Diester **5** (3.9 g, 19.6 mmol) was dissolved in $CHCl_3$–MeOH (1:1, 250 mL) and an O_2/O_3 mixture was bubbled through the stirred solution at −78 °C until a faint blue coloration appeared. N_2 was then bubbled through the solution at −78 °C until the blue coloration disappeared, whereupon $Na_2S_2O_4$ (14 g, 54 mmol, 2.8 equiv) dissolved in H_2O (20 mL) was added to the cold solution to reduce the ozonide. (Ph_3P also can be used as the reductant.) The resulting mixture was warmed slowly to 22 °C and the solvents were removed in vacuo. An oily gum-like residue was obtained that was dissolved in ice-cold saturated aqueous K_2CO_3 (58 mL) and extracted with EtOAc (2 × 100 mL) to remove neutral compounds. The remaining aqueous phase was cooled to ice-bath temperatures and was acidified carefully with 6 N HCl to pH 1 such that the temperature of the solution remained at <10 °C. After saturation of the ice-cold acidic solution with solid KCl, it was extracted thoroughly with Et_2O (4 × 150 mL), and the combined ether extracts were worked up as described in method A to give **1** (2.6 g, 51%).

Acknowledgment. We thank Drs. Milan R. Uskokovic and John J. Partridge, Hoffman-La Roche, Inc., Nutley, N.J., for an authentic sample of **1** and Professor S. W. Baldwin, Duke University, for the information regarding the preparation of **1** from methyl propiolate.

Registry No. 1, 39947-70-1; 2, 38330-80-2; 3, 44205-36-9; 4, 1515-23-7; 5, 38201-52-4; terephthalic acid, 100-21-0.

Useful Route to Alkenyl *S*-Phenyl Thiocarbonates: Reagents for the Introduction of the Enyloxycarbonyl Moiety in Synthesis

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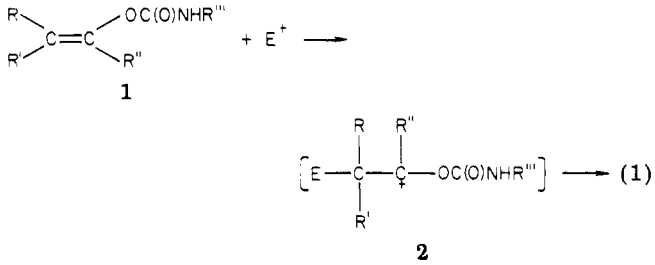
In recent publications from this laboratory,[1-3] vinyl chloroformate (H_2C=CHOC(O)Cl, VOC-Cl) was introduced as a useful reagent for amino protection, especially in peptide synthesis.[1] The utility of VOC-Cl in masking hydroxyls[3] and in selective tertiary amine N-dealkylation also has been reported.[2,3]

In peptide chemistry, certain substituted (vinyloxy)carbonyl groups might be expected to be even more valuable than the VOC moiety itself. For example, substituents in **1** (eq 1) could be incorporated (a) to increase crystal-



1 **2** (1)

linity and so simplify isolation or (b) to inductively and/or sterically reduce the sensitivity of **1** (vs. VOC-NHR) toward alkaline hydrolysis, a significant limitation. By stabilizing the intermediate cation **2** (e.g., with an α-alkyl residue), the normal electrophilic cleavage–removal of the blocking group also could be facilitated.

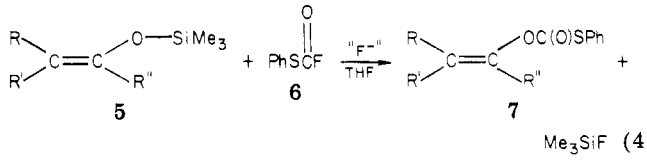
Efforts to test these possibilities have been thwarted in the past by the inaccessibility of substituted enol haloformates using the pyrolytic route to VOC-Cl[4] and by the lack of an alternative practical synthesis of such reagents.[5] Recently, however, Duggan and Roberts described the preparation of VOC-SPh (**4**) as in eq 2 and 3 and showed

$$\text{THF} + n\text{-BuLi} \rightarrow n\text{-BuH} + H_2C{=}CH_2 + \underset{\mathbf{3}}{H_2C{=}CHOLi} \quad (2)$$

$$\mathbf{3} + \text{PhSC(O)Cl} \rightarrow \underset{\mathbf{4}\ (\text{VOC-SPh})}{H_2C{=}CHOC(O)SPh} \xrightarrow[\text{pH 9.5}]{\text{AA}} \text{VOC-AA} + PhS^- \quad (3)$$

that this reagent readily transferred its VOC unit to the amino function of amino acids.[6] In this transacylation, loss of the enolate, vinyl oxide, did not compete with thiophenoxide elimination, a somewhat surprising and very useful discovery.

We now report a second, efficient synthesis of **4** which unlike the Duggan–Roberts process also can be generalized to the economical preparation of substituted vinyl *S*-phenyl thiocarbonates (**7**). In the new method, **7** is formed by the room temperature reaction of a trimethylsilyl enol ether precursor (**5**) in THF with phenyl thiofluoroformate (**6**) in the presence of a "naked fluoride" ion catalyst (eq 4). The process is analogous to a synthesis of enol car-



5 **6** **7** Me_3SiF (4)

bonates and carbamates previously developed in this laboratory and shown to be both regiospecific and stereospecific with respect to the enol surrogate, **5**.[7] Both $PhCH_2NMe_3{}^+F^-$ (BTAF) and KF/18-crown-6 have been utilized as the "naked fluoride"[8] source (the latter is better; see below), and the fluoroformate reagent (**6**) is readily available from the corresponding chloroformate by halide exchange with NaF in acetonitrile (92% yield).[9] All Me_3Si ethers (**5**) were easily prepared by standard procedures[10-14] except the parent, H_2C=CHOSiMe_3, which finally was made in 62% yield by a substantially modified version of the general House method.[10]

The results for several syntheses of thiocarbonates **7** by the new methodology are summarized in Table I. Reaction times were determined by periodic VPC assay, and

(1) R. A. Olofson, Y. S. Yamamoto, and D. J. Wancowicz, *Tetrahedron Lett.*, 1563 (1977).
(2) R. A. Olofson, R. C. Schnur, L. Bunes, and J. P. Pepe, *Tetrahedron Lett.*, 1567 (1977); R. A. Olofson and J. P. Pepe, *ibid.*, 1575 (1977).
(3) R. A. Olofson and R. C. Schnur, *Tetrahedron Lett.*, 1571 (1977).
(4) Reaction of ethylene glycol with phosgene to give the bis(chloroformate) followed by pyrolysis: F. E. Kung, U.S. Patent 2 377 085 (1945); L.-H. Lee, *J. Org. Chem.*, **30**, 3943 (1965).
(5) For an impractical route which does, however, yield some of these compounds, see: R. A. Olofson, B. A. Bauman, and D. J. Wancowicz, *J. Org. Chem.*, **43**, 752 (1978); R. A. Olofson, J. Cuomo, and B. A. Bauman, *ibid.*, **43**, 2073 (1978).
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Table I. Alkenyl S-Phenyl Thiocarbonates: Synthesis and Selected Spectral Data

rxn	ROCOSPh product R	yield,[a] %	amt reagent, equiv ROSiMe$_3$	PhSCOF	KF	18-C-6[d]	time, h	IR stretch (CCl_4), μm C=O	C=C	NMR ($CDCl_3$) vinyl H, δ (J in Hz[b])
A1	H_2C=CH	68	1.2	1.0	0.4	0.01	6	5.75	6.06	4.52 (dd; 7, 1)
A2		65	1.0	1.1	0.2	0.01	24			4.85 (dd; 14, 1)
										7.08 (dd; 14, 7)
B	Me_2C=CH	69	1.2	1.0	0.8	0.006	23	5.76	5.89	6.85 (qq; 1.47, 1.47)
C1	H_2C=C(Me)	70	1.2	1.0	0.3	0.025	7	5.77	5.99	4.5–4.6 (m)
C2		60	1.0	1.3	0.2	0.013	25			4.7–4.8 (m)
D	1-cyclohexenyl	66	1.0	1.2	0.2	0.005	6	5.78	5.92	5.3–5.5 (m)
E	H_2C=C(Ph)	74	1.0	1.2	0.5	0.02	2	5.73	6.10	5.05 (d; 2.4)
										5.36 (d; 2.4)
F1	MeCH=CH	59	1.1	1.0	0.3	0.003	20	5.78	5.98	4.82 (dq; 7, 7; Z)
F2		57	1.0	1.2	0.4	0.007	3			5.26 (dq; 12, 7; E)
										6.8–7.05 (m; E,Z)
G	EtCH=CH	63	1.0	1.0	0.2	0.002	23	5.79	5.99	4.91 (dt; 7, 7; Z)
										5.50 (dt; 13, 7; E)
										6.95–7.2 (m; E,Z)
H	Me_2CHCH=CH	72[c]	1.0[c]	1.1[c]	1.3[c]	0.05[c]	23[c]	5.76	5.99	4.87 (dd; 9, 7; Z)
										5.46 (dd; 12, 7; E)
										6.9–7.1 (m; E,Z)

[a] For methodology, see text, Experimental Section, and variables listed in the table; yields are based on the limiting reagent, either ROSiMe$_3$ or PhSCOF. [b] Multiplet = m, quartet = q, etc.; for geometrical isomer ratios, see the Experimental Section. [c] Reaction of PhSCOCl and KF/18-C-6 and then addition of ROSiMe$_3$; see text and Experimental Section; time is for last step. [d] 18-Crown-6.

optimum yields varied from 59 to 74%. Either **5** or **6** could be present in slight excess with minimal effect on the yield (see A1 vs. A2, C1 vs. C2, F1 vs. F2, and also G). The only significant side product was diphenyl dithiocarbonate,[6] and this was readily separated by distillation or crystallization from **7** except in reaction D where the cyclohexanone-derived product codistilled with the $(PhS)_2C$=O (ratio 88:12). No complications with competing aldol condensations, even in aldehyde systems (A, B, and F through H), were observed. When geometric isomers were possible (F through H), the *E*,*Z* ratios in the product mixtures[15] paralleled the data for the enol silane precursors, even when the reactions only were run to partial completion. Thus one isomer does not seem more reactive than the other.

The process is very sensitive to both the type and concentration of the fluoride catalyst. Best results were obtained with a mixture of KF and just enough 18-crown-6 to complete the reaction in a convenient time span. For example, the yield of (isobutenyloxy)carbonyl product in B was 69% with 0.6 mol % of 18-crown-6 but only 57 and 48%, respectively, with 3 and 7 mol %, though the required reaction time was shorter in the latter experiments. With a single crystal of 18-crown-6, the yield was 63% after 30 h. As anticipated in this heterogeneous system, the amount of KF above a minimum value had no effect on yield: 69% with 0.8 equiv of KF and 67% with 0.3 equiv of KF in B. Also as predicted,[16] NaF/18-crown-6 was a less reactive catalytic species: 33% yield after 15 days at ca. 70 °C in B. Though BTAF was a more active catalyst than KF/18-crown-6, lower yields were obtained with this species. The inverse effect of catalyst concentration on yield also was evident here: yields of 57, 53, 46, and 47% in B were isolated with one crystal and 0.2, 0.5, and 4 mol % of BTAF, respectively (24-, 24-, 2-, and 1-h reaction times). These results were reproduced in other syntheses. For example, in process C1, the 70% yield with 2.5% 18-crown-6 fell to 58% with 8% 18-crown-6 and to 55% with BTAF (0.2 or 0.8%), while in A1, the 68% yield decreased to 30% with 16% BTAF. Also in D, the yield reduction (66% with 0.5% 18-crown-6, 60% with 1.5% 18-crown-6, 51% with 4% 18-crown-6, 48% with 8% 18-crown-6) was accompanied by a rise in the amount of $(PhS)_2C$=O contaminant, an indication that a greater catalyst concentration somehow facilitates this side reaction.

An important reaction variant is illustrated in process H of Table I. In this 72% overall yield experiment, the PhSCOCl was first converted to **6** with KF/18-crown-6 in THF (2 days at room temperature), and then the enol silane was added directly to the reaction mixture. Thus, it is not necessary to isolate **6** or remove the KCl by-product prior to formation of **7**. This alternate process could be valuable in the future should modified-phenyl thiocarbonates prove to be superior reagents for the attachment of substituted VOC groups to amino acids (vide supra). In a further shortcut, the yield in A was 66% when PhSC(O)Cl (1.1 equiv) in THF was treated directly with a mixture of KF (1.3 equiv), 18-crown-6 (4 mol %), and enol silane (1 equiv). The yield in H fell to 61% in a similar experiment. Only minor effects on yield were observed in related telescoped variations of D and G.

Efforts to design improved VOC-type amine masking schemes by using the substituted (alkenyloxy)carbonyl

(15) When a single enol silane isomer is used in the referenced enol carbonate/carbamate synthesis,[7] both the regiochemistry and the stereochemistry of this precursor are preserved in the product.

(16) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, 11, 16 (1972).

reagents introduced here are underway and will be reported elsewhere.[17]

Experimental Section

Melting points were taken in a Thomas-Hoover apparatus equipped with a calibrated thermometer. Infrared spectra were obtained on a Perkin-Elmer 267 spectrophotometer and mass spectra at 70 eV on an AEI MS-902 high-resolution spectrometer. Proton magnetic resonance (NMR) spectra were recorded on a Varian A-60A, a Varian EM-360, or a Bruker WP 200 Super Con spectrometer while ^{13}C NMR spectra were obtained on a JEOL PFT-100 Fourier transform NMR spectrometer equipped with a Nicolet 1080E computer. Gas chromatographic analyses were performed on a Varian Aerograph Model 920 chromatograph equipped with thermal conductivity detectors and fitted with a 5 ft × 0.25 in. 20% SE-30 on Gas Chrom Q column unless otherwise noted.

The THF was refluxed and distilled from LAH before use. Potassium fluoride (Mallinckrodt) was dried at 150 °C for 24 h, finely pulverized, and redried overnight at the same temperature in the reaction vessel. The BTAF was made from commercial Triton B and 48% HF by the method of Kuwajima.[7] The residue was dried at 100 °C and ca. 1 torr for 24 h, finely pulverized, redried for another 24 h under the same conditions, and stored and transferred over P_2O_5 in a glovebag. Glassware was dried at 150 °C, assembled hot in a stream of dried N_2, and set up to maintain a slight positive N_2 pressure during the main reaction sequences.

(Cyclohexenyloxy)trimethylsilane [95% yield, bp 76–79 °C (20 torr); lit.[10] bp 74–75 °C (20 torr)] and (α-styryloxy)trimethylsilane [76% yield, bp 53–54 °C (0.3 torr); lit.[10] bp 89–91 °C (12 torr)] were prepared by the method of House.[10] The following enol silanes were made by a modified procedure in which an excess of the carbonyl compound (ca. 1.5 equiv) was added (1–2 h) to a stirred mixture (at ca. 25 °C) of Me_3SiCl (1 equiv) and Et_3N (1.5 equiv) in DMF which was then warmed at ca. 50 °C for 10–48 h followed by the standard House workup. (Isopropenyloxy)trimethylsilane: bp 92–94° C (lit.[11] bp 93–94 °C). (Isobutenyloxy)trimethylsilane: bp 118–122 °C (lit.[11] bp 119 °C). (Propenyloxy)trimethylsilane: 64% yield of a 75:25 *Z*/*E* isomer mixture;[18] bp 98–103 °C (no boiling point or spectral data in ref 13). The isomers were separated by preparative VPC on a 20 ft × 0.25 in. 20% Carbowax 20M on Gas Chrom Q column at 75 °C (65 cm³/min of He). *Z* isomer: retention time 23.4 min; NMR ($CDCl_3$) δ 0.19 (9 H, s), 1.59 (3 H, dd, *J* = 7, 1.5 Hz), 4.62 (1 H, dd, *J* = 7, 7 Hz), 6.1–6.4 (1 H, m). *E* isomer: 29.6 min; NMR ($CDCl_3$) δ 0.19 (9 H, s), 1.56 (3 H, dd, *J* = 7, 1.5 Hz), 4.85 (1 H, dd, *J* = 13, 7 Hz), 6.1–6.4 (1 H, m). (Butenyloxy)trimethylsilane: 73% yield of a 61:39 *Z*/*E* mixture; bp 120–124 °C (lit.[11] bp 120 °C). [(3-Methylbutenyl)oxy]trimethylsilane: 67% yield of a 55:45 *Z*/*E* mixture; bp 132–137 °C (no boiling point or spectral data in ref 14); NMR ($CDCl_3$) δ 0.17 (9 H, s), 1.00 and 1.03 (6 H, 2 d, each *J* = 6.5 Hz), 1.8–3.1 (1 H, m), 4.32 (0.55 H, dd, *J* = 9, 6 Hz, *Z*), 4.92 (0.45 H, dd, *J* = 12, 7.5 Hz, *E*), 6.04 and 6.18 (1 H, d, *J* = 6 Hz, for *Z*, and d, *J* = 12 Hz, for *E*, respectively).

(Vinyloxy)trimethylsilane. A three-necked flask fitted with an efficient condenser topped by the N_2 pressure-leak system, a septum cap, and in the third neck an adjustable glass tube (destined to have one end under the surface of the reaction mixture) connected as the receiver to a distillation apparatus (15-cm Vigreux column) containing acetaldehyde (dried over $CaSO_4$; 56 mL, 1.0 mol) was charged (via syringe) successively with DMF (100 mL), Et_3N (dried over KOH and distilled; 70 mL, 0.50 mol), and Me_3SiCl (redistilled; 51 mL, 0.402 mol). The acetaldehyde then was distilled slowly (4.5 h) into the stirred reaction mixture. (**Warning**: pressures and distillation rate must be maintained constant enough to avoid backup, and the distilling setup must be disconnected before all the acetaldehyde is gone). After another 24 h at room temperature, anhydrous xylenes (50 mL) was added to the stirred brown reaction slurry, and the apparatus was refitted for distillation (10-cm Vigreux column), including a thermometer which reached under the reaction mixture surface. The stirred slurry then was distilled and the fraction of boiling point 25–90 °C was collected (mixture temperature should not rise above 135 °C).[19] Next, the distillate was diluted with xylenes (200 mL), washed with water (150 mL), ice cold 1.5 N HCl (3 × 75 mL), and aqueous saturated $NaHCO_3$ (50 mL), dried (Na_2SO_4), and carefully distilled through a 30-cm vacuum-jacketed Vigreux column: yield 29.3 g (62%); bp 72–75 °C (lit.[11] 74 °C); IR (CCl_4) 6.13, 7.99 μm; NMR ($CDCl_3$) δ 0.19 (9 H, s), 4.12 (1 H, d, *J* = 6 Hz), 4.43 (1 H, d, *J* = 13 Hz), 6.43 (1 H, dd, *J* = 13, 6 Hz).

When acetaldehyde was dripped into the mixture, the yield was only 15–20%. Inferior results were obtained with toluene instead of xylene as the chaser and a standard House workup[10] gave impure product in 35–50% yield. The yield was <10% by the Rhone–Poulenc process[11] and 19% by the Runge–Abel method.[12]

***S*-Phenyl Thiofluoroformate.** (**Caution**: stench, use hood.) A mixture of NaF (dried at 150 °C for 24 h; 41 g, 0.98 mol), *S*-phenyl thiochloroformate[20] (68.2 g, 0.395 mol, transferred via two-headed needle), and anhydrous MeCN (250 mL) was stirred at reflux until no chloroformate remained (20 h, IR). After cooling, the mixture was filtered, the filtercake washed with anhydrous CH_2Cl_2, and the filtrate distilled: 56.2 g (92% yield); bp 59–61 °C (4 torr) [VPC pure, lit.[15] 73 °C (9 torr)]; IR (CCl_4) 5.54, 6.75, 6.92 μm. Though reaction occurred below 0 °C when neat *S*-phenyl thiochloroformate was stirred with KF and 18-crown-6,[21] the product yield was much lower and diphenyl dithiocarbonate[6] was an important side product.

***O*-Alkenyl *S*-Phenyl Thiocarbonates. General Procedure. *O*-Isobutenyl *S*-Phenyl Thiocarbonate.** (Except for the variations indicated in Table I, all alkenyl thiocarbonates were synthesized by the method presented here. The effect of changes in reaction conditions is described in the text. Note especially that either reactant may be limiting and that only 0.2–0.3 equiv of KF may be used with little or no effect on yield.) A mixture of *S*-phenyl thiofluoroformate (2.67 g, 0.0168 mol), (isobutenyloxy)trimethylsilane (2.83 g, 0.0196 mol), KF (0.8 g, 0.014 mol), and 18-crown-6 (0.03 g, 0.6 mol %) in 25 mL of THF was stirred at room temperature until VPC analysis indicated that no fluoroformate remained (23 h). Then the mixture was diluted with pentane (50 mL), washed with water (20 mL) and brine (15 mL), dried (Na_2SO_4), and distilled: yield 2.5 g (69%), bp 86–88 °C (0.3 torr) (white needles, mp 18–22 °C, when crystallized from pentane at −10 °C); IR (CCl_4) 5.76, 5.89, 6.78, 6.95 μm (the last two peaks, found in all products, indicate the presence of the thiophenyl unit); NMR ($CDCl_3$) δ 1.60 and 1.62 (6 H, 2 d's with extra fine structure, both *J*'s = 1.47 Hz), 6.85 (1 H, qq, both *J*'s = 1.47 Hz [seven lines 1:6:15:20:15:6:1]), 7.3–7.6 (5 H, m); ^{13}C NMR methyls at δ 15.5 and 19.4; mass spectrum, *m*/*e* (relative intensity) 210.0544 ($M^+[^{34}S]$, 1; calcd 210.0515), 208.0568 ($M^+[^{32}S]$, 21; calcd 208.0557), 180.0611 (M^+ − CO, 33; calcd 180.0608), 151 (6), 137.0096 ($PhSCO^+$, 41; calcd 137.0061), 109 (PhS^+, 100%).

***O*-Isopropenyl *S*-phenyl thiocarbonate**: bp 79–82 °C (0.4 torr); NMR ($CDCl_3$) δ 1.92 (3 H, br s), 4.5–4.6 (1 H, m), 4.7–4.8 (1 H, m), 7.1–7.6 (5 H, m); mass spectrum, *m*/*e* (relative intensity) 194.0421 (M^+, 60; calcd 194.0402), 167 (8), 166.0457 (M^+ − CO, 75; calcd 166.0453), 137.0084 ($PhSCO^+$, 87; calcd 137.0061), 110.0182 ($PhSH^+$, 78; calcd 110.0191), 109.0134 (PhS^+, 100; calcd 109.0113).

***O*-Cyclohexenyl *S*-phenyl thiocarbonate**: bp 128–136 °C (0.2 torr) with diphenyl dithiocarbonate contaminant; white solid; mp 34–37 °C, but still impure after two recrystallizations from pentane; purified by preparative VPC; NMR ($CDCl_3$) δ 1.4–2.4 (8 H, m), 5.3–5.5 (1 H, m), 7.1–7.6 (5 H, m); mass spectrum, *m*/*e* (relative intensity) 234.0732 (M^+, 73; calcd 234.0714), 206.0774 (M^+ − CO, 98; calcd 206.0764), 190.0791 (M^+ − CO_2, 47; calcd

(17) R. A. Olofson, J. T. Martz, and J. Cuomo, to be submitted for publication. In systems tested so far, amino acids are acylated by 7.

(18) The isomer ratio in this and all other aldehyde enol silanes and enol thiocarbonates was determined by VPC and NMR analysis. In all systems studied, the *Z* isomers moved faster on Carbowax or SE-30, and the chemical shift for the vinyl H β to the ether group was at higher field.

(19) Some product is present in fractions throughout this distillation range.

(20) W. A. Thaler, *Chem. Commun.*, 527 (1968).

(21) Adapted from a high-yield synthesis of fluoroformates from chloroformates: J. Cuomo and R. A. Olofson, *J. Org. Chem.*, **44**, 1016 (1979).

190.0815), 189 (41), 188 (41), 137.0079 ($PhSCO^+$, 100; calcd 137.0061), 125.0620 (c-$HxOCO^+$, 50; calcd 125.0602).

***O*-α-Styryl *S*-phenyl thiocarbonate**: crude oil obtained after standard workup and evaporation crystallized from pentane and then ether; mp 50–51 °C; NMR ($CDCl_3$) δ 5.05 (1 H, d, J = 2.4 Hz), 5.36 (1 H, d, J = 2.4 Hz), 7.1–7.6 (10 H, m); mass spectrum, m/e (relative intensity) 256.0556 (M^+, 72; calcd 256.0557), 229 (72), 228.0605 (M^+ – CO, 100; calcd 228.0608), 212.0677 (M^+ – CO_2, 50; calcd 212.0659), 196.0883 (M^+ – COS, 15; calcd 196.0887).

***O*-*n*-Butenyl *S*-phenyl thiocarbonate**: bp 80–88 °C (0.2 torr) (62:38 Z/E[18] from the enol silane, 61:39 Z/E); NMR ($CDCl_3$) δ 0.98 (3 H, t, J = 7.5 Hz), 1.8–2.5 (2 H, m), 4.91 (0.62 H, dt, J = 7, 7 Hz, Z), 5.50 (0.38 H, dt, J = 13, 7 Hz, E), 6.95–7.2 (1 H, m), 7.3–7.8 (5 H, m); ^{13}C NMR ($CDCl_3$) for Me δ 13.7 (Z) and 13.8 (E), for CH_2 δ 17.7 (Z) and 20.5 (E), for EtCH= δ 116.4 (Z) and 117.3 (E), for C=O δ 167.2 (Z) and 167.4 (E), for =CHO and aryl δ 129.2 (Z), 129.7 (E), and, in common, 134.2, 134.7, 134.8, 135.1, 135.6, 135.7; mass spectrum, m/e (relative intensity) 208.0557 (M^+, 100; calcd 208.0557), 181 (53), 180.0612 (M^+ – CO, 79; calcd 180.0608), 179.0532 (M^+ – COH, 16; calcd 179.0530), 151 (49), 149 (25). Product Z/E ratios (VPC) at partial reaction times of 15, 27, 35, and 45 h were 65:35, 66:34, 63:37, and 63:37, respectively.

***O*-Propenyl *S*-phenyl thiocarbonate**: bp 89–91 °C (0.6 torr) (75:25 Z/E[18] from the enol silane, 74:26 Z/E); NMR ($CDCl_3$) δ 1.57 and 1.61 (3 H, 2 d's, each J = 7 Hz), 4.82 (0.75 H, dq, J = 7, 7 Hz, Z), 5.26 (0.25 H, dq, J = 12, 7 Hz, E), 6.8–7.05 (1 H, m), 7.15–7.6 (5 H, m); mass spectrum, m/e (relative intensity) 194.0418 (M^+, 32; calcd 194.0401), 170 (20), 137 (70), 110 ($PhSH^+$, 34), 109.0107 (PhS^+, 100; calcd 109.0112).

***O*-Vinyl *S*-Phenyl Thiocarbonate. Alternate Procedure.** This was made in 68 and 65% yields by the standard method (Table I). The compound also was prepared by stirring a mixture of *S*-phenyl thio*chloro*formate (12.9 g, 0.0746 mol), (vinyloxy)-trimethylsilane (8.26 g, 94% pure, 0.0668 mol), KF (5.2 g, 0.09 mol), and 18-crown-6 (0.74 g, 4 mol %) in 50 mL of THF at room temperature followed by the usual workup: yield 7.95 g (66%, VPC pure); bp 69–73 °C (0.5 torr) [lit.[6] 67–69 °C (0.4 torr)]; NMR ($CDCl_3$) δ 4.52 (1 H, dd, J = 7, 1 Hz), 4.85 (1 H, dd, J = 14, 1 Hz), 7.08 (1 H, dd, J = 14, 7 Hz), 7.2–7.6 (5 H, m).

***O*-(3-Methylbutenyl) *S*-Phenyl Thiocarbonate. Second Alternate Procedure.** *S*-Phenyl thiochloroformate (3.59 g, 0.0208 mol) was stirred with KF (1.6 g, 0.028 mol) and 18-crown-6 (0.3 g, 5 mol %) in THF (30 mL) at room temperature until no chloroformate remained (51 h, VPC assay). Then [(3-methylbutenyl)oxy]trimethylsilane (3.11 g, 0.0196 mol, 54:46 Z/E) was added, stirring was continued for 23 h, and the title compound was isolated by the standard workup: yield 3.36 g (72%, 54:46 Z/E[18]); bp 99–106 °C (0.4 torr); NMR ($CDCl_3$) δ 1.00 and 1.03 (6 H, 2 d's, each J = 7 Hz), 2.0–3.0 (1 H, m), 4.87 (0.54 H, dd, J = 9, 7 Hz, Z), 5.46 (0.46 H, dd, J = 12, 7 Hz, E), 6.9–7.1 (1 H, m) 7.3–7.8 (5 H, m); mass spectrum, m/e (relative intensity) 222.0738 (M^+, 75; calcd 222.0724), 194.0760 (M^+ – CO, 84; 194.0775), 137 ($PhSCO^+$, 100). This product was also made in 61% yield (54:46 Z/E) by the first alternate procedure using *S*-phenyl thiochloroformate (0.073 mol), KF (0.15 mol), 18-crown-6 (2 mol %), the enol silane (0.051 mol), and THF (40 mL) (92 h at room temperature).

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Registry No. **5** (R = R′ = R″ = H), 6213-94-1; **5** (R = R′ = Me, R″ = H), 6651-34-9; **5** (R = R′ = H, R″ = Me), 1833-53-0; **5** (R = H, R′ = R″ = (–$CH_2CH_2CH_2CH_2$–)), 6651-36-1; **5** (R = R′ = H, R″ = Ph), 13735-81-4; (*E*)-**5** (R = Me, R′ = R″ = H), 39162-68-0; (*Z*)-**5** (R = Me, R′ = R″ = H), 50300-18-0; (*E*)-**5** (R = Et, R′ = R″ = H), 19980-23-5; (*Z*)-**5** (R = Et, R′ = R″ = H), 19980-22-4; (*E*)-**5** (R = $CHMe_2$, R′ = R″ = H), 73397-84-9; (*Z*)-**5** (R = $CHMe_2$, R′ = R″ = H), 73397-85-0; **6**, 2286-39-7; **7** (R = R′ = R″ = H), 70872-45-6; **7** (R = R′ = Me, R″ = H), 73397-86-1; **7** (R = R′ = H, R″ = Me), 73397-87-2; **7** (R = H, R′ = R″ = (–$CH_2CH_2CH_2CH_2$–)), 73397-88-3; **7** (R = R′ = H, R″ = Ph), 73397-89-4; (*E*)-**7** (R = Me, R′ = R″ = H), 73397-90-7; (*Z*)-**7** (R = Me, R′ = R″ = H), 73397-91-8; (*E*)-**7** (R = Et, R′ = R″ = H), 73397-92-9; (*Z*)-**7** (R = Et, R′ = R″ = H), 73397-93-0; (*E*)-**7** (R = $CHMe_2$, R′ = R″ = H), 73397-94-1; (*Z*)-**7** (R = $CHMe_2$, R′ = R″ = H), 73397-95-2; *S*-phenyl thiochloroformate, 13464-19-2.

Flash Vacuum Pyrolysis of 2-Methylbenzophenones and 2-Methyldiphenyl Ketimines

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The solution-phase pyrolysis of 2-methylbenzophenone at 300–400 °C—the Elbs reactions—gives low yields of anthracene and water.[1-15] We hoped that the gas-phase pyrolysis of 2-methylbenzophenones would give higher yields and fewer side products than the Elbs reaction carried out in solution phase.

Gas-phase vacuum pyrolysis of 2-methylbenzophenone in a flow system at temperatures below 750 °C resulted only in recovery of starting material. At temperatures between 800 and 900 °C, reaction occurred, with higher conversions of starting material to products being obtained at higher temperatures: 800 °C (7%), 900 °C (36%) (see Table I). The highest yield of volatile products was only 40–50%. Anthracene, the expected product, was obtained in 7 to 11% yield while fluorene was found in 32 to 39% yield. We believe that the formation of anthracene and fluorene may occur as outlined in Scheme I. Tautomerization of 2-methylbenzophenone yields the previously proposed dienol intermediate (I).[16,17] Electrocyclic reaction of the dienol and the benzene nucleus may result in formation of 4a,10-dihydro-9-anthranol (II),[18-25] which reacts further to yield both anthracene and fluorene. Consecutive 1,5-sigmatropic hydrogen rearrangements[26]

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