group absorption of **1** was at 1680 cm$^{-1}$, the same position as in previously reported silanecarboxylates.[2]

The ultraviolet spectra of **1**, methyl pivalate, trimethylacetylsilane, and 3,3-dimethyl-2-butanone are shown in Table I. The position of the absorption for **1** shows a small shift to shorter wavelength in more polar solvents, and thus it is reasonable to assign it to the n → π* transition.[17] The absorption of both silicon compounds shows exaltation and large bathochromic shifts in position relative to that of their carbon analogs. In addition the absorption of the esters occurs at higher energy than that of the ketones. Previous workers[18,19] have suggested that the n → π* transition of the esters occurs at higher energy due to a lowering in the energy of the n orbital and an increase in the energy of the π* orbital of the ester relative to those of the ketone. Calculations based upon the ionization potential[20] and the electronic spectra of a series of related esters and ketones such as methyl acetate, acetone, and ethyl acetate and methyl propanoate and 2-butanone indicate that the energy of the n orbitals of the esters is approximately 0.6 eV lower than those of the ketones while the π* orbitals of the esters are approximately 0.9 eV higher in energy than those of the ketones. Since previous MO calculations[10] have shown that the 3d orbitals of silicon are even higher in energy, there should be better matching in energy between the π* orbital of the ester and the 3d orbitals of silicon than between the π* orbital of the ketone and the 3d orbital of silicon.

**Table I.** The Electronic Spectra of Esters and Ketones

| Compound | n → π* transition mμ (ε) | eV | ΔeV |
|---|---|---|---|
| $Me_3SiCOOMe$ (**1**)[a,c] | 245 (330) | 5.06 | |
| | 250 (330) | 4.96 | 0.81 |
| $Me_3SiCOOMe$[b] | 245 (320) | | |
| $Me_3CCOOMe$[a] | 212 (100) | 5.85 | |
| $Me_3SiCOMe$[a,c,d] | 372 (126) | 3.33 | 1.02 |
| $Me_3CCOMe$[a] | 285 (25) | 4.35 | |

[a] In cyclohexane. [b] In 95% ethanol. [c] Shows additional fine structure. [d] A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Amer. Chem. Soc.*, **89**, 431 (1967).

As a result, if stabilization of the π* orbital due to dπ–pπ bonding were a major factor in producing the observed bathochromic shifts, a larger shift would be expected for silanecarboxylates than for silyl ketones. However, as shown in Table I, the effect of the silicon is actually less in **1** than in trimethylacetylsilane.

**Acknowledgment.** We are grateful to the National Research Council of Canada for partial support of this work.

---

(17) W. D. Closson and P. Haug, *J. Amer. Chem. Soc.*, **86**, 2384 (1964).

(18) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 179–187.

(19) K. Higashi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry," Interscience Publishers, New York, N. Y., 1965, pp 175–212.

(20) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, pp 162–203, 308–318.

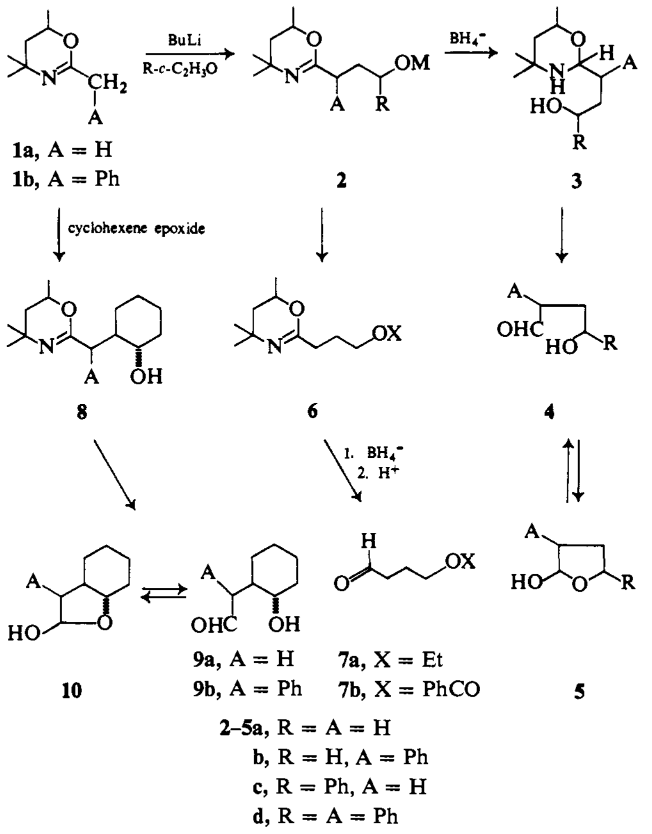
**G. J. D. Peddle, R. W. Walsingham**
*Department of Chemistry, University of Alberta*
*Edmonton, Alberta, Canada*
*Received December 23, 1968*

---

## Aldehydes from Dihydro-1,3-oxazines. IV. A New Synthesis of γ-Hydroxy Aldehydes and Their γ-Oxo Derivatives

*Sir:*

Recently, the lithio salt of **1a,b** was shown to be an excellent nucleophile in the reaction with alkyl halides and carbonyl compounds producing ultimately acyclic, alicyclic, and α,β-unsaturated aldehydes and their C-1 deuterated derivatives.[1] We now report that the reaction of **1a,b** with typical epoxides (ethylene, styrene, and cyclohexene) produces precursors to γ-hydroxy aldehydes and their γ-oxo derivatives.[2]



Addition of the epoxides to a THF solution of the lithio salt **1** (**a** or **b**) at −78° followed by hydrolytic work-up results in excellent yields (Table I) of the adducts **2** (M = H) and **8**. These oxazinylcarbinols were sufficiently pure (tlc, nmr, ir) to be utilized directly for reduction at −35° by sodium borohydride,[1] affording the corresponding tetrahydro-1,3-oxazines **3** in high yield (Table I). Cleavage of **3** or reduced **8** in aqueous oxalic acid and recovery of the aldehyde by extraction or steam distillation produced the γ-hydroxy derivatives **4** or **9** in 57–69% over-all yields (Table I). The hydroxy aldehydes were expected to exist primarily as the cyclic hemiacetals **5** and **10**, and their spectral characteristics (ir, nmr) confirmed this.[3] The sequence is therefore a

---

(1) A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzer, *J. Am. Chem. Soc.*, **91**, 763 (1969); A. I. Meyers, A. Nabeya, I. R. Politzer, H. W. Adickes, J. M. Fitzpatrick, and G. R. Malone, *ibid.*, **91**, 764 (1969); A. I. Meyers, H. W. Adickes, I. R. Politzer, and W. N. Beverung, *ibid.*, **91**, 765 (1969).

(2) The C-1 deuterated derivatives reported in ref 1 can also be obtained for this class of compounds, using sodium borodeuteride in place of borohydride. We did not attempt to prepare the deuterio derivative for the oxo aldehydes reported herein.

**Table I.** γ-Hydroxyaldehydes from Dihydro-1,3-oxazines and Epoxides[a]

| Oxazine | Epoxide | % crude **2** (M = H) | % crude **3** | % aldehyde pure, over-all | 2,4-DNP mp, °C |
|---|---|---|---|---|---|
| **1a** | Ethylene | 96 | 98 | 63 (**4a**)[b] | 116–118[c] |
| **1a** | Styrene | 93 | 95 | 68 (**4c**)[d] | 106–107 |
| **1a** | Cyclohexene | 92[e] | 97[f] | 57 (**9a**) | 78–79 |
| **1b** | Ethylene | 98 | 93 | 69 (**4b**)[g] | 99–101 |
| **1b** | Styrene | 89 | 90 | 61 (**4d**)[h] | 146–147 |
| **1b** | Cyclohexene | 99[e] | 93[f] | 59 (**9b**) | 174–175 |

[a] All new compounds gave satisfactory analyses. [b] Isolated as the dinitrophenylhydrazone derivative. [c] Lit. mp 118°: R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. France*, 197 (1948). [d] B. Helferich and O. Lecher, *Ber.*, **54**, 930 (1921); lit. bp 138° (4 mm), observed 142° (5 mm). [e] Described by structure **8**. [f] Described by structure **8** with C=N reduced. [g] Contains a 1:1 mixture of the dehydrated product, 3-phenyl-4,5-dihydrofuran, which was isolated *via* tlc. [h] Pure aldehyde mp 119–120° (ether–hexane).

three-step operation requiring no purification of the intermediates and can be accomplished in a day or two using the commercially available oxazines, **1a,b**.[4,5] It was found that the initial adduct **2** (M = Li) in the original reaction vessel failed to react either with added ethyl iodide, benzoyl chloride, or ethylene oxide. However, γ-oxo derivatives **6** (X = ethyl, benzoyl) were obtained by treating the crude oxazinylcarbinol **2** (M = H) with sodium hydride in THF at room temperature followed by the addition of the alkyl or acyl halide. Subsequent reduction and hydrolysis gave the γ-substituted aldehydes **7**. In this manner, 4-ethoxybutanal, **7a** (2,4-DNP mp 88–89°, lit.[6] mp 88–89), and 4-benzoyloxybutanal,[7] **7b** (2,4-DNP mp 103–105°), were obtained in 59 and 67% over-all yields, respectively. The highly covalent nature of the oxygen–lithium bond is reflected in its inability to function as a nucleophile leading to **6**, whereas the more ionic sodium salt, **2** (M = Na), behaves in the expected manner.

This approach to γ-oxygenated aldehydes represents a distinct improvement over previous methods[8] which involve oxidative cleavage of 4-alken-1-ols and are sparsely described in the literature. It is also of interest that a search of the literature failed to produce any previous reports of 3-phenyltetrahydrofuran derivatives [*i.e.*, **5** (A = Ph) and **10** (A = Ph)].[9]

**Acknowledgments.** We acknowledge partial financial assistance from the National Institutes of Health (RG-06248-09) and the Petroleum Research Fund, administered by the American Chemical Society.

---

(3) C. D. Hurd and W. H. Sanders, *J. Am. Chem. Soc.*, **74**, 5324 (1952).

(4) The over-all yields are not necessarily optimum since most of the reactions were performed only once on a 50–100-mmol scale. All of the aldehydes described in Table I were obtained pure (nmr, tlc, ir, mass spectroscopy) in the yields stated.

(5) Columbia Organic Chemicals, Columbia, S. C.

(6) H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, 71, 3051 (1949).

(7) Nmr ($CCl_4$), δ 9.8 (t, 1, $J = 0.6$ Hz, $CHO$), 7.4–8.0 (m, 3, aryl H), 4.3 (t, 2, $J = 6$ Hz, $OCH_2$), 2.6 (m, 2, $CH_2C{=}O$), 2.16 (m, 2, $-CH_2-$); ir (neat) 1718 $cm^{-1}$ (broad ester and aldehyde C=O).

(8) Table I, ref *c* and *d*.

(9) The authors would be pleased to furnish complete experimental details regarding this method upon request.

**H. Wayne Adickes, Ieva Ruks Politzer, A. I. Meyers**
*Department of Chemistry, Louisiana State University in New Orleans*
*New Orleans, Louisiana 70122*

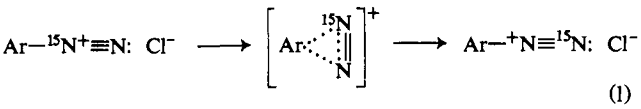
*Received February 3, 1969*

---

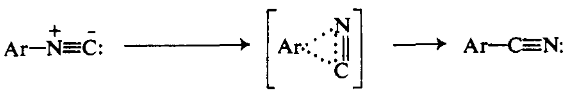
## On the Thermal Stability of the Phenylacetylide Anion

*Sir:*

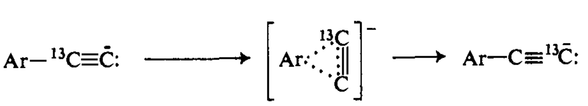
The thermal rearrangement of a series of substituted benzenediazonium chlorides has been shown[1] to occur to the extent of 1–4% at moderate temperatures (eq 1), and the rearrangement of isoelectronic aryl isocyanides has also been shown to take place with facility[2] (eq 2). Extended Hückel analyses of the energetics of these rearrangements were reported by Hoffmann in a recent paper.[3] He also calculated an activation energy for the third possible isoelectronic rearrangement of this series, the rearrangement of phenylacetylide anion (eq 3). This calculation has stimulated us to search for such a rearrangement.



(1)



(2)



(3)

Phenylacetylene-1-$^{13}C$ was prepared in good yield by a conventional reaction sequence from $^{13}C$-enriched barium carbonate.[4] In outline, the synthesis is shown in eq 4–6. A detailed description of this synthesis will appear

$$Ba^{13}CO_3 \xrightarrow{H^+} {}^{13}CO_2 \xrightarrow{PhMgBr} Ph^{13}CO_2H \qquad (4)$$

---

(1) (a) E. S. Lewis and R. E. Holliday, *J. Am. Chem. Soc.*, **88**, 5043 (1966); (b) E. S. Lewis and J. M. Insole, *ibid.*, **86**, 32 (1964); (c) E. S. Lewis, L. D. Hartung, and B. M. McKay, *ibid.*, **91**, 419 (1969); (d) E. S. Lewis and R. E. Holliday, *ibid.*, **91**, 426 (1969); (e) E. S. Lewis, R. E. Holliday, and L. D. Hartung, *ibid.*, **91**, 430 (1969).

(2) (a) G. Kohlmaier and B. S. Rabinovitch, *J. Phys. Chem.*, **63**, 1793 (1959); (b) J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).

(3) G. W. Van Dine and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 3227 (1968).

(4) Bio-Rad Laboratories, Richmond, Calif., 61.2 atom % enriched.