diazomethane was added until the initial blue color of the solution had disappeared. After 2 h, the mixture was allowed to warm to room temperature. The solution was evaporated and purified by preparative thin layer chromatography (PLC, silica gel, hexane/ether 8:1) to afford 185 mg (77%) of **3**. ^{1}H-NMR ($CDCl_3$) δ 0.14 (9H, s), 1.06 (9H, s), 5.60 (2H, s); ^{13}C-NMR ($CDCl_3$) δ −0.24, 28.35, 41.15, 83.91, 118.74; IR (neat) 1550 (N=N), 1250 (Me_3Si) cm^{-1}.

2-*t*-Butyl-2-trimethylsilylthiirane (5). A benzene (5 m*l*) solution of **3** (168 mg, 0.78 mmol) was refluxed for 2 h. The solution was concentrated and the residue was chromatographed on silica gel (hexane) to give **5** (117 mg, 80%). ^{1}H-NMR ($CDCl_3$) δ 0.13 (9H, s), 0.97 (9H, s), 2.13 (1H, d, J=7.8 Hz), 2.16 (1H, d, J=7.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 0.68, 28.60, 28.75, 35.34, 45.72; MS m/e 188 (M$^+$, 16), 173 (6), 146 (4), 131 (16), 91 (38), 83 (29), 73 (100%).

Reaction of 3 with *N*-phenylmaleimide. A benzene (4 m*l*) solution of **3** (105 mg, 0.50 mmol) and N-phenylmaleimide (200 mg, 1.16 mmol) was refluxed for 10 h. The solution was evaporated and the residue was purified by PLC (silica gel hexane/ether 1:1) to yield the adduct **6** (80 mg, 45%). ^{1}H-NMR (270 *M*Hz, $CDCl_3$) δ 0.22 (9H, s), 1.16 (9H, s) 3.24 (1H, dd, J=12.2 and 7.8 Hz), 3.40 (1H, dd, J=12.2 and 3.2 Hz), 3.78~3.92 (2H, m), 7.2~7.5 (5H, m); MS m/e 361 (M$^+$, 11) 346 (39), 73 (100%).

Reaction of 2 with Diphenyldiazomethane.

(a) To a solution of **2** (151 mg, 0.86 mmol) in benzene at room temperature was added a solution of diphenyldiazomethane (169 mg, 0.89 mmol) in benzene (2 m*l*). After 10 minutes, the initial red color of the solution had changed to blue. The solution was concentrated in vacuo and then chromatographed on silica gel (hexane/ether 8:1) to afford thiobenzophenone **9** (151 mg, 88%), thiirane **10** (10.2 mg, 3%), and tetraphenylthiirane **11** (20 mg, 6%). Thiobenzophenone was partially converted to benzophenone during the separation.

9: MS m/e 198 (M$^+$, 72%)

10: ^{1}H-NMR (CCl_4) δ −0.15 (9H, s), 0.95 (9H, s) 6.85~7.80 (10H, m); MS m/e 340 (M$^+$, 18), 308 (2), 235 (10), 166 (12), 73 (100%).

11: MS m/e 364 (M$^+$, 5), 332 (8), 214 (60), 197 (20), 165 (100), 121 (42), 105 (87), 77 (50), 32 (51%).

(b) To a benzene (2 m*l*) solution of **2** (108 mg, 0.62 mmol) was added the benzene (1 m*l*) solution of diphenyldiazomethane (122 mg, 0.63 mmol) at room temperature, and then the resulting mixture was refluxed for 6 h. The solution was treated as described above to give **10** (163 mg, 77%). When the reaction of **2** with diphenyldiazomethane in benzene carried out at room temperature for 40 h, **10** (55%) and thiobenzophenone (32%) was obtained.

(c) To a solution of **2** (303 mg, 1.74 mmol) in ether (3 m*l*) was added diphenyldiazomethane (602 mg, 3.5 mmol) in ether (2 m*l*) at room temperature. After 10 minutes, the solution was distilled in vacuo into a cold trap in dry ice-acetone bath. The yellow distillate was redistilled (110~113℃, 760 mmHg) to afford *t*-butyl(trimethylsilyl)-diazomethane **8** (130 mg, 44%). ^{1}H-NMR (CCl_4) δ 0.20 (9H, s), 1.14 (9H, s). IR (neat) 2031 (N=N), 1250 (Me_3Si) cm^{-1}. The residue chromatographed on silica gel (hexane/ether 8:1) to give **11** (545 mg, 86%).

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