125879-76-7; indole, 120-72-9; 1-methylindole, 603-76-9; 2-methylindole, 95-25-5; pyrrole, 109-97-7; 2,5-dimethylpyrrole, 625-84-3; phenyloxirane, 96-09-3; 4-methoxyphenyloxirane, 6388-72-3; 1a*H*-6,6a-dihydroindeno[1,2-*b*]oxirane, 768-22-9; *trans*-diphenyloxirane, 1439-07-2; 7-oxabicyclo-2-heptene, 6705-51-7.

Improved Synthesis of Dimethylketene Trimethylsilyl Acetals by Rhodium-Catalyzed Hydrosilylation

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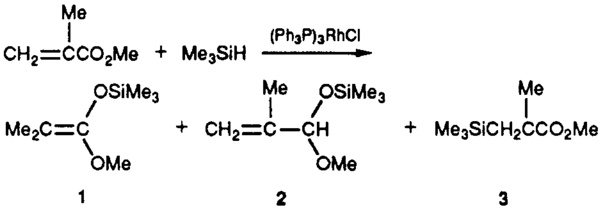
Silyl ketene acetals have received much attention in the literature since the early work of McElvain and co-workers.[1,2] These ester enolate equivalents are used extensively in Michael additions[3] and aldol condensations.[4] Webster and co-workers have used silyl ketene acetals in an acrylate polymerization technique known as group-transfer polymerization (GTP).[5] In GTP, a silyl ketene acetal initiates condensation polymerization of acrylates and continues through sequential Michael additions.

One route to silyl ketene acetals involves the reaction of an alkali-metal enolate with a chlorosilane.[6] Transition-metal-catalyzed hydrosilylations of α,β-unsaturated esters have also been used.[7-9] While the use of platinum catalyst has been reported,[9] rhodium catalysts are more frequently used.[8] The disadvantage of the rhdoium catalysis method is the formation of inseparable isomers, which reduce the purity of the isolated product. Ojima and co-workers,[8] for example, reported the $(Ph_3P)_3RhCl$-catalyzed preparation (sealed ampule) of several dimethylketene silyl acetals in GC yields of 80–96%. The silyl acetals were not isolated as pure compounds but contained 5–25% of a 1,2-carbonyl adduct. Nevertheless, the overall benefits of a catalytic procedure led us to reinvestigate the rhodium catalysis route.

A solution of methyl methacrylate (MMA), 16% molar excess of trimethylsilane, and 400 molar ppm $(Ph_3P)_3RhCl$ was stirred under nitrogen in a Parr pressure reactor for 5 h at 100 °C. Gas chromatographic–mass spectral (GC–MS) examination of the product mixture showed 1-methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (**1**),[10] as the major product, the 1,2-carbonyl adduct **2**,[11] and the vinyl addition product **3**[12] (eq 1). The GC (with FID) area ratio

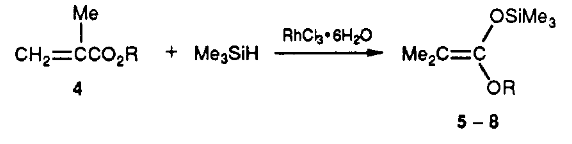


(1)

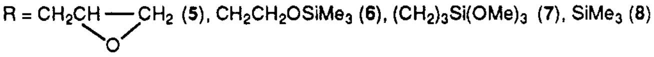
was 7:1:1, respectively, with an isolated yield of 50–60% for **1** and a substantial amount of poly(MMA). Lowering the temperature favored less polymer formation, with only a slight increase in the **1**:**2** ratio. Silyl ketene acetal **1** could not be isolated from **2** by distillation.

The total amount of trimethylsilane used and its rate of consumption up to the stoichiometric end point had a significant effect on the product distribution. For example, a reaction of MMA with a stoichiometric amount of trimethylsilane and a reaction with 30% molar excess of trimethylsilane were each carried out. Only the reaction with 30% excess showed a loss of adduct **2** after 5 h at 50 °C. Treatment of an isolated mixture of **1**, **2**, and **3** with excess trimethylsilane and $(Ph_3P)_3RhCl$ results in a decrease in **2**, without change in **1** or **3**. On the other hand, a slower addition rate of the silane afforded an 80% yield of **1** and a 0.3% yield of **3**. The rate of trimethylsilane consumption was faster with $RhCl_3{\cdot}6H_2O$, and conversion to product was almost instantaneous at 50 °C. Thus, the reaction could be carried out at a faster addition rate, and it could be done in a standard round-bottom flask, instead of a sealed ampule or pressure reactor. A modest increase in the yield of **1** to 85% was also obtained with $RhCl_3{\cdot}6H_2O$, and the product did not contain **2** or **3** after distillation (>98% pure).

The verstaility of this improved procedure was demonstrated when excess trimethylsilane and $RhCl_3{\cdot}6H_2O$ were used to prepare the dimethylketene trimethylsilyl acetals shown in eq 2. Furthermore, synthesis of a difunctional silyl ketene acetal **9** was achieved in 75% isolated yield from ethylene glycol dimethylacrylate (see Experimental Section). The amount of polymer formed was ~1% when 2,6-di-*tert*-butyl-4-methylphenol was added, and the reaction was conducted under nitrogen containing 2% oxygen.



(2)



Experimental Section

Reagents and chemicals were used as received from the manufacturers unless otherwise specified. Trimethylsilane, trimethylsilyl methacrylate, 3-(trimethylsiloxy)ethyl methacrylate, and 3-(trimethoxysilyl)propyl methacrylate were obtained from

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(1) (a) McElvain, S. M. *Chem. Rev.* **1949**, *49*, 453. (b) McElvain, S. M. *J. Am. Chem. Soc.* **1959**, *81*, 2579.

(2) See also: Petrov, A. D.; Sudykh-Zade, S. I.; Filatova, E. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1959**, *29*, 2898.

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(5) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473 and references cited therein.

(6) (a) Ainsworth, C.; Chen, F.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46* (1), 59. (b) Kuo, Y. N.; Chen, F.; Ainsworth, C.; Bloomfield, J. J. *J. Chem. Soc., Chem. Commun.* **1971**, 136.

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(10) Adam, N.; del Fierro, J. *J. Org. Chem.* **1978**, *43*, 1159.

(11) The spectral data were similar to those reported elsewhere for analogous compounds: GC–MS *m/e* (% rel int) 159 (22, P – 15), 143 (24), 133 (94), 89 (69), 73 (100); GC FT-IR 1060 cm^{-1} for SiOC; NMR ($DCCl_3$) 1.7 (s, 3 H), 3.2 (s, 3 H), 3.6 (s, 1 H), 5.0 (m, 2 H) as a mixture containing **1**. See ref 8.

(12) The spectra of **3** matched that of an independently synthesized sample. See: Chalk, A. *J. Organomet. Chem.* **1970**, *21*, 207. Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

0022-3263/90/1955-2972$02.50/0

Dow Corning Corp. Methyl methacrylate and glycidyl methacrylate were obtained from Aldrich Chemical Co.

GC analyses were performed either on a Varian 3700 gas chromatograph equipped with a flame ionization detector (FID) and a 60- or 12-m fused-silica capillary silica column. Routine GC–MS analyses were performed on a Hewlett-Packard 5970A MSD instrument. Chemical ionization mass spectra were obtained on a Finnigan 4610 mass spectrometer with CH_4 as the reagent gas. IR spectra were obtained on a Perkin-Elmer 1330 spectrophotometer or on a Nicolet 60SX GC FTIR. ^1H NMR were obtained on a Varian EM-390 90-MHz spectrometer and are reported on the δ scale. High-resolution mass spectra were obtained from Iowa State University Analytical Services.

1-Glycidoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (5). General Synthesis of Dimethylketene Trimethylsilyl Acetals. Preparation of 5 is exemplary of the procedure used to prepare the other silyl ketene acetals. A stirred solution of 1000 g (7.0 mol) of glycidyl methacrylate, 0.28 g (1.06×10^{-3}) of $RhCl_3 \cdot 6H_2O$, 0.5 g of 2,6-di-*tert*-butyl-4-methylphenol, and 38 mL of THF was heated to 38 °C, under nitrogen containing 2% oxygen, in a 2-L round-bottom flask equipped with a dry ice cooled condenser. The heating mantle was removed, and the addition of trimethylsilane was started from a stainless steel tank at 20 psi. When about 30 mL of trimethylsilane had been added, an exothermic reaction occurred, causing a temperature rise to about 50 °C before cooling was applied. The remainder of the trimethylsilane was added over a 1.5-h period; the temperature was maintained between 40 and 50 °C by compressed-air cooling. A dark brown mixture was removed from the flask and sealed in a half-gallon bottle. GC of the mixture after 24 h showed 5 and the corresponding vinyl adduct in a 75:1 ratio. After fractional distillation (bp 82 °C at 9 mmHg), 1512 g (80%) of 5 was obtained in 98% purity:[13] NMR ($DCCl_3$) 0.20 (s, 9 H), 1.45 (s, 3 H), 1.55 (s, 3 H), 2.6 (m, 2 H), 3.1 (m, 1 H), 3.7 (m, 2 H); IR (neat) 1700 cm^{-1}; GC–MS *m/e* (% rel int) (216 (3), 73 (100), 70 (40), 57 (17), 23 (13); high-resolution mass for $C_{10}H_{20}O_3Si$ measured 216.0072, calculated 216.3544.

1-Methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (1). Silyl ketene acetal 1 was obtained in 85% isolated yield (42 °C at 13 mmHg). The spectra of 1 matched those reported in the literature:[5,10] NMR ($DCCl_3$) 0.20 (s, 9 H), 1.50 (s, 3 H), 1.57 (s, 3 H), 3.45 (s, 3 H); IR (neat) 1704, 1183 cm^{-1}; chemical ionization MS (CH_4) *m/e* 175 (P + 1); GC–MS *m/e* 174 (13), 89 (26), 73 (76), 70 (100).

1-(2-(Trimethylsiloxy)ethyl)-1-(trimethylsiloxy)-2-methylprop-1-ene (6). Silyl ketene acetal 6 was obtained in 77% isolated yield (bp 100 °C at 4 mmHg). The spectra of 6 matched those reported in the literature:[5] NMR ($DCCl_3$) 0.10 (s, 9 H), 0.20 (s, 9 H), 1.50 (s, 3 H), 1.57 (s, 3 H), 3.70 (s, 2 H); IR (neat) 1710 cm^{-1}; GC–MS *m/e* (% rel int) 276 (5), 147 (10), 117 (20), 116 (12), 75 (12), 73 (100), 70 (11); high-resolution mass for $C_{12}H_{28}O_3Si_2$ measured 276.1577, calculated 276.6021.

1-(2-(Trimethoxysilyl)propyl)-1-(trimethylsiloxy)-2-methylprop-1-ene (7). Silyl ketene acetal 7 was obtained in 66% isolated yield (bp 110 °C at 3 mmHg): NMR ($DCCl_3$) 0.16 (s, 9 H), 0.60 (m, 2 H), 1.50 (s, 3 H), 1.56 (s, 3 H), 1.70 (m, 2 H), 3.50 (s, 9 H), 3.60 (t, J = 6 Hz, 2 H); IR (neat) 1705 cm^{-1}; GC–MS *m/e* (% rel int) 322 (4), 176 (11), 163 (18), 122 (18), 121 (100), 91 (39), 75 (18), 73 (42), 70 (23), 61 (10), 45 (16), 41 (12); high-resolution mass for $C_{13}H_{30}O_5Si_2$ measured 322.1629, calculated 322.5517.

1,1-Bis(trimethylsiloxy)-2-methylprop-1-ene (8). Silyl ketene acetal 8 was obtained in 78% isolated yield (bp 86 °C at 14 mmHg):[11] NMR ($DCCl_3$) 0.20 (s, 18 H), 1.47 (s, 6 H); IR (neat) 1705 cm^{-1}; GC–MS *m/e* (% rel int) 232 (10), 217 (20), 147 (45), 75 (21), 70 (70), 69 (21), 45 (44); high-resolution mass for $C_{10}H_{30}O_2Si_2$ measured 238.1864, calculated 238.5203.

1,2-Bis(1-(trimethylsiloxy)-2-methylprop-1-enoxy)ethane (9). Silyl ketene acetal 9 was obtained in 75% isolated yield (bp 110 °C at 2–3 mmHg). The spectra of 9 matched those reported in the literature:[5] NMR ($DCCl_3$) 0.20 (s, 18 H), 1.50 (s, 6 H), 1.56 (s, 6 H), 3.80 (s, 4 H); IR (neat) 1710 cm^{-1}; GC–MS *m/e* (% rel int) 188 (10), 117 (10), 103 (10), 75 (13), 73 (100), 70 (13).

Independent Removal of the Carbonyl Adduct. The removal of carbonyl adduct 2 is exemplary of the method used for the other silyl ketene acetals. Excess trimethylsilane was added to a solution containing 0.0409 g (4.4×10^{-5} mol) of $(Ph_3P)_3RhCl$ and 20.0 g (0.115 mol) of a distilled mixture of 1, 2, and 3 (40:2:1 ratio) to which was added toluene as an internal GC standard. The mixture was stirred 3 days at room temperature. After this time GC analysis showed a loss of 2 with no change in 1 or 3. Subsequent experiments showed 24 h to be sufficient for removal of 2 at room temperature or 5 h at 50 °C.

Acknowledgment. We thank the Dow Corning Analytical Research Department personnel for obtaining GC–FTIR and chemical ionization GC–MS spectra. Special thanks are given to Dow Corning's Process Engineering group for supplying trimethylsilane and to Dr. W. X. Bajzer of Dow Corning for helpful discussions.

Addition of α-Oxyradicals to 1-Fluoro-1-(phenylsulfonyl)ethylene

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The utility of free-radical reactions in organic synthesis has received considerable attention in the past decade.[1] Particularly important in this regard has been a resurgence in the use of carbon radical addition to olefins for the formation of carbon–carbon bonds. We have focused our attention on the utility of free-radical chemistry for the synthesis of fluorinated compounds of biological interest. Herein we report a convenient synthesis of 1-fluoro-1-(phenylsulfonyl)ethylene (3) and the addition of α-oxyradicals to 3 as a new method to synthesize fluoroorganics.

The synthesis of 3 was recently reported by a method requiring perchloryl fluoride, freshly prepared from potassium perchlorate and fluorosulfonic acid.[2] A new synthesis of 3 was developed (Scheme I), which utilizes the fluoro-Pummerer reaction[3] and provides a safe and convenient method to multigram quantities of 3 from commercially available materials. β-Chloroethyl phenyl sulfoxide (1) was treated with diethylaminosulfur trifluoride (DAST)[3] and a catalytic amount of antimony trichloride for 1 h at room temperature to provide the corresponding α-fluoro sulfide. The use of antimony trichloride as a catalyst for the fluoro-Pummerer reaction was recently introduced by Robins,[4] and we concur that this catalyst is superior to zinc iodide.[3] The α-fluoro sulfide was oxidized to the sulfone 2, without isolation, in an overall yield of 64%. Elimination of hydrogen chloride from 2 was readily effected with DBU to provide crystalline 3 in 86% yield.

While investigating the utility of 3 for the synthesis of fluorinated tetrahydrofurans, we found that the addition of a catalytic amount of benzoyl peroxide to a mixture of THF and 3 (reflux for 9 h) led to a diastereomeric mixture of 1-(2-fluoro-2-(phenylsulfonyl)ethyl)tetrahydrofuran (4a

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[13] The distilled purity was typically >98%, but hydrolysis to hexamethyldisiloxane and the corresponding isobutyrate ester occasionally occurred. See ref 8.

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