with synthetic *dl*-prostaglandin $F_{2\alpha}$ also was chromatographically identical with a sample similarly prepared from the natural hormone.

The stereoselective formation of the *cis*-$\Delta^{5,6}$ olefin is in accord with expectations from previous experience[18] with the dimethyl sulfoxide procedure and also with model experiments involving a number of simple aldehydes and the ylide from 5-triphenylphosphoniopentanoic acid.

Oxidation of **14** by chromic (two-phase) reagent[19] and removal of the tetrahydropyranyl protecting groups using acetic acid–water (2:1) at 37° for 3 hr afforded in 70% yield *dl*-prostaglandin E_2 (**16**) obtained in pure form (as an oil) by chromatography on acid-washed silica gel. The synthetic *dl*-prostaglandin E_2 exhibited the same ir and nmr spectra as the natural hormone and identical chromatographic behavior. The mass spectra and chromatographic behavior of the methyl ester obtained from *dl*-**16** with diazomethane and natural prostaglandin E_2 methyl ester were identical.[20]

Selective reduction of the *cis*-Δ^5 bond of the intermediate bistetrahydropyranyl ether **16** would afford a precursor of prostaglandins E_1 and $F_{1\alpha}$. Although preliminary results (using P-1 nickel boride catalyst[21]) indicate that these monounsaturated prostaglandins can be obtained in this manner, discussion of this aspect of the synthetic work is deferred pending completion of the hydrogenation studies.[22] We also plan to utilize the optically active hydroxy acid derived by hydrolysis of the lactone **3** for the synthesis of natural prostaglandins; preliminary experiments demonstrate that the hydroxy acid is easily resolved.[23]

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[18] See E. J. Corey and E. Hamanaka, *J. Amer. Chem. Soc.*, **89**, 2758 (1967), and also E. Hamanaka, Ph.D. Thesis, Harvard University, 1967, for additional examples.

[19] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 143.

[20] Bioassay of the synthetic (racemic) prostaglandins E_2 and $F_{2\alpha}$ by measurement of smooth muscle contraction showed responses at concentrations in the range 10^{-9} to 10^{-8} g/ml, corresponding to a potency one-half that of the natural hormones. We are indebted to Dr. Peter Ramwell and Mr. Reginald Jessup for these biological tests.

[21] C. A. Brown and H. C. Brown, *J. Amer. Chem. Soc.*, **85**, 1003 (1963).

[22] Hydrogenation of prostaglandin $F_{2\alpha}$ to form prostaglandin $F_{1\alpha}$ using a palladium catalyst has been already realized by Professor Bengt Samuelsson [*J. Biol. Chem.*, **239**, 4091 (1964)] and applied to the synthesis of tritium-labeled prostaglandin $F_{1\alpha}$.

[23] This work was supported by the National Institutes of Health.

E. J. Corey, Ned M. Weinshenker
Thomas K. Schaaf, Willy Huber
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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A New Synthesis of Vinyl Halides and Vinylsilanes *via* Alkaline Decomposition of 5,5-Dialkyl-3-nitrosooxazolidones

Sir:

Vinyl cations (B) or unsaturated carbenes (D) have been suggested as intermediates in the basic decomposition of 5,5-dialkyl-3-nitrosooxazolidones.[1,2] As it was expected that halide ions would react with B but not D,[3] several nitrosooxazolidones were treated with alkoxide in the presence of a large excess of halide ions. The vinyl halides listed in Table I were obtained in high yield.

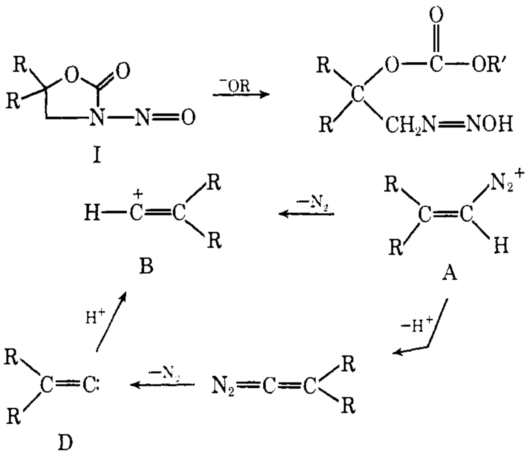
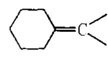
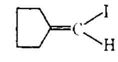
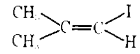
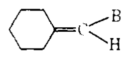
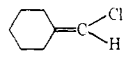
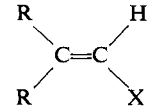


Table I. Vinyl Halides[a–c]

Compd	Structure	Bp, °C (mm)[d]	Yield, %[e]
IIa		45–47 (0.2)	82
III		83–85 (15)	81
IV		126–127 (753)	80
IIb		78–80 (20)	73
IIc		160–161 (755)	78

[a] Satisfactory elemental analyses were obtained for the new compounds III and IV. [b] The authors are indebted to Professor Dietmar Seyferth for furnishing infrared spectra of authentic IIa–c. [c] Saturated solutions (room temperature) of the alkali metal halides in 2-methoxyethanol employed had the following approximate concentrations: NaI (27.4 g/100 ml), LiBr (22.3 g/100 ml), LiCl (13.3 g/100 ml). [d] Boiling point ranges were determined on a short-path distillation apparatus. Isolated products all were of >96% purity by glpc. Analytical samples were isolated by preparative glpc. [e] Yields (isolated, ±3%) are reported as an average of two or more runs.

Thus a new synthesis of vinyl halides (II–IV) is at hand.



II, R = $-(CH_2)_5-$
a, X = I
b, X = Br
c, X = Cl

III, R = $-(CH_2)_4-$
X = I

IV, R = CH_3
X = I

In a typical reaction (synthesis of IIb), a 20% solution of lithium 2-methoxyethanolate in 2-methoxyethanol was added over a period of about 15 min to a well-stirred solution of 9.2 g (0.05 mol) of nitrosooxazolidone in 120 ml of 2-methoxyethanol saturated with anhydrous lithium bromide at room temperature (22.3 g/100 ml). The temperature was held at or below 40° after the initiation of the vigorous exothermic reaction. The theo-

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[1] M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, 73, 4199 (1951).

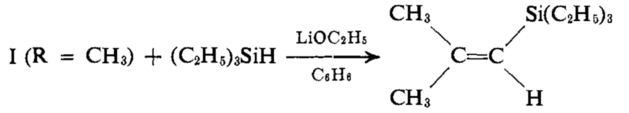
[2] M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969)

[3] Lithium bromide and other strong nucleophiles have been used to trap the 3-phenylcyclopropyl cation generated from N-nitroso-N-2-phenylcyclopropylurea using experimental conditions very similar to those presented herein: W. Kirmse and H. Schütte, *J. Amer. Chem. Soc.*, **89**, 1284 (1967).

retical volume of nitrogen was collected soon after the addition of a slight excess of alkoxide and the vinyl halide isolated by distillation after a suitable work-up.

Although a bimolecular mechanism with attack of halide ion on A cannot be excluded on the basis of the experimental evidence,[4] we favor the intermediacy of the vinyl cation B which reacts with halide ion rather than the weakly nucleophilic 2-methoxyethanol.[5] The postulated vinyl cation could arise either by loss of nitrogen from A or by protonation of D.[6,7] Although trapping of B by strong nucleophiles appears likely, other reaction pathways are possible and currently under investigation.

Carbenes are reported to react by insertion with the silicon-hydrogen bond,[8,9] whereas carbonium ions generally abstract a hydride ion to yield a hydrocarbon.[10] When I was treated with lithium ethoxide in the presence of excess triethylsilane, vinylsilane V[11] was obtained in 61% yield. This result is consistent with the insertion of D into the silicon-hydrogen bond. Further work on the stereochemistry and mechanism of this insertion is in progress.



$$\text{I } (R = CH_3) + (C_2H_5)_3SiH \xrightarrow[C_6H_6]{LiOC_2H_5} (CH_3)_2C{=}C(H)Si(C_2H_5)_3$$

V

From our experience to date apparently unsaturated carbonium ions (such as B) are involved in protic solvents whereas unsaturated carbenes (such as D) are involved in aprotic media.[12]

Acknowledgment. This work was supported by Special Fund 178107 from The Ohio State University and by National Science Foundation Grant 5552.

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(4) The possibility of the vinyl equivalent of the S_N2 reaction has been suggested in the solvolysis of vinyldiazonium ions generated by acidic treatment of triazenes: W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, **89**, 1960 (1967).

(5) Solvolysis of several triaryliodoethylenes in aqueous dimethylformamide have been postulated to involve intermediate vinyl cations which react preferentially with iodide ions: L. L. Miller and D. A. Kaufman, *ibid.*, **90**, 7282 (1968).

(6) W. Kirmse, *Ann.*, **666**, 9 (1963).

(7) J. W. Wilt, C. A. Schneider, H. F. Dabek, J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966).

(8) D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.* (Amsterdam), **7**, 405 (1967).

(9) D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *J. Amer. Chem. Soc.*, **90**, 2944 (1968).

(10) F. A. Carey and H. S. Tremper, *ibid.*, **91**, 2967 (1969).

(11) A. D. Petrov and G. I. Nikishin, *Zh. Obshch. Khim.*, **26**, 123 (1956).

(12) Compare with results on other systems: F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *J. Amer. Chem. Soc.*, **88**, 3870 (1966).

Melvin S. Newman, Charles D. Beard
Evans Chemistry Laboratory, The Ohio State University
Columbus, Ohio 43210

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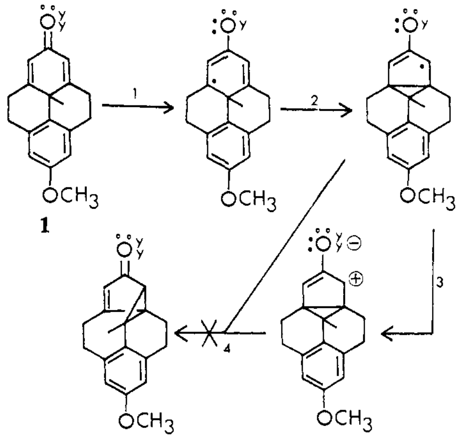
Mechanistic and Exploratory Organic Photochemistry. XLVI.[1] A Constrained 2,5-Cyclohexadienone Which Cannot Rearrange Photochemically

Sir:

The type A rearrangement of 2,5-cyclohexadienones is known[2] to be one of the most facile of photochemical transformations. We wish to report: (1) a cyclohexadienone specifically designed so that the latter stages of the type A rearrangement are geometrically impossible, (2) the actual photochemistry of this compound, (3) a marked photochemical similarity of this constrained dienone to benzophenone, (4) elucidation of the next most favored reaction which is ordinarily obscured by the facile type A rearrangement, (5) information about the nature of the zwitterionic intermediates generally postulated[2] for the type A process, and (6) an intriguing correlation between rates of excited-state reaction and radiationless decay.

7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (**1**) was selected for study[3] since it is constrained in such a way that, although 3,5 bonding[2] should not be inhibited, the 1,4 migration[4] generally accepted as the last stage of the rearrangement is geometrically impossible (note Chart I). Additionally, we synthesized[3] for comparison 4-methyl-4-phenylcyclohexadienone (**2**) as an unconstrained but otherwise structurally similar dienone.

Chart I. Inhibition of the Type A Reaction in the Constrained Dienone[a]



[a] Step 1, excitation; 2, 3,5 bonding; 3, demotion; 4, 1,4 migration.

Indeed, the constrained dienone (**1**) proved totally unreactive (*i.e.*, ϕ <0.005) on irradiation[5] in benzene as well as in *t*-butyl alcohol. This contrasts with the usual near-unit efficiency of the type A rearrangement of dienones.

Photolyses of dienone **1** in isopropyl alcohol solvent did reveal a reaction, namely hydrogen abstraction. This hydrogen abstraction was followed by a methyl radical expulsion, and the methane generated was identified by mass spectral analysis. The over-all transformation is depicted in eq 1. This is in dramatic contrast to the typical type A rearrangement exhibited by 4-methyl-4-phenylcyclohexadienone (**2**) which showed no sign

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(1) For paper XLV see H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **91**, 5307 (1969).

(2) (a) H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4484 (1961); **84**, 4527 (1962); (b) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., June 1961, Abstracts, p 31; (c) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

(3) The synthesis of **1**, mp 132–133°, and **2**, mp 53–55°, will be described in our full paper along with other details; all compounds analyzed correctly.

(4) (a) H. E. Zimmerman, D. Dopp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **88**, 5352 (1966); (b) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968); (c) H. E. Zimmerman, D. S. Crumrine, D. Dopp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

(5) Photolyses were carried out in a parabolic reflector-linear beam AH6 apparatus with filter solutions, all as described by us earlier.[6]

(6) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).