2,2-Dichloro-1-hydroxycyclopropaneacetic Acid (4). A suspension of **3** (3.1 g) in 10% hydrochloric acid (12 mL) was heated at 50–60 °C on a steam bath with stirring. The reaction mixture was condensed under reduced pressure to give a viscous residue which was allowed to stand at room temperature to form a crystalline substance. Recrystallization from petroleum ether (bp 60–70 °C) afforded **4** as needles, 2.1 g (60%): mp 99–100 °C; IR ($CHCl_3$) 3600–2400, 3530, 1715 cm^{-1}; NMR (acetone-d_6) δ 1.69 (s, 2 H, cyclopropane ring protons), 2.97 (s, 2 H CH_2CO_2H), 5.55 (br s, 1 H, D_2O exchangeable, OH), 7.30 (br s, 1 H, D_2O exchangeable, COOH).

Anal. Calcd for $C_5H_6Cl_2O_3$: C, 32.45; H, 3.24; Cl, 38.35. Found: C, 32.47; H, 3.15; Cl, 38.29.

Ethyl 2,2-Dichloro-1-hydroxycyclopropaneacetate (5). A solution of **3** (4.0 g, 0.024 mol) in absolute ethanol (10.0 g, 0.22 mol) was saturated with dry hydrogen chloride under ice–salt cooling. The reaction mixture was heated at 50–60 °C on a steam bath for 7 h. Evaporation of ethanol left an oily residue which was distilled under reduced pressure to give **5** as a colorless oil, 4.2 g (81%): bp 82–83 °C (4 mm); IR ($CHCl_3$) 3500, 2970, 1715 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (t, 3 H, J = 7.2 Hz, OCH_2CH_3), 1.41–1.80 (AB q, 2 H, J = 9.6 Hz, cyclopropane ring protons), 2.58–3.34 (AB q, 2 H, J = 18.0 Hz, CH_2CO_2Et), 4.25 (br s, 1 H, D_2O exchangeable, OH), 4.31 (q, 2 H, J = 7.2 Hz, OCH_2CH_3).

Anal. Calcd for $C_7H_{10}Cl_2O_3$: C, 39.46; H, 4.70; Cl, 33.30. Found: C, 39.74; H, 4.73; Cl, 32.93.

General Procedure for the Synthesis of 2,2-Dichloro-1-hydroxycyclopropaneacetamide Derivatives 6–13. A solution of **3** and the chosen amine in the organic solvent shown in Table I was stirred. Precipitates were collected by suction filtration. Purification by recrystallization gave compounds **6–13**. Reaction conditions, results, and physical data are summarized in Tables I and II.

Acknowledgment. Thanks are due Mrs. R. Koyanagi, Mr. K. Kawamura, and Miss K. Mushiake for elemental analyses and spectral measurements. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture in Japan.

Registry No. 3, 73090-43-4; **4**, 73090-44-5; **5**, 73090-45-6; **6**, 73090-46-7; **7**, 73090-47-8; **8**, 73090-48-9; **9**, 73090-49-0; **10**, 73090-50-3; **11**, 73104-81-1; **12**, 73090-51-4; **13**, 73090-52-5; benzylamine, 100-46-9; aniline, 62-53-3; *p*-toluidine, 106-49-0; *p*-anisidine, 104-94-9; *p*-chloroaniline, 106-47-8; morpholine, 110-91-8; phenylhydrazine, 100-63-0; hydroxylamine hydrochloride, 5470-11-1; phenyl(trichloromethyl)mercury, 3294-57-3; diketene, 674-82-8; ethanol, 64-17-5.

Syntheses of α-Chloro Ketones by Reaction of Silyl Enol Ethers with $CuCl_2$ and $FeCl_3$

Yoshihiko Ito, Masashi Nakatsuka, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

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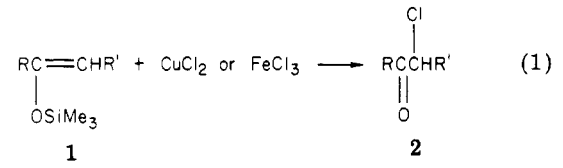
We have already reported a series of reactions of silyl ethers of enols and cyclopropanols with metal salts,[1] in which metal enolates and metal cyclopropoxides may be assumed as key intermediates. Now we wish to report the reactions of silyl enol ethers with cupric chloride and ferric chloride to produce α-chloro ketones according to eq 1. The reaction provides a simple and convenient synthetic method for the preparation of α-chloro ketones under mild conditions. For the chlorination of silyl enol ethers we have obtained some results which are taken to suggest a reaction



1 2 (1)

mechanism involving a vinyloxy radical generated from the collapse of the copper(II) or iron(III) enolate which was formed initially.

Reaction of Silyl Enol Ethers with Anhydrous $CuCl_2$. When silyl enol ethers (**1**) were treated with a 2 or 3 molar excess of cupric chloride in dimethylformamide (DMF), α-chloro ketones (**2**) were produced in moderate yields together with the starting ketones.

The selection of specific solvents was very important for all of the reactions of silyl ethers of enols and cyclopropanols with metal salts. The use of DMF in the present reaction played a decisive role. No reaction occurred in other common organic solvents. Some results are summarized in Table I. Interesting features of the chlorination of silyl enol ethers with cupric chloride are as follows: (i) α-chlorination of unsymmetrical ketones can be regiospecifically performed via their silyl enol ethers, (e.g., Table I, **2d** and **2e**); (ii) selective α-chlorination of ketones having an extra olefin can be performed, leaving the extra olefin intact (e.g., Table I, **2f–i**). Although it has been shown[2] that ketones are chlorinated with cupric chloride in DMF to produce α-chloro ketones, the direct chlorination of unsymmetrical ketones gives mixtures of α- and α′-chloro ketones. Therefore, the present chlorination reaction of silyl enol ethers complements the direct chlorination of ketones.

Reaction of Silyl Enol Ethers with Anhydrous $FeCl_3$. Silyl enol ethers were also reacted with $FeCl_3$ in acetonitrile to give α-chloro ketones in moderate yields (Table I). The use of DMF, which was a crucial solvent for the chlorination with $CuCl_2$, brought about unsatisfactory results.

A large excess of $FeCl_3$ is necessary for the chlorination of silyl enol ethers. For example, the use of a 4 or 5 molar excess of $FeCl_3$ resulted in satisfactory yields of α-chloro ketones, but the use of a 2 molar excess of $FeCl_3$ gave lower yields of α-chloro ketones together with the regeneration of the starting ketones. It is noteworthy that unlike the chlorination with $CuCl_2$, the reaction of a silyl enol ether having an extra olefin with $FeCl_3$ afforded a mixture of α-chloro ketone (**2**), cyclic chloro ketone (**3**), and dimeric 1,4-diketone (**4**) (Scheme I). The ratio of these three products depends upon the reaction conditions employed. The formation of cyclic chloro ketone was more favored when the silyl enol ether was added at once to a refluxing solution of a 5 molar excess of $FeCl_3$ in acetonitrile and then quenched within 1 min. For instance, the reaction of 2-[(trimethylsilyl)oxy]-1,5-hexadiene (**1g**) with a 5 molar excess of $FeCl_3$ in acetonitrile afforded a mixture of 1-chloro-5-hexen-2-one (**2g**), 4-chlorocyclohexanone (**3g**),[3] and dodeca-1,11-diene-5,8-dione (**4g**)[4] in 10, 24, and 1%

(1) (a) Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc.* **1975**, *97*, 649–51. (b) Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073–4. (c) Ito, Y.; Saegusa, T. *Ibid.* **1977**, *42*, 2326. (d) Ito, Y.; Sugaya, T.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *99*, 8366.

(2) Kosower, E. M.; Cole, W. J.; Wu, G.-S.; Cardy, D. E.; Meisters, G. *J. Org. Chem.* **1963**, *28*, 630–3.

(3) **3g**: IR (neat) 1720 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 2.0–3.0 (m, 8 H), 4.44 (m, 1 H).

(4) Ito, Y.; Konoike, T.; Harada, T.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *99*, 1487–93.

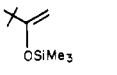
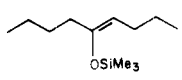
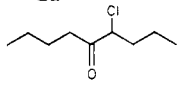
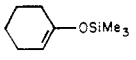
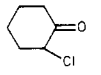
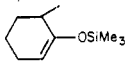
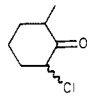
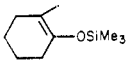
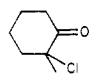
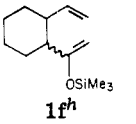
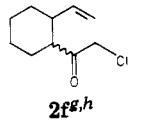
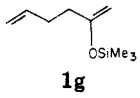
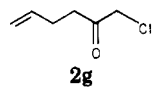
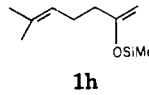
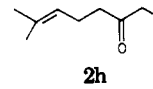
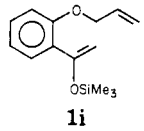
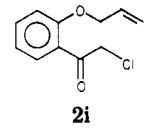
(5) (a) Cook, C. D.; Woodworth, R. C. *J. Am. Chem. Soc.* **1953**, *75*, 6242–4. (b) Bacon, R. G. R.; Hill, H. A. O. *Q. Rev., Chem. Soc.* **1965**, *19*, 95–125.

(6) Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 2nd ed.; Aldrich Chemical Company Inc.: Milwaukee, WI, 1975.

(7) Warnhoff, E. W.; Martin, D. G.; Johnson, W. S. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. 4, pp 162–6.

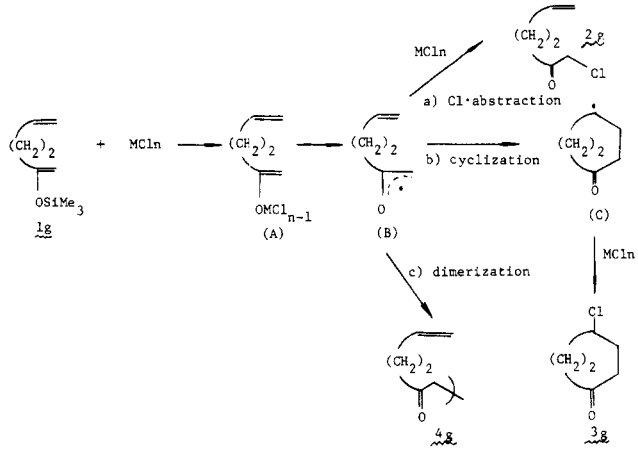
0022-3263/80/1945-2022$01.00/0

Table I. Reactions of Silyl Enol Ethers with $CuCl_2$[a] and $FeCl_3$[b]

silyl enol ethers	metal chloride	α-chloro ketones	yield, %[c]
 1a	$CuCl_2$ $FeCl_3$	 2a	65 62
 1b[h]	$CuCl_2$	 2b	70
 1c	$CuCl_2$ $FeCl_3$	 2c[d]	58 52
 1d	$CuCl_2$ $FeCl_3$	 2d[e]	58 45
 1e	$CuCl_2$ $FeCl_3$	 2e[f]	66 76
 1f[h]	$CuCl_2$	 2f[g,h]	61
 1g	$CuCl_2$	 2g	68
 1h	$CuCl_2$	 2h	80
 1i	$CuCl_2$	 2i	61[g]

[a] A mixture of 1.5 mmol of silyl enol ether and 4.5 mmol of $CuCl_2$ in 6 mL of DMF was stirred for 3 h at room temperature and then for 30 min at 50 °C. [b] A mixture of 1.5 mmol of silyl enol ether and 7.5 mmol of $FeCl_3$ in 13 mL of acetonitrile was stirred for 1.5 h at room temperature. [c] Yields were determined by GLC unless otherwise stated. [d] Reference 6. [e] Stereochemistry was not determined. [f] Reference 7. [g] Isolated yield. [h] A cis and trans mixture.

Scheme I



yields, respectively. Similarly, 1-[1-[(trimethylsilyl)oxy]-vinyl]-2-vinylcyclohexane (**1f**), in which both the olefinic group and silyl enol ether group are located close to each other, was cyclized to 2-chloro-5-oxodecahydronaphthalene (**3f**) in a 58% yield.

The chlorination of silyl enol ethers with $CuCl_2$ or $FeCl_3$ may reasonably be explained by Scheme I which involves a vinyloxy radical (B). The vinyloxy radical (B), which may be assumed to be generated via collapse of metal enolate (A) formed initially, proceeds competitively in three directions: (a) a chlorine abstraction producing an α-chloro ketone, (b) a cyclization followed by chlorine abstraction producing a cyclic chloro ketone, and (c) a coupling reaction to give a dimeric 1,4-diketone. The formation of vinyloxy radicals from metal enolates may be reminiscent of that of phenoxy radical from metal phenoxides in the oxidation of phenol with transition metals.[5]

Experimental Section

Materials. Anhydrous $CuCl_2$ was prepared by heating $CuCl_2 \cdot 2H_2O$ at 100 °C for several hours. Anhydrous $FeCl_3$ was commercially available and heated at 70–80 °C in vacuo prior to use. Dimethylformamide was distilled over calcium hydride. Acetonitrile was distilled over P_2O_5. Silyl enol ethers were prepared according to the procedure reported by House et al.[8]

General Procedure for Chlorinations of Silyl Enol Ethers with Anhydrous $CuCl_2$. (1) Reaction of 2-[(Trimethylsilyl)oxy]-1,5-hexadiene (1g) with $CuCl_2$. To a solution of 605 mg (4.5 mmol) of $CuCl_2$ in 6 mL of DMF was added 255 mg (1.5 mmol) of **1g** dropwise at room temperature. The mixture was stirred at room temperature for 3 h and at 50 °C for 0.5 h and then quenched with ice-cold water. The mixture was extracted with ether and washed with 5% aqueous HCl and brine. The ether extract was dried over $MgSO_4$ and distilled. Preparative gas chromatography of the residue afforded 1-chloro-5-hexen-2-one (**2g**) in a 68% yield with 5-hexen-2-one (20%). For **2g**: IR (neat) 1720–1740, 1645 cm^{-1}; NMR ($CDCl_3$) δ 2.0–2.8 (m, 4 H), 3.95 (s, 2 H), 4.7–5.1 (m, 2 H), 5.3–6.1 (m, 1 H).

(2) Reaction of o-[1-[(Trimethylsilyl)oxy]vinyl]phenyl Allyl Ether (1i) with $CuCl_2$. To a solution of 605 mg (4.5 mmol) of $CuCl_2$ in 6 mL of DMF was added 372 mg (1.5 mmol) of **1i** dropwise at room temperature, and the mixture was stirred at room temperature for 3 h and at 50 °C for 0.5 h. The mixture was quenched with ice-cold water, extracted with ether, and washed with 5% aqueous HCl and brine. The ether extract was dried over $MgSO_4$ and evaporated. The residue was subjected to preparative TLC to give o-(allyloxy)phenacyl chloride (**2i**) (mp 59–62 °C; TLC on silica gel with chloroform solvent, R_f 0.4) in a 61% yield with the starting o-(allyloxy)phenyl methyl ketone (26%). For **2i**: IR (KBr disk) 1680 cm^{-1}; NMR ($CDCl_3$) δ 4.56 (br d, 2 H), 4.67 (s, 2 H), 5.1–5.5 (m, 2 H), 5.7–6.4 (m, 1 H), 6.7–7.9 (m, 4 H).

General Procedure for Chlorinations of Silyl Enol Ethers with Anhydrous $FeCl_3$. Reaction of 1-[(Trimethylsilyl)-oxy]-2-methyl-1-cyclohexene (1e) with $FeCl_3$. To a solution of 1.22 g (7.5 mmol) of $FeCl_3$ in 13 mL of acetonitrile was added 276 mg (1.5 mmol) of **1e** dropwise, and the mixture was stirred at room temperature for 1.5 h. The reaction mixture was quenched with ice-cold water, extracted with ether, and washed with 5% aqueous HCl and brine. The ether extract was dried over $MgSO_4$ and evaporated. The residue was subjected to preparative gas chromatography to give 2-chloro-2-methylcyclohexanone (**2e**) in a 76% yield: IR (neat) 1723 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.5 (m, 7 H), 1.61 (s, 3 H), 2.9–3.2 (m, 1 H).

Spectral data of other α-chloro ketones (**2**) are summarized as follows. **2a**: IR (neat) 1725 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 1.17 (s, 9 H), 4.30 (s, 2 H). **2b**: IR (neat) 1725 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 0.7–2.1 (m, 14 H), 2.78 (t, 2 H), 4.25 (t, 1 H). **2d**: IR (neat) 1719 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 1.00 (d, 3 H), 1.2–2.4 (m, 6 H), 2.6–3.3 (m, 1 H), 4.0–4.2 (m, 1 H). **2f**: IR (neat) 1720 cm^{-1}; NMR (100 MHz, CCl_4 with Me_4Si) δ 1.0–2.0 (m, 8 H), 2.5–2.8 (m, 1 H), 2.8–3.1 (m, 1 H), 3.90 (s, 2 H), 4.8–5.1 (m, 2 H), 5.81 (m, 1 H). **2h**: IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$ with Me_4Si)

(8) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324–36.

δ 1.62 (br s, 3 H), 1.67 (br s, 3 H), 2.0–2.8 (m, 4 H), 4.02 (s, 2 H), 5.02 (t, 1 H).

Reaction of 1-[1-[(Trimethylsilyl)oxy]vinyl]-2-vinylcyclohexane (1f) with $FeCl_3$. To a stirring solution of 1.21 g (7.5 mmol) of $FeCl_3$ in 13 mL of acetonitrile at 50 °C was added 340 mg (1.5 mmol) of **1f** at once. After 1 min, the reaction mixture was quenched with ice-cold water, extracted with ether, and washed with 5% aqueous HCl and brine. The ether extract was dried over $MgSO_4$ and evaporated. Preparative gas chromatography of the residue furnished 2-chloro-5-oxodecahydronaphthalene (**3f**) in a 58% yield: IR (neat) 1715–1725 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.1 (m, 14 H), 3.6–4.4 (m, 1 H).

Registry No. **1a**, 17510-46-2; *cis*-**1b**, 64682-31-1; *trans*-**1b**, 64682-32-2; **1c**, 6651-36-1; **1d**, 19980-33-7; **1e**, 19980-35-9; *cis*-**1f**, 73193-03-0; *trans*-**1f**, 73193-04-1; **1g**, 57711-32-7; **1h**, 59058-13-8; **1i**, 69879-37-4; **2a**, 13547-70-1; **2b**, 61295-53-2; **2c**, 822-87-7; **2d**, 73193-05-2; **2e**, 10409-46-8; *cis*-**2f**, 73193-06-3; *trans*-**2f**, 73193-07-4; **2g**, 73193-08-5; **2h**, 73193-09-6; **2i**, 73193-10-9; **3f**, 73193-11-0; $CuCl_2$, 7447-39-4; $FeCl_3$, 7705-08-0.

Synthesis of 1,3-Dithiol-2-yl and 1,3-Benzodithiol-2-yl Azides and Their Reaction with Trityl Salt

Juzo Nakayama,* Kazuo Fujiwara, and Masamatsu Hoshino

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

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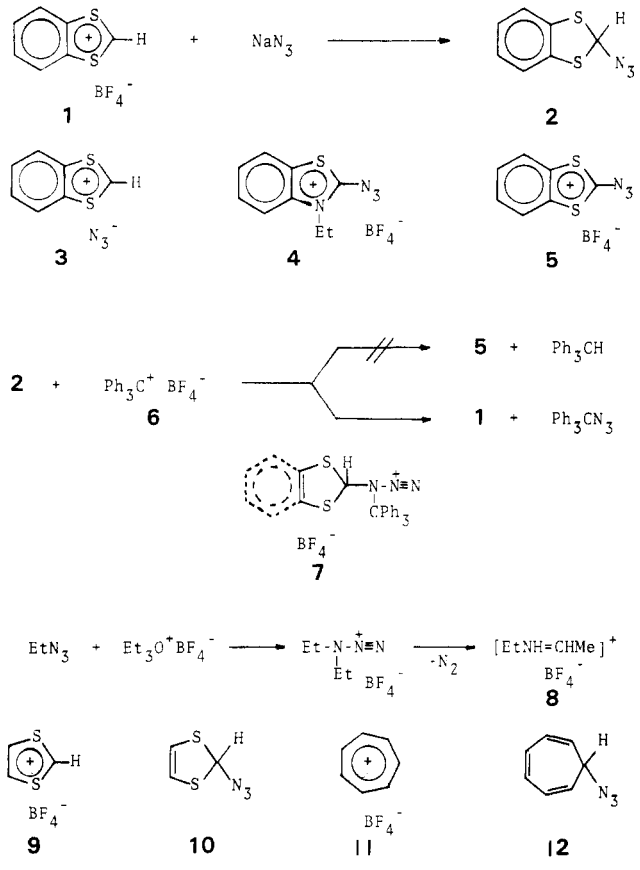
Compound **4** can serve as a diazo donor toward active methylene compounds in a nonbasic medium.[1] Since 1,3-benzodithiole and trityl tetrafluoroborate (**6**) gave 1,3-benzodithiolium tetrafluoroborate (**1**) in good yield,[2] 1,3-benzodithiol-2-yl azide (**2**), on treatment with **6**, might be expected to give the dithiolium salt **5**, which might serve as a diazo donor since it is isoelectronic with **4**.

The azide **2** was prepared in 89% yield from sodium azide and **1**.[2,3] The structure of this azide may be represented as covalent **2**, 1,3-dithiolium azide **3**, or an equilibrium mixture of the two. The chemical shifts of the methine and benzene ring protons of the azide in carbon tetrachloride are comparable with those of 2-alkoxy-[4] and 2-(alkylthio)-1,3-benzodithioles,[5] suggesting that it exists as **2** in a nonpolar solvent as does tropyl azide (**12**).[6] However, an equilibrium mixture cannot be ruled out since its methine proton signal appeared as a rather broad singlet. Similarly, the methine proton of 1,3-dithiol-2-yl azide (**10**), prepared from 1,3-dithiolium tetrafluoroborate (**9**) and sodium azide in a 73% yield, appeared at a position comparable with that of 2-(methylthio)-1,3-dithiole,[7] but as a broad singlet.

An acetonitrile solution of **6** was added dropwise to a stirred, ice-cooled solution of **2** in acetonitrile. The reaction occurred rapidly and the color of **6** disappeared immediately. Much to our surprise, work-up of the mixture gave **1** (87%) and trityl azide (90%). We could not detect the presence of the desired product **5**. Similarly **9** (81%) and trityl azide (70%) were obtained from the azide **10** and **6**.



These results indicate that trityl cation reacts with the α-nitrogen atom of the azide in preference to the methine hydrogen. Studies on reactions of azides with carbonium ions are scarce, but an analogy can be seen in the reaction of ethyl azide with triethyloxonium tetrafluoroborate in which the imine **8** is obtained.[8] In the present case, the formation of the stable 1,3-dithiolium ion must serve as the driving force of the decomposition of **7** to 1,3-dithiolium ion and trityl azide. Tropyl azide (**12**) also reacted with **6** to give a 78% yield of tropylium tetrafluoroborate (**11**) and a 63% yield of trityl azide. However, the possibility that the reaction proceeds via azide ion transfer from the ionized form **3** to trityl cation still remains.

Experimental Section

1,3-Dithiolium[9] and 1,3-benzodithiolium[2] tetrafluoroborates (**9** and **1**) and tropyl azide (**12**)[6] were prepared by reported methods. Acetonitrile was refluxed over and distilled from calcium hydride.

Synthesis of 1,3-Dithiol-2-yl and 1,3-Benzodithiol-2-yl Azides (10 and 2). To a stirred, ice-cooled solution of 2.40 g (10 mmol) of **1** in 10 mL of acetonitrile was added in portions 1.30 g (20 mmol) of sodium azide. The mixture was stirred for 0.5 h and then warmed to room temperature, stirred for an additional 2 h, diluted with 100 mL of ice water, and extracted with 150 mL of hexane. The extract was washed with water, dried over Na_2SO_4, and evaporated under reduced pressure to give 1.73 g (89%) of **2** as a colorless oil, which solidified in a refrigerator and was used

(1) H. Balli and V. Muller, *Angew. Chem., Int. Ed. Engl.*, **3**, 644 (1964); H. Balli and R. Löw, *Tetrahedron Lett.*, 5821 (1966).
(2) J. Nakayama, K. Fujiwara, and M. Hoshino, *Bull. Chem. Soc. Jpn.*, **49**, 3567 (1976).
(3) I. Degani and R. Fochi, *Synthesis*, 471 (1976); J. Nakayama, E. Seki, and M. Hoshino, *J. Chem. Soc., Perkin Trans. 1*, 468 (1978).
(4) J. Nakayama, *Synthesis*, 38 (1975).
(5) J. Nakayama, *Synthesis*, 436 (1975).
(6) C. E. Wulfman, C. F. Yarnell, and D. S. Wulfman, *Chem. Ind. (London)*, 1440 (1960); D. S. Wulfman, L. Durham, and C. E. Wulfman, *Chem. Ind. (London)*, 859 (1962); D. S. Wulfman and J. J. Ward, *Chem. Commun.*, 276 (1967).
(7) K. Sakamoto, N. Nakamura, M. Oki, J. Nakayama, and M. Hoshino, *Chem. Lett.*, 77 (1977).
(8) N. Wiberg and K. H. Schmid, *Angew. Chem., Int. Ed. Engl.*, **3**, 444 (1964). An analogy is also found in the synthesis of isocyanates by reaction of a carboxoyl chloride or carboxylic anhydride with trimethylsilyl azide: S. S. Washburne and W. R. Peterson, *Synth. Commun.*, **2**, 227 (1972); J. H. MacMillan and S. S. Washburne, *J. Org. Chem.*, **38**, 2982 (1973).

$$RCOCl + Me_3SiN_3 \rightarrow RCON_3 \xrightarrow[-N_2]{} RN{=}C{=}O$$

(9) F. Wudl and M. L. Kaplan, *J. Org. Chem.*, **39**, 3608 (1974).

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