1.40; F, 5.28; N, 23.34. Found: C, 16.71; H, 1.59; F, 5.30; N, 23.14.

**2,2,2-Trinitroethyl *N*-(2,2,2-Trinitroethyl)carbamate (6b) and 2,2-Dinitropropyl *N*-(2,2,2-Trinitroethyl)carbamate (6c).** Substitution of 2,2,2-trinitroethanol and 2,2-dinitropropanol for 2-fluoro-2,2-dinitroethanol in the above procedure gives **6b** (mp 165–167 °C) and **6c** (mp 125–126 °C), respectively, in similar yield. For **6b**: $^1$H NMR [$(CD_3)_2C{=}O$] $\delta$ 5.28 (s, 2 H), 5.88 (s, 2 H), 8.22 (br, 1 H); IR (KBr) 3445 (NH), 1770 (C=O) cm$^{-1}$. Anal. Calcd for $C_5H_5N_7O_{14}$: C, 15.51; H, 1.30; N, 25.33. Found: C, 15.48; H, 1.32; N, 25.04.

For **6c**: $^1$H NMR ($CD_2Cl_2$) $\delta$ 2.20 (s, 3 H), 4.90 (d, 2 H) 5.02 (s, 2 H), 5.85 (br, 1 H); IR (KBr) 3445, 3380 (NH), 1760 (C=O) cm$^{-1}$. Anal. Calcd for $C_6H_8N_6O_{12}$: C, 20.23; H, 2.26; N, 23.60. Found: C, 20.37; H, 2.28; N, 23.47.

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## Photoisomerization of 2-(Trimethylsilyl)pyrroles

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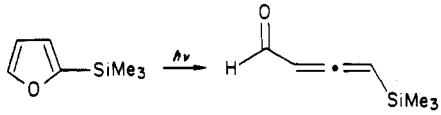
Recently we reported the remarkable effect of silicon substitution on the photochemistry of furans.[1] Thus, the irradiation of silyl-substituted furans leads to unprecedented exclusive formation of acylallenes in high yield.

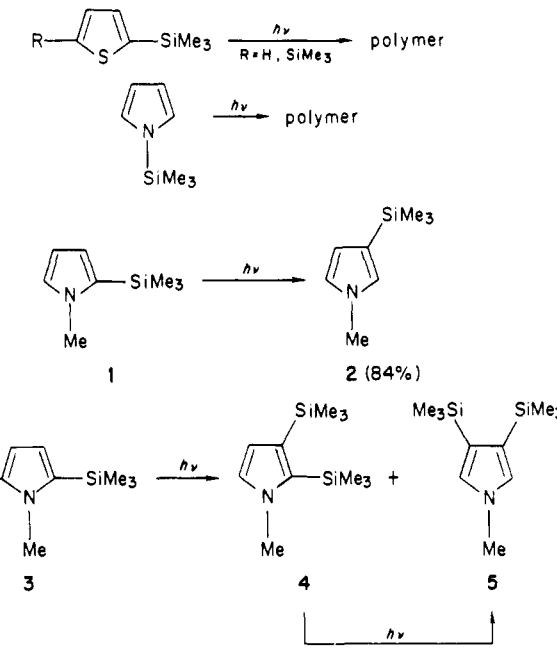


The obvious extensions to the photochemistry of silylthiophenes and silylpyrroles have now been investigated and are reported here. We find that silyl substitution has no apparent positive effect on the photochemistry of thiophenes. Irradiation of either 2-(trimethylsilyl)-thiophene or 2,5-bis(trimethylsilyl)thiophene in degassed pentane yields only intractable polymer.

In contrast to these unremarkable results, photolysis of silyl-substituted pyrroles cleanly affords rearrangement products in high yields. Photolysis of 2-(trimethylsilyl)-*N*-methylpyrrole (**1**) in degassed pentane with a medium-pressure mercury lamp yielded 3-(trimethylsilyl)-*N*-methylpyrrole (**2**, 84%) as the only volatile product. A similar irradiation of 2,5-bis(trimethylsilyl)-*N*-methylpyrrole (**3**) initially afforded two products: 2,3-bis(trimethylsilyl)-*N*-methylpyrrole (**4**, 39%) and 3,4-bis-(trimethylsilyl)-*N*-methylpyrrole (**5**, 41%). Continued irradiation of this reaction mixture, or irradiation of pure **4**, resulted in exclusive formation of **5**.

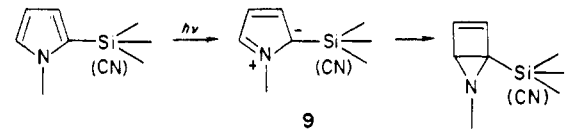
The necessity for silyl substitution to be at the 2-position is indicated by the photochemical inactivity of 3-silylpyrrole **2** and the observation that irradiation (1 h) of *N*-(trimethylsilyl)pyrrole produced only a yellow polymer. NMR and GC analysis of the photolysis solution revealed only unreacted starting material.

Although the photochemistry of pyrroles is usually rather complex,[2] this clean photorearrangement has precedent in the work of Hiraoka[3] who observed formation



of 3-cyano-*N*-methylpyrrole upon photolysis of 2-cyano-*N*-methylpyrrole. There is no reason to suspect actual silyl migration in the rearrangements **1** → **2**, **3** → **4**, and **4** → **5**, and we concur with Day[4] that the most reasonable mechanistic pathway (Scheme I) involves electrocyclic closure to a 5-azabicyclo[2.1.0]pentene **6** followed by 1,3-nitrogen shift and ring opening. Whether **5** is the thermodynamic sink on the energy surface, or whether it is simply the steric bulk of the trimethylsilyl groups that inhibit the back-reaction of **8** → **7** that controls the direction of the isomerization, our data do not reveal. A single attempt to trap a bicyclic intermediate was undertaken when **1** was irradiated in furan. Exclusive formation of **2** was found with no evidence of a furan/5-azabicyclo-[2.1.0]pent-2-ene adduct.

To our knowledge, such rearrangements of substituted pyrroles occur only when the 2-position is substituted by either cyano or silyl groups. The only obvious relationship between these two seemingly disparate groups is their pronounced ability to stabilize adjacent negative charges. Thus, a tentative suggestion is that CN or $SiMe_3$ 2-substitution favors the polarized structure **9** in the excited state and that cyclization occurs more readily from this form.



The photolyses of silicon-substituted pyrroles can be performed with gram quantities and taken to 100% conversion. Pyrroles disubstituted at the 3- and 4-positions are often not readily accessible,[5] and this route should allow for further manipulation at these positions. Investigations are continuing to examine the role of silyl substitution in heterocyclic photochemistry.

## Experimental Section

All mass spectra were recorded at 70 eV. Gas chromatographic (GC) data were obtained on a Varian-Aerograph Model 3700, 1700,

(1) Barton, T. J.; Hussmann, G. *J. Am. Chem. Soc.* **1983**, *105*, 6316.
(2) For an excellent review see: Padwa, A. In "Rearrangements in Ground and Excited States"; Demayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 501.
(3) Hiraoka, H. *J. Chem. Soc., Chem. Commun.* **1970**, 1306.
(4) Barltrop, J.; Day, A. C.; Moxon, P. D.; Ward, R. R. *J. Chem. Soc., Chem. Commun.* **1975**, 786. Barltrop, J. A.; day, A. C.; Ward, R. W. *J. Chem. Soc., Chem. Commun.* **1978**, 131.
(5) Anderson, H. J.; Loader, C. E. *Synthesis* **1985**, 353.

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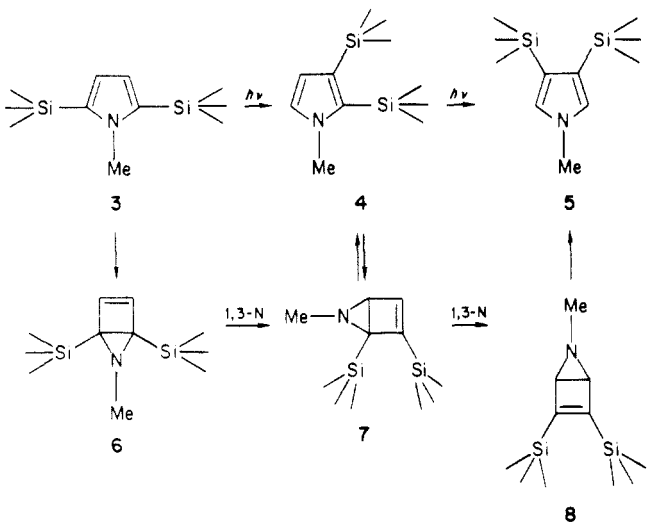
**Scheme I**




or 920 or Fischer/Victoreen Series 4400 gas chromatograph. GC yields were determined with internal standards and predetermined response factors. All melting points (mp) were obtained on a Thomas-Hoover melting point apparatus and are uncorrected.

**Preparation of 2-(Trimethylsilyl)thiophene and 2,5-Bis(trimethylsilyl)thiophene.** To 1.05 g (0.025 mol) of freshly distilled thiophene in 125 mL of $Et_2O$ was added 0.026 mol of *n*-butyllithium in hexane at 0 °C. After the mixture was stirred for 1 h at 25 °C, 3.3 mL (0.026 mol) of trimethylchlorosilane was added and stirring was continued for 8 h. Following extraction of the reaction mixture with saturated aqueous NaCl, the organic layer was dried ($Na_2SO_4$). Removal of the solvent and distillation of the residue (79 °C (35 torr)) afforded pure 2-(trimethylsilyl)thiophene (76%), which was identified by NMR and MS comparison to previously reported spectra.[6] 2,5-Bis(trimethylsilyl)thiophene was prepared in analogous fashion from 1.02 g (0.025 mol) of thiophene, 0.052 mol of *n*-butyllithium, and 0.052 mol (6.6 mL) of trimethylchlorosilane. Distillation (62 °C (15 torr)) afforded 4.3 g (75%) of pure 2,5-bis(trimethylsilyl)thiophene, which was also identified by spectral comparison to those previously reported:[6] UV ($CH_3CN$) $\lambda_{max}$ 235 nm (9951).

**Preparation of *N*-Methyl-2-(trimethylsilyl)pyrrole (1) and *N*-Methyl-2,5-bis(trimethylsilyl)pyrrole (3).** To 5.0 mL (0.056 mol) of *N*-methylpyrrole in 200 mL of $Et_2O$ was added 0.056 mol of *tert*-butyllithium. After the mixture was stirred at 25 °C for 12 h, 6.27 g (0.058 mol) of trimethylchlorosilane was added. Following an additional 2 h of stirring, the crude reaction mixture was extracted with saturated aqueous NaCl, and the organic phase was separated and dried over $Na_2SO_4$. Removal of the solvent and distillation (70 °C (13 torr)) afforded 4.2 g (48%) of pure 1, which was identified by comparison of its NMR and IR spectra to those previously reported.[6] In similar fashion, 3 was prepared from 1.5 mL (0.017 mol) of *N*-methylpyrrole, 0.040 mol of *tert*-butyllithium, and 4.5 mL (0.040 mol) of trimethylchlorosilane. Distillation (95 °C (12 torr)) afforded pure 3 as a solid. Recrystallization from hexane gave 1.7 g (44%) of 3: mp 75–76 °C, lit.[6] mp 76–77 °C. Spectral features matched those previously reported: UV ($CH_3CN$) $\lambda_{max}$ 235 nm (10 471).

**General Procedure for Photolysis.** All solvents were previously distilled from LAH under a nitrogen atmosphere. Irradiations were typically carried out on two scales: NMR and preparative. In a quartz NMR tube sealed with a septum were placed 50 μL of the material being irradiated and 750 μL of pentane. After degassing with a stream of argon, the sample was positioned adjacent to the water-cooled, quartz immersion well of a 450-W Hanovia mercury arc lamp and irradiated. The reaction progress was monitored by $^1H$ NMR and IR. Preparative scale reactions were performed with a 200-mL capacity reaction vessel that jacketed the quartz immersion well. Into the reaction vessel was placed 150 mL of pentane and 1.5 mL of the material being photolyzed. After degassing with argon for 20 min, the solution was irradiated with a 450-W Hanovia lamp. The reaction progress was monitored with $^1H$ NMR, GC, and IR. After irradiation was complete, the photolysate was transferred to a 250-mL flask, via a double-tipped needle, and the pentane removed under vacuum to leave 3–5 mL of residue. Low-temperature irradiations were performed by cooling the NMR tube or reaction vessel with a dry ice/2-propanol bath.

**Irradiation of *N*-Methyl-2-(trimethylsilyl)pyrrole (1).** Pyrrole 1 (1.39 g) in 150 mL of degassed pentane was irradiated for 50 min. $^1H$ NMR and GC analysis of the yellow photolysate revealed trace amounts of unreacted 1 and clean formation of only one product that was isolated by preparative GC (10-ft 15% SE-30). Based on its spectral data, this product was identified as 2: 84%; NMR ($CCl_4$) δ 0.03 (s, 9 H), 3.45 (s, 3 H), 6.03 (t, 1 H, $J$ = 2 Hz), 6.42 (m, 2 H); $^{13}C$ NMR δ −0.1, 35.4, 113.4, 122.9, 127.3; IR (neat) 3100, 2960, 1510, 1420, 1245, 1130, 840 $cm^{-1}$; mass spectrum, $m/e$ (% relative intensity) 153 (22), 138 (100), 94 (6.2), 73 (2.4), 69 (13), 59 (11); calculated for $C_8H_{15}NSi$ 153.09738, measured 153.09730. Irradiation of 1 (50 μL) also afforded exclusive formation of 2.

**Irradiation of *N*-Methyl-2,5-bis(trimethylsilyl)pyrrole (3).** Pyrrole 3 (50 μL in 600 μL of pentane) was entirely consumed after 50-min irradiation, and two products, identified as 4 and 5, were cleanly formed. Continued irradiation resulted in complete disappearance of 4 with a concomitant increase in the amount of 5. A repeat of this reaction on a larger scale (0.50 g of 3, 150 mL of pentane, 35 min of irradiation) allowed isolation of 4 and 5 by preparative GC (10-ft 20% OV101). 4: 39%; NMR ($CCl_4$) δ 0.22 (s, 9 H), 0.35 (s, 9 H), 3.70 (s, 3 H), 6.05 (d, 1 H, $J$ = 3 Hz), 6.58 (d, 1 H, $J$ = 3 Hz); IR (neat) 3100, 2960, 1505, 1410, 1250, 1155, 1110, 945 $cm^{-1}$; mass spectrum, $m/e$ (% relative intensity) 225 (20), 210 (100), 194 (27), 147 (27), 138 (39), 73 (22); calculated for $C_{11}H_{23}NSi_2$ 225.13691, measured 225.13728. 5: 41%; NMR ($CCl_4$) δ 0.21 (s, 18H), 3.71 (s, 3H), 6.58 (s, 2H); IR (neat) 3100, 2960, 1515, 1420, 1245, 1150, 1135, 1095 $cm^{-1}$; mass spectrum, $m/e$ (% relative intensity) 225 (30), 210 (100), 194 (23), 184 (12), 147 (56), 128 (77), 73 (42); calculated for $C_{11}H_{23}NSi_2$ 225.13691, measured 225.13651. Compound 4 (ca. 20 mg) in 400 μL of pentane was placed in a quartz NMR tube, degassed with argon, and irradiated for 1 h. Analysis of the photolysate with $^1H$ NMR indicated clean conversion (ca. 50%) to 5 had occurred. No other products were observed.

**Irradiation of *N*-(Trimethylsilyl)pyrrole.**[7] *N*-(Trimethylsilyl)pyrrole (50 μL in 750 μL of pentane) was irradiated for 1 h. Precipitation of a large amount of a yellow polymer was observed. Analysis of the photolysate by NMR and GC indicated only unreacted starting material. No further photolyses of *N*-(trimethylsilyl)pyrrole were attempted.

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(6) Pratt, J. R.; Pinkerton, F. H.; Thames, S. F. *J. Organomet. Chem.* **1972**, *38*, 24.

(7) Pommier, J. C.; Lucas, D. *J. Organomet. Chem.* **1973**, *57*, 139.

## The Benzoyloxy Radical: Attempted Photochemical Generation for Kinetic Studies and Some Relative Rate Constants[1]

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Benzoyl peroxide has been used for many years as a thermal initiator for the free-radical polymerization of vinyl

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