REACTION OF THIOBENZOYL ISOCYANATES WITH TRIMETHYLSILYL CYANIDE

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Abstract —— Thiobenzoyl isocyanates were found to react with trimethylsilyl cyanide to afford the corresponding 2-phenyl-5-thiobenzoyl-7-trimethylsilylimino-4,5,6,7-tetrahydro-1,3,5-thiadiazepine-4,6-diones (2:1 adducts).

Recently, Ojima and his co-workers have developed versatility of trimethylsilyl cyanide (TMSCN) for syntheses of five-membered heterocyclic compounds by reactions with aryl isocyanates[1], carbodiimides[2], and methyl isothiocyanate[3].

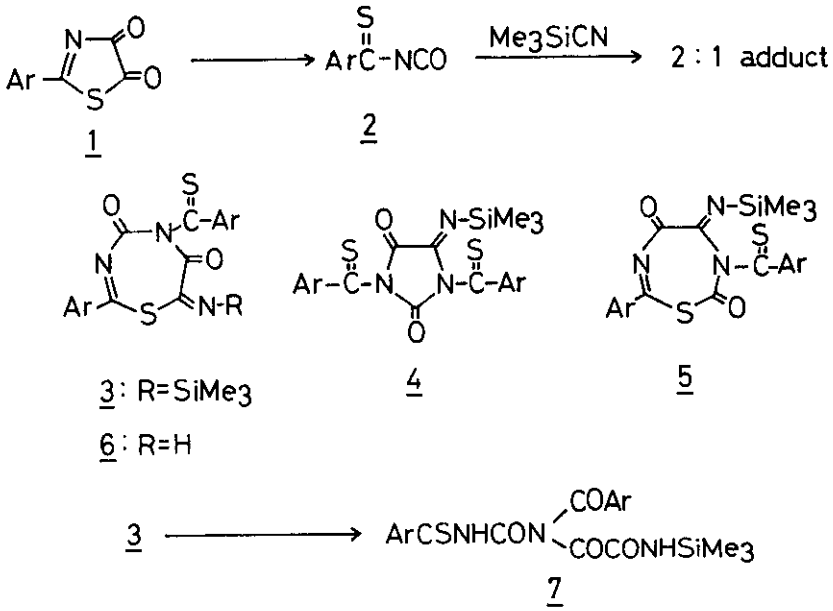
From our previous work on the cycloaddition reactions[4] and chlorination[5] of thiobenzoyl isocyanate, it has become apparent that the isocyanate manifested high reactivity in 1,4-additions. Thus it might be expected that a seven-membered heterocyclic compound would be formed by the reaction of thiobenzoyl isocyanate with TMSCN. We now wish to report on the reaction of thiobenzoyl isocyanates with TMSCN leading to the formation of seven-membered tetrahydro-1,3,5-thiadiazepine derivatives.

Although thiobenzoyl isocyanate (2a), generated in situ from 2-phenylthiazoline-4,5-dione (1a) in xylene[6], reacted with TMSCN at 120° to give the 2:1 adduct 3a of 2a to TMSCN, the yield of 3a was rather low because of the formation of products derived from 2a itself[7]. However, it has been found that the direct reaction of 1a with excess TMSCN in xylene at 120° afforded 3a in good yield. The results under various conditions are shown in Table 1.

Similarly, 2-p-chlorophenyl- (1b) and 2-p-methoxyphenylthiazoline-4,5-dione (1c) reacted with TMSCN to give the corresponding 2:1 adducts 3b and 3c respectively.

On the basis of spectral data and chemical conversions, 2:1 adducts 3a-3c were deduced to be the corresponding 2-phenyl-5-thiobenzoyl-7-trimethylsilylimino-4,5,6,7-tetrahydro-1,3,5-thiadiazepine-4,6-diones, but not 5-iminoimidazolidinediones 4 nor 1,3,6-thiadiazepinediones 5.

Detrimethylsilylation of 2:1 adducts 3 with hydrochloric acid in ethanol at room temperature afforded the corresponding imino compounds 6[8], which readily reverted to 3 on treatment with trimethylsilyl chloride in the presence of triethylamine.



a: Ar=Ph, b: Ar=p-ClC_6H_4, c: Ar=p-$MeOC_6H_4$

Scheme 1

Table 1

1	Conditions			3, Yield %
	1/TMSCN mol/mol	Temp. °C	Time	
1a	1/1	80	2 h	41
1a	1/1	120	5 min	76
1a	2/1	120	1 h	61
1b	1/1	120	5 min	56
1b	1/2	120	5 min	91
1c	1/1	120	5 min	46
1c	1/2	120	5 min	79

As shown below, the carbonyl absorption bands of 3 and 6 appeared at 1670-1680 cm^{-1}. This fact strongly excludes the possibility of 4 for the 2:1 adducts because the carbonyl absorption bands of 1,3-diphenyl-5-iminoimidazolidine-2,4-dione[1] appeared at 1800 and 1750 cm^{-1}. In addition, mass

spectra of 3a, 3b, 6a, and 6b which displayed the fragment ion due to R-N=C=S at m/e 131 ($R=SiMe_3$) or 59 (R=H) supported the 7-imino-1,3,5-thiadiazepine structures for the 2:1 adducts and their detrimethylsilylated products.

3a: mp 156-157°, orange needles. IR (KBr) 1680 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.45 (s, 9H), 7.3-8.1 (m, 10H); MS m/e 425 (M^+), 294 (M^+ - Me_3SiNCS), 262 (M^+ - 2a), 176, 163 (2a$^+$), 131 (Me_3SiNCS^+), 121 ($PhCS^+$), 116, 103, 73 (Me_3Si^+, base peak)[9].

3b: mp 224° (dec), yellow plates. IR (KBr) 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.42 (s, 9H), 7.3-8.0 (m, 8H); MS m/e 497, 495, 493 (M^+), 298, 296 (M^+ - 2b), 212, 210, 199, 197 (2b$^+$), 157, 155 ($ArCS^+$), 139, 137 ($ArCN^+$), 131 (Me_3SiNCS^+), 73 (Me_3Si^+, base peak).

3c: mp 192° (dec), orange needles. IR (KBr) 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.42 (s, 9H), 3.82, 3.87 (each s, 3H), 7.45, 7.55 (each dd, 4H); MS m/e 485 (M^+, base peak), 320 (M^+ - ArCSN), 292 (M^+ - 2c), 151 ($ArCS^+$), 133 ($ArCN^+$), 73 (Me_3Si^+).

6a: mp 160-161° (dec), yellow crystals. IR (KBr) 3200-2300 (NH), 1680 cm^{-1} (C=O); MS m/e 353 (M^+), 294 (M^+ - NHCS), 250 (M^+ - PhCN), 190 (M^+ - 2a), 104, 103, 59 ($NHCS^+$).

6b: mp 220-226° (dec), yellow crystals. IR (KBr) 3300-2800 (NH), 1670 cm^{-1} (C=O); MS m/e 425, 423, 421 (M^+), 286, 284 (M^+ - ArCN), 199, 197 (2b$^+$), 157, 155 ($ArCS^+$), 140, 138 ($ArCNH^+$), 139, 137 ($ArCN^+$), 59 ($NHCS^+$).

6c: mp 190-207° (dec), yellow crystals. IR (KBr) 3300-2200 (NH), 1670 cm^{-1} (C=O); MS m/e 413 (M^+), 193 (2c$^+$), 151 ($ArCS^+$), 134 ($ArCNH^+$), 133 ($ArCN^+$).

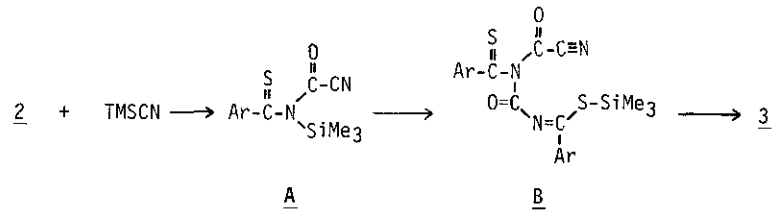
Further evidence for the structures 3 was provided by the reductive hydrolysis of 3. Treatment of 3a with $NaBH_4$ in THF afforded 1-benzoyl-1-(N-trimethylsilyloxamoyl)-3-thiobenzoyl urea (7a) in 44% yield. Similar treatments of 3b and 3c gave the corresponding ureas 7b and 7c in 95 and 93% yields respectively.

7a: mp 196-197°, yellow needles. IR (KBr) 3200, 3100 (NH), 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.42 (s, 9H), 7.2-8.1 (m, 10H), 11.2, 12.98 (each broad, 1H); MS m/e 427 (M^+), 290 (M^+ - $PhCSNH_2$), 264 (M^+ - 2a), 163 (2a$^+$), 137 ($PhCSNH_2^+$), 121 ($PhCS^+$), 105, 73.

7b: mp 237-238° (dec), orange needles. IR (KBr) 3240, 3160 (NH), 1680 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.41 (s, 9H), 7.55 (m, 8H), 11.3, 12.3 (each broad, 1H); MS m/e 499, 497, 495 (M^+), 326, 324 (M^+ - $ArCSNH_2$), 300, 298 (M^+ - 2b), 199, 197 (2b$^+$), 173, 171 ($ArCSNH_2^+$), 157, 155 ($ArCS^+$), 141, 139 ($ArCO^+$), 139, 137 ($ArCN^+$).

7c: mp 196-197° (dec), orange needles. IR (KBr) 3240, 3140 (NH), 1680 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.41 (s, 9H), 3.73, 3.84 (each s, 3H), 7.29, 7.24 (each dd, 4H), 10.9, 12.9 (each broad, 1H); MS m/e 487 (M^+), 320 (M^+ - $ArCSNH_2$), 294 (M^+ - 2c), 193 (2c$^+$), 167 ($ArCSNH_2^+$), 151 ($ArCS^+$), 135 ($ArCO^+$), 133 ($ArCN^+$).

The pathway for the formation of 3 can be readily understood as depicted in the following scheme.



A B

TMSCN adds to 2 in a similar manner as to aryl isocyanate to yield the 1:1 adduct A. The isocyanate 2 reacts with A by a 1,4-addition process to produce B, and subsequent intramolecular insertion reaction in B gives the final product 3.

References and Notes

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7. It is known that 2a dimerizes readily to form the 1,3,5-thiadiazinedione derivative, which on further heating is converted to the 1,3,5-thiadiazinone derivative with the elimination of carbonyl sulfide (J. Goerdeler and H. Schenk, Chem. Ber., 1965, 98, 2954). In the reaction of previously generated 2a with TMSCN in xylene at 120°, dimer and 1,3,5-thiadiazinone derivative were formed besides 2:1 adduct 3a.
8. When a suspension of 3a in methanol was refluxed for 1 h, a new detrimethylsilylated product 8a different from 6a was formed in 74% yield. Under similar conditions 3b and 3c afforded detrimethylsilylated products 8b and 8c in 96 and 65% yields respectively. However, the structures of 8a-8c are not yet established. 8a: mp 162-167° (dec); IR (KBr) 3280, 1760 cm^{-1}; ^{13}C NMR (DMSO-d_6) δ 90.3, 128.5, 129.2, 130.5, 133.6, 147.6, 152.1, 171.9; MS m/e 353 (M^+). 8b: mp 243° (dec); IR (KBr) 3300, 1730 cm^{-1}; ^{13}C NMR (DMSO-d_6) δ 91.1, 129.3, 130.2, 138.5, 147.2, 152.1, 171.2; MS m/e 425, 423, 421 (M^+). 8c: mp 218° (dec); IR (KBr) 3100, 1795 cm^{-1}; ^{13}C NMR (DMSO-d_6) δ 55.6, 90.3, 114.6, 123.0, 130.7, 148.4, 152.4, 163.4, 170.4; MS m/e 413 (M^+)
9. All compounds gave satisfactory analytical values.

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