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-vinyl-cyclohexane (1f) with FeCl₃. To a stirring solution of 1.21 g (7.5 mmol) of FeCl₃ 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 MgSO₄ 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 (CDCl₃) 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; CuCl₂, 7447-39-4; FeCl₃, 7705-08-0.

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

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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
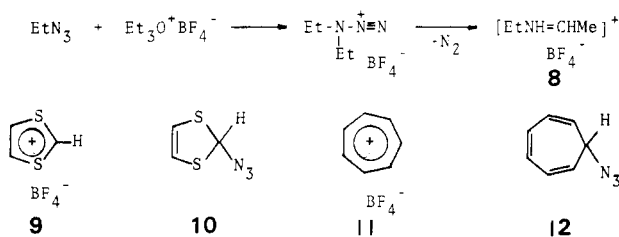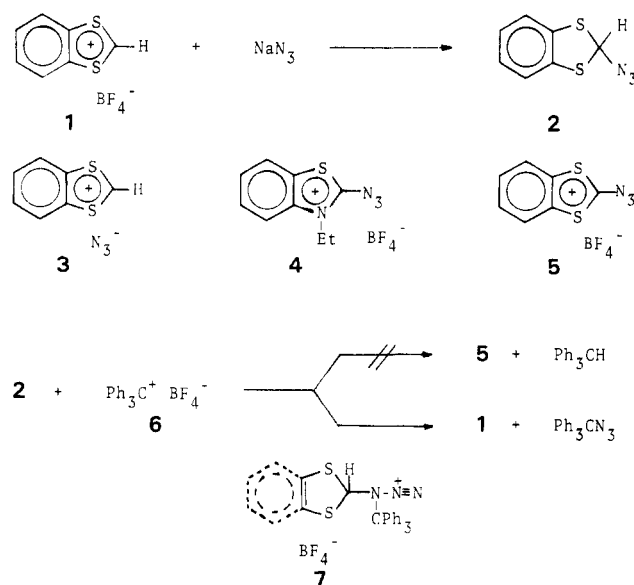
presence of the desired product 5. Similarly 9 (81%) and trityl azide (70%) were obtained from the azide 10 and 6.
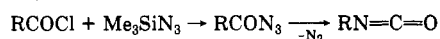
These results indicate that trityl cation reacts with the α-nitrogen atom of the azide in preference to the methine hydrogen. Studies on reactions of azides with carbonium ions are scarce, but an analogy can be seen in the reaction of ethyl azide with triethyloxonium tetrafluoroborate in which the imine 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 Na₂SO₄, 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. Müller, *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 + Me₃SiN₃ → RCON₃ $\xrightarrow{-N_2}$ RN=C=O

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

without further purification: NMR (CCl$_4$ with Me$_4$Si) δ 5.82 (1 H, br s), 6.84–7.44 (4 H, AA'BB' m); IR (neat) 3050, 2990, 2150, 1565, 1450, 1435, 1315, 1200, 1180, 875, 740 cm^{-1}. Anal. Calcd for C$_7$H$_5$N$_3$S$_2$: C, 43.06; H, 2.58; N, 21.52. Found: C, 43.30; H, 2.42; N, 21.30.

Similarly 9 and sodium azide gave a 73% yield of 1,3-dithiol-2-yl azide (10) as a pale yellow liquid, which was unstable at room temperature: NMR (CCl$_4$ with Me$_4$Si) δ 5.95 (1 H, br s), 6.22 (2 H, s); IR (neat) 2180, 1520, 1305, 1295, 1175, 860, 785, 680 cm^{-1}.

Reaction of 1,3-Dithiol-2-yl, 1,3-Benzodithiol-2-yl, and Tropyl Azides (10, 2, and 12) with Trityl Tetrafluoroborate (6). To a stirred, ice-cooled solution of 1.70 g (8.7 mmol) of 2 in 20 mL of anhydrous acetonitrile was added dropwise, over a period of 40 min, a solution of 2.97 g (9 mmol) of 6 in 20 mL of anhydrous acetonitrile. The mixture was stirred for 0.5 h at 0–3 °C and diluted with 250 mL of anhydrous ether. The resulting precipitate was collected and washed with ether to give 1.82 g of 1 as near-white crystals, mp 149–150 °C dec (lit.[2] mp 150–150.5 °C dec). The filtrate was washed with water, dried over Na$_2$SO$_4$, and evaporated. The residue was chromatographed on a silica gel column (eluent hexane) to give 2.23 g (90%) of trityl azide, mp 65–66 °C (lit.[10] mp 64–65 °C).

In a manner similar to that described above, 1.06 g (7.3 mmol) of 10 and 2.64 g (8 mmol) of 6 were allowed to react to give 1.39 g (81%) of 9 and 1.66 g (70%) of trityl azide.

Similarly, 1.18 g (78%) of 11 and 1.53 g (63%) of trityl azide were obtained from 1.13 g (8.5 mmol) of 12 and 2.90 g (8.8 mmol) of 6.

(10) W. H. Saunders, Jr., and J. C. Ware, *J. Am. Chem. Soc.*, 80, 3328 (1958).

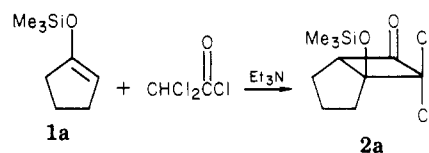## Halogenated Ketenes. 33. Cycloaddition of Ketenes and Trimethylsilyl Enol Ethers

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We recently reported the cycloaddition of dichloroketene with a number of trimethylsilyl enol ethers to produce trimethylsiloxy- and hydroxy-functionalized cyclobutanones.[1] In view of the general synthetic utility of the trimethylsilyl enol ethers as masked enol equivalents[2] and the ease of preparation from readily available aldehydes and ketones,[3] we now report on the cycloaddition of several mono- and disubstituted ketenes with trimethylsilyl enol ethers. The ketenes are generated in the presence of the trimethylsilyl enol, thus resulting in 3-(trimethylsiloxy)-cyclobutanones in good yield. Previous reports of cycloadditions of silyl enol ethers with ketenes are mainly limited to dichloroketene generated by the zinc dechlorination of trichloroacetyl chloride.[1,4a,b]

The generation of dichloroketene by the dehydrochlorination of dichloroacetyl chloride in the presence of the trimethylsilyl enol ether derived from cyclopentanone (1a) resulted in the [2 + 2] cycloaddition product.[5] Vacuum

(1) Brady, W. T.; Lloyd, R. M. *J. Org. Chem.* 1979, 44, 2560.
(2) Rasmussen, J. K. *Synthesis* 1977, 91.
(3) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* 1969, 34, 2324.
(4) (a) Krepski, L. R.; Hassner, A. *J. Org. Chem.* 1978, 43, 3173. (b) Hassner, A.; Pinnick, H. W.; Ansell, J. M. *J. Org. Chem.* 1978, 43, 1774.

distillation provided the siloxycyclobutanone 2a in 77% yield. Spectral data for 2a were in accord with those of an authentic sample prepared by the zinc dehalogenation method.[4a] Several other mono- and disubstituted ketenes were found to react smoothly with trimethylsilyl enol ether 1a to provide the [2 + 2] cycloadducts (see Table I). Reaction of the trimethylsilyl substituent with methanol afforded the bridgehead hydroxycyclobutanones without rearrangement.
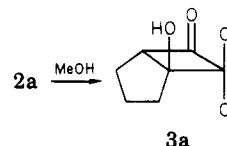
The silyl enol ethers derived from isobutyraldehyde (1b) and 3-cyclohexenecarboxaldehyde (1c) were also found to yield cycloadducts with the halogenated ketenes as seen in Table II. The yields of the cycloadducts of dichloroketene and the three silyl enol ethers were about the same regardless of the method of generation of the ketene, i.e., zinc dehalogenation of trichloroacetyl chloride[6] or dehydrohalogenation of dichloroacetyl chloride. Dichloroketene also gave the highest yield with the silyl enol ethers 1b and 1c, while the yield decreased with methylchloroketene and phenylchloroketene. Although a small amount of cycloadduct could be observed, as evidenced by a band in the infrared at 1800 cm^{-1}, it was not possible to isolate the cycloadduct of phenylchloroketene with either 1b or 1c. The major product in these reactions was a red viscous polymeric material.

The attempted cycloaddition of dichloroketene, generated by the dehydrohalogenation of dichloroacetyl chloride, with the trimethylsilyl enol ether of 2-phenylpropanal (1d) was unsuccessful. However, this cycloaddition proceeds
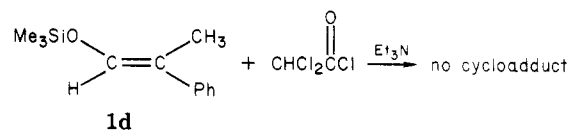
readily when dichloroketene is generated by the zinc dehalogenation of trichloroacetyl chloride and is consistent with an earlier report.[1,4a] Apparently, the zinc or zinc chloride has a catalytic role in the reaction.

The reactions of unsymmetrical ketenes were found to be quite sensitive to steric influences. The cycloaddition of methylchloroketene with trimethylsilyl enol ether 1a yielded two products as evidenced by the NMR spectrum of the crude reaction mixture. These distilled products were found to be in a ratio of 2.5:1. The major isomer was assigned the structure 4a$_1$ with the 7-methyl substituent in the endo position, and the minor isomer, 4a$_2$, has the 7-methyl in the exo position. These assignments were based on the chemical shifts of the 7-methyl and the H$_5$ protons in the NMR spectrum as seen in Table III. This assignment is consistent with literature precedents for the closely related cycloaddition products of cyclopentadiene and alkylhaloketenes, where the downfield proton H$_5$ has

(5) This result conflicts with ref 4a, which states that the cyclobutanone 2a was not observed by the dehydrohalogenation method.
(6) Bak, D. A.; Brady, W. T. *J. Org. Chem.* 1979, 44, 107.