Table I. TBAF-Catalyzed Reaction of 1-[Bis(trimethylsilyl)methyl]-1,2,4-triazole (4) with Carbonyl Compounds 5

entry	carbonyl compd	time, h	products[a] (isomer ratio, % yield)
1	p-ClC_6H_4CHO	2	**7a** p-$ClC_6H_4CH{=}CHT$ (1:1, 89)
2	$C_6H_5COC_6H_5$	4	**7b** $(C_6H_5)_2C{=}CHT$ (89)
3	p-$ClC_6H_4COCH_3$	5	**7c** p-$ClC_6H_4C(CH_3){=}CHT$ (1:1, 80)
4	$C_6H_5CH_2CH_2CHO$	0.5	**7d** $C_6H_5CH_2CH_2CH{=}CHT$ (3:2, 82)
5	cyclohexanone	4	**7e** c-$C_5H_{10}C{=}CHT$ (40)
6[b]	β-tetralone	4	... (0)

[a] T = 1,2,4-triazol-1-yl. Isolated yields as a mixture of isomers whose ratio E/Z was determined by ^1H NMR spectra. No attempt was made to separate and determine the configuration of two components. [b] 98% β-tetralone was recovered.

terson reaction, whereas bis(trimethylsilyl)dichloromethane[5] does not.

In the case of β-tetralone, which has the most enolizable carbonyl group, no product was obtained, and β-tetralone was recovered (97.5%, entry 6) due to formation of the enolate anion by proton transfer to the anion **3**.

Although the anion **3** reacted selectively with **5** to give **7**, anion **1**[1] generated from **2** acted as a base as well as a nucleophile to remove the proton at the 5-position of the triazole ring, which gave the 1,2,4-triazol-5-yl compound **12**, accompanied by the production of 1,2,4-triazol-1-yl compound **11**[6] (Scheme II). This could be attributed to the action of the silicon atom, which stabilizes the adjacent carbanion in anion **3** lowering the basicity of **3** below that of **1**.

Experimental Section

Melting points were determined on a Büchi apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian T-60 or EM-390 instrument with Me_4Si as an internal standard. A Hitachi 260-10 spectrophotometer was used to obtain IR spectra. Chromatography was performed on 230–400-mesh silica gel.

1-[Bis(trimethylsilyl)methyl]-1,2,4-triazole (4). A suspension of 1,2,4-triazole (2 g, 29 mmol), bis(trimethylsilyl)chloromethane[2] (6.2 g, 32 mmol), powdered K_2CO_3 (4.8 g, 35 mmol), and dry DMF (62 mL) was stirred at 60 °C for 40 h. The resulting mixture was poured into ice water and extracted with Et_2O. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel. The fractions eluted with benzene–AcOEt (4:1) gave 3.99 g (61%) of **4**: mp 27–30 °C; bp 100–101 °C (6 mm); ^1H NMR (Me_3SO-d_6) δ 0.03 (s, 18 H, methyl), 3.79 (s, 1 H, methine), 7.86 (s, 1 H, 3-position of triazole), 8.23 (s, 1 H, 5-position of triazole); IR (neat) 2950, 1485, 1250, 1140, 1005, 845, 655 cm^{-1}. This material was converted to its oxalate: 82% yield from the free base; mp (oxalate) 113–122 °C [Et_2O–$(i\text{-}Pr)_2O$]. Anal. Calcd for $C_{11}H_{23}O_4N_3Si_2$: C, 41.61; H, 7.30; N, 13.24. Found: C, 41.48; H, 7.26; N, 13.35.

The fractions eluted with benzene–AcOEt (1:1) gave 195 mg (4%) of **2** as an oil, which was identified by ^1H NMR spectra.

General Procedure for TBAF-Catalyzed Reaction of 1-[Bis(trimethylsilyl)methyl]-1,2,4-triazole (4) with Carbonyl Compounds. To a solution of carbonyl compound (200 mg, 1.1–2.0 mmol) and **4** (1.2 mol equiv/mol of carbonyl compound) in dry THF (2.7 mL/mmol of carbonyl compound) under nitrogen atmosphere at −20 °C was added anhydrous TBAF (0.1 mol equiv/mol of carbonyl compound, 1 M in THF). The mixture was stirred at −20 °C for the period shown in Table I. The reaction mixture was poured into ice water and extracted with Et_2O. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by flash chromatography, and the results are summarized in Table I.

1-(4-Chlorophenyl)-2-(1,2,4-triazol-1-yl)ethylene (7a): 1:1 mixture of E and Z isomers as a semisolid; mp ~102.5 °C; IR (Nujol) 1655 ($\nu_{C=C}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.43 (d, 0.5 H, J = 9.6 Hz, vinyl), 6.84–7.52 (m, 5.5 H, vinyl, phenyl), 7.90 (s, 0.5 H, 3-position of triazole), 7.95 (s, 0.5 H, 5-position of triazole), 7.98 (s, 0.5 H, 3-position of triazole), 8.24 (s, 0.5 H, 5-position of triazole). Anal. Calcd for $C_{10}H_8ClN_3$: C, 58.41; H, 3.92; Cl, 17.24; N, 20.43. Found: C, 58.40; H, 3.82; Cl, 17.33; N, 20.22.

1,1-Diphenyl-2-(1,2,4-triazol-1-yl)ethylene (7b): mp 65–67 °C [$(i\text{-}Pr)_2O$–petroleum ether]; IR (Nujol) 1645 ($\nu_{C=C}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08–7.48 (m, 12 H, vinyl, phenyl, 3-position of triazole), 7.89 (s, 1 H, 5-position of triazole). Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.92; H, 5.18; N, 16.96.

2-(4-Chlorophenyl)-1-(1,2,4-triazol-1-yl)-1-propene (7c): 1:1 mixture of E and Z isomers as an oil; IR (neat) 1650 ($\nu_{C=C}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (d, 1.5 H, J = 1.7 Hz, methyl), 2.28 (d, 1.5 H, J = 1.4 Hz, methyl), 6.83–7.43 (m, 5 H, vinyl, phenyl), 7.51 (s, 0.5 H, 3-position of triazole), 7.89 (s, 0.5 H, 5-position of triazole), 8.04 (s, 0.5 H, 3-position of triazole), 8.24 (s, 0.5 H, 5-position of triazole). Anal. Calcd for $C_{11}H_{10}ClN_3$: C, 60.14; H, 4.59; Cl, 16.14; N, 19.13. Found: C, 60.13; H, 4.80; Cl, 16.14; N, 18.92.

4-Phenyl-1-(1,2,4-triazol-1-yl)-1-butene (7d): 3:2 mixture of E and Z isomers as an oil; IR (neat) 1670 ($\nu_{C=C}$) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.30–2.89 (m, 4 H, methylene), 5.32–5.64 (m, 0.4 H, vinyl), 6.13–6.46 (m, 0.6 H, vinyl), 6.92–7.36 (m, 6 H, vinyl, phenyl), 8.06 (s, 0.6 H, 3-position of triazole), 8.12 (s, 0.4 H, 3-position of triazole), 8.64 (s, 0.4 H, 5-position of triazole), 8.71 (s, 0.6 H, 5-position of triazole). Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.34; H, 6.58; N, 21.09. Found: C, 71.97; H, 6.50; N, 20.76.

(1,2,4-Triazol-1-yl)cyclohexylidenemethane (7e): mp 50.5–52.5 °C (petroleum ether); IR (Nujol) 1670 ($\nu_{C=C}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39–1.82 (m, 6 H methylene), 2.07–2.42 (m, 4 H, allyl), 4.56 (s, 1 H, vinyl), 7.96 (s, 1 H, 3-position of triazole), 8.03 (s, 1 H, 5-position of triazole). Anal. Calcd for $C_9H_{13}N_3$: C, 66.23; H, 8.03; N, 25.74. Found: C, 66.51; H, 7.98; N, 25.64.

Registry No. **2**, 103817-03-4; **4**, 107743-46-4; **4**·oxalate, 107743-47-5; **5**(R^1 = 4-ClC_6H_4, R^2 = H), 104-88-1; **5**(R^1 = R^2 = Ph), 119-61-9; **5**(R^1 = 4-ClC_6H_4, R^2 = Me), 99-91-2; **5**(R^1 = $Ph(CH_2)_2$, R^2 = H), 104-53-0; **5**(R^1 = R^2 = c-C_5H_9), 108-94-1; (*E*)-**7a**, 107743-48-6; (*Z*)-**7a**, 107743-49-7; **7b**, 84595-58-4; (*E*)-**7c**, 107743-50-0; (*Z*)-**7c**, 107743-51-1; (*E*)-**7d**, 107743-52-2; (*Z*)-**7d**, 107743-53-3; **7e**, 107743-54-4; **11**(R^1 = R^2 = Ph), 76674-04-9; **12**(R^1 = R^2 = Ph), 103817-08-9; TBAF, 429-41-4; $(Me_3Si)_2CHCl$, 5926-35-2; 1,2,4-triazole, 288-88-0.

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(6) For example, 1-[(trimethylsilyl)methyl]-1,2,4-triazole (**2**) reacted with benzophenone (**5**, R^1 = R^2 = Ph) in the presence of a catalytic amount of TBAF to give 2-(1,2,4-triazol-1-yl)ethanol (**11**, R^1 = R^2 = Ph; 21%) and (1-methyl-1,2,4-triazole-5-yl)methanol (**12**, R^1 = R^2 = Ph; 46%) after acid-catalyzed hydrolysis.

Preparation of 3-Substituted 4-Methylfurans: 3-Iodo-4-methyl- and 3-Formyl-4-methylfuran

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The furan ring occurs frequently in sesquiterpenes. However, among the many syntheses available,[1] only a few

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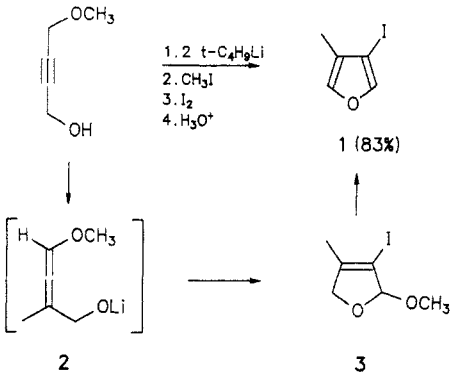
0022-3263/87/1952-2315$01.50/0

Scheme I



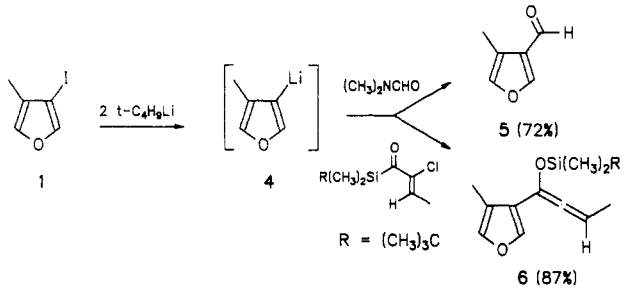
are suitable for the preparation of furans with substituents only at the 3- and 4-positions. This is because most electrophilic substitutions occur at the 2,5-positions, and many acyclic precursors (e.g., 1,4-dicarbonyl compounds) are more easily prepared with substituents at those positions destined to become the 2- and 5-positions of the furan. Successful approaches include,[2] among others, the modification of the commercially available 3,4-furandicarboxylic acid[2a] and Diels–Alder—retro-Diels–Alder sequences.[2b] We required a convenient route to 3-substituted 4-methylfurans for a synthetic project and have developed an efficient process starting from 2-butyne-1,4-diol.

The procedure (Scheme I) is related to a furan synthesis reported by Schlosser and Stähle,[3] which has also been utilized in various forms by other workers.[4] Our procedure involves methylation of the dianion formed by metalation of the monomethyl ether of 2-butyne-1,4-diol.[5,6] Iodination of the intermediate allenol ether **2** followed by acidification gave an 83% yield of 3-iodo-4-methylfuran (**1**). The reaction proceeds as shown in Scheme I. The intermediate allene **2** (as its silyl ether) or the methoxydihydrofuran **3** could be isolated if the reaction mixture was worked up at the appropriate stage.

The metalation and methylation reactions must be performed with good temperature control to avoid the formation of significant amounts of 2,4-dimethyl-3-iodofuran and 2-methyl-3-iodofuran. A second metalation of **2** by the starting dianion during the methylation step is probably responsible for the formation of these products.

Metal–halogen exchange of **1**[7] proceeded smoothly on treatment with 2 equiv of *tert*-butyllithium to give the lithium reagent **4**.[8] We have used it for the preparation

Scheme II



of the formyl derivative **5** and the siloxyallene **6**[9] (R = *t*-C_4H_9) as shown in Scheme II.

We had hoped that the intermediate allene alkoxide **2** could be directly trapped with carbon electrophiles (in the same sense that the iodination occurred),[10] but reaction of it or the derived trimethylsilyl ether with dimethylchloroiminium chloride (DMF–oxalyl chloride),[11] trimethyl orthoformate–$TiCl_4$,[12] or DMF–dialkyl acetals[13] did not give the expected formyl derivatives.

The furans **1**, **4**, and **5** should provide convenient access to a wide variety of other furans by derivatizations of the iodo, lithio, and formyl groups.

Experimental Section

General Procedures. All reactions were run under a positive pressure of nitrogen with oven-dried (110 °C) glassware. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Infrared spectra were recorded as neat liquids between salt plates.

3-Iodo-4-methylfuran (1). To a solution of 1.93 mL (2.00 g, 20.00 mmol) of 4-hydroxy-1-methoxy-2-butyne[5] in 40 mL of THF at −78 °C was added 23 mL of a 1.75 M solution of *t*-BuLi (40 mmol). The orange solution was stirred 75 min and then added over 25 min, via Teflon cannula, to a cold (−78 °C) flask to which had been added (in order) 50 mL of Et_2O, 0.3 mL of 1.5 M *n*-BuLi (0.45 mmol, proton scavenger), and 3.7 mL (8.5 g, 60 mmol) of methyl iodide. A white precipitate began forming immediately. The mixture was stirred 1 h at −78 °C and 30 min at 0 °C and treated with a solution of 5.08 g (20 mmol) of I_2 in 20 mL of THF. After 30 min, the brown mixture was added to 100 mL of rapidly stirred 2 N HCl. After 30 min, 14 g of $Na_2CO_3 \cdot H_2O$ was added (foaming), and the mixture was transferred to a separatory funnel and treated with 10 g of $NaHSO_3$ (foaming). The aqueous layer was extracted with 2 × 20 mL of Et_2O–pentane (1:1), and the organic extracts were washed with 25 mL of brine and dried (Na_2SO_4, K_2CO_3). Most of the solvent was removed through Vigreux columns (18 in., then 6 in.), and the residue was briefly placed on a rotary evaporator and then distilled [Kugelrohr; 65 °C (20 mm)] to give 3.44 g (83%) of 3-iodo-4-methylfuran (**1**): ^1H NMR ($CDCl_3$, 100 MHz) δ 1.96 (s, 3 H), 7.20 (br s, 1 H), 7.40 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 15 MHz) δ 10.7, 71.3, 123.0, 138.9, 145.2; IR 3130, 2910, 1587, 1138, 1050, 1030, 880, 785 cm^{-1}; MS, (M^+) 207.9388, calcd for C_5H_5IO 207.9386. Small amounts of 4-hydroxy-1-methoxy-2-butyne (~4%) and 3-iodo-2-methylfuran were visible in the NMR spectrum. The isomeric iodofuran was isolated from a previous reaction mixture by preparative gas

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chromatography (20% SE-30 on Chromasorb W, AW-DMCS, 80 °C): NMR ($CDCl_3$, 270 MHz) δ 2.33 (br s, 3 H), 6.37 (br d, J = 2 Hz, 1 H), 7.28 (d, J = 2 Hz, 1 H). Small amounts of 2,4-dimethyl-3-iodofuran were also detected in previous reaction mixtures: ^1H NMR (270 MHz, $CDCl_3$) δ 1.92 (d, J = 1.1 Hz, 3 H), 2.31 (s, 3 H), 7.13 (q, J = 1.1 Hz, 1 H).

3-Iodo-2-methoxy-4-methyl-2,5-dihydrofuran (3). A solution of 0.484 mL (500 mg, 5.00 mmol) of 4-hydroxy-1-methoxy-2-butyne[5] was metalated (5.7 mL, 1.75 M t-BuLi, 10 mmol), methylated (0.620 mL, 1.42 g, 10 mmol of methyl iodide), and iodinated (1.52 g, 6.00 mmol of I_2) as in the previous procedure. The solution was poured into 10% $Na_2S_2O_3$–7% $NaHCO_3$/Et_2O–pentane. The organic layer was washed with brine, dried (Na_2SO_4), evaporated, and distilled [Kugelrohr; 85 °C (20 mm)] to give **3**: ^1H NMR (CCl_4, 100 MHz) δ 1.92 (br s, 3 H), 3.24 (s, 3 H), 4.48 (m, 2 H), 5.50 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.3, 53.0, 77.0, 85.9, 112.4, 146.1; ^{13}C NMR (benzene-d_6, 15 MHz) δ 13.8, 52.6, 76.7, 86.7, 112.6, 145.7; IR 3440 (br), 2920, 1658, 1437, 1378, 1193, 1123, 1048, 995, 826 cm^{-1}; MS, (M^+) 239.9647, calcd for $C_6H_9IO_2$ 239.9648. A small amount of 3-iodo-4-methylfuran (~10%) was visible in the ^1H NMR spectrum.

1-Methoxy-3-methyl-4-[(trimethylsilyl)oxy]-1,2-butadiene. To a solution of 0.29 mL of 2-butyne-1,4-diol monomethyl ether[5] (0.30 g, 3.0 mmol) in 6 mL of THF at −78 °C was added 4.2 mL of 1.5 M t-BuLi (6.3 mmol). After 1 h, 0.25 mL (0.57 g, 4.0 mmol) of methyl iodide was added, followed in 20 min by 0.51 mL (0.43 g, 4.0 mmol) of chlorotrimethylsilane. After 15 min, the reaction mixture was warmed to 0 °C, stirred 15 min, then treated with 0.15 mL of triethylamine, and partitioned between cold aqueous 7% $NaHCO_3$ and 1:1 Et_2O–pentane. The organic layer was washed with brine, dried (Na_2SO_4, then K_2CO_3), and evaporated. A few milligrams of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide was added, and the crude product was distilled [Kugelrohr; 80 °C (20 mm)] to give 0.51 g (91%) of 1-methoxy-3-methyl-5-[(trimethylsilyl)oxy]-1,2-butadiene as a clear oil: NMR (CCl_4, 100 MHz) δ 1.94 (d, J = 2 Hz, 3 H), 3.34 (s, 3 H), 4.08 (br s, 2 H), 6.52 (pentet, J = 2 Hz, 1 H); IR 2970, 1951, 1462, 1260, 1135, 1080, 885, 850, 764 cm^{-1}.

4-Methyl-3-furancarboxaldehyde. To a solution of 16.1 mL of 1.74 M t-BuLi (28 mmol) in 100 mL THF was added 1.50 mL (2.87 g, 13.8 mmol) of 3-iodo-4-methylfuran (1) over 5 min. After 30 min, 1.16 mL (1.10 g, 15.0 mmol) of N,N-dimethylformamide was added. The mixture was stirred 30 min at −78 °C and 30 min at 0 °C and then poured into Et_2O–pentane (1:1)—7% $NaHCO_3$ (50 mL each). The aqueous layer was extracted with 50 mL of Et_2O–pentane, and the combined organic layers were washed with brine and dried (Na_2SO_4). The solvent was removed by distillation and the residue purified by Kugelrohr distillation [67 °C (20 mm)] to give 1.10 g (72%) of 4-methyl-3-furancarboxaldehyde: NMR ($CDCl_3$, 100 MHz) δ 2.08 (s, 3 H), 7.08 (br s, 1 H), 7.82 (s, 1 H), 9.82 (s, 1 H); IR 3120, 2820, 2725, 1685, 1540, 1141, 1041, 863, 752 cm^{-1}; MS, (M^+) 110.0368, calcd for $C_6H_6O_2$ 110.0368.

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Registry No. 1, 107658-18-4; 3, 107658-20-8; 5, 107658-19-5; $H_3COCH_2C{\equiv}CCH_2OH$, 18857-03-9; $H_3COCH{=}C{=}C(CH_3)CH_2OSi(CH_3)_3$, 107658-21-9.

A Mild Method for the Reductive Desulfurization of α-Phenylthio and α-Phenylsulfinyl Carbonyl Compounds

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In the last two decades α-phenylthio and α-phenylsulfinyl ketones and esters have become very popular synthetic intermediates. They have been found to serve effectively as reagents or intermediates for a wide variety of transformations in many different situations.[3] One of the attractive features of these groups is their ease of removal; several different reagents have been used for this purpose.[4]

During the course of our studies directed toward aphidicolin[5] total synthesis[6] as well as our efforts to explore diastereoselectivity and enantioselectivity in the kinetic Michael addition,[7] we encountered the necessity for reductive removal of phenylthio or phenylsulfinyl groups on many occasions. In several of these cases the existing methods gave unacceptably poor results due either to competing side reactions or to reactivity with other functional groups present in the compound of interest.

We have, therefore, developed a mild method for reductive desulfurization of α-phenylthio and α-phenylsulfinyl carbonyl compounds that we have found to be unusually effective, particularly in the presence of other functional groups. The method is based upon the original observations of Russell and Mikol, who found that (methylsulfinyl)acetophenones were reduced to the corresponding acetophenones in 83–88% yields by zinc in acetic acid.[4k,8] In many cases these conditions are too acidic to permit the survival of other acid-labile functional groups. We have overcome this problem by the use of activated zinc in a mixture of THF and saturated aqueous ammonium chloride solution at 25 °C. Results for the reduction of a series of representative α-phenylthio and α-phenylsulfinyl ketones and esters under these conditions are listed in Table I.

Several features of this reductive desulfurization are

(1) ACS/PRF Visiting Faculty Fellow from Tennessee Technological University.

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