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Ionic Hydrogenation with Organosilanes under Acid-Free Conditions. Synthesis of Ethers, Alkoxysilanes, Thioethers, and Cyclic Ethers via Organosilyl Iodide and Triflate Catalyzed Reductions of Carbonyl Compounds and Their Derivatives[1]

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Abstract

The general ether synthesis method based on the trialkylsilane/trialkylsilyl iodide or triflate reagent system has been extended to the syntheses of alkoxysilanes from ketones, tetrahydrofurans and tetrahydropyrans from dicarbonyl compounds, and thioethers by reductive cleavage of O-silylhemithioacetals.

Introduction

Ionic hydrogenation[2] had its inception over forty years ago, when Whitmore first observed the ease in which hydride is transferred from triethylsilane to the incipient carbocation formed by the action of aluminum chloride on 1-chlorohexane.[3]

$$CH_3(CH_2)_5Cl + Et_3SiH \xrightarrow{AlCl_3\ (cat)} CH_3(CH_2)_4CH_3 + Et_3SiCl$$

The potential of such a transformation, however, remained virtually unexplored for another twenty years, when Kursanov applied the principle to hydrogenation of alkenes and carbonyl compounds in trifluoroacetic acid to obtain alkanes in the former case and trifluoroacetate esters in the latter.[4]

Doyle has shown that carbonyl compounds may be reduced to alcohols, ethers, carboxylate esters and acetamides in strongly acidic media under appropriate conditions.[5] Reductive coupling of carbonyls to obtain moderate to good yields of symmetrical ethers, has, likewise, been achieved with a number of Lewis acid catalysts.[6-8] In addition, several groups have obtained excellent yields of methyl or ethyl ethers by reductive cleavage of the corresponding acetals with organosilanes and various catalysts; Kursanov with trifluoroacetic acid,[9] Noyori with trimethylsilyl triflate,[7] and Olah with the solid superacid Nafion-H®.[10]

Our group has recently investigated the use of trimethylsilyl iodide and trimethylsilyl triflate catalyzed reductions of carbonyls with various organosilanes.[11] With either trimethyl or triethylsilane, aliphatic ketones are reductively coupled to give quantitative conversion to symmetrical ethers with either catalyst.

$$2\,R_2C{=}O \xrightarrow[Me_3SiX]{R'_3SiH} R_2CH\text{-}O\text{-}CHR_2$$

R' = Me or Et
X = I or OTf

Aromatic carbonyls, on the other hand, give aryloxysilanes as minor products with the triflate but are cleanly coupled with the milder iodide catalyst. The latter (but not the former) is also extremely effective in promoting the reductive condensation of alkoxysilanes with carbonyls to effect quantitative conversion to unsymmetrical ethers.

$$R_2C{=}O \;+\; R'OSiMe_3 \xrightarrow[TMSI]{R''_3SiH} R_2CH\text{-}OR'$$

R'' = Me or Et
TMSI = trimethylsilyl iodide

Two important aspects of the proposed mechanism, to which we will refer later in this paper, may be gleaned from Scheme I.

Scheme I

$$R_2C{=}O + Me_3SiX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2C{=}\overset{\oplus}{O}SiMe_3\,X^{\ominus} \qquad (1)$$

$$R_2C{=}\overset{\oplus}{O}SiMe_3\,X^{\ominus} + Me_3SiH \xrightarrow{k_2} R_2CH\text{-}OSiMe_3 + Me_3SiX \qquad (2)$$

$$R_2CH\text{-}OSiMe_3 + R_2C{=}\overset{\oplus}{O}SiMe_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R_2CH\text{-}\overset{\oplus}{O}(SiMe_3)\text{-}CR_2\text{-}OSiMe_3 \qquad (3)$$

$$R_2CH\text{-}\overset{\oplus}{O}(SiMe_3)\text{-}CR_2\text{-}OSiMe_3 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R_2CH\text{-}O\text{-}CR_2\text{-}\overset{\oplus}{O}(SiMe_3)_2 \qquad (4)$$

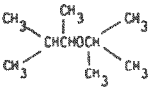
$$R_2CH\text{-}O\text{-}CR_2\text{-}\overset{\oplus}{O}(SiMe_3)_2 \xrightarrow{k_5} R_2CH\text{-}\overset{\oplus}{O}{=}CR_2 + (Me_3Si)_2O \qquad (5)$$

$$R_2CH\text{-}\overset{\oplus}{O}{=}CR_2\;X^{\ominus} + Me_3SiH \xrightarrow{k_6} R_2CH\text{-}O\text{-}CHR_2 + Me_3SiX \qquad (6)$$

The first is that all nucleophilic attacks occur on stabilized carboxonium ions (Scheme-I, equations 2, 3 and 6). The second, which allows for reductive condensation with alkoxysilanes, is that nucleophilic attack on the carboxonium ion is more rapid for alkoxysilanes than for silanes (i.e., $k_3 > k_2$).

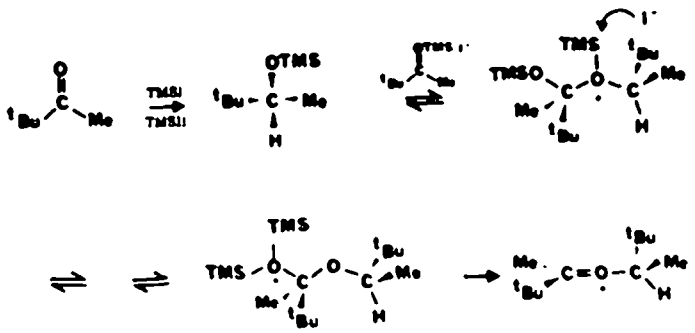
The carboxonium ion also plays an important role in the remarkable diastereoselectivity observed. The symmetrical coupling of α-substituted methyl ketones with trimethylsilyl iodide and trimethylsilane, yields a single pair of enantiomers (see Table I).

Table I: Diastereoselectivity in Ether Synthesis

Ketone	Product	Diastereomer Distribution
$CH_3C(O)C(CH_3)_3$	$(CH_3)_3CCH(CH_3)\text{-}O\text{-}CH(CH_3)(CH_3)_3$	100% (R,S/S,R)
$CH_3C(O)CH(CH_3)_3$		100% (R,R/S,S)

Mutual avoidance of bulky groups, together with π-stabilization, produces a relatively planar intermediate with restricted rotational freedom, as in Scheme II.

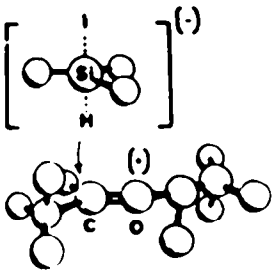
Scheme II



The silane hydride donor then enters from the face offering the least steric hindrance (see Figure I) to yield the stereochemically pure product.

Figure I

(alkyl hydrogens not shown)



In this paper we report our continuing studies of ionic hydrogenation of carbonyls and their derivatives under acid-free conditions, which lead to syntheses of alkoxysilanes, thioethers and cyclic ethers.

Results and Discussion

Alkoxysilanes. The advantage of using a silane in conjunction with a catalyst possessing identical alkyl substitution (at least in principle) is that a single disiloxane by-product will be formed, thereby simplifying the isolation of the desired product. Reactions utilizing trimethylsilane and the corresponding iodide or triflate, which yield the volatile hexamethyldisiloxane as a by-product, are unsurpassed in convenience and simplicity of product isolation. We have found, however, that trimethylsilane (which may be prepared from chlorotrimethylsilane by reduction with lithium aluminum hydride[12] or tertiary amine hydrochlorides and magnesium[13]) is not always readily available from commercial sources. We therefore investigated the use of triethylsilane in conjunction with triethylsilyl iodide.[14]

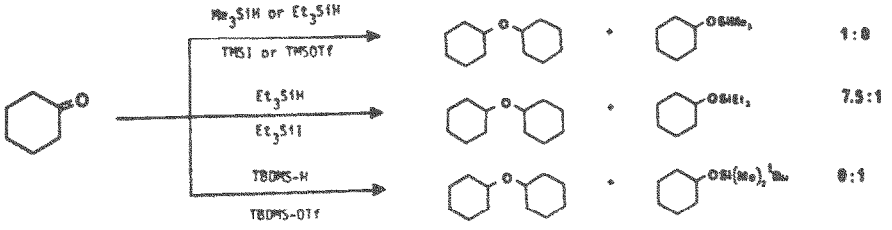
The reaction of cyclohexanone with triethylsilane and catalytic triethylsilyl iodide was extremely slow in comparison to what we observed with trimethylsilyl iodide, requiring 24 hrs. at room temperature to reach completion. In contrast to the

reactions where trimethylsilyl iodide or triflate were used with triethylsilane, analysis of the final reaction mixture by NOE suppressed ^{13}C NMR, showed the molar ratio of dicyclohexyl ether to cyclohexoxytriethylsilane to be 7.5 to 1 (see Scheme III).

This implied that the increase in steric bulk, though minimal, attenuated the rate of nucleophilic attack of the alkoxysilane. We further surmised that with an additional increase in the size of the silicon reagents, symmetrical coupling of carbonyls could be entirely eliminated.

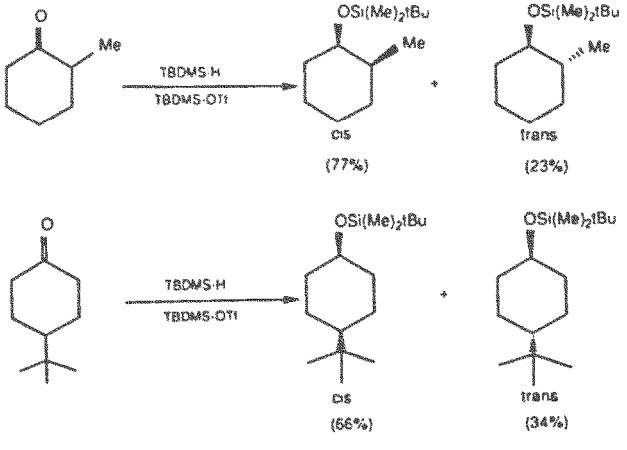
The reaction of cyclohexanone with 3.0 equivalents of t-butyldimethylsilane and catalytic *t*-butyldimethylsilyl triflate supported our conjecture and gave a 90% conversion to the cyclohexoxysilane with no symmetrical ether detectable in the product, the remaining 10% being unreacted starting material (see Scheme III).

Scheme III: Ionic Hydrogenation of Cyclohexanone



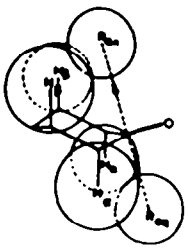
TMS = Trimethylsilyl
TBDMS = t-Butyldimethylsilyl

Similarly, reactions with 2-methylcyclohexanone and 4-*t*-butylcyclohexanone gave 85% and 81% conversions to their respective alkoxysilanes. Analysis by ^{13}C NMR and GLC showed an uneven distribution of stereoisomers in each case. Both ketones showed a preponderance for the formation of the less thermodynamically stable cis isomer; 2-methylcyclohexanone giving 77% *cis* and 23% *trans*, 4-*t*-butylcyclohexanone giving 66% *cis* and 34% *trans*.



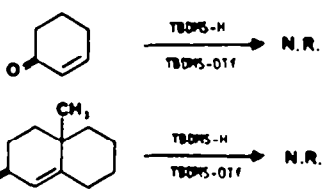
The preference for equatorial rather than axial attack on cyclohexanones by large reagents has been evaluated in terms of "congestion functions" by Wipke[15] (see Figure II). Calculations show the axial β-hydrogens contribute more steric

Figure II



congestion the axial α-hydrogens, thus the cis isomer predominates in each of the aforementioned cases. Doyle has also studied stereoselectivity in reductions with organosilanes in aqueous sulfuric acid-ether mixtures, obtaining similar results with 2-methyl and 4-*t*-butylcyclohexanone.[16] We attribute the higher proportion of cis in 2-methylcyclohexanone (compared to 4-*t*-butyl) to a shift in the conformational equilibrium caused by interaction with the bulky catalyst to avoid an "allylic" type strain. Further studies on the stereochemistry of reduction are currently underway.

Unlike the ketones studied both benzaldehyde and propionaldehyde yielded only symmetrical ethers. 2-Cyclohexene-1-one and 4a-methyl-4,4a-5,6,7,8-hexahydronaphthalen-2(3H)-one gave no reaction under identical conditions.

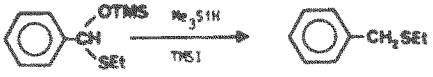


Thioethers. An estimation using the approximate bond dissociation energies[17] in Table II suggests that reductive cleavage of O-trimethylsilyl hemithioacetals should occur at the carbon-oxygen bond rather than the carbon-sulfur bond, and be favored by over 100 kcal mol^{-1}. We have investigated this possibility for thioether synthesis.

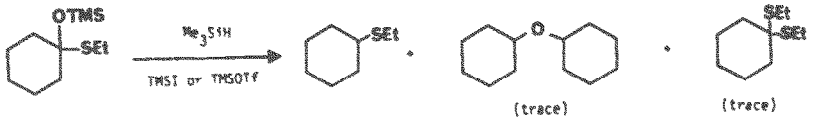
Table II: Approximate Bond Dissociation Energies[17]

Bond	Compound	D, kcal mol^{-1}	Bond	D, kcal mol^{-1}
Si-C	Me_3Si	76	C-C	80
Si-H	Me_3SiH	81	C-H	100
Si-O	Me_3SiOMe	127	C-O	81
	$(Me_3Si)_2O$	194		
Si-S	$(H_3Si)_2S$	70	C-S	76
Si-N	$(Me_3Si)NH$	76	C-N	80
Si-F	Me_3SiF	193	C-F	106
Si-Cl	Me_3SiCl	112	C-Cl	80
Si-Br	Me_3SiBr	96	C-Br	64
Si-I	Me_3SiI	77	C-I	51

Treatment of O-trimethylsilylbenzaldehyde hemiethylthioacetal with excess trimethylsilane and catalytic trimethylsilyl iodide gave benzyl ethyl sulfide with no detectable side products.



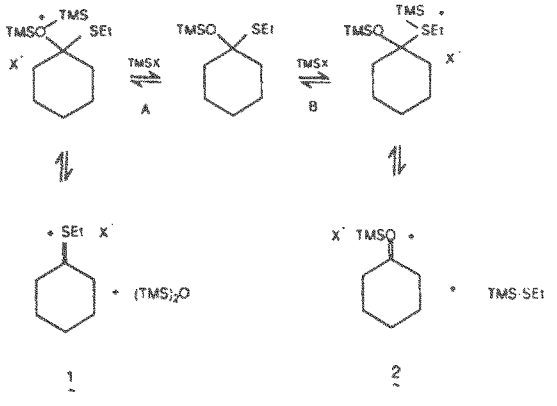
O-Trimethylsilylcyclohexanone hemiethylthioketal, under the same conditions gave not only the expected cyclohexyl ethyl sulfide, but traces of both dicyclohexyl ether and diethylthioketal. Similar results were obtained with trimethylsilyl triflate as the catalyst.



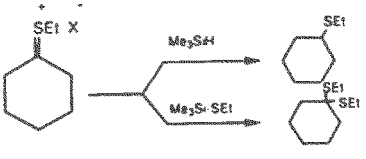
No reduction products were obtained with the weaker triethylsilane-triethylsilyl iodide system. The starting material underwent complete disproportionation to give the diethylthioketal and cyclohexanone within sixty minutes. Trimethylsilyl triflate, iodide, and bromide with no silane present, all promoted rapid disproportionation.

It is evident that two pathways are open to the initial interaction with the catalyst, one leading to an ethylthiocarboxonium intermediate 1 (Pathway A, Scheme IV), the other to an O-trimethylsilylcarboxonium ion 2 (Pathway B, Scheme IV).

Scheme IV



Depending on the catalyst, 2 either undergoes symmetrical coupling as in Scheme I, or is desilylated to form the ketone. The ethylthiocarboxonium ion 1, is either reduced by the silane, or if Pathway B is in operation, preferentially undergoes nucleophilic attack by the thiosilane formed, in a manner analogous to the alkoxysilane in Scheme I.



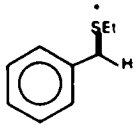
Again, the rate of nucleophilic attack apparently supercedes that of reduction. Why the thiosilane prefers to add to 1 rather than reversibly add to 2 and ultimately

arrive at the thermodynamically preferred product, attests to the relative stabilities of the two intermediates, desilylation of 2 being an extremely facile process.

Evans has observed that the reaction of carbonyls or O-trimethylsilyl hemithioacetals with trimethylsilyl thioethers under Lewis acid catalysis gives complete conversion to dithioacetals. If an amine "buffer", such as imidazole, is used in conjunction with the Lewis acid, the O-trimethylsilyl hemithioacetal (which has been shown to be an intermediate in the formation of the dithioacetal) does not undergo any further reaction, even in the presence of excess thiosilane.[18]

We sought to depress Pathway B in Scheme IV by employing Evans' methodology. The addition of catalytic amounts of imidazole, 1-(trimethylsilyl)-imidazole, or tri-*n*-butylphosphine to the previously mentioned system, however, completely prevented any reduction from taking place.

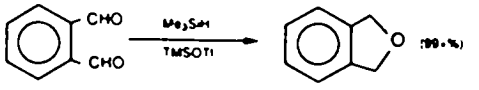
The facility by which O-trimethylsilylbenzaldehyde hemiethylthioacetal is converted to benzyl ethyl sulfide is attributable to the enhanced stability of the thiocarboxonium intermediate.



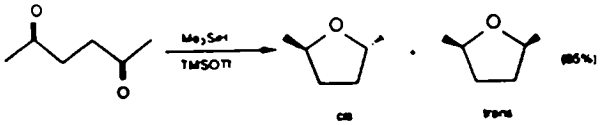
Olah has analogously observed a 12 ppm shielding effect in the ^{13}C NMR spectrum for protonated aromatic thiocarbonyl carbons relative to their neutral precursors, due to extensive charge delocalization into the aromatic ring.[19] Implicit in these observations is that the course of the reaction (Pathway A versus Pathway B in Scheme IV) is, at least in part, controlled by the relative energetics of the two carbocationic intermediates. While the secondary reaction leading to the dithioketal and symmetrical ether does not present a major contamination problem, we are currently investigating the possibilities of totally eliminating the minor pathway.

Cyclic Ethers. The dominance of substituted tetrahydrofuran and tetrahydropyran units in natually occurring polyether antibiotics[20] prompted us to explore the potential for cyclizations of dicarbonyl compounds. Our work with reductive condensations demonstrated that the rate of nucleophilic attack by alkoxysilanes is faster than the rate of reduction (vide supra) and so we felt that the 5- or 6-*Exo*-Trig ring closures would be extremely facile processes. We employed a two to three-fold excess of organosilane in our experiments in order to test this hypothesis. In no case, did we observe polymerization or reduction to bis-alkoxysilanes.

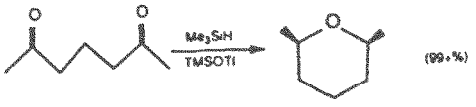
The reaction of phthalic dicarboxaldehyde with excess trimethylsilane and catalytic trimethylsilyl triflate, gave a quantitative conversion to 1,3-dihydro-isobenzofuran.



Under the same conditions, 2,5-hexanedione underwent an 85% conversion to 2,5-dimethyl tetrahydrofuran. Analysis by NOE suppressed ^{13}C NMR showed the remaining 15% to be starting material and the product to be a 50:50 mixture of *cis* and *trans* isomers.



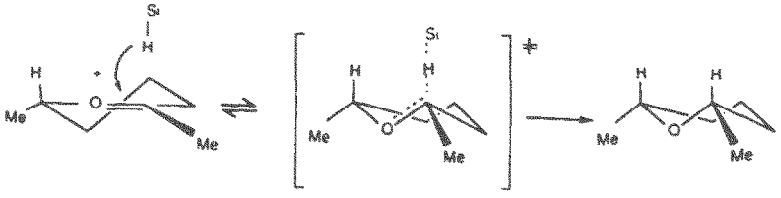
In contrast to the lack of stereoselectivity observed for the 5-membered ring, cyclization of 2,6-heptanedione gave a quantitative yield of *cis*-dimethyl tetrahydropyran.



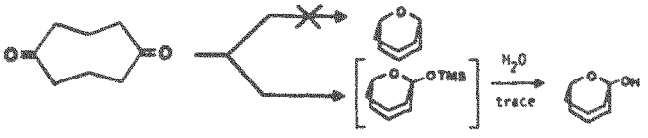
This appears not to be the result of a steric barrier, but due to the thermodynamics of the intermediate and the transition state. The methyl group attached to the sp^3 carbon in the carboxonium intermediate, is in an energetically more favorable configuration when pseudoequatorial.

Progression through a chair-like transition state provides the lowest energy pathway for reduction and yields the observed product (see Scheme V).

Scheme V



Cyclization of 1,5-cyclooctanedione with either trimethylsilyl triflate or trimethylsilyl iodide as the catalyst did not give the expected bicyclic ether. Instead, we quantitatively obtained a stable bicyclic hemiketal, which was desilylated by traces of moisture during workup.



The structure of the final product was confirmed through independent synthesis by partial oxidation of *cis*-1,5-cyclooctanediol with chromic acid. Its stability is not surprising, in that any further reduction would involve a bridgehead carboxonium ion, in violation of Bredt's rule. We were not able to isolate the O-trimethylsilyl hemiketal, nor were we able to silylate the final product by conventional methods.

The moisture-lability of the trimethylsilyl group is, no doubt, due to a weakening of the O-Si bond through an intramolecular interaction with the second oxygen, as in the case of silyl nitronates.[21] The hydroxyl proton, in fact, shows evidence of intramolecular hydrogen bonding with a sharp band in the IR at 3338 cm^{-1} and a pronounced downfield chemical shift in the proton NMR at δ 7.6.

Summary

Ketones may be reduced to *t*-butyldimethylsilyl ethers in good yields by the use of *t*-butyldimethylsilane and catalytic *t*-butyldimethylsilyl triflate. Substituted cyclohexanones show preference for forming the less thermodynamically stable product.

Trimethylsilane in combination with trimethylsilyl iodide or triflate is effective in C-O cleavage of O-trimethylsilyl hemithioacetals to effect transformation to thioethers.

Synthesis of 5 and 6-membered cyclic ethers from dicarbonyl compounds is an extremely facile process using trimethylsilane and catalytic trimethylsilyl triflate.

Experimental

Proton and carbon-13 magnetic resonance experiments were performed on a Varian VXR-200 (200 MHz) NMR spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 1550 FT-IR. Mass spectra were obtained using a Finnigan MAT INCOS™ 50 GC/MS system; GLC analyses were done on a Varian Model 3700 chromatograph equipped with a 30 meter DB-1 (methylsilicone) capillary column.

1,5-Cyclooctanedione[22] and 2,6-heptanedione[23] were prepared by published procedures. Trimethylsilane was supplied by SCM Specialties, Gainesville, FL. All other compounds were purchased from Aldrich, Milwaukee, WI.

General Procedures

Alkoxysilanes. The ketone (1.00 mmol) and *t*-butyldimethylsilane (348 mg, 3.00 mmol) are combined in a 10 mL round bottom flask equipped with a magnetic stir-bar and rubber septum. *t*-Butyldimethylsilyl triflate (2.5 µL, 0.01 mmol) is introduced via syringe and the reaction stirred 2 hours at room temperature under argon. The excess silane is then removed under reduced pressure or may be recovered by distillation. The product may then be purified by distillation or chromatography

Thioethers. The O-trimethylsilyl hemithioacetal (5.00 mmol) is dissolved in 15 mL CH_2Cl_2 and cooled to 0°C under nitrogen. To this added trimethylsilane from a 2.6 M stock solution, kept at 0°C (6 mL, 15 mmol), and followed by the addition of trimethylsilyl iodide (7 µL, 0.05 mmol). The reaction mixture is maintained at 0°C for 60 minutes and then allowed to stand 8 hours at room temperature. The reaction solution is then washed with 10% $Na_2S_2O_3$ (2 x 5 mL), water (2 x 5 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The product may then be purified by conventional methods.

Cyclic Ethers. The dicarbonyl compound (5.00 mmol) in 15 mL CH_2Cl_2 is placed in a 50 mL 3-neck flask equipped with a magnetic stir-bar, rubber septum, thermometer and nitrogen inlet. To this is added 2.6 M trimethylsilane (7.7 mL, 20 mmol) followed by trimethylsilyl triflate (15 µL, 0.08 mmol). The addition of the catalyst produces a 5-6°C rise in temperature, which returns to 0°C within 2 minutes. The reaction is maintained at 0°C for 4 hours and then allowed to stand 2 hours at room temperature. It is then washed with 10% $NaHCO_3$ (1x5 mL), water (1x5 mL), dried over $MgSO_4$ and concentrated.

Physical Data

Cyclohexoxy-*t*-butyldimethylsilane: ^{13}C NMR 70.0, 35.9, 25.9, 25.6, 24.0, 18.2, 4.7

Benzyl ethyl sulfide: ^{13}C NMR 138.5, 128.7, 128.3, 126.7, 35.7, 25.1, 14.2

Cyclohexyl ethyl sulfide: ^{13}C NMR 42.9, 33.5, 26.0, 25.7, 23.8, 14.9

1,3-Dihydroisobenzofuran: ^{13}C NMR 138.8, 127.1, 120.8, 73.4; lit.[24]

2,5-Dimethyltetrahydrofuran: ^{13}C NMR *cis*- 76.7, 34.8, 23.0; *trans*- 76.1, 35.9, 23.1; lit[25]

cis-2,6-Dimethyltetrahydropyran: ^{13}C NMR 73.9, 33.0, 23.6, 22.1; lit[26]

1-Hydroxy-9-oxa-bicyclo[3.3.1]nonane: ^{13}C NMR 93.7, 72.4, 36.2, 28.2, 20.5;

^{1}H NMR 7.6 (broad s, 1H, exchanges w/D_2O), 4.3 (broad, 1H), 1.7 (m, 12H); IR (cm^{-1}) 3338, 2946, 1228, 1154, 1030, 995; MS (m/e) 142, 124, 114, 96, 82, 73, 68, 60, 55.

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