

Organosilicon Compounds XIII.
Cleavage of the Silicon-Carbon Bond of 2-Trimethylsilylbenzothiazole

Frank H. Pinkerton and Shelby F. Thames (1)

Department of Polymer Science, University of Southern Mississippi,
Hattiesburg, Mississippi 39401

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The high-yield synthesis of 2-trimethylsilylbenzothiazole is described, and the labile nature of this silicon-heterocyclic bond is proved when cleavage is affected by aldehydes, acid halides, chloroformates and anhydrides. Justification for this unusual reactivity and further insight into the reaction mechanism is offered.

Previous studies in this laboratory have dealt with the labile reactivity of various silicon-aromatic bonds. In this connection we have recently reported (2,3) the novel cleavage of the silicon-carbon bond of 2-silylpyridines by four neutral reagents, namely benzaldehyde, benzoyl chloride, ethyl chloroformate and phthalic anhydride. Ogawa, Yasui, and Matsui (4) have subsequently published data concerning the cleavage of 2-trimethylsilylpyridine by various aldehyde moieties and in their work have referred to this reaction as "... highly specific for the aldehyde carbonyl group ...", presumably due to the absence of a reaction with acetophenone, cyclohexanone and benzonitrile. Due to the fact that there indeed exist at least three other carbonyl moieties capable of this cleavage, in addition to our initially reported cleavage by benzaldehyde, we strongly suggest that the term, "highly specific", should not be too closely associated with this reaction type.

In addition to our continuing investigation of possible cleavage reagents, we report herein an extension of this general reaction sequence to yet another silylheterocycle, 2-silylbenzothiazole. Gilman and Beel (5) have reported

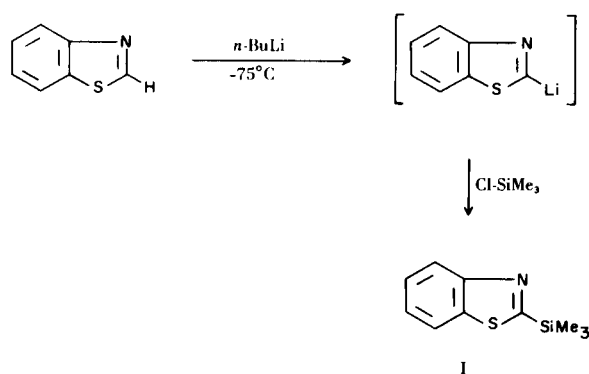
the formation of 2-benzothiazolyl lithium and the appropriate precaution that this anion is not stable above -35° . This instability severely limited (6) the yield of 2-triphenylsilylbenzothiazole (maximum yield of 19%) capable of being produced by condensation of the 2-anion with various triphenylhalosilanes. However, we have discovered that the addition of trimethylchlorosilane to 2-benzothiazolyl lithium at -75° with subsequent gradual warming to room temperature over a 4-5 hour period produced 2-trimethylsilylbenzothiazole (I) in yields of 75-80% (Scheme I).

The silicon-heterocyclic bond of (I) proved to be unusually labile as cleavage was affected by benzaldehyde, benzoyl chloride, ethyl chloroformate and phthalic anhydride in excellent yields (Scheme II).

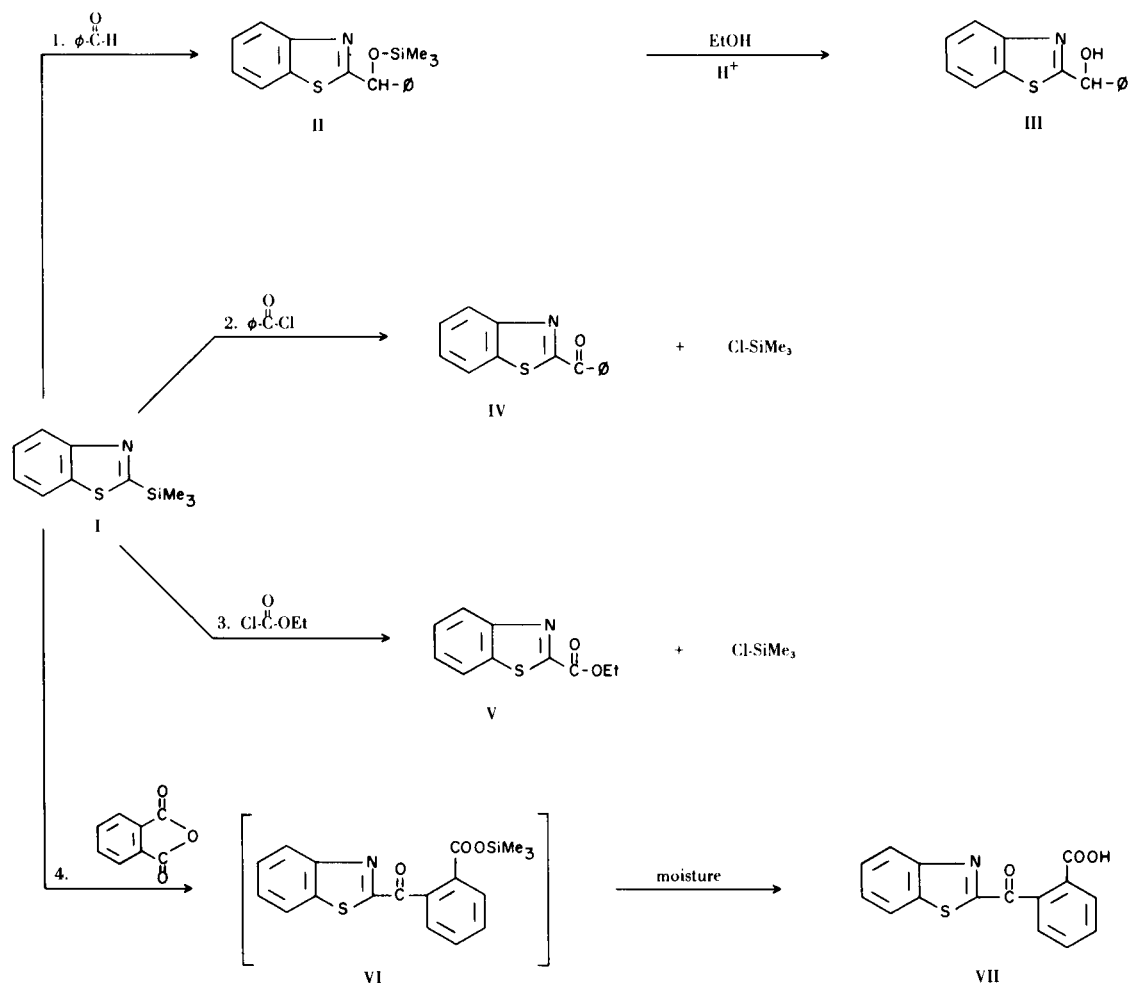
The cleavage by benzaldehyde proceeded smoothly to produce the silyl ether (II) whose identity was proven by IR, NMR, elemental analysis and hydrolysis to the known alcohol (III). The cleavage by benzoyl chloride and ethyl chloroformate proceeded very readily to produce the corresponding ketone (IV) and ester (V) respectively, and trimethylchlorosilane which was distilled from the mixture during the course of the reaction. It is noted that these two reactions occurred in excellent yields and with little discoloration in contrast to the cleavage of 2-silylpyridines by benzoyl chloride and ethyl chloroformate. It is felt that the silyl ester (VI) was formed initially in the reaction of (I) with phthalic anhydride and, as a result of the facile nature of the Si-O bond, was cleaved by moisture to the keto-acid (VII), although, isolation of the silyl ester was not attempted. Thus, as with 2-silylpyridines, the silicon-carbon bond of 2-silylbenzothiazole has proven to be unusually labile in that cleavage can be affected by a variety of carbonyl-containing reagents.

Previously (3) we have described these reactions as pro-

SCHEME I



SCHEME II



ceeding through a cyclic 4-member transition state, the formation and reactivity of which is highly dependent upon the polarity of both the attacking reagent and also the silyl-aromatic bond. In support of this concept, it is significant to note that 2-trimethylsilylthiophene (7) and 2-trimethylsilyltrichlorothiophene (8) fail to react with benzaldehyde. However, in the case of 2-silylbenzothiazoles a more polar silicon-heterocyclic bond exists as a result of the presence of the second heteroatom, nitrogen, and also the fused benzene ring; and thus, cleavage occurs readily. A similar result has been reported in the excellent work by Gilman, *et al.*, (9) in that phenyltrimethylsilane failed to react with benzaldehyde while the silicon-carbon bond of both pentafluorophenyl- and pentachlorophenyltrimethylsilane cleaved in good yields upon prolonged heating with benzaldehyde.

We are continuing our efforts to extend this reaction to other cleavage reagents and silylaromatics as well.

EXPERIMENTAL

2-Trimethylsilylbenzothiazole (I).

To a solution of *n*-butyllithium (50 ml., 2*M*) in 200 ml. of ether cooled to -75° under a dry nitrogen atmosphere was added benzothiazole (13.5 g., 0.1 mole) dropwise over a 15-20 minute period, with caution to prevent an increase in temperature, to produce 2-benzothiazolyllithium (5). Immediately thereafter, trimethylchlorosilane (10.8 g., 0.1 mole) was added dropwise to this -75° ethereal solution. The solution was subsequently allowed to warm to room temperature over a 4-5 hour period, the LiCl filtered, and the solution concentrated *in vacuo* and distilled to afford 16 g. (77.4%) of (I), b.p. $146^\circ/30$ mm, $n_D^{25} = 1.5708$.

Anal. Calcd. for $C_{10}H_{13}NSSi$: C, 57.91; H, 6.33; N, 6.76. Found: C, 57.92; H, 6.25; N, 6.97.

The NMR spectra of I obtained on a Varian A-60D spectrometer exhibited multiplets from 7.8-8.3 δ integrating for 2 aromatic protons, multiplets from 7.2-7.5 δ integrating for 2 aromatic protons, and a singlet at 0.4 δ integrating for the 9 protons of the trimethylsilyl group.

2-Benzothiazolylphenylmethyl Trimethylsilyl Ether (II).

The reaction of 2-trimethylsilylbenzothiazole (11 g., 0.053 mole) with an excess of benzaldehyde (10.6 g., 0.1 mole) under a dry nitrogen atmosphere at a temperature of 160° for 40 hours afforded after recrystallization from heptane 13 g. (78.5%) of II, m.p. 97-99°.

Anal. Calcd. for C₁₇H₁₉NOSSi: C, 65.12; H, 6.12. Found: C, 65.24; H, 6.00.

Compound II upon heating with 95% ethanol with a catalytic trace of hydrochloric acid provided for quantitative conversion to 2-benzothiazolylphenylcarbinol (III) m.p. 119-121°. Literature (5) reports m.p. 121.5°.

The NMR spectra of II exhibited multiplets from 7.1-8.0 δ integrating for the 9 aromatic protons, a singlet at 6.1 δ integrating for the 1 methine proton and a singlet at 0.15 δ integrating for the 9 protons of the trimethylsilyl group.

2-Benzothiazolyl Phenyl Ketone (IV).

Benzoyl chloride (7 g., 0.05 mole) and 2-trimethylsilylbenzothiazole (10 g., 0.05 mole) were heated at 110° for 4 hours under an atmosphere of dry nitrogen, during which time the trimethylchlorosilane produced was collected. The reaction mixture was then washed with a sodium bicarbonate water solution, the water decanted and the resultant solid recrystallized from 95% ethanol to yield 9.6 g. (80.6%) of (IV) m.p. 101-102°. Literature (5) reports m.p. 102.5°.

Ethyl 2-Benzothiazolecarboxylate (V).

Ethyl chloroformate (7.4 g., 0.068 mole) was added cautiously, dropwise with stirring into 2-trimethylsilylbenzothiazole (14 g., 0.068 mole) under an atmosphere of dry nitrogen at 20° due to the apparent exothermic nature of the reaction. The mixture was then heated to 90° for 3 hours during which time the trimethylchlorosilane was collected. The product was then washed with a bicarbonate solution, extracted into ether, dried over anhydrous magnesium sulfate, concentrated *in vacuo*, and recrystallized from petroleum ether to yield 12.6 g. (90%) of (V), m.p. 68-70°. Literature (10) reports m.p. 69.8-70.5°.

2-Carboxyphenyl 2-Benzothiazolyl Ketone (VII).

The reaction of phthalic anhydride (11.1 g., 0.075 mole) with 2-trimethylsilylbenzothiazole (15.5 g., 0.075 mole) at 150° for 11 hours afforded, after exposure to the atmosphere and recrystallization from acetone, 18.8 g. (88.7%) of (VII), m.p. 207-209°.

Anal. Calcd. for C₁₅H₉NO₃S: C, 63.59; H, 3.21; N, 4.94. Found: C, 63.67; H, 3.16; N, 4.87.

The NMR spectra of (VII) in DMSO exhibited multiplets in the aromatic region from 7.5-8.4 δ ; however, the spectra must be considered inconclusive for structural determination as a standard proton absorption for integration purposes was nonexistent since the acid proton did not appear with the solvent employed. Similar failure to detect the acid proton in this type of compound when using DMSO has previously been noted (3). The IR spectra of (VII) exhibited no bands in the O-H stretch region from 2.8-3.1 μ but did exhibit strong bands from 3.7-4.2 μ indicative of the salt formation between the benzothiazolyl nitrogen and the carboxylic acid proton.

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