Experimental Section

Melting points were uncorrected. Thin-layer chromatography was performed on silica gel [GF_{254} (Type 60), Merck] or aluminum oxide [GF_{254} (Type 150), Merck], using a mixture of chloroform and methanol in the following volume ratios: solvent A, 17:3; B, 5:1; C, 5:2. Column chromatography was carried out using silica gel [Merck (art. 7734), 70–230 mesh].

Commercially available uracil (**1**), thymine (**2**), cytosine (**5**), uridine (**7**), thymidine (**10**), inosine (**13**), and cytidine (**16**) were used without further purification.

Preparation of Trimethyloxosulfonium Hydroxide (MOSH). Trimethyloxosulfonium iodide[7] (5.0 g, 22.7 mmol) was dissolved in a hot mixture of methanol and water (500 mL–1 mL). Excess silver oxide (5.3 g, 23.0 mmol) was added to the solution and the mixture was stirred at room temperature. After 1 h, a few drops of the supernatant was removed, acidified with dilute nitric acid, and tested for iodide with a silver nitrate solution. The checking was repeated until the reaction was complete. The reaction mixture was filtered, concentrated to 100 mL, and used for the subsequent methylation reactions. The concentration of MOSH was determined by titration with 0.1 N hydrochloric acid to be 0.216 N; the yield was calculated as 95%. MOSH was stable in methanol for several months upon storage in a refrigerator.

The neat sample of MOSH gave the following spectral data: IR (KBr) 3350 (s), 2950 (m), 1645 (bm), 1480 (m), 1210 (s), 1105 (s), 1047 (s), and 950 (m) cm^{-1}; NMR (Me_2SO-d_6) τ 2.98 (s, CH_3); mass spectrum (75 eV) *m/e* 92 (M − H_2O), 78 (92 − CH_2), 77 (92 − CH_3) and 63 ($CH_3S{=}O$).

Reaction of the methanol solution of MOSH with equivalent amounts of hydrochloric acid or hydroiodic acid gave trimethyloxosulfonium chloride or iodide, respectively, in quantitative yields.

Methylation Reactions. The following are isolation procedures. The mobilities (R_f) of products in thin-layer chromatography are shown in Table I with references on the UV spectral peak at pH 7. UV spectra at pH 1 and 13 as well as the melting points of all known compounds agreed in most cases with literature values. The NMR spectra were obtained in all compounds and coincided with the assigned structures. Yields are calculated after recrystallization and are based on the isolated amounts of products. Spectroscopic yields of products in reaction mixtures were determined in a manner similar to that employed in our previous study.[18]

Products (**9**, **12**, and **15**) were identified by a comparison of R_f values and UV spectra of the aqueous extracts of the corresponding spots in thin-layer chromatography of reaction mixtures with those of authentic samples.[19]

Reaction conditions and results are summarized in Table I.

A. Pyrimidines (1, 2, and 5). These heterocycles (5.0 mmol) were dissolved in the methanol solution of MOSH prepared as above (20.0 mmol). The solvent was removed under reduced pressure and the residues were dissolved in DMF (30 mL) and warmed at 80 °C for 2 h. The reaction mixtures were concentrated and the resulting substances were purified by recrystallization from suitable solvents (ethanol–diethyl ether, ethanol–water, and water for **3**, **4**, and **6**, respectively).

B. Uridine (7). The nucleoside (1.22 g, 5.0 mmol) was mixed with the methanol solution of MOSH (7.0 mmol). The solvent was removed from the mixture and the residue in DMF (30 mL) was heated at 60 °C for 3 h. The reaction mixture was concentrated under reduced pressure and applied to a silica gel chromatograph (1.5 × 55 cm) using chloroform–methanol (8:1 v/v) as a solvent. The fraction (200–530 mL) gave crude 3-methyluridine (**8**), which was recrystallized from ethyl acetate–methanol: 0.78 g (60%); mp 118.5–119 °C (lit.[20] 119–120 °C).

C. Thymidine (10). The treatment of **10** (1.21 g, 5.0 mmol) with MOSH (7.0 mmol) in DMF (30 mL) at 60 °C for 4 h provided 3-methylthymidine (**11**) after processing the reaction mixture in a manner similar to that mentioned above: 0.95 g (75%); mp 130–131 °C (chloroform) (lit.[21] 128.5–132 °C).

D. Cytidine (16). Compound **16** (1.22 g, 5.0 mmol) was allowed to react with the methanol solution of MOSH (7.0 mmol) in DMF (30 mL) at 100 °C for 1 h. Thereafter, 3 mmol, 3 mmol, and 2 mmol of the reagent solution were added at hourly intervals to the reaction mixture. After the last of the MOSH solution was added, heating was continued for 2 h. The resulting solution was concentrated and applied to a silica gel column chromatograph (1.5 × 70 cm), using a mixture of chloroform and methanol (3:1 v/v) as a solvent. $O^{2'}$-Methylcytidine (**17**) was eluted in the fraction (70–110 mL): 0.54 g (43%); mp 257–258 °C (ethanol) (lit.[14] 256–257 °C).

E. Inosine (13). The nucleoside (1.34 g, 5.0 mmol) was treated with MOSH (7.0 mmol) in DMF (30 mL) at 60 °C for 7.5 h. The reaction mixture was concentrated under reduced pressure to give the residue, which was washed with diethyl ether and then extracted with hot acetone. 1-Methylinosine (**14**) was obtained as a white precipitate from the cooled extract: 0.70 g (50%); mp 207–208 °C (ethanol–methanol) (lit.[22] 209–210 °C).

Registry No.—3-Methylcytidine, 2140-64-9; trimethyloxosulfonium hydroxide, 65150-70-1; trimethyloxosulfonium iodide, 1774-47-6.

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(*Z*)-2-Ethoxyvinyllithium: A Remarkably Stable and Synthetically Useful 1,2-Counterpolarized Species[1]

Kreisler S. Y. Lau and Manfred Schlosser*

Institut de Chimie Organique de l'Université de Lausanne, CH-1005 Lausanne, Switzerland

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(*Z*)-2-Ethoxyvinyllithium ((*Z*)-**1**) can easily be prepared by halogen/metal exchange between (*Z*)-2-ethoxyvinyl bromide and butyllithium in diethyl ether at −80 °C.[2] Addition of an aldehyde or a ketone followed by hydrolysis leads to the formation of (*Z*)-3-hydroxy enethers (**2**) which may be alkylated to afford alkenyl diethers (**3**) or to be converted, by acid treatment, into α,β-unsaturated aldehydes (**4**). Examples are listed in Table I.

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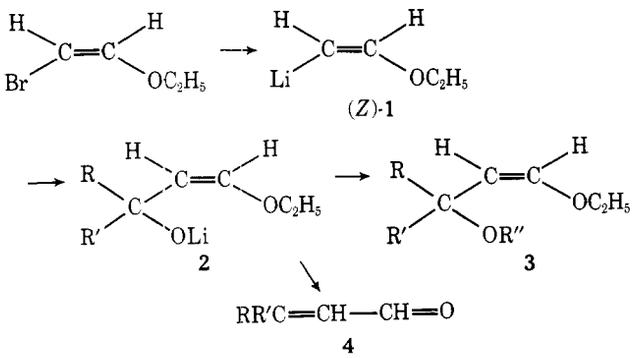
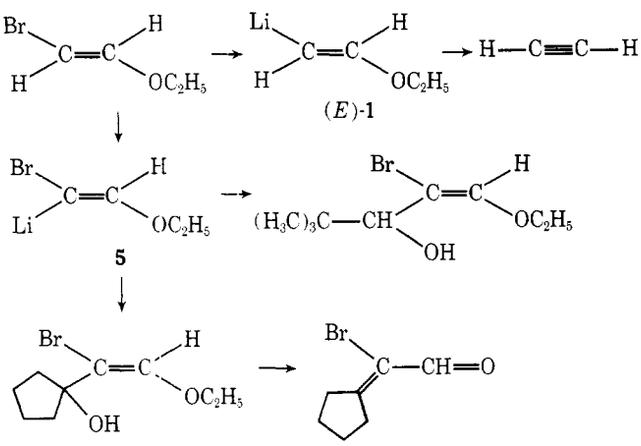
Table I. Products Derived from (*Z*)-2-Ethoxyvinyllithium[g] and Carbonyl Compounds RR'C=O

	Formula	Registry no.	Yield[a,b]
2,[c]	R = C_6H_5; R' = H	65275-94-7	84%
3,	R = C_6H_5; R' = H; R'' = CH_3	65275-93-6	63%[d]
3,	R = C_6H_5; R' = H; R'' = $CH_2C_6H_5$	65392-07-6	54%[d]
4,	R = C_6H_5; R' = H	14371-10-9	46% (62%)[e]
4,	R = $C(CH_3)_3$; R' = H	926-37-4	60% (70%)
4,	R = $C(CH_3)_3$; R' = CH_3	65275-95-8	25% (30%)[f]
4,	R, R' = $-(CH_2)_4-$	5623-82-5	44% (50%)

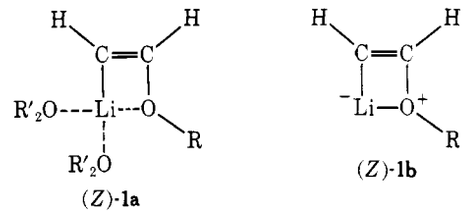
[a] Yield of pure, distilled product; values in parentheses are yields as determined by GC techniques. [b] All (*Z*)-3-hydroxy enethers (**2**) are fairly unstable, the favorite decomposition mode being the loss of water. [c] After hydrolysis, i.e., OH instead of OLi. [d] With respect to **2**. [e] The product (cinnamaldehyde) was compared with an authentic sample by GC on two different columns; it had exclusively the *E* configuration. [f] The product, apparently being homogeneous (see Experimental Section), is supposed to possess the thermodynamically favored *E* configuration. [g] Registry no.: 64724-28-3.



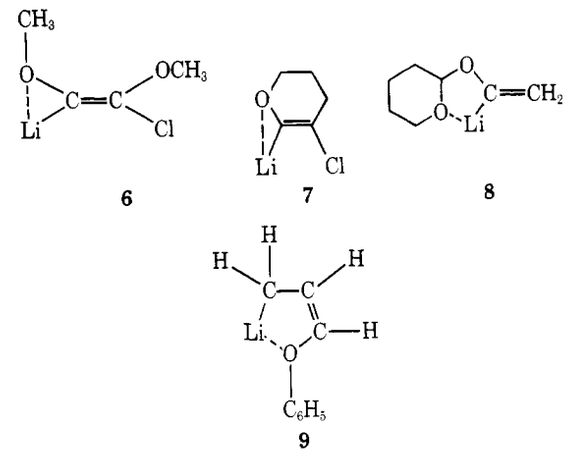
On the contrary, (*E*)-2-ethoxyvinyl bromide undergoes hydrogen/lithium rather than bromine/lithium exchange when treated with butyllithium. The resulting (*E*)-1-bromo-2-ethoxyvinyllithium[4] (**5**) was trapped by addition



onto pivalaldehyde (yielding 58% (*E*)-1-ethoxy-2-bromo-4,4-dimethyl-1-penten-3-ol) and cyclopentanone (yielding 30% cyclopentylidene-α-bromoacetaldehyde, mp 91–92 °C, after acid hydrolysis). Upon interaction of lithium dihydrobiphenylylide ("biphenyl/lithium 1:1 adduct"), (*E*)-2-ethoxyvinyl bromide does produce (*E*)-2-ethoxyvinyllithium ((*E*)-**1**) which cannot, however, be intercepted. At −80 °C it instantaneously decomposes to afford lithium ethoxide and acetylene, the latter being identified by its conversion to 2,2,7,7-tetramethyl-4-octyne-3,6-diol (22%, after consecutive addition of 2 equiv of butyllithium and pivalaldehyde). (*Z*)-**1** is stable in diethyl ether up to −50 °C or even to −30 °C in the presence of tetrahydrofuran and 1,2-dimethoxyethane. This exceptional stability may be contrasted with the lability of (*E*)-**1** or that of 2-methoxyethyllithium (trapped in only 5.3% yield at −130 °C[5]) and can be attributed to the interplay of two factors: the lack of a favorable trans-(anti-) elimination mode[6,7] and an optimum geometry for intramolecular solvation. The latter effect may be depicted in terms of an oxygen–lithium partial bond[3] ((*Z*)-**1a**, externally solvated by two ether molecules) or an ate complex[8] ((*Z*)-**1b**).



Intramolecular solvation of lithium by an oxygen atom is well established, the hetero element being either directly attached to the metal-bearing carbon atom or situated in the next position but one. 1-Ethoxyvinyllithium,[9,10] (*E*)-2-chloro-1,2-dimethoxyvinyllithium (**6**),[11] 1,2-dimethoxyvinyllithium (configuration undefined)[12] or 3-chloro-2-lithio-5,6-dihydro-4*H*-pyran (**7**),[13] and 1-(2-tetrahydropyranyloxy)vinyllithium (**8**)[14] or (*Z*)-3-phenoxyallyllithium (**9**)[15] represent typical examples for each pattern of interaction.



As the formation of α,β-unsaturated aldehydes demonstrates, (*Z*)-**1** is equivalent to the acetaldehyde anion. Other substitutes for this unaccessible species are α-metalated ethylideneamines[16,17] or bromomagnesium ethoxyacetylide[18] (when allowed to perform a carbon–carbon linking step followed by a Lindlar hydrogenation). Because of the ease of its preparation and the mild reaction conditions (*Z*)-**1** compares favorably with those reagents.

Experimental Section

For general remarks, see ref 15 and 19.

1-Bromo-2-ethoxyethylene. The isomeric mixture was prepared according to a modified literature procedure.[20] Bromine (160 g, 1.00 mol) was added dropwise to ethyl vinyl ether (72 g, 1.00 mol) in dichloromethane (100 mL) at −78 °C. The slightly yellow solution was slowly added to tributylamine (200 g, 1.08 mol) kept at 100 °C and under 75 mmHg over a period of 4 h. A distillate was continuously collected in a cold trap. Distillation of this liquid through a Vigreux column (30 cm) afforded two fractions: 59 g, bp 56–61 °C (46 mmHg), *Z*:*E* = 64:36 and 66.8 g, bp 62–64 °C (46 mmHg), *Z*:*E* = 95:5, total yield 84%; GC (3 m, 15% UCC-W, glass column, 70 °C) permitted clean separation of the isomers; NMR (CCl_4) of the *Z* isomer, δ 6.65 (d, *J* = 4 Hz, 1 H), 5.10 (d, *J* = 4 Hz, 1 H), 4.02 (q, *J* = 7.5 Hz, 2 H), 1.36 (t, *J* = 7.5 Hz, 3 H); NMR (CCl_4) of the *E* isomer, δ 6.78 (d, *J* = 12 Hz, 1 H), 5.38 (d, *J* = 12 Hz, 1 H), 3.82 (q, *J* = Hz, 2 H), 1.31 (t, *J* = 7 Hz, 3 H).

(Z)-3-Ethoxy-1-phenyl-2-propen-1-ol and Its Derivatives. (Z)-1-Bromo-2-ethoxyethylene (3.57 g, 23.7 mmol) was dissolved in diethyl ether (10 mL) and treated at −80 °C under nitrogen with a 1.56 N hexane solution (16.7 mL) of butyllithium (26.1 mmol). The mixture was kept 24 h at −80 °C before benzaldehyde (1.55 g, 14.6 mmol) was added. At 25 °C it was hydrolyzed with water (20 mL). The aqueous phase was extracted with diethyl ether (2 × 10 mL); the combined organic fractions were washed with water (2 × 10 mL), dried ($MgSO_4$), and concentrated. Careful bulb-to-bulb (Kugelrohr) distillation gave 3.55 g (84%) of colorless (Z)-3-ethoxy-1-phenyl-2-propen-1-ol, bp 120–125 °C (0.5 mmHg); IR (film) 3380 (br), 1665 (s) cm^{-1}; NMR (CCl_4) δ 7.5 (m, 5 H), 6.00 (d × d, J = 6, 1.5 Hz, 1 H), 5.68 (d × d, J = 8.5, 1.5 Hz, 1 H), 4.64 (d × d, J = 8.5, 6 Hz, 1 H), 3.80 (q, J = 7 Hz, 2 H), 1.23 (t, J = 7 Hz, 3 H); mass spectrum *m/e* 132 (100%, $M^+ - H_2O$, C_2H_4).

The alcohol (3.38 g, 19.0 mmol) was added to a vigorously stirred suspension of sodium hydride sand (0.52 g, 21.7 mmol) in 20 mL of diethyl ether. After 3 h the reaction mixture was treated with methyl iodide (12 g, 85 mmol), first at 25 °C and then 2 h at reflux temperature. After filtration the liquid was concentrated and distilled to afford 2.31 g (63%) of (Z)-1-ethoxy-3-methoxy-3-phenylpropene: bp 58.0–58.5 °C (0.5 mmHg); IR (film) 3120–2810 (m), 1660 (s) cm^{-1}; NMR (CCl_4) δ 7.4 (m, 5 H), 6.12 (d × d, J = 6.5, 1.5 Hz, 1 H), 5.21 (d × d, J = 9.5, 1.5 Hz, 1 H), 4.50 (d × d, J = 9.5, 6.5 Hz, 1 H), 3.31 (s, 3 H), 3.85 (q, J = 7 Hz, 2 H), 1.25 (t, J = 7 Hz, 3 H); mass spectrum *m/e* 192 (34%, M^+), 121 (100%).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.09; H, 8.23.

Analogously, by consecutive treatment with sodium hydride (0.33 g, 14 mmol) and benzyl bromide (2.35 g, 13.7 mmol) in tetrahydrofuran (15 mL), (Z)-3-ethoxy-1-phenyl-2-propen-1-ol was converted into (Z)-3-benzyloxy-1-ethoxy-3-phenylpropene, yield 1.89 g (54%): bp 120–125 °C (0.5 mmHg); IR (film) 3080–2860 (s), 1660 (s) cm^{-1}; NMR (CCl_4) δ 7.3 (m, 10 H), 6.08 (d × d, J = 6.5, 1.5 Hz, 1 H), 5.44 (d × d, J = 9.5, 1.5 Hz, 1 H), 4.6 (m, br, 3 H), 3.78 (q, J = 7 Hz, 2 H), 1.21 (t, J = 7 Hz, 3 H); mass spectrum *m/e* 197 (100%, $M^+ - C_4H_7O$).

In another experiment the (Z)-3-ethoxy-1-phenyl-2-propen-1-ol, without being isolated, was acidified to pH 2. After 2 h of stirring, the reaction mixture was extracted with diethyl ether (2 × 10 mL). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate solution (10 mL) and water (10 mL), dried, and concentrated. Distillation of the residual oil gave pure cinnamaldehyde. The yield, based on (Z)-1-bromo-2-ethoxyethylene, was 0.89 g (46%): bp 145–150 °C (4 mmHg).

4,4-Dimethyl-2-pentenal.[21] To a solution of *tert*-butyllithium (35.2 mmol) in tetrahydrofuran (75 mL) and hexane (25 mL), cooled to −80 °C, (Z)-1-bromo-2-ethoxyethylene (2.57 g, 17.0 mmol) and, after 30 min, pivaldehyde (2.9 g, 40 mmol) were added. After the mixture had reached room temperature, it was hydrolyzed (20 mL of 15% hydrochloric acid) and worked up by extraction (2 × 20 mL of diethyl ether) and distillation. The crude product (1.15 g, 60%; bp 138–140 °C) was further purified by GC (3 m, 15% Carbowax 20M, glass column, 90 °C): IR (film) 2900 (s), 2880 + 2830 + 2740 (m), 1700 (s), 1130 (s), 995 (m) cm^{-1}; NMR ($CDCl_3$) δ 9.53 (d, J = 7.5 Hz, 1 H) 6.83 (d, J = 16 Hz, 1 H), 6.04 (d × d, J = 16 + 7.5 Hz, 1 H), 1.13 (s, 9 H); mass spectrum *m/e* 112 (14%, M^+), 97 (100%).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.71; H, 10.83.

In a series of similar runs (Z)-2-ethoxyvinyllithium (prepared as usual at −80 °C) was kept 15 min at a given temperature in the range between −60 and −20 °C before being treated with pivalaldehyde. As evidenced by the yields of 4,4-dimethyl-2-pentenal, (Z)-2-ethoxyvinyllithium is stable in tetrahydrofuran solution up to −45 °C; in an ethylene glycol dimethyl ether/tetrahydrofuran mixture (1:1) it is perfectly stable up to −35 °C and fairly stable up to −30 °C.

3,4,4-Trimethyl-2-pentenal. Consecutive treatment of (Z)-1-bromo-2-ethoxyethylene (2.86 g, 18.9 mmol) in diethyl ether (10 mL) with butyllithium (20.8 mmol in 16.5 mL of hexane, 24 h at −78 °C), 2,2-dimethyl-3-butanone (pinacolone, 1.80 g, 18.0 mmol, at −78 °C) and hydrochloric acid (10%, 24 h at 25 °C) gave 3,4,4-trimethyl-2-pentenal, which was purified by preparative GC (6 m, 20% C-20-M, glass column, 130 °C): IR (film) 2960 (s), 2870 (m), 1680 (s) cm^{-1}; NMR (CCl_4) δ 10.08 (d, J = 7.5 Hz, 1 H), 5.91 (d × q, J = 7.5, 1.5 Hz, 1 H), 2.19 (d, J = 1.5 Hz, 3 H), 1.15 (s, 9 H); mass spectrum *m/e* 126 (50%, M^+), 111 (100%).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.05; H, 10.99.

Cyclopentylideneacetaldehyde. Using the same procedure described above and starting out with (Z)-1-bromo-2-ethoxyethylene (1.44 g, 9.5 mmol), butyllithium (10.5 mmol), and cyclopentanone (0.76 g, 9.1 mmol), 0.44 g (44%) cyclopentylideneacetaldehyde was obtained; bp 30–35 °C (0.5 mmHg); IR (film) 2960 (m), 2885 (m), 1685 (s) cm^{-1}; NMR (CCl_4) δ 9.92 (d, J = 7.5 Hz, 1 H), 6.01 (d × pentet, J = 7.5, 2.5 Hz, 1 H), 3.3–2.2 (m, 4 H), 2.2–1.3 (m, 4 H); mass spectrum *m/e* 110 (100%, M^+).

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.46; H, 9.07.

Cyclopentylidene-α-bromoacetaldehyde. (E)-1-Bromo-2-ethoxyethylene (1.0 g, 6.6 mmol) in diethyl ether (5 mL) and butyllithium (7.4 mmol) in hexane (6 mL) were mixed at −78 °C. After 6 h at −50 °C, cyclopentanone (0.53 g, 6.3 mmol) was added. At 25 °C the reaction mixture was acidified with 10% hydrochloric acid to pH 2 and stirred for 5 h. Extraction with ether (2 × 10 mL), washing (10 mL of $NaHCO_3$ solution, 10 mL of water), drying ($MgSO_4$), and solvent evaporation yielded a viscous oil which was taken up in 20 mL of petroleum ether and stored at −5 °C. The white crystalline solid formed overnight was recrystallized from pentane: yield, 0.37 g (30%); mp 91–92 °C; IR (KBr) 2970 (m), 2880 (m), 1700 (s), 1675 (s), 1610 (s) cm^{-1}; NMR (CCl_4) δ 9.63 (s, 1 H), 2.8 (m, 4 H), 2.0 (m, 4 H); mass spectrum *m/e* 190 (95%, M^+), 109 (100%).

Anal. Calcd for C_7H_9BrO: C, 44.50; H, 4.80. Found: C, 44.10; H, 5.25.

(E)-1-Ethoxy-2-bromo-4,4-dimethyl-1-penten-3-ol.[21] At −80 °C a hexane solution (2.1 mL) of butyllithium (3.2 mmol) was added dropwise to (E)-1-bromo-2-ethoxyethylene (0.44 g, 2.9 mmol) in diethyl ether (5 mL). After 16 h at −60 °C, pivalaldehyde (0.44 g, 6.0 mmol) was added. The reaction mixture was briefly shaken with 5 N hydrochloric acid (5 mL), washed, dried, and evaporated. The residual, almost colorless oil (0.4 g) was purified by GC (3 m, 15% UCC-W, 145 °C): IR (film) 3450 (s), 2950 + 2870 (s), 1645 (s), 1190 + 1075 (s) cm^{-1}; NMR ($CDCl_3$) δ 6.49 (s, 1 H), 4.33 (s, 1 H), 3.86 (q, J = 7 Hz, 2 H), 2.47 (s, 1 H), 1.26 (t, J = 7 Hz, 3 H), 0.99 (s, 9 H).

Anal. Calcd for $C_9H_{17}BrO_2$: C, 45.58; H, 7.23. Found: C, 45.30; H, 6.41.

2,2,7,7-Tetramethyl-4-octyne-3,6-diol.[21] Upon dropwise addition of (E)-1-bromo-2-ethoxyethylene (0.21 g, 1.4 mmol) to a fresh solution of lithium dihydrobiphenylylide[22] (3 mmol) in tetrahydrofuran (15 mL) at −80 °C, the deep-blue "radical-anion" color changed to light red. The reaction mixture was consecutively treated with butyllithium (2.8 mmol) in hexane at −80 °C and pivalaldehyde (1.1 g, 15 mmol) at −30 °C and then hydrolyzed (10 mL of 1 N hydrochloric acid). According to GC (2 m, 15% Carbowax 20M, glass column, 80–200 °C; 2 m, 15% UCC-W, 130–200 °C; octanol as an "internal standard") the organic layer contained *meso*- and *dl*-2,2,7,7-tetramethyl-4-octyne-3,6-diol (22% yield), identified by comparison with an authentic sample.[23]

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Registry No.—(Z)-1-Bromo-2-ethoxyethylene, 23521-49-5; (E)-1-bromo-2-ethoxyethylene, 16339-88-1; benzaldehyde, 100-52-7; benzyl bromide, 100-39-0; pivaldehyde, 630-19-3; 2,2-dimethyl-3-butanone, 75-97-8; cyclopentanone, 120-92-3; cyclopentylidene-α-bromoacetaldehyde, 65275-96-9; (E)-1-ethoxy-2-bromo-4,4-dimethyl-1-penten-3-ol, 65275-97-0; *meso*-2,2,7,7-tetramethyl-4-octyne-3,6-diol, 54277-04-2; *dl*-2,2,7,7-tetramethyl-4-octyne-3,6-diol, 54277-05-3.

References and Notes

(1) Part 7 of the series "Selective Syntheses with Organometallics." For the preceding paper see M. Stähle, J. Hartmann, and M. Schlosser, *Helv. Chim. Acta*, **60**, 1730 (1977).

(2) Previously (Z)-**1** had been only obtained as a by-product (10%) accompanying (Z)-1-bromo-2-ethoxyvinyllithium when (Z)-2-ethoxyvinyl bromide was treated with butyllithium in a tetrahydrofuran/hexane mixture at −100 °C (J. Ficini and J. C. Depezay, *Tetrahedron Lett.*, 937 (1968)). It is a general rule[3] that low temperatures and solvent polarity facilitate the hydrogen/metal exchange more than other reactions including halogen/metal exchange. Tetrahydrofuran, however, turned out to be a very suitable solvent if *tert*-butyllithium is applied to bring about the bromine/lithium exchange (see Experimental Section: preparation of 4,4-dimethyl-2-pentenal). According to two reports which have just appeared (R. H. Wollenberg, K. F. Albizati, and R. Peries, *J. Am. Chem. Soc.*, **99**, 7365 (1977); J. Ficini, S. Falou, A. M. Touzin, and J. d'Angelo, *Tetrahedron Lett.*, 3589 (1977)), (Z)-**1** can also be obtained by metal/metal exchange between tributyl-(Z)-2-ethoxyvinyltin and butyllithium at −70 °C.

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(4) A mixture of (Z)- and (E)-1-bromo-2-ethoxyvinyllithium had previously been generated by treatment of 1,1-dibromo-2-ethoxyethylene with butyllithium (J. Ficini, personal communication; see J. C. Depezay, Ph.D. thesis, Université de Paris, 1969).

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(13) This compound is stable up to 80 °C (M. Schlosser and Nguyen Dinh Ly, unpublished) whereas 2-fluoro-1-cyclohexenyllithium appears to cleave off lithium fluoride already around −120 °C (G. Wittig and U. Meyer, *Chem. Ber.*, **96,** 329 (1963)).
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Chemistry of Alkali Metal Tetracarbonylferrates. Synthesis of Aldehydes and Reductive Dehalogenation by a Polymer-Supported Iron Carbonyl Complex

Gianfranco Cainelli,* Francesco Manescalchi, and Achille Umani-Ronchi

Istituto Chimico "G. Ciamician", Università di Bologna, Bologna, Italy

Mauro Panunzio

Laboratorio dei composti contenenti eteroatomi, C.N.R., Ozzano Emilia, Italy

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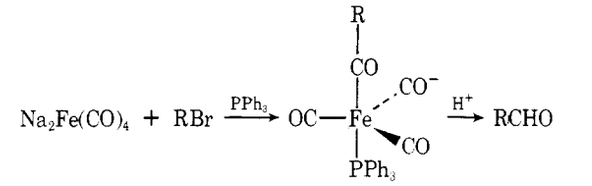
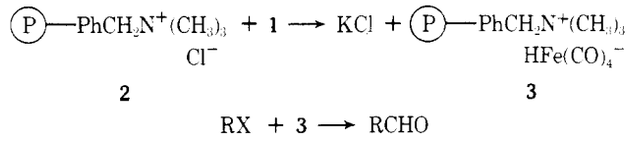
Recently several works have demonstrated that alkali metal tetracarbonylferrates ($M_2Fe(CO)_4$) and the corresponding alkali metal tetracarbonylhydridoferrates ($MHFe(CO)_4$) are useful reagents in organic synthesis.[1] The treatment of an aldehyde or a ketone containing the partial structure CH_3COR or $R'CH_2COR$ with an aldehyde in the presence of $MHFe(CO)_4$ in ethanol or water results in reductive alkylation of the carbonyl compound in high yield.[2] Moreover, $M_2Fe(CO)_4$ is able to convert alkyl halides, acid chlorides, and carboxylic anhydrides into ketones and carboxylic acid derivatives.[3] Aldehydes are also obtained in high yield from alkyl halides in the presence of added triphenylphosphine or CO.[4] We now find that similar results can be obtained supporting the reagent on a polymeric matrix by an exchange process with an ion-exchange resin (Amberlyst A-26) in the chloride form. The tetracarbonylhydridoferrate anion, prepared in alcoholic solution from iron pentacarbonyl and potassium hydroxide as described elsewhere,[5] rapidly and quantitatively exchanges, under an inert atmosphere, with the chloride ion simply on stirring the resin **2** a few minutes with the solution of hydride **1**. The resin **3** prepared by this method, filtered off and washed



$$Fe(CO)_5 + 3KOH \longrightarrow \underset{\mathbf{1}}{KHFe(CO)_4} + K_2CO_3 + H_2O$$



$$RX + 3 \longrightarrow RCHO$$

as indicated in the Experimental Section, was directly utilized to convert alkyl halides to homologous aldehydes in THF solution under reflux. The choice of the solvent is critical to avoid side reactions. In fact, in benzene, isooctane, and petroleum ether the autocondensation of aldehyde was prevailing. Hexane seems to be useful, although the yield is, in this case, lower. The results of the application of this system to several alkyl halides are summarized in Table I. The yields of the aldehydes are very high and the ease and simplicity of the method seem to provide an improvement over other existing procedures. We have to note, however, that alkyl chlorides fail to react while secondary alkyl halides are subjected to E2 elimination in the presence of the basic iron complex **3**.

The most remarkable advantages of our technique are the possibility of a facile drying of the reagent and the ease of separation of the reaction products, which are simply recovered by filtering off the resin while the iron complex remains bound to the polymer. As a matter of fact the separation of iron-containing byproducts from the organic compounds constitutes a hard to solve problem which limits the usefulness of the usual procedure in solution.[4] Moreover, with our resin **3** there is no need for added ligand to perform the reaction as is necessary with Cooke's procedure.[4]

A possible explanation of this remarkable difference is that on the resin the migratory insertion required is induced by the halogen anion formed. It has been indeed demonstrated that the nucleophilicity of halogen ions is strongly enhanced if they are bonded on the resin.[6]

Table I. Reaction of the Polymer-Supported $FeH(CO)_4^-$ Anion with Alkyl Halides

Alkyl halide	Registry no.	Product[a]	Registry no.	Solvent[b,c]	Yield, %[d]
n-$C_7H_{15}Br$	629-04-9	n-$C_7H_{15}CHO$	124-13-0	THF	90
n-$C_8H_{17}Br$	111-83-1	n-$C_8H_{17}CHO$	124-19-6	THF	90
n-$C_8H_{17}Br$		n-$C_8H_{17}CHO$		Hexane[e]	60
n-$C_8H_{17}I$	629-27-6	n-$C_8H_{17}CHO$		THF	95
$C_6H_5CH_2CH_2Br$	103-63-9	$C_6H_5CH_2CH_2CHO$[f]	104-53-0	THF	80
$EtOCO(CH_2)_3Br$	2969-81-5	$EtOCO(CH_2)_3CHO$[g]	22668-36-6	THF	85

[a] All products were identified by comparison with authentic samples and by spectroscopic data. [b] At reflux for 4 h. [c] The use of other solvents as benzene, isoctane, and petroleum ether (75–120) caused the formation of autocondensation products. [d] Yields were determined by GLC using an internal standard. [e] At reflux for 10 h. [f] Product isolated and identified as 2,4-dinitrophenylhydrazone.

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