= 6.4 Hz), 3.66 (t, 2 H, J = 5.4 Hz), 2.02–1.93 (m, 4 H), 1.66 (s, 3 H), 1.56–1.27 (m, 10 H), 1.05 (s, 9 H), 0.88 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 135.0, 134.2, 129.5, 127.6, 125.6, 63.8, 32.5, 31.6, 31.4, 29.8, 27.8, 26.9, 24.2, 23.3, 22.6, 19.2, 14.1; MS (EI) m/z 365 (M – t-Bu$^+$) 183, 41. Anal. Calcd for $C_{28}H_{42}OSi$: C, 79.56; H, 10.01. Found: C, 79.78; H, 10.22.

1-[(*tert*-Butyldiphenylsilyl)oxy]-5-methyl-5(*E*)-undecene (12j): oil (0.83 g, 62%); 99:1 mixture of E/Z isomers; IR (film) 3071, 2930, 2858, 1590, 1472, 1112 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67–7.65 (m, 4 H), 7.43–7.33 (m, 6 H), 5.10 (dt, 1 H, J = 1.2, 7.2 Hz), 3.66 (t, 2 H, J = 6.1 Hz), 1.95 (m, 4 H), 1.66–1.28 (m, 13 H), 1.05 (s, 9 H), 0.88 (t, 3 H, J = 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 134.8, 134.2, 129.5, 127.6, 125.6, 124.8, 63.9, 39.3, 32.1, 31.6, 29.6, 27.9, 26.9, 24.1, 22.6, 19.2, 15.8, 14.1; MS (EI) m/z 365 (M – t-Bu$^+$) 183, 41. Anal. Calcd for $C_{28}H_{42}OSi$: C, 79.56; H, 10.01. Found: C, 79.91; H, 10.24.

6-Butyl-6(*Z*)-dodecene (12k): oil (0.24 g, 65%); >95:<5 mixture of Z/E isomers; IR (film) 2926, 2858, 1560, 1466, 1378, 727 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.09, (t, 1 H, J = 7.0 Hz), 1.95 (m, 6 H), 1.40–1.22 (m, 16 H), 0.89 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 124.8, 37.0, 36.7, 32.1, 31.7, 30.8, 30.6, 30.0, 29.9, 28.3, 27.7, 22.6, 22.5, 14.1, 14.0; MS (EI) m/z 224 (M$^{\bullet+}$), 182, 167, 154, 41. Anal. Calcd for $C_{16}H_{32}$: C, 85.63; H, 14.37. Found: C, 85.76; H, 14.45.

6-Butyl-6(*E*)-dodecene (12l): oil (0.49 g, 63%); >95:<5 mixture of E/Z isomers; IR (film) 2957, 2927, 2858, 1466, 1378, 727 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.09, (t, 1 H, J = 6.8 Hz), 2.01–1.92 (m, 6 H), 1.39–1.22 (m, 16 H), 0.90 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 124.8, 37.0, 31.8, 31.7, 30.8, 29.9, 29.8, 28.0, 27.7, 22.9, 22.6, 14.1; MS (EI) m/z 224 (M$^{\bullet+}$), 196, 182, 167, 55. Anal. Calcd for $C_{16}H_{32}$: C, 85.63; H, 14.37. Found: C, 85.85; H, 14.40.

8-Methyl-8(*Z*)-hexadecene (12m): oil (0.39 g, 54%); 90:10 mixture of Z/E isomers; IR (film) 2957, 2855, 1465, 1377, 842, 722 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (t, 1 H, J = 7.0 Hz), 2.02–1.92 (m, 4 H), 1.66 (s, 3 H), 1.37–1.27 (m, 20 H), 0.88 (t, 6 H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 125.3, 31.9, 31.8, 30.2, 29.6, 29.4, 29.35, 29.29, 28.1, 27.8, 23.4, 22.7, 14.1; MS (EI) m/z 238 (M$^{\bullet+}$), 139, 125, 97, 83, 55, 41. Anal. Calcd for $C_{17}H_{34}$: C, 85.63; H, 14.37. Found: C, 85.44; H, 14.73.

8-Methyl-8(*E*)-hexadecene (12n): oil (0.54 g, 68%); 95:5 mixture of E/Z isomers; IR (film) 2925, 2854, 1466, 1378 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (tq, 1 H, J = 1.2, 7.0 Hz), 1.97–1.92 (m, 4 H), 1.57 (s, 3 H), 1.39–1.26 (m, 20 H), 0.88 (t, 6 H, J = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 124.6, 39.7, 31.9, 29.9, 29.30, 29.27, 28.0, 27.9, 22.7, 15.8, 14.1; MS (EI) m/z 238 (M$^{\bullet+}$), 139, 126, 97, 83, 55, 41. Anal. Calcd for $C_{17}H_{34}$: C, 85.63; H, 14.37. Found: C, 85.75; H, 14.79.

5-(Methyl-d_3)-5(*E*)-tridecene (12o): oil (0.33 g, 51%); 98:2 mixture of E/Z isomers; IR (film) 2957, 2856, 2234, 2193, 1466 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (t, 1 H, J = 7.1 Hz), 1.98–1.93 (m, 4 H), 1.39–1.23 (m, 14 H), 0.91–0.85 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.0, 124.6, 39.4, 31.9, 30.2, 30.0, 29.31, 29.29, 27.9, 22.7, 22.3, 14.1, 14.0; MS (EI) m/z 199 (M$^{\bullet+}$), 171, 157, 142, 129, 114, 86, 72, 58, 41. Anal. Calcd for $C_{14}H_{25}D_3$: C, 85.63; H, 14.37. Found: C, 85.30; H, 14.73.

5-(Methyl-d_3)-5(*Z*)-tridecene (12p): oil (0.38 g, 50%); 97:3 mixture of Z/E isomers; IR (film) 2957, 2856, 2223, 2193, 1466, 1378 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (t, 1 H, J = 7.1 Hz), 1.97 (app quintet, 4 H, J = 7.5 Hz), 1.37–1.23 (m, 14 H), 0.93–0.86 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 125.3, 31.9, 31.5, 30.4, 30.2, 29.4, 29.3, 27.8, 22.7, 14.09, 14.07; MS (EI) m/z 199 (M$^{\bullet+}$), 171, 157, 142, 129, 114, 86, 72, 58, 41. Anal. Calcd for $C_{14}H_{25}D_3$: C, 85.63; H, 14.37. Found: C, 85.11; H, 14.39.

1-Cyclohexyl-1(*Z*)-nonene (12q): oil (0.41 g, 61%); 92:8 mixture of Z/E isomers; IR (film) 2924, 2852, 1448, 1378, 967, 889 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.2 (m, 2 H), 2.25 (app tq, 1 H, J = 3.6, 11.1 Hz), 2.05–1.99 (m, 2 H), 1.72–1.57 (m, 6 H), 1.35–1.02 (m, 14 H), 0.88 (t, 3 H, J = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 128.1, 36.3, 33.5, 31.9, 30.0, 29.28, 29.25, 29.2, 27.5, 26.18, 26.16, 26.0, 22.7, 14.1; MS (EI) m/z 208 (M$^{\bullet+}$), 180, 166, 152, 124, 109, 96, 81, 67, 41. Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.76; H, 13.69.

1-Cyclohexyl-1(*E*)-nonene (12r): oil (0.44 g, 60%); 94:6 mixture of E/Z isomers; IR (film) 2924, 2852, 1448, 1378, 967 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35–5.33 (m, 2 H), 1.98–1.88 (m, 3 H), 1.73–1.60 (m, 6 H), 1.35–1.01 (m, 14 H), 0.88 (t, 3 H, J = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 127.8, 40.7, 33.3, 32.7, 31.9, 29.7, 29.3, 29.2, 29.1, 26.3, 26.2, 26.0, 22.7, 14.1; MS (EI) m/z 208 (M$^{\bullet+}$), 109, 96, 81, 67, 41. Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.47; H, 13.71.

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Registry No. **8a**, 66-25-1; **8b**, 124-13-0; **8c**, 2043-61-0; **8d**, 100-52-7; **9a**, 125950-71-2; **9b**, 115672-04-3; **9c**, 2043-61-0; **9d**, 135987-50-7; **10a**, 135987-51-8; **10b**, 135987-52-9; **10c**, 135987-53-0; **10d**, 135987-54-1; **11a**, 137466-51-4; **11b**, 137466-52-5; **11c**, 137466-53-6; **11d**, 137466-54-7; **11e**, 137466-55-8; **11g**, 137466-56-9; **11h**, 137466-57-0; **11i**, 137466-58-1; **12a**, 57024-93-8; **12b**, 57024-92-7; **12c**, 101165-44-0; **12d**, 101146-61-6; **12e**, 137466-59-2; **12f**, 137466-60-5; **12g**, 53109-17-4; **12h**, 53109-16-3; **12i**, 137466-61-6; **12j**, 137466-62-7; **12k**, 137466-63-8; **12l**, 137466-64-9; **12m**, 137466-65-0; **12n**, 137466-66-1; **12o**, 137466-67-2; **12p**, 137466-68-3; **12q**, 127392-75-0; **12r**, 127392-74-9; $Me_2PhSiLi$, 3839-31-4; BuCOCl, 638-29-9; $C_5H_{11}COCl$, 142-61-0; $C_7H_{15}COCl$, 711-64-8; PhCOCl, 98-88-4; t-$BuPh_2SiO(CH_2)_4COCl$, 118715-28-9; CD_3COCl, 19259-90-6.

New Reactions of Potassium Naphthalenide with β-, γ- and δ-Lactones: An Efficient Route to α-Alkyl γ- and δ-Lactones and α,β-Unsaturated Carboxylic Acid Esters

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It is known that potassium naphthalenide can transfer a single electron to a suitable organic acceptor molecule.[1] Potassium naphthalenide can also act as a Lewis base (e.g., in its reaction with water[2,3]).

Here, we describe the outcomes of the reactions of the γ-lactones (2-oxotetrahydrofurans) **1a,b**, the δ-valerolactone (tetrahydro-2*H*-pyran-2-one) **1c**, and the β-lactones (2-oxetanones) **3a,b** with potassium naphthalenide and the potassium naphthalenide/18-crown-6 complex.

The potassium naphthalenide/18-crown-6 complex is stable for several days at room temperature, as analysis by ^{39}K NMR and ESR spectroscopy shows.[4]

Potassium naphthalenide, in either the absence or the presence of 18-crown-6, reacts with γ- and δ-lactones (mole ratio 1:1) to yield the lactone enolates which, upon alkylation, give the corresponding α-alkyl γ- and δ-lactones derivatives in high yield (Scheme I, Table I).

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(4) The ^{39}K NMR spectrum of the 0.2 M THF solution of potassium naphthalenide recorded at 20 °C showed a signal due to the potassium cation at δ = 20 ppm. After introduction of the crown ether, the signal remained at the same position, although its line width increased due to complexation of the cation by 18-crown-6. The signal due to the complexed potassium cation retained both its intensity and its line width over 72 h, as repeated measurements showed. The concentration of the naphthalene radical anion in the potassium naphthalenide/18-crown-6 solution remained unchanged as the solution's ESR spectra revealed.

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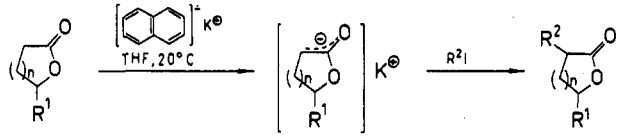
Scheme I



1a-c 2a-f

1a: R^1=H; n=1
1b: R^1=CH_3; n=1
1c: R^1=H; n=2

2a: R^1=H; R^2=CH_3; n=1
2b: R^1=H; R^2=C_2H_5; n=1
2c: R^1=CH_3; R^2=CH_3; n=1
2d: R^1=CH_3; R^2=C_2H_5; n=1
2e: R^1=H; R^2=CH_3; n=2
2f: R^1=H; R^2=C_2H_5; n=2

Table I. Products of the Reaction of Potassium Naphthalenide with γ-, δ-, and β-Lactones in THF at 20 °C

lactone	alkylating agent	product	R^1	R^2	yield[a] in % b	c
1a	CH_3I	2a	H	CH_3	94	96
1a	C_2H_5I	2b	H	C_2H_5	80	89
1b	CH_3I	2c	CH_3	CH_3	92	95
1b	C_2H_5I	2d	CH_3	C_2H_5	75	86
1c	CH_3I	2e	H	CH_3	89	94
1c	C_2H_5I	2f	H	C_2H_5	63	87
3a	CH_3I	4a	H	CH_3	82	0
3a	C_2H_5I	4b	H	C_2H_5	81	0
3b	CH_3I	4c	CH_3	CH_3	88	0
3b	C_2H_5I	4d	CH_3	C_2H_5	85	0

[a] Yield of isolated products based on the lactone. [b] Reaction performed in the presence of 18-crown-6. [c] Reaction performed in the absence of 18-crown-6.

In the reaction of equimolar quantities of potassium naphthalenide and the β-lactones **3a** and **3b**, the unstable enolate of the β-lactone is cleaved to an α,β-unsaturated carboxylate. The latter, after alkylation by methyl or ethyl iodide in the presence of 18-crown-6, yields the corresponding α,β-unsaturated acid ester (Scheme II, Table I).

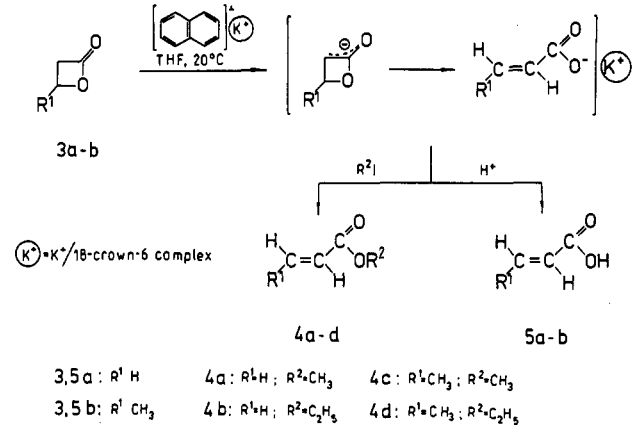
The esters **4c** and **4d**, derived from the β-alkyl β-lactone **3b**, are *E* isomers, as GC–MS analysis showed (see Experimental Section). It has been reported[5] that the reaction of β-lactones with lithium diisopropylamide also shows a tendency to form *E* isomers of α,β-unsaturated carboxylic acids.

The results indicate that, in its reactions with γ- and δ-lactones, potassium naphthalenide acts as a strong base and abstracts an α-proton from the lactone. The lactone enolate, upon treatment with methyl or ethyl iodide, yields the corresponding α-alkyl γ- or δ-lactone. Moreover, no side reactions, e.g., α,α-dialkylation or self-condensation are observed, in contrast to some other methods of enolate alkylation.[6]

No significant influence by the crown ether on the course of the reaction was observed. That this is so is probably due to the fact that the presence of the crown ether leads not only to an increase in the solubility of the enolate but also to an increase in the enolate's basisity, which enables it to abstract a proton from the solvent.[7]

In the case of β-lactones, the enolates initially formed by ring cleavage yield α,β-unsaturated carboxylate salts

Scheme II



3a-b

4a-d 5a-b

3,5a: R^1 H 4a: R^1=H; R^2=CH_3 4c: R^1=CH_3; R^2=CH_3
3,5b: R^1 CH_3 4b: R^1=H; R^2=C_2H_5 4d: R^1=CH_3; R^2=C_2H_5

which, after protonation or alkylation (in presence of 18-crown-6), yield the corresponding acids or esters, respectively (Scheme II). However, the reaction of the β-alkyl β-propiolactone **3b** with potassium naphthalenide/18-crown-6 complex, followed by alkylation with methyl iodide, yields ester **4c** and a small amount of methyl butyrate (7% yield by GC–MS). The latter is possibly the result of a side reaction that involved the transfer of a single electron from potassium naphthalenide to the carbonyl carbon of the lactone, cleavage of the alkyl carbon–oxygen bond of the radical anion so formed, and, finally, disproportionation of the butyrate radical anion.

The results demonstrate the ambivalent reactivity of potassium naphthalenide. That is, it can act either as a base or as an electron-transfer agent.

The abstraction of an α-proton from β-, γ-, and δ-lactones by potassium naphthalenide is accompanied by the partial reduction of naphthalene. Thus, the formation of 1,2- and 1,4-dihydronaphthalene (mole ratio = 1:4) was detected by GC–MS.[8]

These new reactions of potassium naphthalenide with γ-, δ-, and β-lactones represent alternative, simple routes to α-alkyl γ- and δ-lactones as well as to α,β-unsaturated carboxylic acids and esters.

Experimental Section

NMR spectra were recorded with a Varian VXR-300 multinuclear spectrometer. ^1H NMR spectra are of $CDCl_3$ solutions. TMS served as an internal standard. ^{39}K NMR spectra are of THF solutions. Aqueous KF served as an external standard. IR spectra were recorded with a Specord M80 Carl Zeiss Jena spectrophotometer. ESR spectra were recorded with a Bruker ESP-300 spectrometer at 9.62 GHz. GC–MS analyses were performed with a 30-m DB-1701 fused silica capillary column, in conjunction with a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800AT ion-trap detector. Preparative GC was performed with a 7-mm i.d. 4-m glass column packed with 20% OV-17 on 45–60 mesh Chromosorb W, in conjunction with a Varian 2800 semipreparative gas chromatograph.

General Procedure. Preparation of Dihydro-3-methyl-2(3*H*)-furanone (α-Methyl γ-Butyrolactone, 2a). A 0.2 M THF solution of potassium naphthalenide was prepared at 20 °C by exposing a THF solution of naphthalene to a potassium mirror. Then to the solution (40 mL) was added drop-by-drop a solution of γ-butyrolactone (0.69 g, 0.008 mol) in dry THF (8 mL) with vigorous magnetic stirring. A glass-covered magnetic stirring bar was used. After 10 min, a solution of CH_3I (0.54 mL, 0.0085 mol)

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(8) 1,2-Dihydronaphthalene MS: *m/z* (relative intensity) 28 (13.2), 51 (5.4), 63 (3.7), 64 (4.1), 65 (4.2), 77 (8.1), 78 (3.9), 89 (2.8), 102 (7.8), 115 (44.0), 116 (4.1), 126 (4.3), 127 (21.6), 128 (43.6), 129 (73.0), 130 (100.0, M^+), 131 (11.0). 1,4-Dihydronaphthalene MS: *m/z* (relative intensity) 77 (4.5), 85 (4.1), 87 (4.6), 102 (11.1), 115 (50.6), 116 (5.5) 127 (13.2), 128 (31.0), 129 (93.7) 130 (100.0, M^+), 131 (8.2).

in THF (2 mL) was added. The precipitate that formed was removed by filtration and was washed with THF. The filtrate and the washing were combined, and the solvent was evaporated. Distillation of the residue under reduced pressure afforded 768 mg (96%) of **2a**: IR (capillary cell) ν_{max} = 1770 cm^{-1}; ^{1}NMR ($CDCl_3$) δ 1.2 (d, 3 H, J = 6 Hz), 1.4–3.3 (m, 3 H), 4.1–4.3 (m, 2 H); MS m/z (relative intensity) 41 (100), 42 (41), 56 (70), 100 (16, M$^+$). Anal. Calcd for $C_5H_8O_2$: C, 59.99; H, 8.05. Found: C, 59.97; H, 8.05.

Reaction in the presence of the crown ether was performed in similar manner. However, in this case, a THF solution of equimolar quantities of the γ-lactone and the crown ether was added drop-by-drop to the potassium naphthalenide solution.

The following α-alkyl γ- and δ-lactones were obtained in a similar manner:

Dihydro-3-ethyl-2(3*H*)-furanone (α-ethyl γ-butyrolactone, 2b): yield, 811 mg (89%); IR (capillary cell) ν_{max} = 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0 (t, 3 H, J = 7.5 Hz), 1.5–2.7 (m, 5 H), 4.2–4.6 (m, 2 H); MS m/z (relative intensity) 114 (10, M$^+$). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.15; H, 8.80.

Dihydro-3,5-dimethyl-2(3*H*)-furanone (α-methyl γ-valerolactone, 2c): mixture of two stereoisomers (mole ratio = 3:2 by GC); yield, 866 mg (95%); IR (capillary cell) ν_{max} = 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2 (d, 3 H, J = 6.4 Hz), 1.4 (d, 3 H, J = 6.3 Hz), 1.5–2.9 (m, 3 H), 4.2–4.6 (m, 1 H); MS m/z (relative intensity) 114 (16, M$^+$). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.14; H, 8.85.

Dihydro-3-ethyl-5-methyl-2(3*H*)-furanone (α-ethyl γ-valerolactone, 2d): mixture of two stereoisomers (mole ratio = 2:1 by GC); yield, 880 mg (86%); IR (capillary cell) ν_{max} = 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0 (t, 3 H, J = 7.0 Hz), 1.2–2.6 (m and d, 8 H, J = 6.2 Hz), 4.1–4.5 (m, 1 H); MS m/z (relative intensity) 128 (4, M$^+$). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.61; H, 9.46.

Tetrahydro-3-methyl-2*H*-pyran-2-one (α-methyl δ-valerolactone, 2e): yield, 857 mg (94%); IR (capillary cell) ν_{max} = 1733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 3 H), 1.38–2.80 (m, 5 H), 4.20–4.50 (m, 2 H); MS m/z (relative intensity) 114 (3.7, M$^+$). Anal. Calcd for $C_6H_{10}O_2$: C,63.14; H, 8.83. Found: C, 63.12; H, 8.85.

Tetrahydro-3-ethyl-2*H*-pyran-2-one (α-ethyl δ-valerolactone, 2f): yield, 890 mg (87%); IR (capillary cell) ν_{max} = 1733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, 3 H), 1.20–2.70 (m, 7 H), 4.20–4.50 (m, 2 H); MS m/z (relative intensity) 128 (2.7, M$^+$). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.63; H, 9.41.

The reaction of the potassium naphthalenide/18-crown-6 complex with β-propiolactone (2-oxetanone) **3a** and β-butyrolactone (4-methyl-2-oxetanone) **3b** to yield the esters **4** was conducted in a similar manner. The following compounds were obtained after treatment of the enolate solutions with methyl and ethyl iodide, respectively.

2-Propenoic acid methyl ester (4a): yield, 564 mg (82%); IR (capillary cell) ν_{max} = 1740, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H), 5.75–6.43 (m, 3 H); MS m/z (relative intensity) 42 (12), 55 (100), 56 (70), 85 (12), 86 (2, M$^+$). Anal. Calcd for $C_4H_6O_2$: C, 55.81; H, 7.02. Found: C, 55.83; H, 7.08.

2-Propenoic acid ethyl ester (4b): yield, 648 mg (81%); IR (capillary cell) ν_{max} = 1730, 1670 cm^{-1}; ^{1}H NMR ($CDCL_3$) δ 1.30 (t, 3 H, J = 7.1 Hz), 4.21 (q, 2 H, J = 7.1 Hz), 5.76–6.44 (m, 3 H); MS m/z (relative intensity) 29 (15), 55 (100), 57 (12), 73 (8), 85 (5), 100 (2, M$^+$). Anal. Calcd for $C_5H_8O_2$: C, 59.99; H, 8.05. Found: C, 59.97; H, 8.04.

2-Butenoic acid methyl ester ((*E*)-4c): yield, 704 mg (88%); IR (capillary cell) ν_{max} = 1745, 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.89 (dd, 3 H), 3.73 (s, 3 H), 5.86 (dq, 1 H), 6.9–7.1 (m, 1 H); MS m/z (relative intensity) 15 (10), 28 (5), 29 (4), 38 (3), 39 (25), 41 (48), 43 (3), 53 (2), 55 (3), 59 (5), 68 (3), 69 (100), 70 (5), 85 (23), 100 (19, M$^+$), 101 (2). Anal. Calcd for $C_5H_8O_2$: C, 59.99; H, 8.05. Found: C, 59.99; H, 8.06.

2-Butenoic acid ethyl ester ((*E*)-4d): yield, 775 mg (85%); IR (capillary cell) ν_{max} = 1740, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (t, 3 H, J = 7.0 Hz), 1.88 (dd, 3 H), 4.2 (q, 2 H, J = 7.0 Hz); 5.85 (dq, 1 H), 6.9–7.2 (m, 1 H); MS m/z (relative intensity) 39 (17), 41 (22), 45 (4), 68 (6), 69 (100), 70 (5), 86 (8), 99 (30), 100 (4), 114 (2, M$^+$). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.16; H, 8.80.

2-Propenoic acid (5a) was prepared according to the general procedure. However, when the reaction of potassium naphthalenide with lactone **3a** was complete, the THF was partly evaporated and the precipitate that formed was collected by filtration and was washed with THF. Then, the precipitate was dissolved in Et_2O which also contained ion-exchange resin (Lewatit S 1080), acid form, Merck). The mixture was filtered to remove the resin. Evaporation of solvent from the filtrate afforded 461 mg (80%) of **5a**: IR (capillary cell) ν_{max} = 1700, 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.7–6.8 (m, 3 H), 10.2 (s, 1 H); MS m/z (relative intensity) 55 (60), 72 (70, M$^+$). Anal. Calcd for $C_3H_4O_2$: C, 50.01; H, 5.60. Found: C, 50.03; H, 5.58.

Similarly obtained was the following.

2-Butenoic acid ((*E*)-5b): yield, 571 mg (83%); IR (capillary cell) ν_{max} = 1700, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.9 (d, 3 H), 5.9 (d, 1 H), 7.0–7.2 (m, 1 H), 9.1 (s, 1 H); MS m/z (relative intensity) 69 (30), 86 (100, M$^+$). Anal. Calcd for $C_4H_6O_2$: C, 55.81; H, 7.02. Found: C, 55.80; H, 7.09.

Registry No. **1a**, 96-48-0; **1b**, 108-29-2; **1c**, 542-28-9; **2a**, 1679-47-6; **2b**, 13888-01-2; **2c**, 5145-01-7; **2d**, 19639-00-0; **2e**, 10603-03-9; **2f**, 32821-68-4; **3a**, 57-57-8; **3b**, 3068-88-0; **4a**, 96-33-3; **4b**, 140-88-5; **4c**, 623-43-8; **4d**, 623-70-1; **5a**, 79-10-7; **5b**, 110-17-8; potassium naphthalenide, 4216-48-2.

Hypochlorite-Induced Substitution of Chlorine for Bromine in Aromatic Compounds

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Aqueous hypochlorite and phase-transfer catalysts induce oxidation of aldehydes, amines, and primary and secondary alcohols,[1] oxidative decarboxylation of certain trisubstituted acetic acids with oxidative cleavage of corresponding tertiary alcohols,[2] and formation of alkyl and aromatic chlorides from alkanes and activated aromatics via substitution for hydrogen.[3]

In research focusing on defining the role of pH in such hypochlorite reactions, chlorinated benzenes show considerable utility as internal standards for gas and liquid chromatographic analysis.[2,4] Specifically, chlorobenzene and 1,4-dichlorobenzene are stable to conditions and have suitable retention times for inclusion with reactants to serve as quantitative and qualitative "bench marks" for monitoring the course of reactions.

In contrast, the present research has revealed that brominated benzenes are demonstrably unstable, reacting with aqueous hypochlorite in a biphasic system including the phase-transfer catalyst, tetra-*n*-butylammonium bisulfate, to give the corresponding chloroaromatics. At ambient temperature and pH 7.5–9, conventional for hypochlorite oxidations, bromobenzene is converted to chlorobenzene with a reaction half life of 2–5 h. The

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