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.

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(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, C*H*O), 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.

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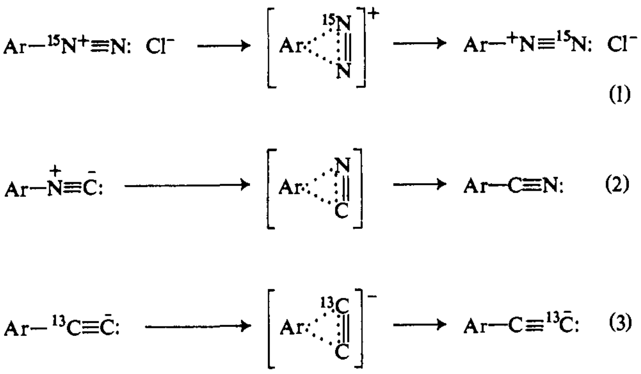
## On the Thermal Stability of the Phenylacetylide Anion

*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.



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

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

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(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.

Table I. Extent of Rearrangement of Phenylacetylene-1-$^{13}$C and Phenylacetylide-1-$^{13}$C Anion

| Entry | Base | Solvent | Temp, °C | Time, hr | % 1-$^{13}$C Initial | % 1-$^{13}$C Final |
|---|---|---|---|---|---|---|
| 1 | None | Benzene | 178 ± 5 | 4.1 | 56.0[a] | 56.0 |
| 2 | $NaNH_2$[b] | THF[c] | 65 ± 1 | 17.5 | 56.0 | ~56 |
| 3 | $NaNH_2$ | THF | 160 ± 2 | 2.0 | 32.6 | 32.0[d] |
| 4 | KOBu-*t* | *t*-BuOH | 130 ± 2 | 1.5 | 32.3 | 32.3 |
| 5 | $LiNHC_6H_{11}$ | *c*-$C_6H_{11}NH_2$ | 160 ± 1 | 2.0 | 32.6 | 32.3[d] |

[a] All values are calculated from several integrations of the $^1$H nmr and are ±~2%. [b] The ratio of base:phenylacetylene in all cases was 2:1 or 3:1. [c] Several milliliters of solvents per millimole of phenylacetylene. [d] However, mass spectral analysis of carbon dioxide obtained from the permanganate oxidation [V. N. Krestinskii and M. K. Kelbovskaya, *Ber.*, **68B**, 512 (1935)] of phenylacetylene recovered from runs 3 and 5 showed 2.62 ± 0.14% $^{13}$C and 1.60 ± 0.12% $^{13}$C, respectively. Since a control sample showed 2.34 ± 0.80% $^{13}$C, the extent to which these results represent carbon skeleton rearrangement rather than excessive oxidation is not known.

$$Ph^{13}CO_2H \xrightarrow{SOCl_2} Ph^{13}COCl \xrightarrow{Me_2Cd} Ph^{13}COMe \qquad (5)$$

$$Ph^{13}COMe \xrightarrow{PCl_5} Ph^{13}CCl_2CH_3 + Ph^{13}CCl{=}CH_2 \xrightarrow{NaNH_2} Ph^{13}C{\equiv}CH \qquad (6)$$

elsewhere.[5] Isotopic analysis of samples of enriched phenylacetylene was carried out using the $^2J_{^{13}CCH}$[6a] and the $^1J_{^{13}CH}$[6a,b] coupling, by $^1$H nmr, both before and after attempted rearrangement of the anion. Isolation of phenylacetylene was accomplished by hydrolysis and extraction or by precipitation of the insoluble silver phenylacetylide.

Both phenylacetylene-1-$^{13}$C and the anion produced therefrom by three different bases in solvents of disparate polarity maintained their isotopic integrity even under the most severe conditions which would still permit recovery of a practical amount of phenylacetylene. The results are summarized in Table I. Using the data from entries 3 and 5 of Table I and making the reasonable[7] assumption that $\Delta S^{\neq} \cong 0$ and that first-order kinetics would prevail for this rearrangement, it is possible to calculate a value for $\Delta H^{\neq}$ (minimum) of 37.4 kcal/mol for the rearrangement. This result fully supports the theoretical conclusion of Hoffmann that the activation energy for this rearrangement should be highly unfavorable.[8]

**Acknowledgment.** The authors are indebted to the National Science Foundation and to California State College, Los Angeles, for financial support of this work.

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(5) J. Casanova, Jr., and R. N. Morris, "Organic Preparations and Procedures," in press.

(6) (a) P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," Vol 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, Chapter 7; (b) N. Muller and D. E. Pritchard. *J. Chem. Phys.*, **31**, 768 (1959).

(7) Kohlmaier and Rabinovitch[2a] have determined $\Delta S^{*} = -4.8$ eu for the gas-phase rearrangement of *p*-tolyl isocyanide, and have suggested a somewhat higher value for the solution reaction.

(8) Van Dine and Hoffmann[3] have calculated $\Delta H^{*} = 58$ kcal/mol for this reaction.

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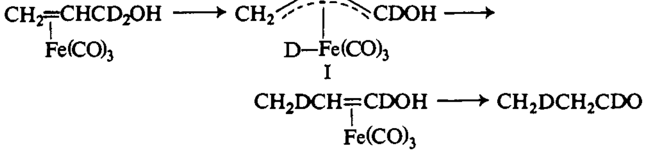
## The Mechanism of Iron Pentacarbonyl Catalyzed 1,3-Hydrogen Shifts

*Sir:*

Several examples have recently been reported[1] which indicate that electrocyclic and cycloaddition transformations which are symmetry "forbidden" by the Woodward–Hoffmann rules[2] become "allowed" when the reaction is catalyzed by various transition metal complexes. An explanation for the contradictory behavior of systems catalyzed by metals has been given by Pettit[1a] and Mango and Schachtschneider.[1c] In essence, it is concluded that interaction of appropriate metal orbitals with those of the olefin forms a new set of occupied molecular orbitals which provide a symmetry-allowed reaction pathway.

Concerted, thermally induced, sigmatropic hydrogen shifts of order [1,3] are "allowed" to proceed only *via* the sterically unfavorable antarafacial mode,[2a] and it is significant that no such migrations have been reported. However, 1,3-hydrogen shifts brought about by the influence of a metal catalyst could conceivably occur through the sterically favorable suprafacial pathway since back donation[3] of metal d electrons to the olefinic ligand could result in a molecular orbital of proper symmetry being the highest occupied one. Such a process would then be analogous to the photochemical process where such 1,3-hydrogen shifts have been reported.[2a] Indeed, it has been suggested[1c] that such a process is operative in the $DCo(CO)_4$-catalyzed isomerization of allylbenzene to β-methylstyrene[4] since only about 5% deuterium was found to be incorporated in the product.

We have previously reported the occurrence of a 1,3-hydrogen shift in the $Fe(CO)_5$-induced isomerization of allyl alcohol to propionaldehyde.[5] Thus, rearrangement of [1,1-$^2H_2$]allyl alcohol with $Fe(CO)_5$ produced propionaldehyde with deuterium appearing in the methyl but *not* in the methylene group. Similar results have been reported in the rearrangement of allyl alcohol with $DCo(CO)_4$.[6] Our results were found to be consistent with the rearrangement proceeding *via* a π-allyl–hydroiron tricarbonyl complex (I), as had been suggested earlier by Pettit[7] and Manuel.[8] However, the data are



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(1) (a) W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4788 (1967); (b) H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967); (c) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967), and references therein.

(2) (a) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395, 2511, 4389 (1965), and references therein; (b) *ibid.*, **87**, 2046 (1965); (c) *ibid.*, **87**, 4388 (1965); (d) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); (e) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (f) J. A. Berson, *ibid.*, **1**, 152 (1968); (g) G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

(3) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18c**, 79 (1951).

(4) L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965).

(5) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, 97 (1968).

(6) R. W. Goetz and M. Orchin, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

(7) G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).