the recovered liquid treated with *N,O*-bis[(trifluoromethyl)silyl]trifluoroacetamide to convert all the aromatic phenols to their TMS derivatives. The products were analyzed by GC on a 50-ft methylsilicone capillary column at 150 °C. The three dihydroxybenzenes elute in the order 1,2 < 1,3 < 1,4.

Registry No. 2-HOC_6H_4OH, 120-80-9; 4-HOC_6H_4OH, 123-31-9; 3-HOC_6H_4OH, 108-46-3; C_6H_5OH, 108-95-2; $C_6H_5OC_6H_5$, 101-84-8; $HOC_6H_4OC_6H_5$, 54774-79-7; dibenzofuran, 132-64-9; α-naphthol, 90-15-3; β-naphthol, 135-19-3.

Regioselective Alkylations of 4,6-Dialkyl-Substituted 2*H*-Pyran-2-ones

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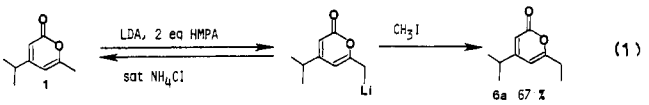
Recently, we reported[1] a versatile synthesis of α-pyrones[2] from vinylogous thiol esters which were readily prepared[3] by reaction of α-oxo ketene dithioacetals[4] with organocuprates. The alkyl substitution pattern at all four olefinic carbon atoms of the pyrone ring could be altered simply by choice of starting α-oxo ketene dithioacetal, organocuprate, or ester enolate anion. In addition, the method permitted annulation of the pyrone ring system onto an existing cycloalkanone framework. In an effort to functionalize these readily prepared alkyl-substituted α-pyrones, we examined the kinetic deprotonation of these substrates and the subsequent alkylation of the resonance stabilized carbanions. We now report that deprotonation can be effected at the 4- and 6-alkyl substituents by the use of lithium diisopropylamide and that good to excellent regioselectivity can be achieved in the alkylation reactions.

Although deprotonation of alkyl-substituted α-pyrones has been described by several groups, low yields and severe limitations have been noted.[5-7] These limitations generally involve the instability of the pyrone ring system under the reaction conditions. The general origin of the instability appears to be ring-opening reactions followed by subsequent base-catalyzed transformations.[8] Despite these limitations Harris has achieved some success with alkylations at the C6-methyl substituent of polyanions generated from 4-hydroxy-2-pyrones in yields ranging from 30% to 72%.[6] Deprotonation of the 4-hydroxy substituent in these compounds may protect the ring from nucleophilic cleavage reactions. An alternative approach involved the use of a phosphonium ylide generated from 4-methoxy-6-bromomethyl-2*H*-pyran-2-one.[9] 4-Methoxy-6-methyl-2*H*-pyran-2-one, however, has been reported to undergo deprotonation in the ring via an ortho-lithiation process, and the resulting vinyl anion has been successfully quenched with chlorotrimethylsilane.[10] 3-Bromo-2-pyrone could not be converted into the lithium derivative but did afford an organocopper species upon reaction with lithium dimethylcuprate.[11]

In an initial experiment, addition of 4-isopropyl-6-methyl-2*H*-pyran-2-one (1) to a cold (−78 °C) solution of lithium diisopropylamide (LDA) and HMPA gave the 6-ethyl derivative in 67% yield after quenching with methyl iodide (eq 1). The stability of the intermediate



(1)

carbanion was examined as a function of time and temperature by treating the carbanion containing solution with acid and measuring the yield of recovered α-pyrone. In marked contrast to vinyl anions generated from α-pyrones,[10] the resonance-stabilized anion generated from **1** was relatively stable and the α-pyrone was recovered in 83% yield upon quenching the anion after 2 h at 20 °C. Similar treatment of several alkyl-substituted α-pyrones with LDA and 2 equiv of HMPA in THF generated the resonance-stabilized carbanions, which could be alkylated with alkyl iodides, aldehydes, and acid chlorides in good to excellent yields (Table I). Alkylation could not be effected with benzyl bromide, epoxides, or enoates; very low yields of the 6-bromo derivative **6e** were achieved with molecular bromine. Interestingly, ethyl bromide did not afford the alkylation product, while ethyl iodide did, in 68% yield (entry 3). This result suggests the possibility that these alkylation reactions may proceed by an electron-transfer pathway,[12] although it may also merely reflect relative reactivities of carbanion and electrophile. The yield of alkylation product obtained with benzoyl chloride could be increased by utilizing 2 equiv of the reagent (entries 5-6). This observation is consistent with a moderately reactive, resonance-stabilized carbanion where product deprotonation by pyrone carbanion becomes competitive when 1 equiv of acid chloride is employed.

The regioselectivity of carbanion formation showed a preference for deprotonation at the C4-alkyl substituent. Deprotonation and alkylation of **4** gave **9** and **10** as a 73:27 mixture (entry 14). Analysis of the mass and 200-MHz NMR spectra of the mixture permitted structure assignments. The major isomer **9** clearly shows an isopropyl substituent [δ 1.17 (d, J = 6.8 Hz, 6 H), 2.82 (sept, J = 6.8 Hz, 1 H)] and a methyl resonance at δ 2.25 consistent with the 6-methyl resonances found in **1** and **4** (δ 2.25 and 2.23, respectively). The minor isomer **10** displays two methylene absorptions at δ 2.44 (qd, J = 1.08 Hz, J = 7.39 Hz, 2 H) and 2.56 (q, J = 7.52 Hz, 2 H); the quartet of doublets is similar to that observed for the methylene group in **4**. The mass spectrum shows an intense peak at m/e 123 for sequential loss of CO and the C6-Me for the major isomer and a small peak at m/e 109 for the similar fragmentation of the minor isomer. A small peak at m/e 137 corresponds

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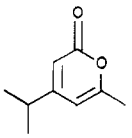
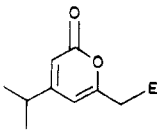
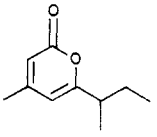
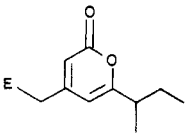
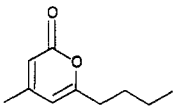
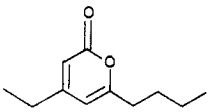
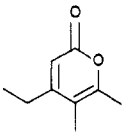
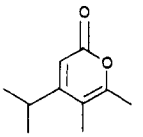
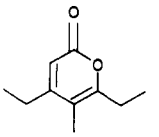
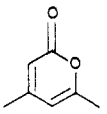
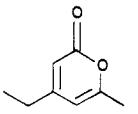
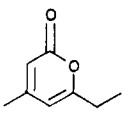
Table I. Regioselective Alkylation of Resonance-Stabilized Carbanions Generated from α-Pyrones

entry	substrate	electrophile	products: major	products: minor	% yield[a] (ratio)
					
1	**1**	CH_3I	**6a**, E = Me		51
2		(2.0 equiv)			67
3		EtI	**b**, E = Et		68
4		PhCHO	**c**, E = PhCHOH		98
5		PhCOCl	**d**, E = PhCO		64
6		(2.0 equiv)			89
7		Br_2	**e**, E = Br		5
8		CH_2=CH-CO_2CH_3			0
9		$PhCH_2Br$			0
					
10	**2**	CH_3I	**7a**, E = Me		70
11		PhCHO	**b**, E = PhCHOH		84
12		PhCOCl	**c**, E = PhCO		70
					
13	**3**	CH_3I	**8**		80
					
14	**4**	CH_3I	**9**	**10**	54 (73:27)[b]
					
15	**5**	CH_3I	**11**	**12**	53 (77:23)[b]

[a] Yields are based upon isolated products purified by MPLC. [b] Determined by NMR.

to loss of the C6-ethyl group from the M^+ ion of **10**. Peaks are observed at m/e 95 and 81 for the isopropylmethyl- and ethylmethylcyclopropenium ions[13] derived from fragmentation of **9** and **10**, respectively. Similarly, deprotonation and alkylation of **5** afforded a 77:23 mixture of **11** and **12**, respectively. The 200-MHz NMR spectrum of the mixture shows methyl resonances at δ 2.14 (d, J = 1.33 Hz) and 2.23 for the minor and major isomers, respectively, consistent with the methyl signals in the spectra of **2** [δ 2.10 (d, J = 1.0 Hz)], **3** [δ 2.13 (d, J = 0.98 Hz)], **4**, and **1**. The methylene resonances at δ 2.41 (qd, J = 1.01, J = 7.5 Hz) and 2.51 (q, J = 7.6 Hz) for the major and minor isomer, respectively, are consistent with those found in the spectra of **3**, **7a**, and **8**. Analysis of the GC–mass spectrum permitted evaluation of the individual components of the mixture. The minor peak in the GC trace shows peaks at m/e 109 for loss of the C6-ethyl group and m/e 53 for the methylcyclopropenium ion expected for the fragmentation of **12**. The major peak in the GC trace shows peaks at m/e 123 (loss of C6-Me) and m/e 95 (ethylcyclopropenium ion) consistent with structure **11**.

Although the 4-ethyl-6-methyl derivative **4** underwent selective deprotonation to afford a secondary carbanion in preference to a primary carbanion (entry 14), the regioselectivity of deprotonation appears to be governed by both carbanion substitution and possibly by net atom electron densities and frontier molecular orbital coefficients.[14,15a] Molecular orbital considerations could account for the selective deprotonation of the more substituted position in **4**. If the choice is between deprotonation of a methyl vs. a secondary alkyl substituent, then regiospecific formation of the primary carbanion occurs regardless of its location (entries 1–12). These results indicate that α-pyrones can form extended enolates which

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undergo alkylation at the terminus (generally γ-alkylation) of the conjugated system in a manner similar to that observed for β-amino enones and enoates,[15] copper enolate dianions of unsaturated acids,[16] and 3(2*H*)-furanones.[17] Many of these substrates which undergo γ-alkylation contain a heteroatom at the β-carbon atom, and the α-pyrones may be viewed as vinylogous analogues.

In summary, 4,6-dialkyl-substituted α-pyrones can be easily deprotonated and alkylated with good regioselectivity. Reaction preferentially occurs at the 4-alkyl substituent unless it is more highly branched, and the resulting carbanions display modest reactivity. The method provides a convenient procedure for functionalization of readily prepared alkyl-substituted α-pyrones.

Experimental Section

Proton NMR spectra were recorded as $CDCl_3$ solutions on a JEOL-FX90Q or, when indicated, an IBM-NR-200 AF series instrument. Chemical shifts are reported as values in parts per million relative to tetramethylsilane as internal standard. The carbon NMR chemical shifts are reported in parts per million downfield from tetramethylsilane and are referenced with respect to internal $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer 710B grating spectrophotometer as $CHCl_3$ solutions unless otherwise noted. Combustion analysis were determined by Atlanta Microlab Inc., Atlanta, GA. High-resolution mass spectra were run on a Dupont CEC-110 mass spectrometer at the Massachusetts Institute of Technology Mass Spectrometry Laboratory. GC–mass spectra were run on a Hewlett-Packard 59-85B system employing a 6-ft Carbowax 20M column and measured under electron impact conditions (EI).

Ethyl iodide, methyl iodide, benzaldehyde, benzoyl chloride, and methyl acrylate were purchased from Aldrich and used without further purification. The concentration of alkyllithium reagents was determined by titration of diphenylacetic acid to the yellow end point.[18] Diisopropylamine was distilled over CaH_2 and stored over potassium hydroxide. Hexamethylphosphoramide (HMPA) was distilled over CaH_2 and stored over 3-Å molecular sieves. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone prior to use.

General Procedure. Lithium diisopropylamide was generated at 0 °C under nitrogen from diisopropylamine (0.80 mL, 0.575 mmol) and *n*-butyllithium (0.24 mL, 2.40 M) in 2.0 mL of THF. The solution was stirred for 15 min at 0 °C and then cooled to −78 °C, whereupon HMPA (0.21 mL) was added and the solution was stirred for an additional 30 min. The 2*H*-pyran-2-one (0.50 mmol) in 1 mL of THF was added to the solution, cooled to −78 °C via double tipped needle, and stirred for 45 min to generate the carbanion. The electrophile (0.60 mmol) was then added, and the solution was stirred at the temperature and for the time indicated. The reaction was then quenched with 1.5 mL of 1 N HCl, warmed to room temperature, poured into 25 mL of Et_2O/20 mL of 1 N HCl mixture, and separated, and the aqueous phase was extracted with 2 × 25 mL of Et_2O. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuo, and the crude material was purified by medium-pressure liquid chromatography (MPLC).

6-Ethyl-4-(1-methylethyl)-2*H*-pyran-2-one (6a). The general procedure was employed with the exception that the enolate was treated with methyl iodide (0.07 mL, 1.1 mmol, 2.2 equiv), warmed to 0 °C over 1 h, stirred for 2 h at 0 °C, and then quenched with 2.0 mL of 2 M HCl. Workup and MPLC purification (R_f 0.70; petroleum ether/30% ethyl acetate, v/v) afforded a 67% yield: IR 3030 (m), 2980 (s), 2950 (m), 2890 (w), 1720 (vs), 1640 (m), 1565 (w), 1470 (m), 1430 (m), 1390 (m) cm^{-1}; NMR δ 1.18 (d, J = 6.84 Hz, 6 H), 1.09–1.31 (m, 3 H), 2.50–2.87 (m, 1 H), 2.52 (q, J = 7.57 Hz, 2 H), 5.90 (br s, 1 H), 5.96 (br s, 1 H); ^{13}C NMR δ 166.2, 165.8, 163.8, 107.6, 102.5, 33.6, 26.9, 21.3 (2 C), 11.1; mass spectrum, m/e 152.0843 (M^+) (calcd for $C_{10}H_{14}O_2$ 152.0837).

4-(1-Methylethyl)-6-propyl-2*H*-pyran-2-one (6b). The general procedure was employed, and the enolate (0.30 mmol) was reacted with ethyl iodide (0.08 mL, 1.0 mmol, 3.3 equiv) at −78 °C, warmed to 0 °C over 30 min, stirred for 1 h, and then quenched with 2 mL of 2 M HCl. Workup and MPLC purification (R_f 0.48; petroleum ether/10% ethyl acetate) afforded a 68% yield: IR 3020 (s), 2980 (s), 2945 (s), 1720 (br s), 1645 (s), 1565 (s) cm^{-1}; NMR δ 0.96 (t, J = 7.32 Hz, 3 H), 1.18 (d, J = 6.83 Hz, 6 H), 1.67 (sext, J = 7.33 Hz, 2 H), 2.45 (t, J = 7.69 Hz, 2 H), 2.45–2.78 (m, 1 H), 5.89 (br s, 1 H), 5.95 (br s, 1 H); ^{13}C NMR δ 165.7, 164.9, 163.8, 107.7, 103.5, 35.7, 33.5, 21.3 (2 C), 20.2, 13.4; mass spectrum m/e 180.1147 (M^+) (calcd for $C_{11}H_{16}O_2$: 180.1150).

6-(2-Hydroxy-2-phenylethyl)-4-(1-methylethyl)-2*H*-pyran-2-one (6c). The general procedure was employed with the exception that the enolate (0.39 mmol) was treated with benzaldehyde (0.07 mL, 0.68 mmol, 1.7 equiv), warmed to −20 °C over 1 h, and then quenched with 1 mL of 2 M HCl. Workup and purification by MPLC (R_f 0.13; petroleum ether/20% ethyl acetate, v/v) afforded a 98% yield: IR 3500–3300 (br, m), 3020 (s), 2980 (s), 2940 (m), 1715 (vs), 1645 (s), 1565 (s) cm^{-1}; NMR δ 1.10 (d, J = 6.84 Hz, 6 H), 1.99 (sept, J = 6.85 Hz, 1 H), 2.80–2.87 (m, 2 H), 3.70–4.00 (br s, 1 H), 5.10 (t, J = 6.85 Hz, 1 H), 5.89 (br s, 2 H), 7.25–7.37 (m, 5 H); ^{13}C NMR δ 165.9, 163.8, 161.2, 143.1, 128.2 (2 C), 127.5, 125.4 (2 C), 107.8, 105.8, 71.1, 43.6, 33.3, 21.1, 20.4.

4-(1-Methylethyl)-6-(2-oxo-2-phenylethyl)-2*H*-pyran-2-one (6d). The general procedure was employed except that the enolate (0.39 mmol) was treated with benzoyl chloride (0.065 mL, 0.55 mmol, 1.4 equiv) at −78 °C, stirred for 15 min, and then quenched with 1 mL of 2 M HCl. Workup and MPLC purification (R_f 0.20; petroleum ether/20% ethyl acetate, v/v) afforded a 64% yield: IR 3040 (m), 2990 (s), 2940 (s), 2900 (s), 1720–1690 (br, vs), 1610 (vs), 1450 (m), 1390 (m) cm^{-1}; NMR δ 1.16 (d, J = 6.84 Hz, 6 H), 2.61 (sept, J = 6.85 Hz, 1 H), 4.15 (s, 2 H), 6.01 (br s, 1 H), 6.12 (br s, 1 H), 7.43–7.57 (m, 3 H), 7.90–8.03 (m, 2 H); ^{13}C NMR δ 193.4, 165.3, 163.0, 157.4, 135.8, 133.7, 128.7 (2 C), 128.2 (2 C), 108.6, 106.7, 43.0, 33.4, 21.0 (2 C); mass spectrum, m/e 256.1102 (M^+) (calcd for $C_{16}H_{16}O_3$ 256.1100).

6-(Bromomethyl)-4-(1-methylethyl)-2*H*-pyran-2-one (6e). The general procedure was employed, and the enolate (0.39 mmol) was treated with bromine (0.025 mL, 0.49 mmol) at −78 °C, stirred for 5 min, and then quenched with 2 mL of 2 M HCl. Workup and MPLC purification (R_f 0.30; petroleum ether/30% ethyl acetate, v/v) afforded a 5% yield: IR 3020 (m), 2980 (s), 2940 (m), 1720 (br, vs), 1645 (s), 1475 (m), 1395 (m), 1300 (m), 1190 (m), 1160 (m) cm^{-1}; NMR δ 1.21 (d, J = 6.83 Hz, 6 H), 2.69 (sept, J = 6.85 Hz, 1 H), 3.82 (s, 2 H), 6.13 (br s, 1 H), 6.26 (br s, 1 H); ^{13}C NMR δ 164.6, 162.4, 155.2, 110.5, 109.1, 57.4, 33.5, 21.1 (2 C).

4-Ethyl-6-(1-methylpropyl)-2*H*-pyran-2-one (7a). The general procedure was employed with the exception that the enolate (0.20 mmol) was treated with methyl iodide (0.03 mL, 0.48 mmol, 2.4 equiv), warmed to 0 °C over 1 h, and then stirred for an additional hour before quenching with 1 mL of 2 M HCl. Workup and MPLC purification (R_f 0.68; petroleum ether/20% ethyl acetate, v/v) afforded a 70% yield: IR 3030 (m), 2990 (vs), 2970 (s), 2930 (m), 2880 (m), 1710 (br, s), 1640 (s), 1560 (s), 1460 (m), 1420 (m) cm^{-1}; NMR δ 0.88 (t, J = 7.20 Hz, 3 H), 1.15 (t, J = 7.35 Hz, 3 H), 1.19 (d, J = 6.87 Hz, 3 H), 1.40–1.77 (m, 2 H), 2.22–2.65 (m, 3 H), 5.79 (br s, 1 H), 5.90 (br s, 1 H); ^{13}C NMR δ 168.5, 163.7, 161.5, 109.0, 103.7, 39.8, 28.2, 27.4, 17.8, 12.2, 11.5.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.20; H, 8.95.

4-(2-Hydroxy-2-phenylethyl)-6-(1-methylpropyl)-2*H*-pyran-2-one (7b). The general procedure was employed with the exception that the enolate (0.20 mmol) was treated with benzaldehyde (0.04 mL, 0.4 mmol, 2 equiv) at −78 °C, warmed to 0 °C over 90 min, and then quenched with 1 mL of 2 M HCl. Workup and purification by MPLC (R_f 0.15; petroleum ether/20% ethyl acetate, v/v) afforded an 84% yield: IR 3600 (br, w), 3050 (m), 3000 (vs), 2970 (m), 1715 (vs), 1640 (m), 1560 (m), 1520 (m), 1420 (m) cm^{-1}; NMR δ 0.83 (t, J = 7.20 Hz, 3 H), 1.14 (d, J = 6.84 Hz, 3 H), 1.52 (p, J = 6.96 Hz, 2 H), 2.40 (sext, J = 6.84 Hz, 1 H), 2.70–2.81 (m, 2 H), 3.41 (br s, 1 H), 4.81 (t, J = 6.84 Hz, 1 H), 5.79 (br s, 1 H), 5.92 (br s, 1 H), 7.30 (s, 5 H); ^{13}C NMR δ

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168.3, 163.6, 156.6, 143.1, 128.4 (2 C), 127.8, 125.6 (2 C), 111.5, 104.6, 72.9, 44.8, 39.6, 27.3, 17.6, 11.4.

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.78; H, 7.45.

6-(1-Methylpropyl)-4-(2-oxo-2-phenylethyl)-2*H*-pyran-2-one (7c). The general procedure was employed, and the enolate (0.20 mmol) was reacted with benzoyl chloride (0.03 mL, 0.26 mmol, 1.3 equiv) at −78 °C, stirred for 15 min, and then quenched with 1 mL of 2 M HCl. Workup and purification by MPLC (R_f 0.28; petroleum ether/20% ethyl acetate, v/v) afforded a 69% yield: IR 3050 (m), 3000 (vs), 2970 (m), 1715 (vs), 1690 (m), 1550 (m), 1520 (m), 1480 (m), 1420 (m) cm^{-1}; NMR δ 0.87 (t, J = 7.32 Hz, 3 H), 1.21 (d, J = 6.84 Hz, 3 H), 1.58 (p, J = 7.08 Hz, 2 H), 2.44 (sext, J = 6.84 Hz, 1 H), 4.08 (s, 2 H), 5.95 (br s, 1 H), 6.05 (br s, 1 H), 7.45–7.65 (m, 3 H), 7.90–8.03 (m, 2 H); ^{13}C NMR δ 194.6, 168.8, 162.7, 152.4, 135.9, 133.7, 128.7 (2 C), 128.2 (2 C), 112.4, 104.1, 44.4, 39.7, 27.3, 17.6, 11.4; mass spectrum, m/e 270.1264 (M^+) (calcd for $C_{17}H_{18}O_3$ 270.1256).

6-Butyl-4-ethyl-2*H*-pyran-2-one (8). The general procedure was employed with the exception that the enolate (0.30 mmol) was treated with methyl iodide (0.06 mL, 0.96 mmol, 3.2 equiv) at −78 °C, warmed to −30 °C over 1 h, and then quenched with 1 mL of 2 M HCl. Workup and MPLC purification (R_f 0.65; petroleum ether/20% ethyl acetate, v/v) afforded an 80% yield: IR 3010 (m), 2970 (s), 2940 (s), 2870 (m), 1715 (br, vs), 1640 (s), 1565 (s), 1465 (m), 1435 (m) cm^{-1}; NMR δ 0.93 (t, J = 6.10 Hz, 3 H), 1.18 (t, J = 7.45 Hz, 3 H), 1.28–1.85 (m, 4 H), 2.17–2.65 (m, 4 H), 5.88 (br s, 1 H), 5.95 (br s, 1 H); ^{13}C NMR δ 164.9, 163.5, 161.5, 108.8, 104.5, 33.3, 28.8, 28.1, 22.0, 13.6, 12.1; mass spectrum m/e 180.1150 (M^+) (calcd for $C_{11}H_{16}O_2$ 180.1160).

5,6-Dimethyl-4-(1-methylethyl)-2*H*-pyran-2-one (9) and 4,6-Diethyl-5-methyl-2*H*-pyran-2-one (10). The general procedure was employed. Workup and MPLC purification (R_f 0.22; hexane/20% ethyl acetate, v/v) afforded a 54% yield of **9** and **10** as a 73:27 mixture determined by the average value obtained from NMR integrations and relative peak heights of three absorption pairs. **9**: IR 1720 (vs) cm^{-1}; NMR (200 MHz) δ 1.17 (d, J = 6.8 Hz, 6 H), 1.97 (s, 3 H), 2.25 (s, 3 H), 2.82 (sept, J = 6.8 Hz, 1 H), 6.06 (s, 1 H); mass spectrum, m/e (relative intensity) 166 (17, M^+), 138 (34, $M^+ - CO$), 123 (75, $M^+ - CO - {}^{\bullet}Me$), 95 (12, $C_7H_{11}^+$; cyclopropenium ion), 43 (100, $C_3H_7^+$). **10**: NMR δ 1.22 (t, partly obscured, 3 H), 1.26 (t, partly obscured, 3 H), 1.95 (s, 3 H), 2.44 (qd, J = 1.08 Hz, J = 7.39 Hz, 2 H), 2.56 (q, J = 7.52 Hz, 2 H), 6.03 (s, 1 H); mass spectrum, m/e (relative intensity) 137 (7, $M^+ - {}^{\bullet}C_2H_5$), 109 (11, $M^+ - CO - {}^{\bullet}C_2H_5$), 81 (6, $C_6H_9^+$; cyclopropenium ion).

4-Ethyl-6-methyl-2*H*-pyran-2-one (11) and 6-Ethyl-2-methyl-2*H*-pyran-2-one (12). The general procedure was employed. Workup and MPLC purification gave a 53% yield of **11** and **12** as a 77:23 mixture determined by the average value obtained from NMR integrations and relative peak heights of six absorption pairs. GC analysis (10 ft, Carbowax 20M, 130–200 °C, 30 mL/min) indicated an 85:15 ratio of products. **11**: NMR (200 MHz) δ 1.18 (t, J = 7.5 Hz, 3 H), 2.23 (s, 3 H), 2.41 (qd, J = 1.01 Hz, J = 7.5 Hz, 2 H), 5.89 (br s, 1 H), 5.97 (br s, 1 H); mass spectrum m/e (relative intensity) 138 (27, M^+), 123 (10, $M^+ - {}^{\bullet}Me$), 110 (56, $M^+ - CO$), 95 (100), 67 (51, ethylcyclopropenium ion). **12**: NMR δ 1.23 (t, J = 7.6 Hz, 3 H), 2.14 (d, J = 1.33 Hz, 3 H), 2.51 (q, J = 7.6 Hz, 2 H), 5.86 (br s, 1 H), 5.97 (br s, 1 H); mass spectrum, m/e (relative intensity) 138 (50, M^+), 109 (100, $M^+ - {}^{\bullet}C_2H_5$), 95 (72), 53 (70, methylcyclopropenium ion).

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A Novel Method of Functionalizing the Ethyl Chain of Octaethylporphyrin

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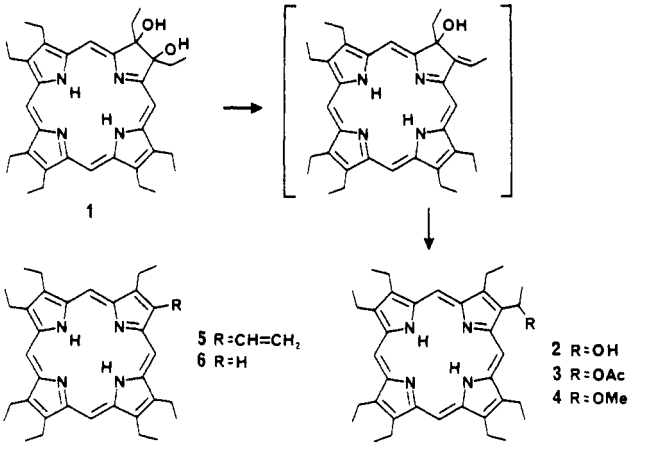
Octaethylporphyrin (OEP), by virtue of its symmetry, high solubility in organic solvents, and excellent spectroscopic correspondence with that of biological heme/porphyrins, has a special place in porphyrin chemistry. Numerous important discoveries concerning heme structure and function can be credited to model studies based on OEP and its metal complexes.[1] The lack of functional groups on OEP, nevertheless, can hinder its application in studies wherein some manipulation of side chains would be required. In such cases, it is often a choice between total synthesis, which is usually lengthy and of low yield, and the natural protoporphyrin or its derivatives, which on the other hand may have too many functional groups all at once. We report here a simple method to functionalize the ethyl chain of OEP so that the broad range of chemical transformations[2] ascribed for the vinyl group of protoporphyrin would become accessible to OEP.

In the study of *vic*-dihydroxychlorins[3] (obtained from OsO_4 oxidation of porphyrins[4]), it was observed that the green pigment often turns grayish brown during heating in aqueous acid. The product is usually a mixture comprising red porphyrins and some purple porphyrinone derived from pinacolic rearrangement of the diol.[5,6] With OEP-diol (**1**), the major porphyrin component is OEP-



alcohol (**2**). This compound is presumably derived via hydration of an ethenylhydroxychlorin intermediate. An analogous reaction has been observed previously in a *vic*-dihydroxybacteriorchlorin.[7] The aqueous acid/dioxane medium employed in the earlier report,[7] however, failed

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