$C_{28}H_{53}NO_3S$: C, 69.51; H, 11.04. Found: C, 69.72; H, 11.14.

***trans*-8-Heptadecenylammonium tosylate (from elaidamide)**: yield, 1.019 g (80%); mp 90–95 °C, 126–127 °C; IR ca. 3253 (sh), 3143 and 3053 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.4 (m, 20 H, prominent peaks at δ 1.12 and 1.25), 1.47 (m, 2 H), 1.92 (m, 4 H), 2.35 (s, 3 H), 2.70 (t, 2 H), 5.35 (m, 2 H), ca. 7.15–7.8 and 7.64 (AA'BB' and br s, 7 H); ^{13}C NMR ($CDCl_3$) δ 14.07, 21.28, 22.63, 26.31, 27.40, 28.85, 28.94, 29.17, 29.27, 29.45, 29.53, 29.62, 31.86, 32.50, 32.58, 39.88, 125.85, 128.96, 130.03, 130.42, 140.60, 141.24 (low-intensity resonances at 29.34 and 29.37, impurities?). Anal. Calcd for $C_{24}H_{43}NO_3S$: C, 67.72; H, 10.18. Found: C, 67.67; H, 10.17.

***cis*-12-Heneicosenylammonium tosylate (from erucamide)**: yield, 0.91 g (63%); mp 68–70 °C, 110–113 °C; IR ca. 3245 (sh), 3125 and 3055 cm^{-1} (NH_3^+); ^1H NMR δ 0.87 (t, 3 H), ca. 1.0–1.38 (m, 29 H, (expected, 28 H) prominent peaks at δ 1.12 and 1.25), 1.47 (m, 2 H), 2.00 (m, 3.6 H), 2.35 (s, 3 H), 2.70 (t, 2 H), 5.34 (m, 2 H), ca. 7.12–7.8 and 7.64 (AA'BB' m and br s, 7 H). Anal. Calcd for $C_{28}H_{51}NO_3S$: C, 69.81; H, 10.67. Found: C, 70.06; H, 10.70.

Reaction of *N*-[(Trimethylsilyl)methyl]azinones

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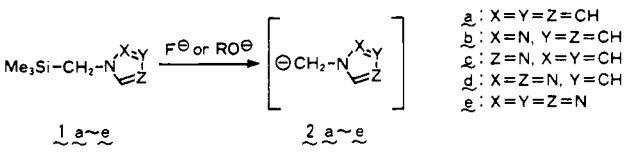
In recent years,[1] we have reported the reaction of carbonyl compounds with azolylmethyl anions **2a–e** derived from the fluoride- or alkoxide-induced desilylation of 1-[(trimethylsilyl)methyl]azoles **1a–e** (Scheme I). The reaction of 1-[(trimethylsilyl)methyl]-1,2,4-triazole (**1d**) with carbonyl compounds in the presence of fluoride catalyst proceeded smoothly, while that of 1-[(trimethylsilyl)-methyl]pyrrole (**1a**) failed. Since the nucleophilic cleavage of C–Si bond is dependent on the stability of the generated carbanion,[2] the difference between **1a** and **1d** was explained by the concept[3] of a dipole-stabilized carbanion. Our interest in this reaction led us to investigate the generation of azinonylmethyl anions **4a–e** by fluoride-induced desilylation of the corresponding *N*-[(trimethylsilyl)methyl]azinones **3a–e** (Scheme II).

Although lithiation of *N*-alkylazinones has been investigated,[4–9] it cannot be used to generate azinonylmethyl anions **4a–e** from the corresponding *N*-methylazinones, except in the case of 1-alkyl-4,6-diphenyl-2-pyridone which is lithiated at N-Cα of the alkyl radical and then made to react with electrophiles.[6]

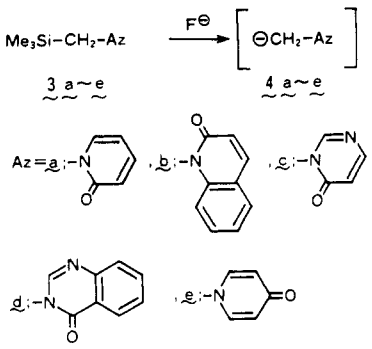
We now report the generation of azinonylmethyl anions **4a–e** derived from the fluoride-induced desilylation of *N*-[(trimethylsilyl)methyl]azinones **3a–e** in the presence of aldehydes and ketones.[10] Also described are the thermal reactions of **3a,e** with ketones and diethyl acetylenedicarboxylate.

Scheme I

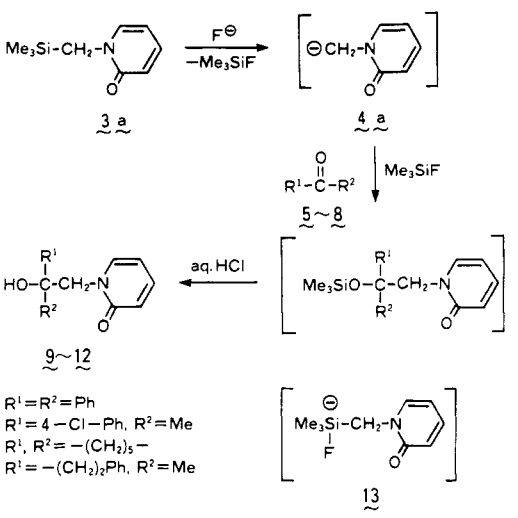


1 a~e 2 a~e

Scheme II



Scheme III



Results and Discussion

Preparation of *N*-[(Trimethylsilyl)methyl]azinones 3a–e. Treatments of 2-pyridone, 2-quinolone, 4-pyrimidinone, and 4-quinazolinone with (chloromethyl)trimethylsilane in the presence of potassium carbonate in dry DMSO led to the (trimethylsilyl)methyl derivatives **3a** (76%), **3b** (64%), **3c** (55%), and **3d** (91%), respectively. The structure of **3c** was confirmed by spectroscopic comparison with 1-methyl-4-pyrimidinone and 3-methyl-4-pyrimidinone[11] and the structure of **3d** was determined by referring to the product of alkylation of 4-quinazolinone.[12] 1-[(Trimethylsilyl)methyl]-4-pyridone (**3e**) was prepared by using a modification of a literature procedure[13] as de-

(1) Shimizu, S.; Ogata, M. *J. Org. Chem.* **1986**, *51*, 3897.
(2) (a) Eaborn, C.; Stamper, I. G.; Seconi, G. *J. Organomet. Chem.* **1981**, *204*, 27. (b) Effenberger, F.; Krebs, A. *J. Org. Chem.* **1984**, *49*, 4687.
(3) Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275.
(4) Katritzky, A. R.; Grzeskowiak, N. E.; Salgado, H. J.; bin Bahari, Z. *Tetrahedron Lett.* **1980**, *21*, 4451.
(5) Katritzky, A. R.; Arrowsmith, J.; bin Bahari, Z.; Jayaram, C.; Siddiqui, T.; Vassilatos, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2851.
(6) Katritzky, A. R.; Arrowsmith, J.; Grzeskowiak, N. E.; Salgado, H. J.; bin Bahari, Z. *J. Chem. Soc., Perkin Trans. 1* **1982**, 143.
(7) Katritzky, A. R.; Salgado, H. J.; Chermprapai, A.; Ponkshe, N. K. *J. Chem. Soc., Perkin Trans. 1* **1982**, 153.
(8) Patel, P.; Joule, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1021.
(9) Meghani, P.; Joule, J. A. *J. Chem. Soc., Perkin Trans 1* **1988**, 1.
(10) After completion of this experiment, the fluoride-induced reaction of **3a** with aldehydes and thermal reaction of **3a** with acid chlorides was reported: Katritzky, A. R.; Sengupta, S. *Tetrahedron Lett.* **1987**, *28*, 5419.
(11) Ring protons of 1-methyl-4-pyrimidinone: ^1H NMR (Me_2SO-d_6) δ 6.02 (5-position of pyrimidone ring), 7.72 (6-position) 8.30 (2-position). Ring protons of 3-methyl-4-pyrimidinone: ^1H NMR (Me_2SO-d_6) δ 6.42 (5-position), 7.95 (6-position), 8.50 (2-position). See: Bauer, L.; Wright, G. E.; Mikrut, B. A.; Bell, C. L. *J. Heterocycl. Chem.* **1965**, *2*, 447.
(12) Bogert, M. T.; Geiger, G. A. *J. Am. Chem. Soc.* **1912**, *34*, 524.

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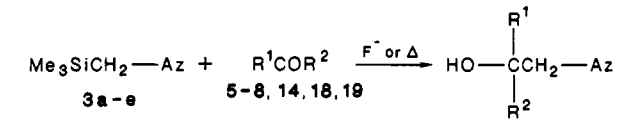
Table I. Reactions of *N*-[(Trimethylsilyl)methyl]azinone 3 with Carbonyl Compounds



3a-e 5-8, 14, 18, 19 9-12, 15-17, 20-24

entry	azinones	carbonyl compound	products[a] condns[b]	products[a] yield (%)	products[a] mp, °C (recryst solv)[c]
1	3a	5: $R^1 = R^2$ = Ph	−20 °C, 2 h	9 (87)	164.5–166 (A)
2	3a	6: R^1 = 4-ClPh, R^2 = Me	−20 °C, 2 h	10 (69)	106–107.5 (A)
3	3a	7: R^1, R^2 = -$(CH_2)_5$-	−20 °C, 2 h	11 (40)	110–111.5 (A)
4	3a	8: R^1 = $(CH_2)_2$Ph, R^2 = Me	−20 °C, 2 h	12 (69)	oil
5	3e	5	rt, 3 h	15 (92)	>290 (B)
6	3e	6	rt, 3 h	16 (70)	223–226 (C)
7	3e	14: R^1 = 4-ClPh, R^2 = H	rt, 1 h	17 (88)	214–219 (C)
8	3b	6	rt, 2 h	20 (79)	112–113 (A)
9	3b	18: R^1 = 4-ClPh, R^2 = Et	rt, 2 h	21 (78)	103.5–105.5 (A)
10	3b	19: R^1 = PhCO, R^2 = Ph	rt, 2 h	22 (35)	149.5–151.5 (A)
11	3c	6	rt, 2 h	23 (39)	142.5–143.5 (A)
12	3d	6	rt, 2 h	24 (43)	148–149 (A)
13	3a	6	145 °C, 9 h[d]	10 (11)	
14	3e	6	145 °C, 4 h[d]	16 (45)	

[a] All products gave satisfactory elementary analyses (C, H, N, Cl ± 0.4%). [b] rt = room temperature. [c] A = AcOEt/*i*-Pr_2O; B = MeOH; C = MeOH/AcOEt. [d] No fluoride ion.

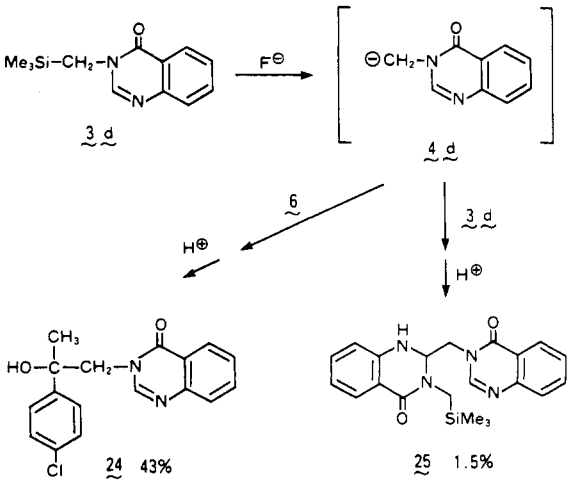
scribed below. Treatment of 4-[(trimethylsilyl)oxy]-pyridine with (iodomethyl)trimethylsilane and subsequent methanolysis gave **3e** (62%).

Reaction of *N*-[(Trimethylsilyl)methyl]azinones 3a–e. 1-[(Trimethylsilyl)methyl]-2-pyridone (**3a**) when treated with a stoichiometric amount of tetrabutylammonium fluoride (TBAF) in THF at −30 °C gave desilylated 1-methyl-2-pyridone accompanied by many byproducts which could not be isolated. The formation of the byproducts could be rationalized as follows. Fluoride-induced desilylation of **3a** generates (2-oxopyrid-1-yl)methyl anion **4a** which reacts with the starting **3a** to give the dimer[8,9] which undergoes further desilylation. However, in the presence of carbonyl compounds **5–8** as electrophiles, TBAF-catalyzed desilylation of **3a** gave only 2-(2-oxopyrid-1-yl)ethanols **9–12** in moderate yields after acid-catalyzed hydrolysis (Scheme III). The results are summarized in Table I (entries 1–4). Fluoride-induced reaction of organosilanes is known to be substrate-dependent[14] and chemoselective.[15] Therefore, the anion **4a** or a pentavalent silicate species **13**,[10] derived from the fluoride-induced reaction of **3a**, may be selectively trapped in the reaction with the carbonyl compound.

Katritzky and Sengupta reported the failure of the fluoride-induced reaction of **3a** with cyclohexanone (**7**).[10] In our hands, however, **3a** reacted with **7** to give 1-[(2-oxopyrid-1-yl)methyl]cyclohexanol (**11**) in 40% yield (entry 3). In the case of the other enolizable ketones **6** and **8**, the product yields were higher.

1-[(Trimethylsilyl)methyl]-4-pyridone (**3e**) smoothly reacted with ketones **5**, **6**, and 4-chlorobenzaldehyde (**14**) in the presence of TBAF catalyst in THF at room temperature to afford 2-(4-oxopyrid-1-yl)ethanols **15**, **16**, and **17**, respectively, in good yields after acid-catalyzed hydrolysis (Table I, entries 5–7). To the best of our knowledge, **3e** is the first example of a synthon of the (4-oxopyrid-1-yl)methyl anion **4e**. The most acidic proton of 1-methyl-4-pyridone is at the 2-position of the pyridone ring,[16] and 1-methyl-4-pyridone lithiates at the 2-position, not at the *N*-methyl group.[8,9]

Scheme IV

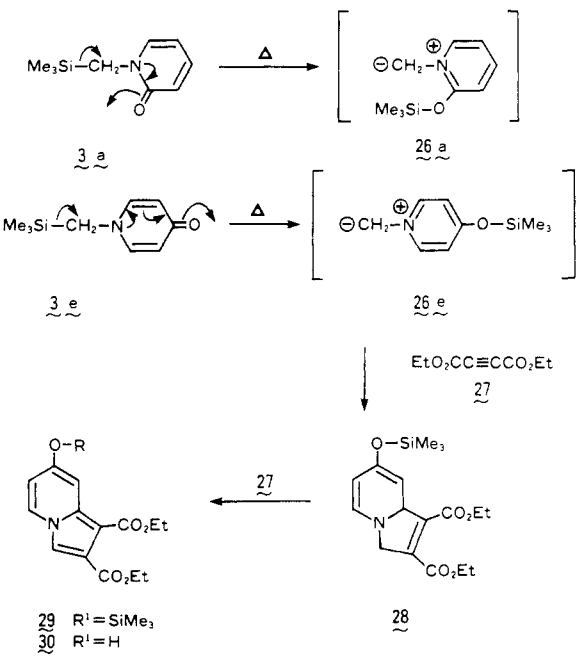


TBAF-catalyzed reactions of the other azinone **3b** and diazinones **3c,d** may be compared with those of **3a,e**. Quinolone **3b** also reacted easily with ketones **6**, **18**, and **19** to give 2-(2-oxoquinol-1-yl) ethanols **20**, **21**, and **22**, respectively, in good yields (Table I, entries, 8, 9, and 10). However, in the case of the reaction of the diazinones **3c,d** with **6**, the yields of the products **23** and **24** were comparatively low (39%, 43%) (Table I, entries 11 and 12). The reaction of **3d** with **6** gave **24** with the accompanying dimer (**25**, 1.5%). Clearly, the formation of the dimer can be attributed to the reaction of the anion **4d** with unreacted **3d**. The results suggest that (*N*-diazinonyl)methyl anions **4c,d**, generated from **3c,d**, competitively reacted with the carbonyl compound and the diazinone ring, respectively (Scheme IV).

We found that, in the absence of TBAF catalyst, **3a,e** also reacted with **6** at 145 °C to give 2-oxopyridylethanols **10** (11%) and **16** (45%) respectively, after acid-catalyzed hydrolysis (Table I, entries 13 and 14). Although this

(13) Guerry, P.; Neier, R. *Synthesis* **1984**, 485.
(14) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *J. Org. Chem.* **1986**, *51*, 1745.
(15) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043.
(16) Beak, P.; Monroe, E. M. *J. Org. Chem.* **1969**, *34*, 589.

Scheme V



thermal reaction gives lower yields than the fluoride-catalyzed reaction, the mechanism is of interest. We assumed the ylides **26a,e** to be intermediates of the thermal reactions of **3a,e** by intra- or intermolecular isomerization (Scheme V). In order to test this assumption the reaction of **3e** with diethyl acetylenedicarboxylate (**27**) was carried out, and bicyclic compound **30** was obtained in 11% yield. The formation of **30** can be explained by the process shown in Scheme V. Namely the thermal isomerization of **3e** may generate ylide **26e** which undergoes 1,3-dipolar cycloaddition with **27** to yield cycloadduct **28**. This cycloadduct is oxidized by **27** to the aromatic compound **29**,[17] and subsequent hydrolysis of **29** may produce the product **30**. 2-Pyridone **3a** did not lead to the 1,3-dipolar cycloadduct. Although the above results only partially support our hypothesis, the actual nature of the thermal reaction intermediate has not yet been determined.

In summary, the fluoride-induced desilylation of *N*-[(trimethylsilyl)methyl]azinones provides (*N*-azinonyl)methyl anions in synthetically useful yields. The thermal reaction of 1-[(trimethylsilyl)methyl]-4-pyridone generates 4-[(trimethylsilyl)oxy]pyridinium methylide which undergoes 1,3-dipolar cycloaddition with dipolarophile.

Experimental Section

Melting points were determined on a Büchi apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian T-60, EM-390, and VXR-200 instruments with Me_4Si as an internal standard. A Hitachi 260-10 spectrophotometer was used to obtain IR spectra. Column chromatography was performed on 230-400-mesh silica gel.

1-[(Trimethylsilyl)methyl]-2-pyridone (3a). A suspension of 2-pyridone (20 g, 210 mmol), (chloromethyl)trimethylsilane (28.4 g, 231 mmol), K_2CO_3 (34.9 g, 253 mmol), and dry Me_2SO (280 mL) was stirred at 25 °C for 72 h. 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 distilled under reduced pressure to give 29.0 g of **3a** (76%): bp 100–102 °C (3 mm); mp 46–50 °C; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H, Me_3), 3.58 (s, 2 H, CH_2), 6.08–6.17 (m, 1 H, 5-position of pyridone ring), 6.55 (d, 1 H, J = 9.2 Hz, 3-position), 7.18–7.33 (m, 2 H, 4- and 6-positions; IR (neat) 1650, 1580 cm^{-1}. Anal. Calcd for $C_9H_{15}NOSi$: C, 59.62; H, 8.34; N, 7.73. Found: C, 59.27; H, 8.43; N, 7.92.

1-[(Trimethylsilyl)methyl]-2-quinolone (3b) was prepared in a similar manner. 2-Quinolone (12.3 g, 85 mmol) was convered into 12.5 g of **3b** (64%): bp 148–151 °C (3 mm); ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9 H, Me_3), 3.92 (s, 2 H, CH_2), 6.72 (d, 1 H, J = 9.4 Hz, 3-position of quinolone ring), 7.16–7.68 (m, 5 H, the other positions of quinolone); IR (neat) 1650, 1590 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NOSi$: C, 67.49; H, 7.41; N, 6.05. Found C, 66.38; H, 7.47; N, 5.98.

3-[(Trimethylsilyl)methyl]-4-pyrimidinone (3c) was prepared in a similar manner. 4-Pyrimidinone (10 g, 104 mmol) gave **3c** (10.0 g, 55%) and 4-[[(trimethylsilyl)methyl]oxy]pyrimidine (950 mg, 5%), which were separated from each other by flash chromatography using AcOEt–benzene (1:3) and AcOEt–MeOH (10:1) as eluents. **3c**: mp 93.5–95.5 °C [(*i*-Pr)$_2$O–petroleum ether]; ^{1}H NMR (Me_2SO-d_6) δ 0.05 (s, 9 H, Me_3), 3.55 (s, 2 H, CH_2), 6.39 (d, 1 H, J = 6.4 Hz, 5-position of pyrimidinone ring), 7.90 (d, 1 H, J = 6.4 Hz, 6-position), 8.47 (s, 1 H, 2-position); IR (Nujol) 1655, 1585 cm^{-1}. Anal. Calcd for $C_8H_{14}N_2OSi$: C, 52.71; H, 7.74; N, 15.37. Found: C, 52.51; H, 7.64; H, 15.27.

In the ^{1}H NMR spectrum of **3c**, the chemical shifts of the pyrimidinone ring protons were similar to that of 3-methyl-4-pyrimidinone.[11]

3-[(Trimethylsilyl)methyl]-4-quinazolinone (3d) was prepared in a similar manner. 4-Quinazolinone (10 g, 68 mmol) was converted into 14.5 g of **3d** (91%): bp 147–149 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H, Me_3), 3.59 (s, 2 H, CH_2), 7.28–8.45 (m, 5 H, quinazolinone ring); IR (Nujol) 1680, 1605 cm^{-1}. Anal. Calcd for $C_{12}H_{16}N_2OSi$: C, 62.03; H, 6.94; N, 12.06. Found: C, 61.91; H, 6.93; N, 12.06.

1-[(Trimethylsilyl)methyl]-4-pyridone (3e). A mixture of 4-[(trimethylsilyl)oxy]pyridine (3 g, 18 mmol) and (iodomethyl)trimethylsilane (4.6 g, 21 mmol) was stirred at 80 °C for 2 h. To the resulting solid was added K_2CO_3 (3 g, 22 mmol) and MeOH (6 mL) with cooling in an ice bath. The suspension was stirred with cooling in an ice bath for 15 min and then filtered to remove any inorganic solid. The filtrate was evaporated under reduced pressure. To the residue was added water (30 mL), and the resulting mixture was extracted three times with $CHCl_3$. The $CHCl_3$ layer was washed with NaCl-saturated water, dried (Na_2SO_4), and evaporated. The residue was recrystallized from CH_2Cl_2–AcOEt to give 1.76 g of **3e** (54%): mp 177–178.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H, Me_3), 3.41 (s, 2 H, CH_2), 6.39 (d, 2 H, J = 7.6 Hz, 3- and 5-positions of pyridone ring), 7.15 (d, 2 H, J = 7.6 Hz, 2- and 6-positions); IR (Nujol) 1645, 1560 cm^{-1}. Anal. Calcd for $C_9H_{15}NOSi$: C, 59.62; H, 8.34; N, 7.73. Found: C, 59.48; H, 8.34; N, 7.65.

General Procedure for TBAF-Catalyzed Reaction of *N*-[(Trimethylsilyl)methyl]azinone 3 with Carbonyl Compounds. To a mixture of carbonyl compound (500 mg, 2.4–5.1 mmol) and **3** (1.2 molar equiv/mol of carbonyl compound) in dry THF (2.0 mL/mmol of carbonyl compound) under nitrogen atmosphere was added anhydrous TBAF (0.1 molar equiv/mol of carbonyl compound, ca. 1 M in THF) and the mixture was stirred under the conditions described in Table I. Then 6 N HCl (2 mL) was added and the mixture was stirred at room temperature for 6 h. The reaction mixture was poured into aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by flash chromatography (entries 1–4, 9–12) and recrystallization, and the results are summarized in Table I (entries 1–12).

2-(4-Chlorophenyl)-2-hydroxy-1-(4-oxoquinazolin-3-yl)-propane (24) and 1,2-dihydro-2-[(4-oxoquinazolin-3-yl)-methyl]-3-[(trimethylsilyl)methyl]-4-quinazolinone (25) were prepared by the above general procedure. 4-Chloroacetophenone (300 mg, 1.94 mmol) and **3e** (541 mg, 2.33 mmol) gave **24** (262 mg, 43%) and **25** (7 mg, 1.5%), which were purified from each other by flash chromatography using AcOEt–benzene (1:2) as an eluent (entry 12). **24**: mp 148–149 °C [(*i*-Pr)$_2$O–AcOEt]; ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 3 H, CH_3), 3.92 (s, 1 H, OH), 3.95 (d, 1 H, J = 14.1 Hz, -C*H*H-), 4.57 (d, 1 H, J = 14.1 Hz, -CH*H*-), 7.21–7.83 (m, 8 H, Ar H) 8.22–8.36 (m, 1 H, Ar H); IR (Nujol) 3220, 1675, 1655, 1615 cm^{-1}. Anal. Calcd for $C_{17}H_{15}ClN_2O_2$: C, 64.87; H, 4.80; Cl, 11.26; N, 8.90. Found: C, 64.75; H, 4.86; Cl, 11.16; N, 9.08.

(17) A similar oxidation was reported, see: Sasaki, T.; Kanematsu, K.; Yukimoto, Y. *J. Chem. Soc. C* **1970**, 481.

25: mp 186 °C (dec, recryst from AcOEt); ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9 H, Me_3), 2.53 (d, 1 H, J = 14.9 Hz, SiCH*H*), 3.73 (dd, 1 H, J = 7.5, 8.8 Hz, CHCH*H*-), 3.83 (d, 1 H, J = 14.9 Hz, SiC*H*H), 4.43 (d, 1 H, J = 4.4 Hz, NH), 4.47 (dd, 1 H, J = 3.2, 7.5 Hz, CHC*H*H-), 4.83-4.88 (m, 1 H, C*H*CH_2), 6.73-8.31 (m, 9 H, Ar H); IR (Nujol) 3280, 1670, 1620 cm^{-1}. Anal. Calcd for $C_{21}H_{24}N_4O_2Si$: C, 64.26; H, 6.16; N, 14.27. Found: C, 63.62; H, 6.16; N, 14.25.

General Procedure for Thermal Reaction of *N*-[(Trimethylsilyl)methyl]azinone 3 with *p*-Chloroacetophenone (6). A mixture of **6** (200 mg, 1.3 mmol) and **3** (1.2 molar equiv/mol of **6**) was stirred under the conditions described in Table I. Then 6 N HCl (2 mL) and MeOH (2 mL) were added and the mixture was stirred at room temperature for 6 h. The reaction mixture was poured into 5% NaOH and extracted with $CHCl_3$. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by flash chromatography (entry 13) and recrystallization, and the results are summarized in Table I (entries 13 and 14).

Thermal Reaction of 1-[(Trimethylsilyl)methyl]-4-pyridone (3e) with Diethyl Acetylenedicarboxylate (27). A mixture of **3e** (200 mg, 1.1 mmol), **27** (235 mg, 1.6 mmol), and dry THF (1 mL) was refluxed for 8 h. The reaction mixture was evaporated to remove THF and chromatographed on silica gel. The fractions eluted with AcOEt-benzene (1:2) gave 24 mg (11%) of diethyl 7-hydroxyindolizine-1,2-dicarboxylate (**30**): mp 194-196 °C (MeOH-AcOEt); ^{1}H NMR (DMSO-d_6) δ 3.70 (s, 3 H, Me), 3.75 (s, 3 H, Me), 6.53 (dd, 1 H, J = 2.4 and 6.9 Hz, 6-position of indolizine ring) 7.24 (d, 1 H, J = 2.4 Hz, 8-position), 7.70 (s, 1 H, 3-position), 8.25 (d, 1 H, J = 6.9 Hz, 5-position); IR (Nujol) 3125, 1725, 1645, 1635 cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_5$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.80; H, 4.51; N, 5.68.

Registry No. **3a**, 116059-99-5; **3b**, 116211-37-1; **3c**, 116211-38-2; **3d**, 116211-39-3; **3e**, 116211-40-6; **5**, 119-61-9; **6**, 99-91-2; **7**, 108-94-1; **8**, 2550-26-7; **9**, 116211-41-7; **10**, 116211-42-8; **11**, 116211-43-9; **12**, 116211-44-0; **14**, 104-88-1; **15**, 116211-45-1; **16**, 116211-46-2; **17**, 116211-47-3; **18**, 6285-05-8; **19**, 134-81-6; **20**, 116211-48-4; **21**, 116232-46-3; **22**, 116232-47-4; **23**, 116211-49-5; **24**, 116211-50-8; **25**, 116211-51-9; **27**, 762-21-0; **30**, 116211-52-0; TBAF, 429-41-4; 2-pyridone, 142-08-5; (chloromethyl)trimethylsilane, 2344-80-1; 2-quinolone, 59-31-4; 4-pyrimidinone, 4562-27-0; 4-quinazolinone, 491-36-1; 4-[(trimethylsilyl)oxy]pyridine, 27248-04-0; (iodomethyl)trimethylsilane, 4206-67-1.

Oxidative Coupling of Methyl 6-Hydroxyindole-2-carboxylate with Primary Amines: Preparation of 2-Substituted Methyl Pyrrolo[2,3-*e*]benzoxazole-5-carboxylates

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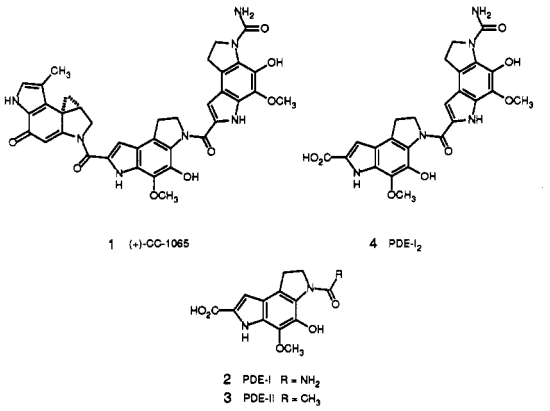
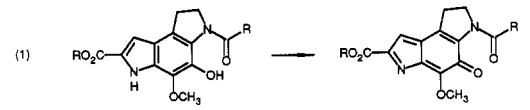
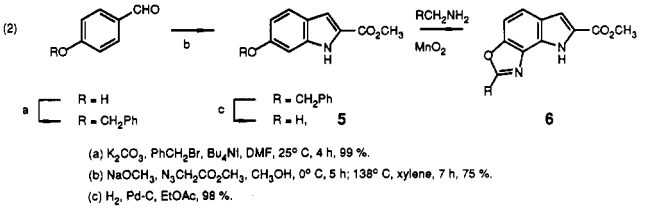
In the conduct of synthetic efforts on the antitumor antibiotic (+)-CC-1065 (**1**) and functionally related agents we have noted the instability of PDE-I (**2**), PDE-II (**3**), PDE-I dimer (**4**), and structurally related intermediates to mild, oxidative conditions.[2] We have suggested that the oxidative lability of the central and right-hand subunits of (+)-CC-1065 and structurally related agents may be due



to a mild oxidation of the 6-hydroxyindole-2-carboxylate structural subunit to an intermediate, extended *p*-quinonemethide imine, and subsequent capture by nucleophiles, eq 1.[3,4]



Herein we detail the related oxidative susceptibility of methyl 6-hydroxyindole-2-carboxylate (**5**),[5] its use in a mild regioselective, oxidative coupling with primary amines suitable for the preparation of fused oxazoles, eq 2,[6] and the apparent interception of an intermediate *o*-quinone monoimine generated enroute to the methyl pyrrolo[2,3-*e*]benzoxazole-5-carboxylates **6**.



In an initial survey of oxidants including silver(II) oxide,[7] lead(IV) dioxide,[8] nickle peroxide,[9] and manganese dioxide[6]

(1) (a) National Institutes of Health research career development award recipient, 1983-88 (CA 01134). Alfred P. Sloan research fellow, 1985-89. (b) Undergraduate research participant.

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