NMR ($CDCl_3$) δ 159.4, 137.2, 136.9, 128.4, 128.3, 127.9, 127.8, 127.5, 127.4, 127.3, 92.1, 68.5, 68.3, 60.5, 47.3, 46.1, 34.5, 28.5, 28.1, 22.2, 13.9.

Anal. Calcd for $C_{24}H_{30}N_2O_2S$, C, 70.21; H, 7.37; N, 6.82. Found: C, 69.98; H, 7.20; N, 6.98.

Reaction of 2 with (Pentyl)$_2$CuCNLi$_2$. Pentyllithium (1.91 mL, 1.5 M, 2.87 mmol, 510 mol %) containing an equivalent amount of LiBr was added dropwise over 0.5 h to CuCN (128 mg, 1.43 mmol, 254 mol %) in dry THF (5 mL) at -78 °C. The resulting light tan solution of (pentyl)$_2$CuCNLi$_2$ was allowed to warm to 0 °C for 0.5 h and recooled to -78 °C. A solution of **2** (202 mg, 0.563 mmol) in THF (6 mL) was added dropwise over 0.5 h to the solution of (pentyl)$_2$CuCNLi$_2$ at -78 °C under argon. The resulting yellowish solution was stirred an additional 11 h. The reaction was then quenched by addition of water (5 mL) and saturated ammonium chloride (3 mL). The mixture was filtered and extracted with methylene chloride as previously described. Flash chromatography (2:1 hexane/ethyl acetate) afforded *N*,*N'*-dibenzylurea[37] (81.2 mg, 37% yield), **6** (45.5 mg, 21% yield), and a mixture of **1** (35 mg, 19% yield) and **11** (35 mg, 19% yield). When this reaction was begun at -65 °C, warmed to 22 °C over 5 h, and stirred at 22 °C for 11 h, **1** (18%), **6** (2%), **11** (18%), and *N*,*N'*-dibenzylurea (60%) were formed.

***N*-Benzyl-*N*-((benzylamino)carbonyl)-2,3-dihydro-3-thiophenamine (11)** was purified by chromatography on silica gel: mp 74-82 °C; mass spectrum, *m/e* (relative intensity) 324 (26, M^+), 277 (7), 266 (8), 240 (33), 233 (35), 149 (16), 106 (46), 100 (26), 91 (100); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.2-7.4 (10 H, m, Ar), 6.37 (1 H, dd (*J* = 1.7, 5.7), HC=CH), 5.85 (1 H, m, NCH), 5.58 (1 H, dd (*J* = 3.1, 5.7), HC=CH), 5.48 (1 H, br t (*J* = 4.9), NH), 4.40 (1 H, d (*J* = 8), benzylic), 4.29 (2 H, d (*J* = 4.9), benzylic), 4.27 (1 H, d (*J* = 8), benzylic), 3.53 (1 H, dd (*J* = 10.2, 13.0), $CH_{exo}S$), 3.03 (1 H, dd (*J* = 4.3, 13.0), $CH_{endo}S$); ^{13}C NMR ($CDCl_3$) δ 157.7, 139.7, 139.0, 131.0, 128.7, 128.5, 128.2, 127.4, 127.2, 127.0, 126.7, 126.1, 121.3, 62.8, 47.2, 44.6, 35.5.

Anal. Calcd for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63. Found: C, 70.81; H, 6.13; N, 8.95.

(3aα,4α,6aα)-1,3-Dibenzylhexahydro-4-hydroxy-1*H*-thieno[3,4-*d*]imidazol-2(3*H*)-one (12). Aqueous 1 M NaOH (1.3 mL, 1.3 mmol, 250 mol %) was added to a solution of **2** (190.3 mg, 0.530 mmol) in 1,2-dimethoxyethane (1.5 mL). After 1 h at 22 °C, the solvent was evaporated. The residue was dissolved in water and neutralized with 1 M HCl, and the solution was extracted three times with CH_2Cl_2. The organic layer was dried and the solvent was evaporated to afford the product (166.3 mg, 92% yield) as a white crystalline solid: mp 146-148 °C (lit.[3] mp 144-145); IR ($CHCl_3$) 3550, 3020, 2950, 1695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.35 (10 H, m, Ar), 5.17 (s, CH-O), 4.75, 4.68, 4.32, 4.21, (4 H, 4 d (*J* = 15.1), benzylic), 4.22 (1 H, dd (*J* = 7.9, 4.7), NCH), 4.01 (1 H, d, *J* = 8.0, NCH), 3.01 (1 H, dd (*J* = 12.7, 4.7), $CH_{exo}S$), 2.87 (1 H, d (*J* = 12.7), $CH_{endo}S$), 1.7 (1 H, br s, OH); ^{13}C NMR ($CDCl_3$) δ 159.5, 137.2, 137.0, 128.8, 128.2, 128.1, 127.5, 84.3, 69.3, 61.0, 47.4, 46.8, 35.2; mass spectrum, *m/e* (relative intensity) 340 (M^+, 15), 187 (56), 91 (100).

(3aα,6aα)-1,3-Dibenzylhexahydro-1*H*-thieno[3,4-*d*]-imidazole-2(3*H*),4-dione (13). Me_2SO (0.16 mL, 176 mg, 2.26 mmol, 353 mol %) was added over 25 min to trifluoroacetic anhydride (0.30 mL, 444 mg, 1.78 mmol, 278 mol %) in ethanol-free chloroform (washed three times with water, dried over $CaCl_2$, and distilled, 1.0 mL) at -60 °C (bath temperature). The mixture was stirred 5 min and a solution of **12** (218 mg, 0.64 mmol) in $CHCl_3$ (2.0 mL) was added over 20 min via syringe. The reaction was stirred at -60 °C for 2 h and then additional TFAA (0.30 mL) and Me_2SO (0.16 mL) were added as above. After an additional 2 h, the reaction was warmed to 0 °C, water (2 mL) was added, and the mixture was extracted three times with chloroform. The organic layers were dried and the solvent was evaporated to afford crude product (227 mg) which was purified by flash chromatography on silica gel (hexane-EtOAc, 50:50) to afford **13** (154 mg, 72% yield) as a white solid: mp 125-127 °C (lit.[3] mp 126-127 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.35 (10 H, m, Ar), 5.03, 4.68, 4.36, 4.35, (4 H, 4 d (*J* = 15.2), benzylic), 4.13 (1 H, ddd (*J* = 2.2, 5.5, 8.1), CHN), 3.80 (1 H, d (*J* = 8.1), CHN), 3.38 (1 H, dd (*J* = 5.5, 12.8), $CH_{exo}S$), 3.28 (1 H, dd, (*J* = 2.2, 12.8), $CH_{endo}S$); IR ($CHCl_3$) 1800, 1700 cm^{-1}; mass spectrum, *m/e* (relative intensity) 338 (17), 187 (33), 91 (100).

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(37) *Sadtler Standard NMR Spectra*; Sadtler Research Laboratories: Philadelphia, 1974; 18689 M.

A Selective Method for Oxygen Deprotection in Bistrimethylsilylated Terminal Alkynols

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A selective method for oxygen deprotection of bistrimethylsilylated ω-alkynols is described using sulfonic acid type exchange resins in ether solvent. The method offers the advantages of selectivity toward the silicon-oxygen bond, easier monitoring of the reaction and workup, and higher yields (>75%). Comparisons are made between standard aqueous acid procedures and a series of resins.

Synthetic studies in this laboratory recently required ω-alkynols having the terminal alkynyl carbon protected with a trimethylsilyl (Me_3Si) grouping. Since carbon selectivity is not possible in the silylation of these compounds, it is necessary to protect both positions then remove the oxygen-bound silyl moiety.[2] A method was, therefore, sought for selective Si-O cleavage in these doubly protected substrates.

It is well-known that silicon groups are readily, but indiscriminantly, cleaved from both carbon and oxygen in the presence of fluoride ion.[3] Selective removal of the Me_3Si group from oxygen in bistrimethylsilylated terminal alkynols using aqueous 1 M hydrochloric acid[2] and 30%

(1) Address: Department of Chemistry, Southwestern Oklahoma State University, Weatherford, OK 73096.

(2) See footnote 5 in: Corey, E. J.; Tramontano, A. *J. Am. Chem. Soc.* **1984**, *106*, 462-463.

(3) See, for example: (a) Corey, E. J.; Snider, B. B. *J. Am. Chem. Soc.* **1972**, *94*, 2549-2550. (b) Majetich, G.; Hull, K.; Desmond, R. *Tetrahedron Lett.* **1985**, *26*, 2751-2754.

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Table I. Reaction Yields for Selective Cleavage of Bistrimethylsilylated ω-Alkynols

reactant	resin or acid	reacn time, h	product	isolated yield, %
1	30% HOAc	1	2	72
1	1 M HCl	0.05	2	60
1	Rexyn AG 50	3	2	82
1	Amberlyst 15	3	2	86
1	Dowex 50W-X2	3.3	2	91
1	Rexyn 101	19	2	94
3	Rexyn 101	3	4	79
5	1 M HCl	0.5	6	20
5	Dowex 50W-X2	4	6	58
5	Rexyn 101	1	6	80
7	1 M HCl	3	8	67
7	Amberlyst 15	1.15	8	74
7	Rexyn 101	80	8	69

acetic acid[4] has been reported; in our application, however, these methods proved difficult to control, and reproducibility was poor. The present work describes the use of sulfonated polystyrene cation-exchange resins for the selective hydrolysis of Me_3Si protected alcohols in the presence of (trimethylsilyl)alkynes as depicted in eq 1.

$$(CH_3)_3SiC{\equiv}C(CH_2)_nCH(R)OSi(CH_3)_3 \xrightarrow[\text{ether, 20 °C}]{\text{Ⓟ-SO}_3\text{H}} (CH_3)_3SiC{\equiv}C(CH_2)_nCH(R)OH \quad (1)$$

1, n = 3, R = H
3, n = 2, R = H
5, n = 0, R = H
7, n = 0, R = CH_3

2
4
6
8

Ion-exchange resins have found previous use in organic synthesis for the removal of several oxygen protecting groups.[5,6] The present work, however, is the first report of the application of polymer supported acid to the selective hydrolysis of differentially bound Me_3Si groups. Sulfonic acid type exchange resins exhibit several preferred qualities for the hydrolysis of such substrates: (1) greater selectivity toward the Si–O bond, (2) slower conversion with no soluble acid which facilitates direct gas chromatographic monitoring of the reaction, and (3) easier workup involving only filtering, drying, and concentrating. This last point is particularly important for low molecular weight compounds, such as the (trimethylsilyl)alkyne derivative of propargyl alcohol (**5**), where water solubility makes extraction from an aqueous layer difficult. In all cases, with appropriate resin selection, products were isolated in high yield without contamination by silicon-containing residues and could be used in subsequent transformations without further purification.

Table I summarizes our results comparing a series of resins with standard methods employing aqueous acid. It is apparent from these data that the use of exchange resins in this transformation significantly improves the yield of product. Beyond this, experimental operations are simplified and the products obtained are cleaner.

Figure 1 compares the rate of conversion of 1-(trimethylsiloxy)-6-(trimethylsilyl)-5-hexyne (**1**) to 6-(trimethylsilyl)-5-hexyn-1-ol (**2**) using four different resins. Amberlyst 15, an anhydrous resin designed for use as an acid catalyst in organic solvents, possesses enhanced reactivity due to its microporous structure[7] and is consequently less selective than the other catalysts which are wet ion-exchange resins. After an initial sharp rise in product formation, the yield gradually lowers with time due to further cleavage of the (trimethylsilyl)alkyne bond. The wet resins have less tendency to attack the SiC bond and give much more controlled reactions. For doubly protected primary alcohols, it was most convenient to use the mildest resin, Rexyn 101, and leave the reaction stirring overnight. For the bis(trimethylsilyl) derivative of the secondary alcohol, **7**, the more active Amberlyst 15 proved superior. In all cases, the reaction proceeded best when enough resin was used to provide a full equivalent of acidic sites. Finally, when the alcohol was tertiary, as in 1,1-dimethyl-2-propyn-1-ol, only the monosilylated product was formed under the conditions employed for the preparation of the disilylated derivatives.[2,4]

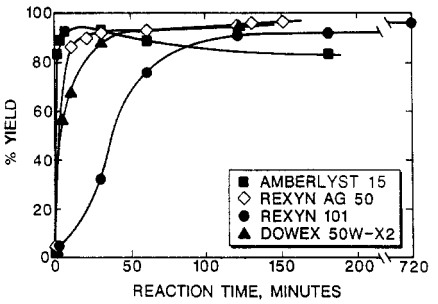

Figure 1. Kinetic study of 1 → 2 comparing four sulfonated polystyrene resins.

The current methodology was found to be effective only in the selective cleavage of bis(trimethylsilyl) terminal alkynols. Attempts to expand the scope of the reaction to include substrates derivatized with the more synthetically versatile *tert*-butyldimethylsilyl group were unsuccessful, giving mostly recovered starting material or completely deprotected alkynol. Similarly, the *tert*-butyldiphenylsilyl-protected compound was completely impervious to resin-promoted hydrolysis even after 6 days of exposure to Amberlyst 15.

In summary, cation-exchange resins have been used to selectively remove oxygen-bound Me_3Si groups in the presence of (trimethylsilyl)alkynes. The method offers many advantages over standard aqueous procedures—higher selectivity and yields, simpler experimental manipulations and cleaner products. The present findings should prove useful in syntheses involving more complex molecules.

Experimental Section[8]

General Procedure for Selective Cleavage of Bistrimethylsilylated ω-Alkynols. 6-(Trimethylsilyl)-5-hexyn-1-ol (2). To a vigorously stirred suspension of 7 mL of Rexyn 101

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(8) Bistrimethylsilylated substrates were prepared by methods previously described.[2,4] The sulfonated polystyrene resins utilized were obtained from the following sources: Dowex 50W-X2, Bio-Rad; Rexyn 101 and Rexyn AG 50,[9] Fisher Scientific; Amberlyst 15 was a generous gift from the Rohm and Haas Co. Anhydrous diethyl ether was used as received. Kinetic measurements were made with a Varian 3400 capillary GC with FI detection (0.25 mm × 3 m DB-1 column programmed between 50–150 °C). IR spectra were recorded with a PE-681 instrument and are referenced to polystyrene. ^1H NMR spectra were measured as solutions in $CDCl_3$ with a Varian XL-300 superconducting FT instrument; chemical shifts are reported in δ units relative to internal Me_4Si. Mass spectra were recorded at 70 eV with a CEC double focusing mass spectrometer.
(9) Rexyn AG 50 is no longer commercially available from Fisher Scientific. Rexyn 101, which is available, is slightly milder but affords very similar results. Rexyn AG 50 was studied due to the fact that we had a large supply on hand and our work was already completed when we learned it had been discontinued.

(analytical grade, 16–50 mesh, 1.99 mequiv of H/mL, 14 mequiv of H) in 10 mL of anhydrous ether was added 3.0 g (12.4 mmol) of 1-(trimethylsiloxy)-6-(trimethylsilyl)-5-hexyne (1). The reaction was monitored by GC analysis of 0.2-μL aliquots removed by syringe directly from the reaction mixture. After 19 h, the reaction was filtered through a coarse sintered-glass frit and the filtrate dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to give 2.12 g of an oil, which was shown by GC to contain 1.4% of starting material and 98.6% of 6-(trimethylsilyl)-5-hexyn-1-ol (2). The product can be used directly or purified by fractional distillation to yield 1.98 g (11.7 mmol, 94%) of pure (trimethylsilyl)alkynol: bp 55–56 °C (0.5 mmHg); IR (neat) 3425, 2180, 1250, 1050, 843 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.68 (t, J = 6 Hz, 2 H), 2.28 (t, J = 6 Hz, 2 H), 1.82 (br s, 1 H), 1.66 (m, 4 H), 0.14 (s, 9 H); mass spectrum, m/z (relative intensity) 170 (M^+, 0.2), 75 (100), 73 (25.5); exact mass calcd for $C_9H_{18}OSi$ m/z 170.1127, found m/z 170.1099.

The above procedure was exactly the same for all the resins utilized in this study.

5-(Trimethylsilyl)-4-pentyn-1-ol (4):[2] bp 47–49 °C (0.5 mmHg); IR (neat) 3330, 2180, 1250, 1045, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.71 (t, J = 6 Hz, 2 H), 2.41 (br s, 1 H), 2.30 (t, J = 6 Hz, 2 H), 1.72 (quintet, J = 6 Hz, 2 H), 0.12 (s, 9 H); mass spectrum, m/z (relative intensity) 156 (M^+, 0.2), 125 (11), 99 (14), 75 (100), 73 (30); exact mass calcd for $C_8H_{16}OSi$ m/z 156.0970, found m/z 156.1010.

3-(Trimethylsilyl)-2-propyn-1-ol (6):[4] bp 51–52 °C (3 mmHg) [lit.[4] bp 71 °C (15 mmHg)]; IR (neat) 3350, 2180, 1250, 1040, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.16 (s, 2 H), 3.12 (br s, 1 H), 0.12 (s, 9 H); mass spectrum, m/z (relative intensity) 124 (M^+, 0.6), 85 (100), 75 (36), 73 (40); exact mass calcd for $C_6H_{12}OSi$ m/z 128.0657, found m/z 128.0695.

4-(Trimethylsilyl)-3-butyn-2-ol (8): bp 49–51 °C (1.5 mmHg); IR (neat) 3330, 2175, 1371, 1250, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.43 (q, J = 6 Hz, 1 H), 3.34 (br s, 1 H), 1.40 (d, J = 6 Hz, 3 H), 0.15 (s, 9 H); mass spectrum, m/z (relative intensity) 124 ($M^+ - H_2O$, 2), 99 (100), 75 (12), 73 (13); exact mass calcd for $C_7H_{14}OSi \cdot H_2O$ m/z 124.0709, found m/z 124.0665.

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Photochemical Reactions of 2,4-Dinitro-6-phenyliodonium Phenolate with Alkenes, Alkynes, and Aromatic Compounds

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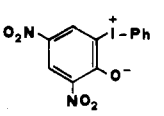
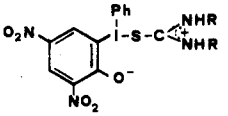
2,4-Dinitro-6-phenyliodonium phenolate, a stable iodonium zwitterion, reacts under photolytic conditions with various alkenes, alkynes, and aromatic compounds to afford 2,3-dihydrobenzo[*b*]furans, benzo[*b*]furans, and 6-aryl-2,4-dinitrophenols. A possible reaction pathway involving the intermediacy of hypervalent iodine compounds is proposed.

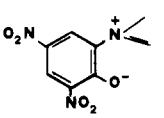
Zwitterionic iodonium compounds constitute an interesting class of hypervalent iodine compounds, the chemistry of which has recently been reviewed.[1] In our continuing exploration of the chemistry of hypervalent iodine compounds we have reported[2] the synthesis and reactivity of some 2-oxidodiaryliodonium zwitterions. Among them 2,4-dinitro-6-phenyliodonium phenolate (1) is easily prepared and fairly stable.[2] The phenyliodonio group in 1 can be displaced by basic nucleophiles,[2] whereas other nucleophiles react with 1 only under photolytic conditions. Thus irradiation of 1 in carbon disulfide affords 5,7-dinitro-1,3-benzoxathiole-2-thione.[3] Similarly phenyl isothiocyanate with 1 gives 5,7-dinitro-2-phenylimino-1,3-benzoxathiole.[4] Stable iodinanes 2 have been isolated from the photochemical reaction of 1 with various thioureas,[4] whereas pyridinium zwitterions 3 have been formed from the photoreaction of 1 with pyridines.[4]



1



2



3

The photochemical reaction of 1 with various alkenes, alkynes, and aromatic compounds are reported here.

Results and Discussion

When a suspension of 1 in acetonitrile was irradiated in the presence of an alkene 4 for several hours, 2,3-dihydrobenzo[*b*]furans 5 and/or 6-alkenyl-2,4-dinitrophenols 6 were isolated (Table I).

The above reaction provides an easy route to various 2,3-dihydrobenzo[*b*]furans, the synthesis of which has attracted much attention because of their interesting pharmacological properties.[5] An analogous reaction involving in situ generated carbenoid species has been described by Huisgen.[6] 2,3-dihydrobenzo[*b*]furans were

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