(peak enhancement) and proton magnetic resonance (on preparative gas chromatography samples).

1,1-Diiodo-2,2-dimethylpropane (1.61 g, 4.98 mmol) in 1,2-dichloroethane (35 mL) was stirred with an aqueous solution of 10% sodium thiosulfate and 10% sodium bicarbonate (10 mL) and irradiated for 31 h. A sample of the organic layer was analyzed by gas chromatography with cyclopentane as an internal standard. Yields are as indicated in Table I. The identity of the major product was confirmed by a proton magnetic resonance spectrum obtained for the first fraction of the distillate of the dried (potassium carbonate) organic layer.

Diiodomethylbenzene (1.72 g, 5 mmol) in solvent (35 mL) as indicated in Table II was irradiated for 20 h. For the cases where no aqueous layer was used during the irradiation, it was added with stirring prior to the analysis. Fluorene (ca. 30 mg) was then added as an internal standard, and the organic layer was analyzed by gas chromatography.

Acknowledgment. We thank Professor Kropp for kindly sharing with us his results and comments during the preparation of this manuscript.

Registry No. 1,1-Diiodo-2,2-dimethylpropane, 2443-89-2; α,α-diiodotoluene, 28000-59-1; 2-methyl-2-butene, 513-35-9; 1-iodo-2,2-dimethylpropane, 15501-33-4; stilbene, 588-59-0; benzyl iodide, 620-05-3; benzaldehyde, 100-52-7.

Reaction of 4-(Iodomethyl)azetidin-2-ones with Tetracarbonylferrate(-II)

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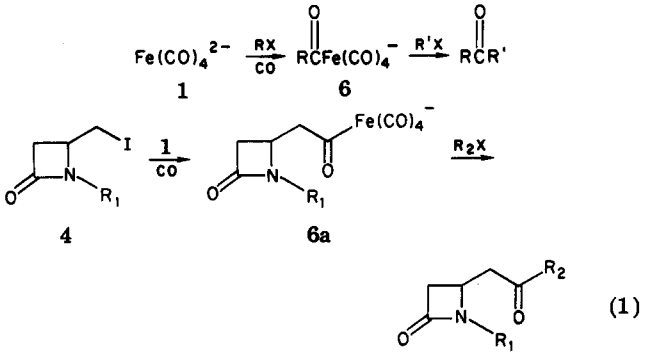
Collman and co-workers have recently introduced the use of disodium tetracarbonylferrate(-II) as a reagent for the preparation of unsymmetrical ketones according to eq



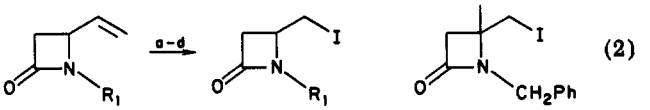
(1)

2, R_2 = alkyl, H
3, R_2 = $CH_2CO_2PNB_2$

1.[1] The tetracarbonyl ferrate dianion, an excellent nucleophile, is first reacted with an alkyl halide to form the acyliron intermediate **6**, the result of initial formation of a carbon–iron bond followed by CO insertion. The intermediate **6** can also be prepared directly from **1** upon reaction with acid halides. It is less reactive than **1** and is alkylated only by the very reactice primary alkyl iodides. The reagent **1** was shown to react cleanly with primary bromides and tosylates without interference from groups such as esters and nitriles.[1] We therefore felt that it should be possible to displace iodide from the 4-(iodomethyl)azetidin-2-ones while retaining the β-lactam ring. The expected intermediates **6a** should have been further alkylated to the desired intermediates **2**[2] and **3**[3] upon treatment with the appropriate alkyl iodides.

Results and Discussion

The β-lactams **4** required for this study were prepared by ozonolysis of the corresponding 4-vinylazetidin-2-ones followed by reduction of the intermediate aldehyde with sodium borohydride, tosylation and subsequent treatment with sodium iodide in acetone (eq 2). 1-Benzyl-4-(iodomethyl)-4-methylazetidinone (**5**) was obtained from 4-(chloromethyl)-4-methylazetidin-2-one via N-benzylation[4] and treatment with sodium iodide in DMF.

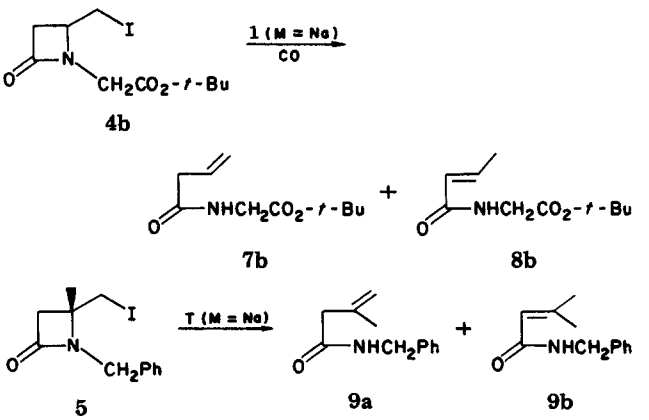


(2)

4a, R_1 = CH_2Ph **5**
b, R_1 = CH_2CO_2-*t*-Bu
c, R_1 = $SiMe_2$-*t*-Bu
d, R_1 = *n*-Bu

Reagents: a, O_3; b, $NaBH_4$; c, TsCl/pyridine; d, NaI

Reaction of **4b** with the potassium salt of **1** in dry THF–10% *N*-methylpyrrolidone at 65 °C for 45 min afforded after chromatography on silica gel a roughly 2:1 mixture of the unsaturated amides **7b** and **8b** in 64% yield; there was no evidence of any of the desired β-lactam-containing product. The yield of **7** + **8** was increased to 98% when the same reaction was carried out at room temperature for 60 h. The structures of **7b** and **8b** followed readily from the NMR spectra which showed the vinylic methyl group of **8b** as a doublets (J = 6 and 2 Hz) at δ 1.13 and the $C(O)CH_2$ group of **7b** as a doublet (J = 7 Hz) at δ 3.02. Furthermore, in the series **4a** → **7a** + **8a**, the product **8a** was synthetized by reaction of methyl crotonate with benzylamine. The ratio of **7**/**8** varied somewhat with the reaction time and temperature, the amount of excess of **1**, and the workup and isolation procedure, since **7** and **8** are readily interconverted by the action of base. Similar results were obtained when **4b** was reacted with Li-*n*-$BuC(O)Fe(CO)_4$, prepared from $Fe(CO)_5$ and *n*-BuLi.[5] Finally, the tosylate corresponding to **4b** and the sodium salt of **1**, as the dioxane complex,[6] gave the above amides



(1) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

(2) (a) Onue, H.; Narisada, M.; Uyeo, S.; Matsumara, H.; Okada, K.; Yano, T.; Nagata, W. *Tetrahedron Lett.* **1979**, 3867. (b) Foxton, M. W.; Mearman, R. C.; Newall, C. E.; Ward, P. *Ibid.* **1981**, *22*, 2497.

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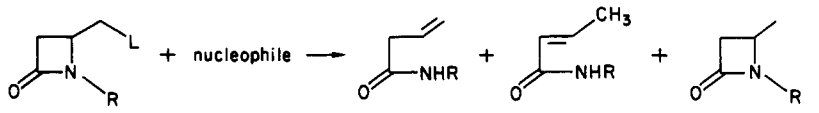
(4) Reuschling, D.; Pietsch, H.; Linkies, H. *Tetrahedron Lett* **1978**, 615.

(5) Siegl, W. O.; Collman, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 2516.

0022-3263/83/1948-2092$01.50/0

Table I



run	L	R	Nu	solvent	reaction time, h/temp, °C	yield, % 7 + 8	16	recov 4
1	I	CH_2CO_2-t-Bu	$K_2Fe(CO)_4$	THF:10% NMP	0.75/65	64		
2	I	CH_2CO_2-t-Bu	$K_2Fe(CO)_4$	THF:10% NMP	60/25	98		
3	I	CH_2CO_2-t-Bu	$LiBuC(O)Fe(CO)_4$	THF:10% HMPA	13/65	53	trace	
4	I	CH_2CO_2-t-Bu	$LiPhC(O)Fe(CO)_4$	THF	12/25			75
5	OTS	CH_2CO_2-t-Bu	$Na_2Fe(CO)_4$	THF	3/25	75		
6	I	CH_2Ph	$Na_2Fe(CO)_4$	THF	3/25	48	trace	
7	I	CH_2Ph	$NaArC(O)Fe(CO)_4$	THF	22/25		50	50
8	I	CH_2Ph	$NaBH_4$	Me_2SO	12/25		65	
9	I	CH_2Ph	n-BuLi	THF	1/−78 → 25	98		
10	I	n-Bu	$Na_2Fe(CO)_4$	THF	3/25	35		
11	I	$Si(Me)_2$-t-Bu	$Na_2Fe(CO)_4$	THF	3/25	26[a]		35
12		5	$Na_2Fe(CO)_4$	THF	3/25	16b (50) + 9 (50)		
13		5	$NaBH_4$	Me_2SO	12/25	16b (44)		

[a] Isolated as a mixture of $CH_3CH=CHCONH_2$ and $CH_2=CHCH_2CONH_2$.

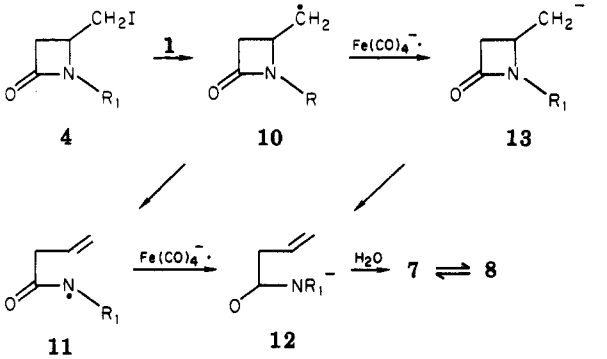
in 75% yield after a 3-h reaction at room temperature in THF. These fragmentation reactions also occurred with the 4,4-disubstituted lactam **5**, affording **9a** and **9b** in 50% yield. A number of other examples are also reported in Table I.

The most likely mechanism that can be suggested to explain the reaction of **1** with 4-halomethyl and 4-(tosyloxy)methyl β-lactams involves electron transfer from **1** to **4**, thereby generating the radical **10**, $Fe(CO)_4^{-}\cdot$, and I^-. Fragmentation of **10** leads to the ring-opened structure **11**, which can accept another electron to form the amide anion **12**, and then be protonated to **7**. Alternatively, **11** could be converted to **7** by a hydrogen transfer from the solvent. The amide anion **12** could also arise by a second electron transfer from $Fe(CO)_4^-$ to **10**, thus generating the anion **13**, followed by fragmentation to **12** (Scheme I).

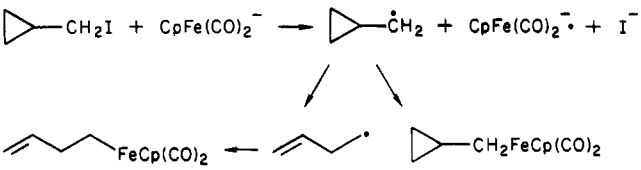
Krusic et al.[7] have provided strong evidence that the reaction of (iodomethyl)cyclopropane with $CpFe(CO)_1^-Na^+$, that which gives a mixture of the allyl and cyclopropyl derivatives **14** and **15**, respectively, proceeds via radical intermediates, (Scheme II). The radical process in our reaction is supported by the observation that traces of the reduction products, the 4-methylazetidin-2-ones (**16**), are obtained in several of the reactions. Indeed, in the reaction of **4a** with the 3,4,5-trimethoxybenzoyltetracarbonyl anion, 1-benzyl-4-methylazetidin-2-one was obtained as the sole product in 50% yield. The aryl fragment was recovered as 3,4,5-trimethoxybenzaldehyde.

The possibility of a displacement by **1** on iodine of **4** to generate directly the anion **13** is made unlikely by the observation that the 4-(tosyloxy)methyl derivative, which cannot undergo such a displacement, gives the same products as the iodo derivatives. Interesteringly, reactin of **4b** with n-BuLi in THF followed by warming to room temperature leads cleanly to **8a**, probably via the mechanism shown in Scheme I. In contrast, 1-benzyl-4-(chloromethyl)-4-methylazetidin-2-one when reacted with n-BuLi in a similar manner gave no trace of either **9a** or **9b** but almost complete recovery of the starting material.

Scheme I



Scheme II



Examples of what constitutes essentially the reverse of the reactions described in this paper, i.e., **7** → **4** have recently been reported by Ganem et al., as a new route to β-lactams. These authors showed that reaction of several *N*-tosylamides of crotonic acid with Br_2 or I_2 in the presence of $NaHCO_3$ furnished 4-(halomethyl)azetidin-2-ones. They reduced the 4-halomethyl groups in their derivatives to methyls by treatment with n-Bu_3SnH. We have found that $NaBH_4$ in Me_2SO for 12 h, at room temperature also effectively reduces both the 4-CH_2I and 4-CH_2OTs groups in β-lactams to the corresponding 4-methyl derivatives (Scheme III).

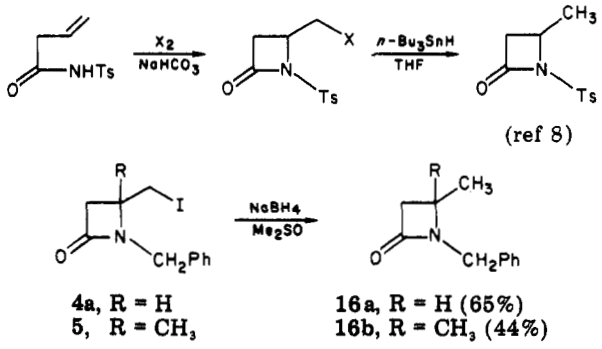
Experimental Section

NMR data were obtained as $CDCl_3$–1% Me_4Si solutions at 60 MHz. Infrared spectra were taken as $CHCl_3$ solutions. Normal workup refers to diluting the reaction with water or in the case of the metal carbonyl anions, reactions with saturated NH_4Cl and extracting with CH_2Cl_2. Purifications were performed either by recrystallization or silica gel chromatography. The yields refer to purified products.

1-Benzyl-4-(hydroxymethyl)azetidin-2-one. A stream of ozone was introduced into a stirred −78 °C solution of 1-benzyl-4-vinylazetidin-2-one (**7a**)[9] (2.1 g, 11.3 mmol) in methylene

(6) Available from Aldrich Chemical Co., Milwaukee WI, and used as received.
(7) *Krusic*, P. J.; Fagan, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 251.
(8) Biloski, A. J.; Wood, R. D.; Ganem, B. *J. Am. Chem. Soc.* **1982**, *104*, 3233.

Scheme III



4a, R = H
5, R = CH_3

16a, R = H (65%)
16b, R = CH_3 (44%)

chloride (30 mL) until the blue color remained. After addition of dimethyl sulfide (1.2 mL), the mixture was stirred for 15 min at −20 °C. Sodium borohydride (214 mg, 5.7 mmol), dissolved in 5 mL of ethanol, was added dropwise, and then the mixture was stirred for an additional hour at 0 °C. The reaction mixture was poured into a saturated ammonium chloride solution (80 mL) and worked up in the usual manner. Column chromatography of the crude product on silica gel (50 g) with ethyl acetate as eluent gave 1.9 g (88%) of the desired alcohol as colorless crystals: mp, 96 °C; IR 1740 cm^{-1}; ^1H NMR (100 MHz) δ 2.8–3.1 (m, 3, $COCH_2$; OH), 3.4–3.9 (m, 2, CH_2OH), 4.40 (AB q, 2, J = 15 Hz, CH_2Ph), 7.3 (m, 5 Ph) Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85. Found C, 68.87, H, 6.90.

1-Benzyl-4-(*p*-tosyloxymethyl)azetidin-2-one. A solution of 1-benzyl-4-(hydroxymethyl)-azetidin-2-one (523 mg, 2.7 mmol) in 10 mL of dry pyridine was treated with tosyl chloride (1.0 g, 5.4 mmol). After the addition was complete, the flask was placed in a refrigerator for 24 h. The mixture was then poured into 25 mL of water, and the organic product was isolated. The crude solid was purified by column chromatography on silica gel (20 g) with ethyl acetate as eluent to yield 871 mg of the title tosylate as colorless crystals: mp 79 °C (CCl_4/petroleum ether); IR 1750 cm^{-1}; ^1H NMR δ 2.43 (s, 3, CH_3), 2.8 (ABX, $COCH_2$), 3.5–3.8 (m, 1, CH), 3.97 (AB q, 2, CH_2OTs), 4.3 (AB q, 2, J = 16 Hz, CH_2Ph), 7.2 (m, 5, Ph), 7.5 (AA′BB′, 4, Ph). Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54. Found C, 62.41; H, 5.72.

1-Benzyl-4-(iodomethyl)-azetidin-2-one. The above tosylate (1.6 g, 4.6 mmol) and 2.8 g (18.4 mmol) of sodium iodide were refluxed in 35 mL of acetone for 4 h. The reaction mixture was diluted with water and then worked up in the usual manner. The crude product was purified by silica gel chromatography (ethyl acetate) to afford 1.3 g (94%) of the required iodide as colorless crystals: mp 90 °C (sublimation); IR 1745 cm^{-1}; ^1H NMR (100 MHz) δ 2.6–3.3 (m, 4, $COCH_2$ CH_2I), 3.4–3.7 (m, 1, NCH), 4.40 (AB q, 2, J = 15. 5 Hz, CH_2Ph), 7.3 (m, 5, Ph). Anal. Calcd for $C_{11}H_{12}INO$: C, 43.87, H, 4.02. Found C, 44.01 H, 3.89.

Lactams 4b–4d. These compounds were synthesized from 4-vinylazetidin-2-one by first protecting the nitrogen with *tert*-butyl bromoacetate (**4b**), *tert*-butyldimethylsilyl chloride (**4c**), and *n*-BuI (**4d**), and then following the sequence described for **4a**. All intermediates were characterized by their NMR spectra, which were readily interpreted and were unambiguous. The spectroscopic properties of **4b–d** are given below.

β-Lactam 4b: colorless crystals, mp 81 °C (sublimation); IR 1735, 1760 cm^{-1}; ^1H NMR δ 1.47 (s, 9, *t*-Bu), 2.8 (ABX, 2, $COCH_2$), 3.4 (AB q, 2, CH_2I), 3.9 (AB, 2, J = 18 Hz, CH_2CO_2), 4.2–3.7 (m, 1, CH). Anal. Calcd for $C_{10}H_{16}INO_3$: C, 36.94, H, 4.96. Found C, 37.06; H, 5.04. Yield, 100%.

β-Lactam 4c: colorless crystals, mp 47 °C (sublimiation); IR 1735 cm^{-1}; ^1H NMR δ 0.23 (s, 3, CH_3) 0.27 (s, 3, CH_3), 0.97 (s, 9, *t*-Bu), 3.9–2.5 (m, 5, $COCH_2$, CH, CH_2I). Anal. Calcd for $C_{10}H_{20}INOSi$: C, 36.93; H, 6.30. Found C, 36.94; H, 6.23. Yield, 88%.

β-Lactam 4d: colorless oil; IR 1740 cm^{-1}; ^1H NMR δ 0.7–1.9 (m, 7, $(CH_2)_2CH_3$), 2.4–3.9 (m, 7, $COCH_2$, CH, CH_2I, NCH_2). Anal. Calcd for $C_8H_{14}INO$: C, 35.97; H, 5.28. Found C, 36.29; H, 5.67. Yield, 100%.

1-Benzyl-4-(chloromethyl)-4-methylazetidin-2-one. To a solution of 4-(chloromethyl)-4-methylazetidin-2-one[10] (1.27 g, 10.4 mmol), benzyl bromide (1.2 mL, 10.4 mmol), and tetrabutylammonium iodide (380 mg, 1 mmol) in dry THF (50 mL) was added powdered potassium hydroxide (640 mg, 11.4 mmol). After 2 h of stirring h at room temperature, the reaction mixture was diluted with methylene chloride and filtered. The solvents were removed under vacuum, and the resulting oil was purified by column chromatography on 75 g of silica gel (1:1 ethyl acetate-/hexane) to give 1-benzyl-4-(chloromethyl)-4-methylazetidin-2-one as colorless crystals (1.76 g, 85%): mp 63 °C (sublimation); IR 1730 cm^{-1}; ^1H NMR 1.3 (s, 3, CH_3), 2.8 (ABX, 2, $COCH_2$), 3.4 (s, 2, CH_2Cl), 4.3 (s, 2, CH_2Ph), 7.3 (s, 5, Ph). Anal. Calcd for $C_{12}H_{14}ClNO$: C, 64.43; H, 6.31. Found C, 64.53; H, 6.22.

1-Benzyl-4-(iodomethyl)-4-methylazetidin-2-one (5). 1-Benzyl-4-(chloromethyl)-4-methylazetidin-2-one (670 mg, 3.2 mmol) and sodium iodide (1.44 g, 9.6 mmol) were dissolved in DMF (15 mL) and kept for 3 days at 50 °C. Then the reaction mixture was poured into water (30 mL), and the aqueous phase was extracted three times with hexane (75 mL). The combined hexane solutions were dried ($MgSO_4$) and evaporated under vacuum. Silica gel chromatography with 1:1 ethyl acetate/hexane as eluent yielded 405 mg (41%) of **5** as colorless crystals: mp 75 °C (sublimation); IR 1730 cm^{-1}; ^1H NMR 1.4 (s, 3, CH_3), 2.8 (ABX, 2, $COCH_2$), 3.1 (s, 2, CH_2I), 4.3 (s, 2, CH_2Ph), 7.3 (s, 5, Ph). Anal. Calcd for $C_{12}H_{14}INO$: C, 45.73; H, 4.48. Found C, 46.19; H, 4.61.

1-Benzyl-4-methylazetidin-2-one (16a). A solution of 1-benzyl-4-(iodomethyl)azetidin-2-one (**4a**), 0.198 g, 0.66 mmol) and sodium borohydride (50 mg, 1.3 mmol) in dry Me_2SO (3 mL) was stirred at room temperature overnight. After the mixture was poured into a saturated ammonium chloride solution (20 mL), the aqueous phase was extracted three times with methylene chloride (15 mL). The combined methylene chloride solutions were dried ($MgSO_4$) and evaporated under vacuum. Column chromatography on silica gel (10 g) with 1:1 ethyl acetate/hexane as eluent gave **16a** as a colorless oil (71 mg, 65%): IR 1735 cm^{-1}; ^1H NMR 1.2 (d, 3, CH_3), 2.8 (ABX, 2, $COCH_2$), 3.6 (m, 1, CH), 4.3 (AB q, 2, J = 15 Hz, CH_2Ph), 7.3 (m, 5, Ph); MS, calcd for $C_{11}H_{13}NO$, M^+ 175, found 175.

1-Benzyl-4,4-dimethylazetidin-2-one (16b): yield 44% following the procedure the procedure for **16a**, colorless oil, ($CHCl_3$) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1,2 (s, 6, CH_3), 2.7 (s, 2, $COCh_2$), 4.2 (s, 2, CH_2Ph), 7.2 (s, 5, Ph), MS, calcd for $C_{12}H_{15}NO$, M^+ 189, found 189.

Reactions Involving Organometallic Reagents. Air- and water-free conditions were maintained at all time throughout the experiments. The handling of the reagents and preparation of solutions were carried out in an inert atmosphere (nitrogen) glovebox. All equipment used in the experiments was dried at 140 °C overnight followed by cooling under argon. Liquid transfers outside the drybox were handled by syringe. THF freshly distilled under nitrogen from sodium/benzophenone. NMP and HMPT were refluxed at reduced pressure over CaH_2 for 2 days, followed by vacuum distillation into a dry flask containing activated 3-Å molecular sieves.

Run 1. **4b** (283 mg, 0.78 mmol) dissolved in THF (1 mL) was added to a stirred suspension of $K_2Fe(CO)_4$ (235 mg, 0.95 mmol) in THF (15 mL) containing 10% NMP. After refluxing for 45 min in a CO atmosphere, the reaction mixture was quenched to a saturated NH_4Cl solution, extracted with methylenechloride, dried ($MgSO_4$), and evaporated under vacuum. After filtration through a short column of silica gel with ethyl acetate as eluent, the reaction mixture was purified by column chromatography on silica gel (10 g) with 1:1 ethyl acetate/hexane to yield a mixture of **7b/8b** (111 mg, 64%).

Run 3. To a stirred solution of $Fe(CO)_5$ (0.3 mL, 1 mmol) in THF (15 mL) containing 10% HMPT at −78 °C was added *n*-BuLi (1 mmol). After warming to room temperature (1 h), **4b** (345 mg, 1.06 mmol) dissolved in THF (2 mL) was added and the reaction mixture was then refluxed for 13 h. After workup as described above, 111 mg (53%) of **7b/8b** was obtained.

Run 7. $Na_2Fe(CO_4)$·1.5dioxane (759 mg, 2.2 mmol) and 3,4,5-trimethoxybenzoyl chloride (503 mg, 2.2 mmol) were stirred

(9) Durst, T.; Van den Elzen, R.; LeBelle, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 9261.

(10) Clauss, K. *Tetrahedron Lett.* **1974**, 1271.

for 3 h in 15 mL of THF at room temperature. Then **4a** (301 mg, 1 mmol) dissolved in THF (2 mL) was added, and the reaction mixture was stirred for 22 h more. Workup as above yielded **12a** (87 mg, 50%), recovered **4a** (152 mg, 50%), and 3,4,5-trimethoxybenzaldehyde (90 mg, 28%).

Run 9. To a solution of 300 mg of **4b** on 10 mL of THF at −78 °C was added 1 equiv of *n*-BuLi. The reaction mixture was kept at −78 °C for 1 h, and then at room temperature for a further 4 h. Usual workup afforded 170 mg (>98%) of **8b**.

All other experiments involving the lactams **4** and **5** with organometallics were carried out following the examples shown above and experimental conditions described by Collman.[1] See also Table I.

Acknowledgment. We acknowledge the financial assistance of the NSERC (Canada), Bristol Laboratories, Syracuse, NY, and the Deutsche Forschungsgemeinschaft for a travel grant to G.G.

Registry No. 1 (M = K), 16182-63-1; 1 (M = Na), 14878-31-0; **4a**, 85390-48-3; **4b**, 85390-49-4; **4c**, 85390-50-7; **4d**, 85390-51-8; **5**, 85390-53-0; **6**-Li (R = Bu), 31627-07-3; **6**-Li (R = Ph), 31627-04-0; **7a**, 85390-58-5; **7b**, 85390-56-3; **7d**, 85390-59-6; **8a**, 51944-67-3; **8b**, 85390-57-4; **8d**, 24698-27-9; **9a**, 85390-60-9; **9b**, 67264-80-6; **16a**, 4391-83-7; **16b**, 85390-54-1; $CH_3CH{=}CHCONH_2$, 23350-58-5; $CH_2{=}CHCH_2CONH_2$, 28446-58-4; 1-benzyl-4-vinylazetidin-2-one, 39919-84-1; 1-benzyl-4-(hydroxymethyl)azetidin-2-one, 85390-46-1; 1-benzyl-4-[(*p*-tosyloxy)methyl]azetidin-2-one, 85390-47-2; 4-(chloromethyl)-4-methylazetidin-2-one, 53598-88-2; 1-benzyl-4-(chloromethyl)-4-methylazetidin-2-one, 85390-52-9; *N*-[(*tert*-butoxycarbonyl)methyl]-4-[(*p*-tosyloxy)methyl]azetidin-2-one, 85390-55-2.

1-Bromo-2-methoxyvinyllithium: A Useful Bromoacetaldehyde Anion Equivalent from 1,1-Dibromo-2-methoxyethene

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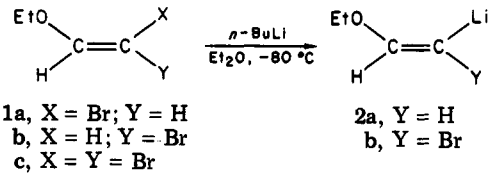
A number of recent reports have concerned the generation of 2-ethoxyvinyllithium systems, which inter alia are of interest as acetaldehyde anion equivalents.[1] One of the methods[1a] utilized to prepare such derivatives involves the reaction of 2-ethoxy-1-bromoethenes with alkyllithiums and is noteworthy because in solvent diethyl ether, formation of the vinyllithium occurs with outstanding regiospecificity. Thus, as shown in Scheme I, while treatment of (*Z*)-1-bromo-2-ethoxyethene (**1a**) leads to (*Z*)-2-ethoxyvinyllithium (**2a**) through halogen–metal exchange, in the case of the *E* isomer **1b**, hydrogen–lithium exchange instead gives (*E*)-1-bromo-2-ethoxyvinyllithium (**2b**).

Although intrinsically interesting, this regiospecificity does have the disadvantage that a requirement for specific generation of either **2a** or **2b** necessitates prior separation of geometric isomers **1a** and **1b**, and only one of them is useful.

We now report that the use of readily available 1,1-dibromo-2-alkoxyethenes[2] as precursors of 1-bromo-2-alkoxyvinyllithiums is advantageous because it circumvents the problem of isomer separation, results in very short reaction times (probably as a consequence of the more

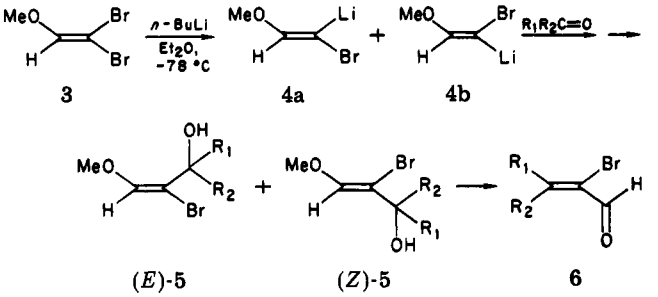
Scheme I



1a, X = Br; Y = H
b, X = H; Y = Br
c, X = Y = Br

2a, Y = H
b, Y = Br

Scheme II



3 **4a** **4b**

(*E*)-**5** (*Z*)-**5** **6**

rapid halogen–metal exchange[3]), and in some instances can provide a simple synthesis of α-bromo α,β-unsaturated aldehydes.

The possibility of regiospecific halogen–metal exchange in these systems[4] was probed by reacting dibromovinyl ether **1c** with butyllithium in diethyl ether at −78 °C, followed by quenching with aqueous ammonium chloride and isolation of the resulting monobromo ethers **1a** and **1b**. Gas chromatographic analysis indicated a 55:45 mixture of (*E*)- and (*Z*)-1-bromo-2-ethyoxethenes **1b**/**1a**, respectively, demonstrating that, in this case, halogen–metal exchange only marginally favors formation of the (*E*)-vinyllithium **2b**. This observation is also interesting in that it constitutes another example which contrasts the relatively stable behavior of (*Z*)-1-halo-2-alkoxyvinyllithiums[5] such as **4b** (Scheme II) with the highly unstable (*E*)-2-ethoxyvinyllithium[1a] which instantly decomposes at −80 °C by a transelimination of LiOEt.[6] The difference is presumably due to the attenuating effect of halogen on the carbanionic character of species such as **4b**.

The usefulness of these systems as bromoacetaldehyde anion equivalents was investigated by utilizing 1,1-dibromo-2-methoxyethene (**3**, Scheme II).

When **3** in diethyl ether was stirred with butyllithium at −78 °C for 15 min, a thin white suspension was formed. Subsequent reaction with acetone (10 min) followed by a workup with aqueous ammonium chloride led to isolation

(1) See for example: (a) Lau, K. S. Y.; Schlosser, M. *J. Org. Chem.* **1978**, *43*, 1595. (b) Ficini, J.; Falou, S.; Touzin, A. M.; D'Angelo, J. *Tetrahedron Lett.* 1977, 3589. (c) Wollenberg, R. H.; Albizati, K. F.; Peries, R. *J. Am. Chem. Soc.* **1977**, *99*, 7365.

(2) See: Neher, F.; Fleece, C. L. *J. Am. Chem. Soc.* **1926**, *48*, 2416.

(3) For bromine and iodine, halogen–metal exchange proceeds several orders of magnitude faster than the corresponding hydrogen–lithium exchange. See: Kobrich, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *74*, 33.

(4) It has been previously noted that treatment of **1c** with butyllithium leads to a mixture of (*Z*)- and (*E*)-1-bromo-2-ethoxyvinyllithiums. However, solvent, conditions, and product distribution were not specified (see ref 1a, footnote 4).

(5) Chloro analogues appear similarly stable. See: Ficini, J.; Depezay J. *Tetrahedron Lett.* **1968**, 937.

(6) It is interesting to note that at −80 °C, not only are species such as **4** quite stable with respect to loss of alkoxide by internal elimination but they also display poor electrophilic reactivity. Specifically, butyllithium-promoted dehydrobromination to the corresponding lithium alkoxyacetylide is an unfavorable process. Thus, when **3** in THF was reacted with 2 equiv of BuLi at −80 °C followed by addition of acetone, the products consisted of 2-methyl-2-hexanol (derived from addition of BuLi to acetone), the alcohols **5**, and only 10–15% of the acetylenic carbinol 4-methoxy-2-methyl-but-3-yn-2-ol. Similar behavior has been reported for monobromide **1a** (see ref 5). The behavior of **3** may be contrasted with that of simple 1,1-dibromo olefins whose reaction with 2 equiv of BuLi constitutes a useful route to lithium alkynides. See: Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.

(7) See: (a) Kingsbury, C. A.; Draney, D.; Sopchick, A.; Rissler, W.; Durham, D. *J. Org. Chem.* **1976**, *41*, 3863. (b) Robert A.; Pommeret, J. J.; Foucaud, A. *Tetrahedron* **1972**, *28*, 2085.

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