Acknowledgment. I acknowledge the encouragement and inspiration provided by the late Professor Robert B. Woodward in whose laboratories the work in this and the following paper was initiated and completed. I also acknowledge the generous financial support provided by the National Science Foundation (Grant CHE 78-25699) to the Woodward Group. I am grateful for the collective support and encouragement of the Harvard Organic Chemistry Faculty after Professor Woodward's death and am especially grateful to Professor Jeremy Knowles for his invaluable advice and encouragement and to Professor Frank Westheimer for his sincere and thoughtful interest and criticism.

Registry No. 4, 38499-08-0; **5a**, 86864-24-6; **5b**, 86864-25-7; **5c**, 86864-26-8; **5d**, 86864-27-9; **5e**, 86864-28-0; **5f**, 86864-29-1; **5g**, 86884-72-2; **5h**, 86884-73-3; **5i**, 86864-30-4; **5j**, 86864-31-5; **6a**, 86864-32-6; **6b**, 86864-33-7; **6c**, 86864-34-8; **6d**, 86864-35-9; **6e**, 86864-36-0; **6f**, 86864-37-1; **6g**, 86864-38-2; **7**, 5824-40-8; **8**, 13733-56-7; **9b**, 86864-39-3; **9d**, 86864-40-6; **10a**, 86864-41-7; **10b**, 86864-42-8; **10c**, 86864-43-9; **10d**, 86864-44-0; **11a**, 86864-45-1; **11b**, 86864-46-2; **11c**, 86864-47-3; **11d**, 86864-48-4; **11e**, 86864-49-5; **11f**, 86864-50-8; **12a**, 5381-93-1; **12b**, 14035-54-2; **12c**, 13161-18-7; **12d**, 42052-56-2; **13a**, 86864-51-9; **13b**, 86864-52-0; **13c**, 86864-53-1; **13d**, 86864-54-2; **13e**, 86864-55-3; **14a**, 86864-56-4; **14b**, 86864-57-5; **14c**, 86864-58-6; $OHCCH_2CH_3$, 123-38-6; $OHCCH_2(CH_2)_7CH_3$, 112-31-2; H_3CCOCH_3, 67-64-1; $H_3CCOCH_2CH_3$, 78-93-3; $-(CH_2)_4COCH_2-$, 108-94-1; $-(CH_2)_2CH(C(CH_3)_3)CH_2COCH_2-$, 936-99-2; $-(CH_2)_4COCH(CH_3)-$, 583-60-8; $H_3CCOCH_2COOCH_3$, 105-45-3; $H_3CCOCH_2COOCH_2CH_3$, 141-97-9; $H_3CCOCH_2(CH_2)_2OSi(CH_3)_2C(CH_3)_3$, 86864-59-7; $OHCCH{=}CHCH_3$, 4170-30-3; $OHCCH{=}C(CH_3)_2$, 107-86-8; OHCPh, 100-52-7; $OHCC_6H_4OCH_3$-4, 123-11-5; $H_3CCOCOOCH_3$, 600-22-6; H_3CCOPh, 98-86-2; $-(CH_2)_2C(CH_3){=}CHCO-$, 2758-18-1; CH_3F, 74-88-4; $H_3C(CH_2)_3Br$, 109-65-9; $(CH_3)_3CSi(CH_3)_2O(CH_2)_2Br$, 86864-60-0; $H_2C{=}CHCH_2I$, 556-56-9; Ph_2CO, 119-61-9.

Supplementary Material Available: Tabulations of ^1H NMR and elemental microanalysis data of compounds **5a-j**, **6a-g**, **9b,d**, **11b-f**, **12a-d**, **13a-e**, and **14a-c** (11 pages). Ordering information is given on any current masthead page.

Studies on the Development of the Tritylsulfenyl Group as a Nitrogen Protecting Group and Application in a Synthesis of δ-Coniceine[1]

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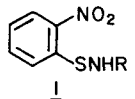
The (triphenylmethyl)sulfenyl (tritylsulfenyl, TRS) group was found to possess properties which should make it useful as a nitrogen protecting group. The almost instantaneous reaction of TrSCl (**6**) with amines produced the corresponding triphenylmethanesulfenamides. The TRS group was found to render the nitrogen atom nonbasic and relatively nonnucleophilic, was stable to aqueous acid, aqueous base, and various reducing agents, and was moderately stable to Moffat oxidation conditions. The TRS group could be cleaved under mild conditions, generating the amine with either $CuCl_2$/EtOH-THF, HI/THF-H_2O, or trimethylsilyl iodide (Me_3SiI)/CH_2Cl_2. A synthesis of δ-coniceine (**16**) illustrates carbon-carbon bond formation with tritylsulfenimine methodology and the utility of the tritylsulfenyl group as a nitrogen protecting group.

The sulfenamide functional group, in particular the *o*-nitrophenylsulfenyl (*o*-NPS) group (see **1**), is known to



1

Ph_3CSNHR = TrSNHR

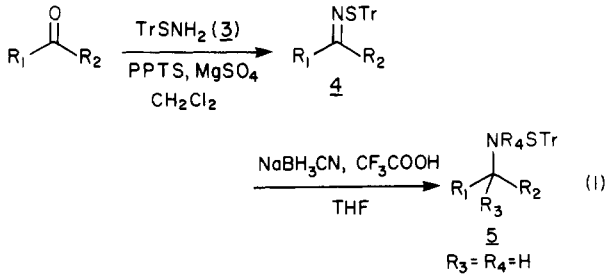
2

be useful as a nitrogen protecting group for peptide synthesis.[3] Zervas[3] examined the (triphenylmethyl)sulfenyl (tritylsulfenyl, TRS) group (see **2**) as an amine protecting group for peptide synthesis, for which it was useful, but the methodology was never widely used due to the superior properties of the *o*-NPS group.

We have found that the TRS group possesses properties which make it useful as an amine protecting group in contexts other than peptide synthesis and in situations where the *o*-NPS group would be inapplicable due to incompatibility of the nitro group with various reagents, in particular strong reducing agents and organometallic reagents.

Results and Discussion

Triphenylmethanesulfenamides are now readily available by reduction of tritylsulfenimines as described in the accompanying paper (eq 1), but the general utility of the



TRS group as a nitrogen protecting group arises from the ease of preparation of triphenylmethanesulfenamides from the corresponding amines. Treatment of an amine with triphenylmethanesulfenyl chloride (TrSCl, **6**)[4] at room

(1) Taken from the Ph.D. thesis of B.P.B., Harvard University, 1981.

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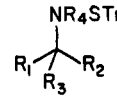
(3) Zervas, L.; Borovas, D.; Gazis, E. *J. Am. Chem. Soc.* **1963**, *85*, 3660.

(4) See accompanying paper.

0022-3263/83/1948-3538$01.50/0

Table I. Formation of Triphenylmethanesulfenamides by Reaction of Amines with Triphenylmethanesulfenyl Chloride



5

entry	amine	R_1	R_2	R_3	R_4	base	solvent	product (isolated yield,[a] %)
1	*n*-decylamine	H	H	$(CH_2)_8CH_3$	H	Na_2CO_3	$THF-H_2O$	**5a** (95)
2	benzylamine	H	H	Ph	H	pyridine	CH_2Cl_2	**5b** (77)
3	benzylamine	H	H	Ph	H	Na_2CO_3	$THF-H_2O$	**5b** (97)
4	cyclohexylamine	H		$-(CH_2)_5-$	H	pyridine	CH_2Cl_2	**5c** (79)
5	cyclohexylamine	H		$-(CH_2)_5-$	H	Na_2CO_3	$THF-H_2O$	**5c** (96)
6	*tert*-butylamine	CH_3	CH_3	CH_3	H	pyridine	CH_2Cl_2	**5d** (80)
7	*tert*-butylamine	CH_3	CH_3	CH_3	H	Na_2CO_3	$THF-H_2O$	**5d** (85)
8	piperidine	H	H	$-(CH_2)_4-$		pyridine	CH_2Cl_2	**5e** (64)
9	piperidine	H	H	$-(CH_2)_4-$		Na_2CO_3	$THF-H_2O$	**5e** (86)

[a] After chromatography on silica gel.

temperature results in the almost instantaneous formation of the triphenylmethanesulfenamide (eq 2, Table I).

6 5 (2)

When hindered amines such as diisopropylamine or 2,2,6,6-tetramethylpiperidine were reacted with **6**, a fairly rapid reaction ensued, but the triphenylmethanesulfenamide was not the isolated product. A compound whose structural data were most consistent with ditrityl peroxide could be crystallized directly from the reaction solutions of 2,2,6,6-tetramethylpiperidine with **6** in as high as 45% yield by trituration with anhydrous EtOH. It seems likely that the triphenylmethanesulfenamide was formed initially but decomposed[5] to triphenylmethyl (trityl radical, which is known to produce ditrityl peroxide upon exposure to oxygen)[6] and the relatively stable 2,2,6,6-tetramethylpiperidine-1-thiyl radical.[7] A sample of *N*,*N*-(Pentamethylene)triphenylmethanesulfenamide (**5e**) underwent partial decomposition (apparently to ditrityl peroxide by ^1H NMR) after storage for 2 weeks at room temperature.

A characteristic of most sulfenamides is the lability of the sulfur–nitrogen bond to a variety of reagents and conditions[8] including aqueous and nonaqueous acid, Lewis acids, aqueous and nonaqueous base, organic and inorganic nucleophiles, and various reducing agents including Raney nickel and diborane. There is also evidence available that sulfenamides can exhibit an α effect,[9] i.e., an enhanced nucleophilicity relative to the parent amine as is the case with hydroxylamines.

In the course of development of conditions to convert triphenylmethanesulfenamides to the corresponding amines to complete a reductive amination sequence for the conversion of carbonyl compounds to primary amines,[4] it eventually became apparent that the TRS group was considerably more stable than expected and that the TRS group could survive a wide range of synthetically useful reaction conditions.

Our studies show that *the TRS group*: (*a*) *renders the nitrogen atom nonbasic*, (*b*) *significantly decreases the nucleophilicity of the nitrogen*, (*c*) *is stable to aqueous acid*, (*d*) *is stable to aqueous base*, (*e*) *is stable to many common reducing reagents, and* (*f*) *is unstable to many common oxidizing reagents.*

From a practical point of view triphenylmethanesulfenamides possess no basic properties. Molecules containing the TRS group have been routinely exposed to aqueous acid during extractive workups with no significant loss of material. For example, the *N*-benzyl-1,1,1-triphenylmethanesulfenamide (**5b**) could not be extracted from an Et_2O solution into aqueous 1 N HCl. The effect must be predominantly the electronic effect of the sulfur since a partially purified sample of tritylamine ($TrNH_2$), prepared by thermolysis of $TrSNH_2$,[4] was purified by an aqueous extractive workup and was found to be freely soluble in aqueous acid.

The decreased nucleophilicity of the nitrogen atom in a triphenylmethanesulfenamide is evident from its demonstrated utility as a nitrogen protecting group for peptide synthesis,[3] although the reaction of $TrSNH_2$ with acetyl chloride in pyridine was reported to form TrSNHAc.[10] We found that $TrSNH_2$ exhibited decreased reactivity toward carbonyl compounds compared to amines, hydroxylamines, and hydrazines.[4] In contrast, the analogous $TrONH_2$ reacts with carbonyl compounds within minutes with no catalyst.[11]

The TRS group routinely survived mild nonaqueous acidic conditions in the preparation of triphenylmethanesulfenamides by the reduction of tritylsulfenimines.[4] The group is moderately stable to aqueous acid, as illustrated in Table II. The anion in the mineral acid plays an important role in determining the acid stability of the TRS group since a reaction run with HI instead of HCl under otherwise identical conditions led to complete cleavage of the TRS group within minutes. These results can be rationalized by using hard–soft acid–base theory,[12]

(5) Force must be used in constructing a space-filling model of *N*-(2,2,6,6-tetramethylpiperidinyl)-1,1,1-triphenylmethanesulfenamide.
(6) Gomberg, M. *Chem. Ber.* **1900**, *33*, 3150.
(7) Bennett, J. E.; Sieper, H.; Tavs, P. *Tetrahedron* **1967**, *23*, 1697.
(8) References to reactions of sulfenamides can be found in the accompanying paper and in: (a) Rheinholdt, H., Mott, F. *Chem. Ber.* **1939**, *72*, 668. (b) Foss, O. *Acta Chem. Scand.* **1947**, *1*, 307. (c) Nith, H.; Mikulaschek, G. *Chem. Ber.* **1961**, *94*, 634. (d) Noth, H.; Mikulaschek, G. *Ibid.* **1964**, *97*, 709. (e) Fontana, A.; et al. *Tetrahedron Lett.* **1966**, 2985.
(9) (a) Welch, W. M. *J. Org. Chem.* **1976**, *41*, 2220. (b) Davis, F. A.; et al. *Ibid.* **1977**, *42*, 967. (c) Gordon, E. M., et al. *J. Am. Chem. Soc.* **1980**, *102*, 1690.
(10) Vorlander, D.; Mittag, E. *Chem. Ber.* **1919**, *52*, 413.
(11) Lutz, W. *J. Org. Chem.* **1971**, *36*, 3835.
(12) (a) Ho, T. L. "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977. (b) Pearson, R. G. "Hard and Soft Acids and Bases"; Dowder, Hutchinson, and Ross Inc.: Stroudsburg, PA, 1973.

Table II. Resistance of *N*-Benzyl-1,1,1-triphenylmethanesulfenamide (5b) to Various Conditions

reaction conditions	coreactant	coproduct (isolated yield,[a] %)	5b, isolated yield,[a] %
3:1 THF/1 N HCl, room temp, 5 h			75
2:3:3 0.5 N NaOH/THF/EtOH, room temp, 24 h			92
$NaBH_4$ (6 equiv)/THF–EtOH (1:4)	4-*tert*-butylcyclohexanone (3 equiv)	4-*tert*-butylcyclohexanol (73)	95
$NaAlH_2Et_2$ (0.052 M)/THF, 0 °C, 2 h			96
$LiAlH_4$ (6 equiv)/Et_2O, 0 °C, 30 min	methyl benzoate (6 equiv)	benzyl alcohol (87)	91
H_2 (1 atm), 10% Pd/C/EtOH–THF (4:1), room temp, 24 h	*trans*-stilbene (1 equiv)	bibenzyl (96)	90
H_2 (1 atm), 10% Pt/C/EtOH–THF (4:1), room temp, 24 h	*trans*-stilbene (1 equiv)	stilbene and bibenzyl (ca. 1:1, ca. 100%)	94
dicyclohexylcarbodiimide (10 equiv), pyridinium trifluoroacetate (3 equiv), Me_2SO, 6 h, room temp.	4-*tert*-butylcyclohexanol (3 equiv)	4-*tert*-butylcyclohexanone (90% by NMR)	59

[a] After chromatography.

in which the hard proton interacts with the hard nitrogen atom, and the soft sulfur center interacts with the halide ion; the softer halide promotes the cleavage reaction.

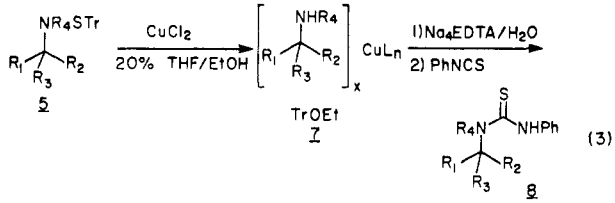
The TRS group is stable to moderately strong aqueous base, as illustrated in Table II and in our synthesis of δ-coniceine in which the group survives exposure to basic sodium peroxide (vide infra).

The TRS group is resistant to exposure to $NaBH_3CN$ in the preparation of triphenylmethanesulfenamides from the corresponding sulfenimines.[4] It also survives exposure to a variety of reducing agents (Table II) including $LiAlH_4$ (triphenylmethanesulfenamides can be reduced to triphenylmethane with $LiAlH_4$ under more forcing conditions).

The TRS group is incompatible with a variety of oxidizing reagents including *m*-chloroperbenzoic acid and various chromium-based oxidants such as pyridinium chlorochromate, Collins reagent, and Jones reagent. The TRS group is moderately stable to Moffat oxidation conditions (Table II). Many of the numerous variants on Me_2SO-based and Me_2SO-type oxidants should be compatible with the TRS group, although reaction conditions may have to be carefully defined to optimize the desired oxidation and minimize the loss of the TRS group.

The stability of the TRS group to various reagents and conditions limits the possibilities for the liberation of the free amine from the corresponding triphenylmethanesulfenamide under mild, synthetically useful conditions. However, ways to effect that transformation have been uncovered.

Treatment of triphenylmethanesulfenamides with anhydrous cupric salts in anhydrous EtOH–THF results in solvolysis, leading after a workup to the free amine, which was determined by conversion to the corresponding phenylthiourea (eq 3, Table III). Trityl ethyl ether (TrOEt, 7) was isolated as a major solvolysis byproduct.



(3)

Exploiting our discovery of the instability of triphenylmethanesulfenamides to HI, we developed a general procedure for the rapid conversion of triphenylmethanesulfenamides to the corresponding amines using excess aqueous HI (eq 4, Table IV).

Table III. Cupric Chloride Mediated Solvolysis of Triphenylmethanesulfenamides Leading to the Corresponding Amines

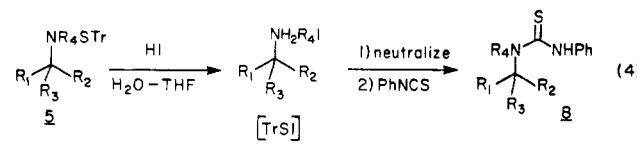
compd[b]	R_2	R_3	amine (isolated yield,[a] %, of the phenylthiourea)
5a	H	$(CH_2)_8CH_3$	8a (67)
5b	H	Ph	8b (61)
5c		$-(CH_2)_5-$	8c (58)
5f	H	4-CH_3OPh	8d (60)
5g	CH_3	$CH_2COOCH_2CH_3$	8e (64)

[a] After chromatography on silica gel. [b] $R_1 = R_4 = H$ in all cases.

Table IV. Conversion of Triphenylmethanesulfenamides to Amines with Hydrogen Iodide

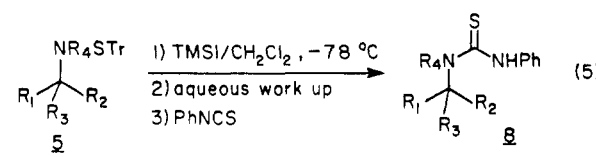
compd[b]	R_2	R_3	amine (isolated yield,[a] %, of the phenylthiourea)
5a	H	$(CH_2)_8CH_3$	8a (86)
5b	H	Ph	8b (95)
5c		$-(CH_2)_5-$	8c (92)
5f	H	4-CH_3OPh	8d (91)
5g	CH_3	$CH_2COOCH_2CH_3$	8e (82)
5h		$-(CH_2)_2CH(C(CH_3)_3)(CH_2)_2-$	8f (86)

[a] After chromatography on silica gel. [b] $R_1 = R_4 = H$ in all cases.



(4)

The conversion of triphenylmethanesulfenamides to amines can also be accomplished by using trimethylsilyl iodide (Me_3Si)[13] in chlorinated solvents at −78 °C (eq 5,



(5)

Table V. Conversion of Triphenylmethanesulfenamides to Amines with Trimethylsilyl Iodide

compd[b]	R_2	R_3	amine (isolated yield,[a] %, of the phenylthiourea)
5a	H	$(CH_2)_8CH_3$	8a (89)
5b	H	Ph	8b (96)
5c		$-(CH_2)_5-$	8c (94)
5f	H	4-CH_3OPh	8d (95)
5g	CH_3	$CH_2COOCH_2CH_3$	8e (77)

[a] After chromatography on silica gel. [b] $R_1 = R_4 = H$ in all cases.

Scheme I

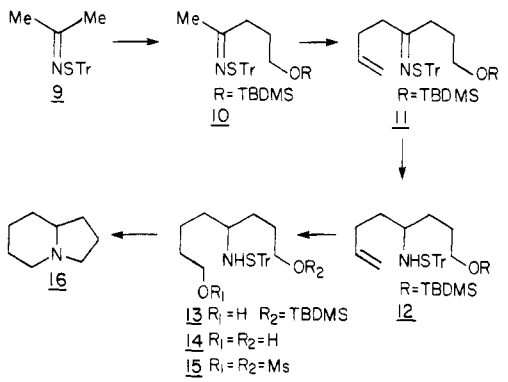


Table V). Using **5b** as a model, it was found that a minimum of 2 equiv of Me_3SiI was necessary for complete reaction. It was also found that the reaction was complete even after exposure of **5b** to Me_3SiI/CH_2Cl_2 at −95 °C for only 5 min. The presence of TrSI was inferred from the formation of $TrSNH_2$ (**3**) when a reaction at −78 °C was quenched with saturated NH_3/EtOH followed by gradual warming to room temperature.

Synthesis of δ-Coniceine

We choose to illustrate various aspects of triphenylmethanesulfenamide-based methodology, as described in this and the accompanying paper, with a synthesis of δ-coniceine[14] (Scheme I).

As detailed in the accompanying paper the following reactions were performed. Deprotonation of acetone tritylsulfenimine (**9**) followed by reaction with $BrCH_2CH_2OTBDMS$ produced **10** (52–77%, purified) which was also prepared by the reaction of the corresponding ketone with $TrSNH_2$ (70%). Deprotonation of **10** followed by reaction with $ICH_2CH{=}CH_2$ then produced **11** (97%, crude).

Reduction of **11** with $NaBH_3CN$ and CF_3COOH in THF at room temperature at pH 4–5 produced **12** (95%, 92% overall from **10**). Several reactions were then performed to both complete the synthesis and illustrate the resistance of the TRS group to various reagents and reaction conditions.

Hydroboration of **12** with B_2H_6/THF at room temperature followed by oxidation with $NaOH–H_2O_2/H_2O$ produced **13** (69%, purified). Removal of the TBDMS group from **13** with n-Bu_4NF in THF at room temperature furnished **14** (69–77%, purified).

Mesylation of **14** with $MsCl/CH_2Cl_2$ at 0 °C in the presence of a stoichiometric (relative to MsCl) amount of 4-(dimethylamino)pyridine (DMAP) produced **15** even when excess (4–5 equiv) MsCl was used. It is noteworthy that the nucleophilicity of the nitrogen atom in the TRS group is reduced sufficiently so that the nitrogen is protected from reacting with methanesulfonyl chloride while two alcohol moieties are converted to methanesulfonate esters. Also, **15**, which is sufficiently stable to allow its isolation, is protected from what would otherwise be an almost instantaneous intramolecular displacement reaction to form five- and/or six-membered rings.

Cleavage of the TRS group of **15** with excess Me_4SiI in $CDCl_3$ at room temperature for 5 min followed by treatment with Na_2CO_3 and Na_2SO_3 in D_2O produced δ-coniceine (**16**, isolated as the picrate; 48% (from **14**) of recrystallized, analytically pure material).

This synthesis of δ-coniceine illustrates a strategy for alkaloid synthesis which results in the formation of previously under-utilized key bonds and illustrates several aspects of the utility of the TRS group as a nitrogen protecting group.

In conclusion it can be seen that the TRS group possesses many desirable attributes as a nitrogen protecting group including rapid, simple introduction, stability to a range of synthetically useful reagents and conditions, and ease of removal under mild conditions which should be compatible with a wide range of functional groups.

Experimental Section

General Methods. Methods and materials were the same as previously detailed.[4]

Formation of Triphenylmethanesulfenamides from the Corresponding Amines. General Information. All yields refer to triphenylmethanesulfenamides which were purified by silica gel preparative TLC. The identity of many of the products was determined by NMR and TLC comparison with triphenylmethanesulfenamides previously prepared by the reduction of tritylsulfenimines.[4]

General Procedure for the Condensation of TrSCl (6) with Amines in the Presence of Pyridine (Method A). To a stirred solution of the amine (1.00 equiv, 0.086 M) and reagent-grade pyridine (7.2 equiv, 0.62 M) in CH_2Cl_2 at room temperature was added dropwise a solution of TrSCl (0.95 equiv, 0.081 M) in CH_2Cl_2. The reaction was completed almost immediately after the addition (yellow TrSCl color vanished, leaving a colorless solution). The CH_2Cl_2 solution was washed with 1 N HCl/H_2O and saturated $NaCl/H_2O$ and then was dried ($MgSO_4$), and the volatiles were removed in vacuo. The crude products were then purified by silica gel preparative TLC.

General Procedure for the Condensation of TrSCl (6) with Amines in the Presence of Sodium Carbonate (Method B). To a stirred solution of the amine (1.00 equiv, 0.043 M) in THF/5% aqueous Na_2CO_3 (2.0 equiv, ca. 0.47 M) was added dropwise a solution of TrSCl (0.95 equiv, 0.040 M) in THF. The reaction was completed almost immediately (yellow TrSCl color vanished, leaving a colorless solution). After the addition of Et_2O (2 volumes), the organic phase was washed with H_2O and then saturated $NaCl/H_2O$ and was dried ($MgSO_4$), and the volatiles were removed in vacuo. The crude products were purified by silica gel prep TLC.

***N*-*n*-*Decyl*-1,1,1-triphenylmethanesulfenamide (5a).** The identity of this **5a** was determined by comparison with authentic material.[4]

***N*-Benzyl-1,1,1-triphenylmethanesulfenamide (5b).** The identity of this **5b** was determined by comparison with authentic material.[4]

***N*-Cyclohexyl-1,1,1-triphenylmethanesulfenamide (5c):** mp 66–69 °C; NMR δ 0.65–1.85 (m, 10 H), 2.05–2.30 (m, 1 H), 2.44 (d, 1 H, J = 6 Hz), 7.00–7.50 (m, 15 H). The identity of this **5c** was determined by comparison with authentic material.[4]

***N*-*tert*-Butyl-1,1,1-triphenylmethanesulfenamide (5d):** mp 67–70 °C; NMR δ 0.82 (s, 9 H), 2.55–2.80 (br s, 1 H), 7.05–7.50

(13) Schmidt, A. H. *Aldrichimica Acta* **1981**, *14*, 31 and references therein.

(14) Recent syntheses of δ-coniceine illustrating synthetic methodology: (a) Hart, D. J.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1982**, *104*, 1430. (b) Khatri, N. A.; Schmitthenner, H. F.; Shringapure, J.; Weinreb, S. M. *Ibid.* **1981**, *103*, 6387 and references therein.

(m, 15 H); IR (CH_2Cl_2) 3300 (NH); high-resolution MS (CI), calcd for $C_{23}H_{26}NS$ (parent + H) m/z 348.1786, found m/z 348.1780.

***N,N*-(Pentamethylene)-1,1,1-triphenylmethanesulfenamide (5e)**: mp ca. 79–85 °C; a new crystalline solid forms, mp ca. 170 °C; NMR δ 1.10–1.50 (m, 6 H), 2.00–2.35 (m, 4 H), 7.00–7.50 (m, 15 H); high-resolution MS (CI), calcd for $C_{24}H_{26}NS$ (parent + H) m/z 360.1786, found m/z 360.1792.

Reaction of 2,2,6,6-Tetramethylpiperidine with TrSCl (6). To a stirred solution of the amine (272 mg, 1.93 mmol) in CH_2Cl_2 (6 mL) was added a solution of TrSCl (200 mg, 0.644 mmol) in CH_2Cl_2 (6 mL) all at once. The yellow solution initially went colorless and then became a darker yellow. After 12 h at room temperature the solution was concentrated in vacuo at or below room temperature until a few milliliters remained, and then anhydrous EtOH (10–15 mL) was added to initiate crystallization (in other runs of this reaction crystallization occurred directly from the reaction solution). After crystallization for several hours at room temperature the white solid was collected by suction filtration and was washed with anhydrous EtOH, and the residual solvent was removed on a vacuum line, leaving white solid (76 mg, 45% as TrOOTr). **Crude white solid**: mp 189–195 °C; NMR δ 7.17 (pseudo s, a trityl peak). Anal. Calcd for $C_{38}H_{30}O_2$: C, 88.00; H, 5.83; O, 6.17. Found: C, 86.84; H, 5.92; N, <0.05; S, 0.13. **Recrystallized product** (a sample from a different run of the reaction was recrystallized by trituration from $CHCl_3$ with anhydrous EtOH): mp 189–191 °C (lit.[6] mp 185–186 °C; NMR δ 7.17 (pseudo s); IR (KBr) 3020, 1600, 1480, 1435 cm^{-1}. Anal. Calcd for $C_{38}H_{30}O_2$: C, 88.00; H, 5.83; O, 6.17. Found: C, 86.64; H, 5.86; N, <0.05; S, 0.03.

Exposure of *N*-Benzyl-1,1,1-triphenylmethanesulfenamide (5b) to Various Conditions. Compound **5b** was exposed to acid, base, and reducing and oxidizing agents as presented in the text and in Table II. In all cases yields refer to recovered **5b** after preparative TLC. The purity and identity of recovered **5b** was determined by NMR and TLC comparison with authentic material. Yields of other products from the reactions refer to material purified by preparative TLC unless otherwise noted. The purity and identity of other products was determined by NMR and TLC comparison with authentic compounds.

Exposure of 5b to Aqueous HCl. A solution of **5b** (100 mg, 0.262 mmol) in THF (3 mL) and 1 N HCl (1 mL) was left at room temperature for 5 h. Silica gel TLC (20% Et_2O/hexanes) indicated at least 3 UV-active decomposition products were present. The reaction mixture was diluted with CH_2Cl_2 (20 mL) followed by an aqueous extractive workup and analysis as described.

Exposure of 5b to Aqueous NaOH. A solution of **5b** (100 mg, 0.262 mmol) in THF (3 mL), anhydrous EtOH (3 mL), and 0.5 N NaOH (2 mL) was left 24 h at room temperature. No decomposition could be detected by TLC. The solution was diluted with Et_2O (20 mL) followed by an aqueous extractive workup and analysis as before.

Exposure of 5b to Sodium Borohydride. A solution of **5b** (100 mg, 0.262 mmol), 4-*tert*-butylcyclohexanone (121 mg, 0.786 mmol), and $NaBH_4$ (60 mg, 1.59 mmol) in anhydrous EtOH (4 mL) and THF (1 mL) was stirred for 30 min at room temperature. The reaction was quenched by the dropwise addition of 0.5 N HCl (10 mL) followed by Et_2O (25 mL), and an aqueous extractive workup and analysis were carried out as before.

Exposure of 5b to Sodium Diethyldihydroaluminate. A solution of **5b** (50 mg, 0.13 mmol) in THF (5 mL) under argon at 0 °C was treated with $NaAlH_2Et_2$ (2.16 M in toluene, 0.12 mL, 0.26 mmol) followed by stirring for 2 h at 0 °C. The reaction was quenched at 0 °C with 1 N HCl (2 mL) followed by a CH_2Cl_2 extractive workup and analysis as before.

Exposure of 5b to Lithium Aluminum Hydride. A solution of **5b** (100 mg, 0.262 mmol) and methyl benzoate (214 mg, 1.57 mmol) in Et_2O (10 mL) was added to a suspension of lithium aluminum hydride (60 mg, 1.58 mmol) in Et_2O (5 mL) maintained at 0 °C; complete transfer was effected with additional Et_2O (5 mL). After 30 min at 0 °C the reaction was quenched with methanol (2 mL) and then diluted with Et_2O (30 mL) followed by an aqueous extractive workup and analysis as before.

Exposure of 5b to Catalytic Hydrogenation Conditions. A solution of **5b** (100 mg, 0.262 mmol) and *trans*-stilbene (47 mg, 0.261 mmol) in anhydrous EtOH (4 mL) and THF (1 mL) under 1 atm of H_2 (balloon) was stirred over catalyst (10% palladium/carbon or 10% platinum/carbon, 25 mg) for 22–24 h as indicated. The catalyst was removed by filtration through Celite followed by evaporation of solvents and analysis as before.

Exposure of 5b to Moffat Oxidation Conditions. A solution of **5b** (100 mg, 0.262 mmol), 4-*tert*-butylcyclohexanone (123 mg, 0.788 mmol), dicyclohexylcarbodiimide (487 mg, 2.36 mmol), and pyridinium trifluoroacetate (152 mg, 0.788 mmol) in dry dimethyl sulfoxide (4 mL) was stirred 6 h at room temperature. A solution of oxalic acid dihydrate (300 mg, 2.46 mmol) in methanol (2 mL) was added with Et_2O (20 mL); the heterogeneous mixture was stirred 45 min after gas evolution had ceased. The precipitate was collected by suction filtration and washed with Et_2O. The filtrate was subjected to an aqueous extractive workup followed by analysis as before.

Conversion of Triphenylmethanesulfenamides to the Corresponding Amines. General Information. All amines were isolated as the phenylthiourea derivatives which were formed by treating the amine, in a homogeneous solution in an organic solvent or a heterogeneous solution in an organic solvent/H_2O mixture, with excess phenyl isothiocyanate (ca. 2 equiv.). All phenylthioureas were purified by silica gel preparative TLC followed by NMR and TLC comparison with authentic phenylthioureas prepared independently.

General Procedure for Cupric Chloride Mediated Solvolysis of Triphenylmethanesulfenamides to the Corresponding Amines. A solution of triphenylmethanesulfenamide **5** (1.0 equiv, 0.08 M) and anhydrous Alfa $CuCl_2$ (1.2 equiv) in 20% dry THF/anhydrous EtOH was left at room temperature for 3–15 h (most reactions are complete by TLC within a few hours).

(A) Workup by Extraction. The green solution was diluted with H_2O (1.5 volumes) and then was extracted with CH_2Cl_2 (3 × 2.5 volumes). The aqueous phase was then treated with Na_4EDTA/H_2O (2 equiv, 0.25 M), leading to a blue solution which was extracted with CH_2Cl_2 (5 × 2.5 volumes). The combined final CH_2Cl_2 extract was treated with PhNCS/CH_2Cl_2 (2 equiv, 0.5 M) followed by removal of volatiles in vacuo at or below room temperature. The crude phenylthioureas were then purified by silica gel preparative TLC.

(B) Direct Conversion to the Phenylthiourea (for Water-Soluble Amines). The green solution was treated directly with Na_4EDTA (1.5 equiv, 0.25 M) and PhNCS/CH_2Cl_2 (2.0 equiv, 0.5 M), and then the heterogeneous mixture was rapidly stirred 1–2 h at room temperature. The solution was treated with Et_2O (3 volumes), the organic phase was washed with H_2O and saturated $NaCl/H_2O$ and dried ($MgSO_4$), and the volatiles were removed in vacuo. The crude phenylthioureas were then purified by silica gel preparative TLC.

The results are summarized in Table III and as follows [triphenylmethanesulfenamide (mass of sulfenamide, method of workup, A or B, isolated yield of purified phenylthiourea)]: **5a** (225 mg, B, 67%), **5b**, (280 mg, A, 61%), **5c** (192 mg, B, 58%), **5f** (100 mg, A, 60%), **5g** (116 mg, B, 64%).

Isolation and Characterization of TrOEt (7) from a Cupric Chloride Mediated Solvolysis of *N*-Benzyl-1,1,1-triphenylmethanesulfenamide (5b). According to the general procedure (method A), **5b** (280 mg, 0.735 mmol) was converted to the corresponding amine (61% isolated phenylthiourea). The combined initial CH_2Cl_2 extract (before Na_4EDTA was added) was dried ($MgSO_4$), the volatiles were removed in vacuo, and then the residual solvent was removed on a vacuum line, leading to a viscous yellow oil (236 mg, 100% as TrOEt). The ^1H NMR of the crude product appeared to be clearly one compound and was identical with a ^1H NMR of purified, recrystallized TrOEt. The compound was purified by silica gel preparative TLC followed by recrystallization by trituration from $CHCl_3$ with anhydrous EtOH. **TrOEt (7)**: mp 84–85 °C (lit.[15] mp 84–85 °C); NMR δ 1.10–1.40 (t, 3 H, J = 7 Hz), 2.90–3.30 (q, 2 H, J = 7 Hz), 7.10–7.60 (m, 15 H); IR (CH_2Cl_2) 3050, 3010, 2980, 2910, 1610, 1495, 1445; MS, m/z (relative intensity) 287 (8, parent − H), 286 (32), 243 (60), 211 (32, parent − Ph), 182 (24, 211 − Et), 165 (38), 105 (100, C_7H_5O); high-resolution MS (EI), calcd for $C_{21}H_{20}O$ m/z 288.1514, found m/z 288.1514.

(15) "Dictionary of Organic Compounds", 4th ed.; Oxford University Press; New York, 1965; p 3200.

General Procedure for the Conversion of Triphenylmethanesulfenamides to the Corresponding Amines with HI. A solution of triphenylmethanesulfenamide **5** (1.0 equiv, 0.08 M) in THF was treated with HI/H_2O (1.0 M, 3 equiv) with stirring at room temperature, leading almost instantly to a brown solution. The reactions appeared by TLC to be complete within a few minutes; most reactions were run for a total of 15 min.

(A) Workup by Extraction. The brown solution was treated with H_2O (2 volumes). The aqueous phase was washed with CH_2Cl_2 (3 × 2.5 volumes), was made basic with solid NaOH, and was extracted with CH_2Cl_2 (5 × 2.5 volumes). The combined final CH_2Cl_2 extract was treated with PhNCS/CH_2Cl_2 (2 equiv, 0.5 M) followed by removal of volatiles at or below room temperature. The phenylthioureas were then purified by silica gel preparative TLC.

(B) Direct Conversion to the Phenylthiourea (for Water-Soluble Amines). The brown solution was treated directly with solid sodium sulfite (Na_2SO_3, excess, sufficient to consume I_2, leading to a clear solution), H_2O (sufficient to dissolve Na_2SO_3), solid Na_2CO_3 (excess, to make aqueous layer basic by pH paper), and PhNCS/CH_2Cl_2 (2.0 equiv, 0.5 M). The heterogeneous mixture was stirred rapidly at room temperature for 1–2 h. The solution was treated with Et_2O (3 volumes), the organic phase was washed with H_2O and saturated NaCl/H_2O and was dried ($MgSO_4$), and the volatiles were removed in vacuo. The crude phenylthioureas were then purified by silica gel preparative TLC.

The results are summarized in Table IV and as follows [triphenylmethanesulfenamide (mass of sulfenamide, method of workup, A or B, isolated yield of purified phenylthiourea)]: **5a** (125 mg, B, 86%), **5b** (100 mg, A, 95%), **5c** (173 mg, B, 92%), **5f**, (100 mg, A, 91%), **5g** (151 mg, B, 82%), **5h** (111 mg, A, 86%).

General Procedure for the Conversion of Triphenylmethanesulfenamides to the Corresponding Amines with Me_3SiI. To a solution of the triphenylmethanesulfenamide (1.0 equiv, 0.025 M) in dry CH_2Cl_2 at −78 °C under argon in a flame-dried flask was added Me_3SiI (3.0 equiv, 0.71 M in CH_2Cl_2, prepared by combining 1 mL of Me_3SiI with 9 mL of CH_2Cl_2) dropwise by syringe, leading to a slightly yellow solution. After 15 min at −78 °C anhydrous EtOH was added, and the solution was warmed to near room temperature, leading to a red-brown solution.

(A) Workup by Extraction. This procedure was identical with that described for the HI cleavage reactions.

(B) Direct Conversion to the Phenylthiourea (for Water-Soluble Amines). This procedure was identical with that described for the HI cleavage reactions.

The results are summarized in Table V and as follows [triphenylmethanesulfenamide (mass of sulfenamide, method of workup, A or B, isolated yield of purified phenylthiourea)]: **5a** (135 mg, B, 89%), **5b** (100 mg, A, 96%), **5c** (154 mg, B, 94%), **5f** (100 mg, A, 95%), **5g** (148 mg, B, 77%).

Preparation of 12. To a stirred solution of tritylsulfenimine **11** (919 mg, 1.74 mmol), sodium cyanoborohydride (219 mg, 3.49 mmol), and Bromocresol Green (a speck) in dry THF (25 mL) at room temperature was added dropwise a solution of trifluoroacetic acid in dry THF (3% w/w) periodically as needed to maintain the pH near the transition pH of the indicator. When the addition of acid was necessary only every 10 min (2.5 h total reaction time), the reaction was quenched with saturated $NaHCO_3$ (25 mL). The heterogeneous mixture was treated with Et_2O (50 mL); the organic phase was washed with H_2O (25 mL), 0.1 N HCl (25 mL), saturated $NaHCO_3$ (25 mL), and twice with saturated NaCl (25 mL each) followed by drying ($MgSO_4$) and evaporation. The crude product was dissolved in Et_2O and filtered through silica gel (5 g) followed by concentration in vacuo and removal of residual volatiles on a vacuum line: 880 mg (95%); ^1H NMR ($CDCl_3$) δ 0.00 (s, 6 H, used as internal standard), 0.85 (s, 9 H), 1.00–1.55 (m, 6 H), 1.55–2.00 (m, 1 H), 2.20–2.60 (m, 3 H), 3.25–3.70 (m, 2 H), 4.70–5.10 (m, 2 H), 5.40–5.95 (m, 1 H), 7.05–7.45 (m, 15 H); IR (CH_2Cl_2) 3340 (NH), 3050, 3010, 2910, 2850, 1960, 1910, 1830, 1780, 1645, 1600 cm^{-1}; exact mass (CI) calcd for $C_{33}H_{46}NOSSi$ (M + H) 532.3069, found 532.3053.

Preparation of 13. Neat triphenylmethanesulfenamide **12** (204 mg, 0.384 mmol) was treated with a solution of borane (1 M, 0.77 mL, 0.77 mmol) in THF at room temperature under argon. The resulting solution was stirred at room temperature for 1 h, and then methanol (1 mL) was added followed by aqueous NaOH (1 N, 0.306 mL, 0.306 mmol) and 30% aqueous H_2O_2 (0.102 mL, 0.99 mmol). The resulting solution was stirred 30 min at room temperature, and then Et_2O (20 mL) and H_2O (10 mL) were added. The organic phase was washed with 0.25 N HCl (10 mL), saturated $NaHCO_3$ (10 mL), and saturated NaCl (10 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by silica gel preparative TLC (50:49.5:0.5 pentane/Et_2O/EtOH development, extraction of band with 4% MeOH/CH_2Cl_2), leading to analytically pure clear oil: 146 mg (69%); ^1H NMR ($CDCl_3$) δ 0.00 (s, 6 H, used as internal standard), 0.85 (s, 9 H), 1.00–1.70 (m, 11 H), 2.20–2.60 (hump, 2 H), 3.30–3.75 (m, 4 H), 7.05–7.40 (m, 15 H); IR (thin film) 3600–3100 (OH), 3030, 2900, 2840, 1600, 1485. Anal. Calcd for $C_{33}H_{47}NO_2SSi$: C, 72.08; H, 8.61; N, 2.55; S, 5.83; Si, 5.11. Found: C, 72.18; H, 8.74; N, 2.61; S, 5.68; Si, 5.36.

Preparation of 14. A solution of triphenylmethanesulfenamide **13** (31.4 mg, 0.057 mmol), $(n\text{-Bu})_4NF$ [50 mg, 0.19 mmol; prepared by neutralizing $(n\text{-Bu})_4NOH$ with HF followed azeotropic removal of H_2O with toluene (2 × 25 mL) immediately prior to use], and *n*-propylamine (excess, several drops) in dry THF (4 mL) was allowed to stand at room temperature for 1.25 h. The solution was diluted with Et_2O (15 mL), followed by washing with H_2O (2 × 10 mL) and saturated NaCl (10 mL), drying (Na_2SO_4), and concentration in vacuo. Silica gel chromatography (Et_2O to 5% EtOH/Et_2O gradient) led to pure product: 19.2 mg (77%); ^1H NMR ($CDCl_3$) δ 0.80–1.80 (m, 13 H), 2.20–2.60 (hump, 1 H), 3.30–3.70 (m, 4 H), 7.10–7.50 (m, 15 H); IR (CH_2Cl_2) 3600, 3450, 3340, 3700–3200 (OH), 3050, 3000, 2910, 2860, 1960, 1910, 1820, 1770, 1600, 1490 cm^{-1}.

Preparation of 15. To a stirred solution of triphenylmethanesulfenamide **14** (19.2 mg, 0.044 mmol) and 4-(dimethylamino)pyridine (22 mg, 0.18 mmol) in dry CH_2Cl_2 (distilled from CaH_2, 5 mL) at 0 °C was added a CH_2Cl_2 solution of methanesulfonyl chloride (0.100 mL of MsCl/0.900 mL of CH_2Cl_2 = 1.29 M, 0.140 mL, 0.18 mmol) all at once by syringe. The solution was stirred 30 min at 0 °C, and then 1 N HCl (1 mL) was added all at once by pipet. The cold solution was transferred to a separatory funnel with H_2O (5 mL) and CH_2Cl_2 (15 mL); the organic phase was washed with saturated NaCl (2 × 10 mL) and then was concentrated in vacuo, producing an oil which was briefly (15 min) dried on a vacuum line. The product **15** was characterized in this experiment by ^1H NMR and in other experiments by conversion to δ-coniceine: ^1H NMR ($CDCl_3$) δ 1.00–1.90 (m, 11 H), 2.15–2.60 (hump, 1 H), 2.80–3.10 (pseudo s, 6 H), 3.85–4.35 (m, 4 H), 7.00–7.50 (m, 15 H).

Preparation of δ-Coniceine (16). A sample of **14** (29.7 mg, 0.0683 mmol) was converted to **15** by using 4-(dimethylamino)-pyridine (42 mg, 0.344 mmol) and methanesulfonyl chloride (1.29 M, 0.267 mL, 0.344 mmol) in CH_2Cl_2 at 0 °C for 45 min according to the preceding experimental method. Crude **15** (49.5 mg) was dissolved in $CDCl_3$; all subsequent reactions were performed in an NMR tube with drawn out capillary pipets for addition and removal of liquids. The solution was treated with neat trimethylsilyl iodide (excess, 1 drop) at room temperature. After 5 min a saturated solution of Na_2CO_3 and Na_2SO_3 in D_2O (ca. 1 mL) was added followed by shaking. The aqueous solution was carefully drawn off, and then a solution of trifluoroacetic acid in D_2O (made from trifluoroacetic anhydride/D_2O) was added followed by shaking. The $CDCl_3$ layer was withdrawn, and the aqueous layer was washed once more with $CDCl_3$. The aqueous layer was made basic with solid Na_2CO_3 followed by extraction with $CDCl_3$. The ^1H NMR spectrum of the $CDCl_3$ solution, in comparison with an NMR spectrum of δ-coniceine provided by Professor Steven Weinreb, indicated that δ-coniceine was essentially the only species present in solution. The $CDCl_3$ solution was transferred to a flask by using CH_2Cl_2, and then picric acid (15.6 mg, 0.068 mmol) was added. Concentration in vacuo followed by recrystallization from anhydrous EtOH produced analytically pure δ-coniceine picrate (11.6 mg, 48% from **14**). For the **16** picrate: mp 226–229 °C (recrystallized from anhydrous EtOH) [lit.[14] mp 224–234 °C (numerous reports are sharp but the range spans 10 °C); MS, *m/z* (relative intensity) 229 (10, picric acid), 228 (86), 199 (13), 125 (57, δ-coniceine), 124 (100), 122 (7), 110 (10), 97 (71), 96 (57), 92 (7), 91 (31), 84 (11), 83 (50), 82 (13), 80

(13), 78 (7), 77 (9), 70 (10), 69 (44), 68 (14), 67 (9), 63 (14), 62 (37), 61 (12), 56 (7) 55 (23), 54 (14), 53 (20), 51 (10), 50 (14); exact mass (EI, measured m/z 125 peak, δ-coniceine, from picrate) calcd for $C_8H_{15}N$ 125.1204, observed 125.1206. Anal. (recrystallized picrate) Calcd for $C_{14}H_{18}N_4O_7$: C, 47.46; H, 5.12; N, 15.81. Found: C, 47.20; H, 5.01; N, 15.69.

Registry No. **5a**, 86864-51-9; **5b**, 86864-57-5; **5c**, 86864-53-1; **5d**, 86884-96-0; **5e**, 86884-97-1; **5f**, 86864-58-6; **5g**, 86864-55-3; **5h**, 86864-54-2; **6**, 24165-03-5; **7**, 968-39-8; **8a**, 79425-06-2; **8b**, 726-25-0; **8c**, 722-03-2; **8d**, 86884-98-2; **8e**, 86884-99-3; **8f**, 86885-00-9; **11**, 86885-01-0; **12**, 86885-02-1; **13**, 86885-03-2; **14**, 86885-04-3; **15**, 86885-05-4; **16**, 13618-93-4; **16** picrate, 5210-66-2; TrOOTr, 596-30-5; HCl, 7647-01-0; NaOH, 1310-73-2; $NaBH_4$, 16940-66-2; $NaAlH_2Et_2$, 17836-88-3; $LiAlH_4$, 16853-85-3; H_2, 1333-74-0; PhNCS, 103-72-0; *n*-decylamine, 2016-57-1; benzylamine, 100-46-9; cyclohexylamine, 108-91-8; *tert*-butylamine, 75-64-9; piperidine, 110-89-4; 2,2,6,6-tetramethylpiperidine, 768-66-1; *m*-chloroperbenzoic acid, 937-14-4; pyridinium chlorochromate, 26299-14-9; Collins reagent, 20492-50-6.

Notes

Improved Synthesis of Selenophene

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Introduction

The use of aluminum oxide as a packing material or support of 450 °C hot columns in the preparation of selenophene from elemental selenium and acetylene gas has dramatically improved the overall yields obtained from prior methods.[1,2] In particular, a recent study of a semi-large-scale method for selenophene using aluminum oxide support revealed that seven batches are required in order to sufficiently condition the support (~8 h/batch) before yields of about 58% can be achieved.[2] Typically, the first four or five batches provide extremely low yields, requiring a long "incubation" time before the reaction becomes sufficiently efficient. During this conditioning, the alumina becomes coated with carbonaceous material, and simultaneously the yields of selenophene increase. We have now found that inert support materials like sand or glass beads assure a high (70%) yield from the start, thus pointing out that alumina does not have a catalytic effect upon the selenophene synthesis, rather it seems to affect the reaction negatively, therefore requiring initial passivation.

Experimental Section

The reaction between selenium and acetylene with various supports was carried out in glass tubes of 25 × 600 mm, as previously described.[2] These were cleaned prior to use with hot concentrated nitric acid and then rinsed with distilled water and acetone. The glass beads (1-mm diameter) and sand (1–3-mm diameter) were similarly cleaned. The tubes were typically loaded with 120 g of support, and these were preheated and maintained at 450 °C for 3 h under nitrogen until all moisture was removed. The sand or glass beads so treated were then mixed thoroughly with 20–25 g (1–2-mm diameter) of selenium each, and the reloaded tubes were placed back into the oven slightly inclined to facilitate collection of the reaction product. A stream of nitrogen was passed through each tube until 400 °C was reached. Then the nitrogen was replaced with acetylene with a flow rate of 0.25 $cm^3\ s^{-1}$, upon which liquid selenophene started to form almost immediately. The temperature was increased slowly to 450 °C and a red liquid (selenophene containing dissolved selenium) was collected during 16 h. During the reaction, the excess acetylene gas was passed through a saturated KOH solution in order to trap any H_2Se. At the end of the reaction, acetylene was replaced with a nitrogen stream, the tubes were allowed to cool, and the glass beads or sand from each tube were then mixed homogeneously with a new portion of 20–25 g of selenium. The tubes were reloaded, and the reaction was restarted, as described above. The crude products from three batches were combined and distilled to give selenophene in 70% yield (based upon the total amount of selenium), bp 109–112 °C (Gronowitz et al.[2] reported bp 105–120 °C). The yields were the same with use of either support, and the product was confirmed via NMR. The crude product also contained ca. 3% toluene, and the residue from the distillation pot contained elemental Se, diphenyl selenide (according to mass spectral data), and other unidentified, high-boiling products.[3]

Results and Discussion

The combined yields of selenophene obtained from three initial batches using glass beads or sand were 70% in either case. Gronowitz et al. reported a combined yield of the first three batches of ca. 8% using aluminum oxide support.[2] They were able to obtain a single batch yield of 58% only after seven batches. Also, all of the supports used here were similarly coated with carbonaecous material. The fact that selenophene forms almost immediately when the reaction is started implies that these carbonaceous coatings, which have been previously suggested to exert a catalytic effect,[1b] in fact, appear to play no catalytic role in the formation of selenophene at all. Moreover, the formation of such carbonaceous material is a common phenomenon in pyrolysis reactions.

These data suggest that the formation of selenophene from selenium and acetylene requires no catalyst, but rather a support that provides an increased surface area to facilitate the reaction, as previously asserted by Gronowitz et al.[2] Thus, we believe that selenium distributes over the surface of the support materials during heating in the glass tube, thereby giving a much greater cross section for reaction with acetylene. However, the nature of the support material itself is also of importance. The comparatively low yields obtained using aluminum oxide as opposed to glass beads or sand bears this out. This may be attributed to the countercatalytic properties of aluminum oxide, which apparently has a destructive effect upon product formation, especially in the initial runs until

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(2) S. Gronowitz, T. Frejd, A. Moberg-Ogard, and L. Trege, *J. Heterocycl. Chem.*, **13**, 1319 (1976).

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