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.

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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

Roger H. Smithers

Department of Chemistry, University of Malaya, Kuala Lumpur 22-11, West Malaysia

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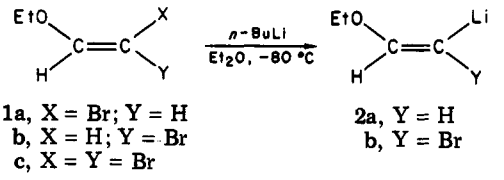
A number of recent reports have concerned the generation of 2-ethoxyvinyllithium systems, which inter alia are of interest as acetaldehyde anion equivalents.[1] One of the methods[1a] utilized to prepare such derivatives involves the reaction of 2-ethoxy-1-bromoethenes with alkyllithiums and is noteworthy 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

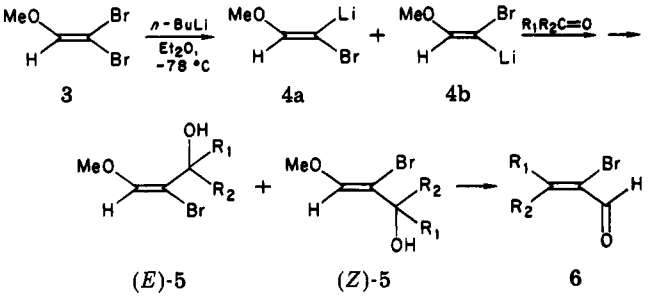
Scheme I



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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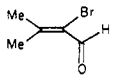
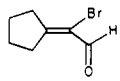
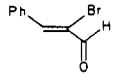
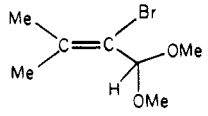
Table I. α-Bromo-α,β-Unsaturated Aldehydes from the Reaction of 1-Bromo-2-methoxyvinyllithium with Carbonyl Compounds

carbonyl substrate	product	% yield[a]
Me_2CO	 **6a**	47
	 **6b**	49
PhCHO	 **6c**	35

[a] Yield of pure distilled or recrystallized product. [b] NMR indicates a single product. The configuration is apparently *Z*;[7] the melting point is identical with literature values.[7,16]

of the alcohols **5** ($R_1 = R_2 = Me$) in 80% yield as a 3:2 mixture of diastereomers. The fact that the NMR spectrum of **5** also showed the presence of small amounts of the aldehyde **6** appeared to suggest that further purification might be problematical, and, indeed, **5** could not be distilled without inception of the allylic rearrangement **5** → **6** (Scheme II). Chromatography on SiO_2, on the other hand, caused quantitative conversion to **6a** and its dimethyl acetal **7** as a 4:1 mixture, respectively.



7

Therefore, as a general procedure, after coupling with the carbonyl compound, the reaction mixture was acidified at −30 °C with aqueous HCl and stirred at room temperature for 1 h. Table I lists representative reactions and yields of isolated α-bromo α,β-unsaturated aldehydes **6**.

While the yields of pure aldehyde were only moderate, the simplicity of the method makes the process attractive. It should be mentioned, however, that this sequence appears most useful when saturated carbonyl compounds are used as substrates. For example, yields were noticeably lower with benzaldehyde, and although initial addition took place smoothly, the subsequent allylic rearrangement was not so clean. With other substrates such as geranial and cyclohex-2-en-1-one, this preculuded the isolation of pure products.

α-Bromo α,β-unsaturated aldehydes **6** have been useful as synthetic intermediates[8] and have also served as model compounds in studies of conjugate addition.[9] Other previously reported methods of synthesis which also incorporate concomitant formation of the α,β-unsaturated linkage include the reaction of brominated alkylidene phosphoranes with aldehydes[10] and, more recently, the ring cleavage of 2,2-dibromo-1-[(trimethylsilyl)oxy]cyclopropanes.[11]

Experimental Section

Solvents. The dryness of solvents and reagents used in these preparations can affect the yields. Diethyl ether,[12] pyridine,[13] and DMF[14] were dried to known residual water levels, and drying of organic extracts was carried out with 4A powdered molecular sieves.[15]

1,1-Dibromo-2-methoxyethene was prepared in two steps according to a modified literature procedure.[2]

2,2,2-Tribromo-1-chloro-1-methoxyethane. This compound was prepared by reaction of 2,2,2,-tribromo-1-methoxyethanol (bromal methyl hemiacetal) with thionyl chloride in the presence of pyridine, essentially by following the published procedure for the ethoxyl derivative.[2] Vigorous agitation with a mechanical stirrer is necessary during addition of the alcohol to prevent occlusion of unreacted starting material by the precipitated complex salt. The yield of the crude almost colorless product was 88%. This material may be distilled [bp 94–96 °C at (6 mmHg)], but the crude product is sufficiently pure for further reaction: ^1H NMR δ 3.72 (3 H, s), 5.62 (1 H, s).

1,1-Dibromo-2-methoxyethene. Dehalogenation of 2,2,2-tribromo-1-chloro-1-methoxyethane was accomplished with zinc in DMF. The conditions and workup method followed the procedure published for the ethoxyl derivative: yield 73%; bp 73–74 °C (19 mmHg); ^1H NMR δ 3.68 (3 H, s), 6.72 (1 H, s).

1,1-Dibromo-2-ethoxyethene was obtained analogously in a similar yield: bp 72–73 °C (11 mmHg) [lit. bp 73–75 °C (15 mmHg)]; ^1H NMR δ 1.3 (3 H, t, $J = 7$ Hz), 3.9 (2 H, q, $J = 7$ Hz), 6.75 (1 H, s).

Preparation of α-Bromo α,β-Unsaturated Aldehydes 6. The preparation of 2-bromo-3-methyl-2-butenal serves as an example. The apparatus used consisted of a 50-mL, two-necked, round-bottomed reaction vessel fitted with a pressure-equalized dropping funnel and a thermometer/gas inlet adaptor. A slow steam of argon was maintained through the apparatus during the experiment. In the flask was placed 1,1-dibromo-2-methoxyethene (2.17 g, 10.02 mmol) in absolute diethyl ether (20 mL), and in the dropping funnel was placed butyllithium (10 mL of a 1.05 M solution in hexane, 10.5 mmol). The flask was then cooled in a dry ice–acetone bath, and when the internal temperature dropped below −72 °C, dropwise addition of butyllithium was begun at a rate so that the temperature did not exceed −70 °C. After the addition was complete, the reaction mixture, a white suspension, was stirred for a further 15 min. Acetone (0.64 g, 11 mmol) in diethyl ether (5 mL) was then added dropwise, after the reaction had been allowed to stir 10 min more, it was warmed to −30 °C, and aqueous hydrochloric acid (20 mL of 1.2 M acid) was then added. After the mixture warmed to room temperature, vigorous stirring was continued for 1 h. The organic layer was then separated, the aqueous layer was washed with portions of ether (2 × 5 mL), and the combined extracts were washed once with dilute potassium carbonate. Drying (4A sieve powder) followed by removal of solvent and distillation gave 0.80 g (47%) of 2-bromo-3-methyl-2-butenal: bp 78–79 °C (12 mmHg) [lit.[11] bp 78–80 °C (15 mmHg)]; ^1H NMR δ 2.1 (3 H, s), 2.3 (3 H, s), 9.6 (1 H, s).

Cyclopentylidenebromoacetaldehyde (6b) was obtained similarly by using cyclopentanone as the substrate: yield 49%; mp 91–92 °C (lit.[1a] mp 91–92 °C).

2-Bromo-3-phenylpropenal (6c) was derived from benzaldehyde: yield 35%; mp 69–71 °C (lit.[16] mp 72–73 °C); ^1H NMR δ 7.4 (3 H, m), 7.9 (3 H, m), 9.25 (1 H, s).

(*Z*)- and (*E*)-3-Bromo-4-methoxy-2-methyl-3-buten-2-ol (5). The procedure was carried out on a 10-mmol scale analogously to that reported above except that quenching at −30 °C was done with saturated aqueous ammonium chloride (5 mL). The ammonium chloride was taken from a 1 L stock solution to which has been added 3 or 4 drops of concentrated ammonium hy-

(8) Grob, C. A.; Spaar, R. *Helv. Chim. Acta* **1970**, *53*, 2119.
(9) Posner, G. H. *Org. React.* **1975**, *22*, 253.
(10) Markl, G. *Chem. Ber.* **1962**, *95*, 3003.
(11) Amice, P.; Blanco, L.; Conia, J. M. *Synthesis* **1976**, 196.
(12) Drying with 4A molecular sieves gives a solvent containing <10 ppm residual water. See: Burfield, D. R.; Gan, G. H.; Smithers, R. H. *J. Appl. Chem. Biotechnol.* **1978**, *28*, 23.
(13) See: Burfield, D. R.; Smithers, R. H.; Tan, A. S. C. *J. Org. Chem.* **1981**, *46*, 629.
(14) Single-stage drying with 3A molecular sieves gives a solvent containing <100 ppm residual water. See: Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.
(15) See: Burfield, D. R.; Smithers, R. H. *J. Chem. Educ.* **1982**, *59*, 703.
(16) Allen, C. F. H.; Edens, C. O., Jr. "Organic Syntheses"; Collect. Vol. III, Wiley: New York, 1955; Collect. Vol. III, p 731.

droxide. A workup as above furnished 1.82 g (80%) of the crude alcohols **5** as a 3:2 mixture of *E*/*Z* diastereomers. The major component was assigned the *E* configuration on the basis of the chemical shift of the olefinic proton which is expected to appear at lowest field, being cis to the vicinal Br: ^{1}H NMR of *E* isomer δ 1.45 (6 H, s), 3.4 (1 H, brs), 3.7 (3 H, s), 6.6 (1 H, s); ^{1}H NMR of *Z* isomer δ 1.45 (1 H, s), 3.4 (1 H, brs), 3.65 (3 H, s), 6.25 (1 H, s). The NMR spectrum showed contamination by ~10% aldehyde **6a**.

Chromatography of **5** (1.82 g) on silica gel with diethyl ether as the eluant furnished 1.75 g of a 4:1 mixture of 2-bromo-3-methyl-2-butenal and its methyl acetal 2-bromo-1,1-dimethoxy-3-methylbut-2-ene (**7**).

Compound **7** was identified from its reaction with aqueous HCl (which produced **6a** as the only product) as well as from its NMR spectrum: ^{1}H NMR δ 1.95 (6 H, m), 3.35 (3 H, s), 3.4 (3 H, s), 4.9 (1 H, s).

Registry No. **1a**, 23521-49-5; **1b**, 16339-88-1; **1c**, 77295-79-5; **2b**, 85371-39-7; **3**, 85371-47-7; **4a**, 85371-40-0; **4b**, 85371-41-1; (*E*)-**5**, 85371-42-2; (*Z*)-**5**, 85371-43-3; **6a**, 31058-93-2; **6b**, 65275-96-9; **6c**, 33603-90-6; **7**, 85371-44-4; Me_2CO, 67-64-1; PhCHO, 100-52-7; cyclopentanone, 120-92-3; 2,2,2-tribromo-1-chloro-1-methoxyethane, 85371-45-5; 2,2,2-tribromo-1-methoxyethanol, 85371-46-6.

Comment on the Purported Photoelectron Spectrum of 1,2-Dimethyl-3,4-dimethylenecyclobutene Dimer

K. Gubernator, J. Spanget-Larsen, and R. Gleiter*

Institut für Organische Chemie der Universität Heidelberg, D-6900 Heidelberg, West Germany

H. Hopf

Institut für Organische Chemie der Universität Braunschweig, D-3300 Braunschweig, West Germany

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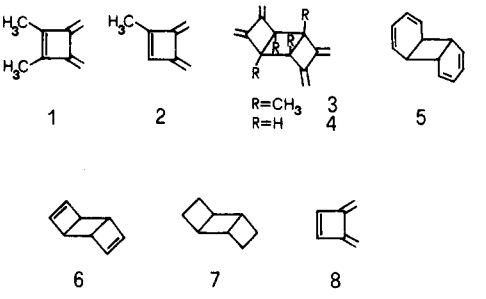
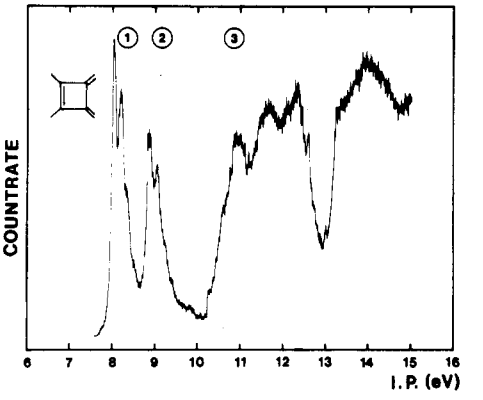
During our photoelectron (PE) spectroscopic investigations of 1,2-bridged cyclobutanes (e.g., **5**–**7**,[1-5] Chart I) we became interested in the PE spectrum of the tetraene **3** published by Borden et al.[6] We were puzzled by the circumstance that only two PE bands are observed below 11 eV. The two peaks close to 8 and 9 eV could possibly be assigned to butadiene π-type levels; however, additional ionizations are expected to occur below 11 eV, corresponding to ejection of electrons from the high-lying Walsh orbitals of the tricyclo[4.2.0.0^{2,5}]octane moiety of **3**. This is strongly suggested by the PE data for **6** and **7**.[1-3,5] We suspected that the spectrum published by Borden et al. was not the spectrum of **3** but of some other compound, most probably the triene **1**, i.e., the precursor in the photosynthesis of **3**.[6] We presently report the PE spectra of 1,2-dimethyl- and 1-methyl-3,4-dimethylenecyclobutene (**1** and **2**). Both spectra are shown in Figure 1. The first ionization potentials are given in Table I. The spectrum of **1** is identical within experimental error with that published by Borden et al., indicating that the spectrum recorded by these authors must be assigned to **1** and not to its dimer **3**. The latter compound is most likely unstable with respect to cycloreversion into two molecules of **1** under the conditions prevailing in the target chamber of the PE spectrometer. This assumption is consistent with the observed photochemical instability of this strained species[6] and is supported by the results of MINDO/3[7] calculations which predict a release of 35 kcal/mol when **3** is cleaved into two molecules of **1** (in contrast, the less crowded parent compound **4** is predicted to be thermo-

Chart I



1 2 3 4 5

6 7 8



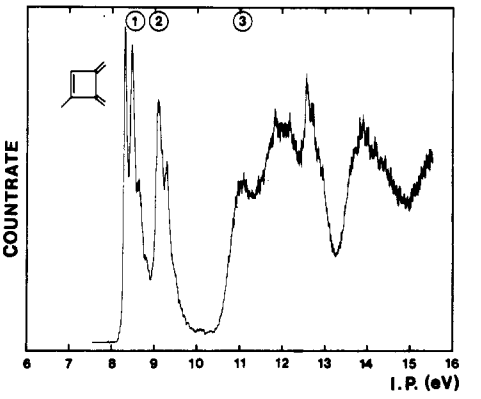


Figure 1. PE spectra of **1** (top) and **2** (bottom).

Table I. Vertical Ionization Potentials of 1 and 2

compd	band	$I_{V,J}$, eV	assignment
1 (C_{2v})	1	8.05	b_1 (π)
		8.20	
	2	8.87	a_2 (π)
		9.07	
	3	10.75 (sh)[a]	
		11.0	
2 (C_s)	1	8.34	a'' (π)
		8.90	
	2	9.12	a'' (π)
		9.32	
	3	11.1	

[a] sh = shoulder.

(1) Gleiter, R.; Heilbronner, E.; Hekman, M.; Martin, H.-D. *Chem. Ber.* **1973**, *106*, 28.
(2) Spanget-Larsen, J.; Gleiter, R.; Paquette, L. A.; Carmody, M. J.; Degenhardt, C. R. *Theor. Chim. Acta* **1978**, *50*, 145.
(3) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197.
(4) Gubernator, K.; Gleiter, R. *J. Org. Chem.* **1981**, *46*, 1247.
(5) Gubernator, K. Thesis, University of Heidelberg, 1982.
(6) Borden, W. T.; Young, S. D.; Frost, D. C.; Westwood, N. P. C.; Jorgensen, W. L. *J. Org. Chem.* **1979**, *44*, 737.
(7) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294. Bischof, P. *Ibid.* **1976**, *98*, 6844; *QCPE* **1979**, *12*, 383.

0022-3263/83/1948-2097$01.50/0