New Syntheses of Vinyl Halides and Vinylsilanes¹

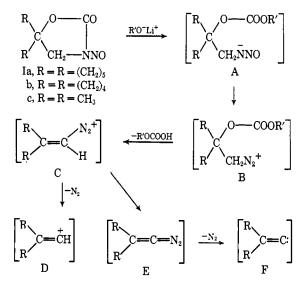
Melvin S. Newman and Charles D. Beard

Contribution from the Evans Chemistry Laboratory of the Ohio State University, Columbus, Ohio 43210. Received January 8, 1970

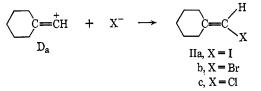
Abstract: Treatment of 5,5-dialkyl-N-nitrosooxazolidones (Ia-c) with lithium 2-methoxyethanolate in 2-methoxyethanol saturated with sodium iodide, lithium bromide, and lithium chloride leads to high yields of vinyl halides. When 5-methyl-5-t-butyl-N-nitrosooxazolidone is similarly treated in the presence of sodium iodide and lithium bromide, mixtures of *trans*- and *cis*-1-iodo-2,3,3-trimethyl-1-butene and the corresponding bromo compounds are obtained in high yields in which the *trans* isomers predominate (94/6 and 92/8, respectively). Treatment of 5,5-dimethyl-N-nitrosooxazolidone (Ic) with alkoxide in benzene containing triethylsilane leads to formation of 2-methylpropenyltriethylsilane (XIV) in high yield. On varying the inorganic salt content of aqueous glyme solutions of the nitrosooxazolidones (Ia-c) alkaline treatment yields varying amounts of compounds containing unrearranged carbon skeletons (aldehydes) and rearranged carbon skeletons (ketones). Mechanisms to account for all of the above reactions are presented.

The products which result from the treatment of 5,5-disubstituted N-nitrosooxazolidones, I, with basic reagents can be explained by mechanisms which proceed via unsaturated carbonium ions,² D, or unsaturated carbenes,³ F. In this paper, we describe separately new reactions of synthetic value which we believe involve unsaturated carbonium ions⁴ and unsaturated carbenes.⁴ The general reactions are shown in Scheme I.

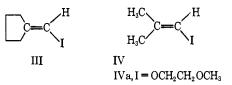
Scheme I



1. Reactions Involving Unsaturated Carbonium Ions. When solutions of 5,5-pentamethylene-N-nitrosooxazolidone (Ia) in 2-methoxyethanol saturated with sodium iodide, lithium bromide, and lithium chloride, respectively, were treated with a solution of lithium 2-methoxyethoxide in 2-methoxyethanol the vinyl halides IIa,b,c were each obtained in about 80% yields. These results are explained by assuming that the unsaturated carbonium ion Da reacts with halide ions to yield the products IIa,b,c.



On similar treatment 5,5-tetramethylene-N-nitrosooxazolidone (Ib) yielded III and 5,5-dimethyl-Nnitrosooxazolidone (Ic) yielded IV in about 80% yields.



Interestingly, the unsaturated carbonium ions involved show a marked preference for reaction with halide ions rather than 2-methoxyethanol as no appreciable amount of vinyl ethers (II, $X = OCH_2CH_2$ - OCH_3) was formed.⁵ Previous work has shown that vinyl ethers are formed in high yield when nitrosooxazolidones are treated with alkoxides in alcoholic media^{3b} in the absence of added halide ions. Similarly, Ic reacts with base in 2-methoxyethanol to give 2-methoxyethyl 2-methylpropenyl ether (IVa) in 70% yield. However, the question as to whether unsaturated carbonium ions or carbenes are involved in the formation of vinyl ethers^{3b} is still open.

In order to find out if there were stereoselectivity in the reactions of an unsymmetrical vinyl cation, the behavior of 5-methyl-5-t-butyl-N-nitrosooxazolidone (V) under similar conditions was studied. Mixtures of vinyl iodides, VIa and VIb, and vinyl bromides, VIIa and VIIb, were obtained in about 80% yield when sodium iodide and lithium bromide were used.

The isomeric iodides were separated by preparative glpc and shown to consist of 94% VIa and 6% VIb. The assignment of the *trans* structure to VIa was made by assuming that the major component in the case of

⁽¹⁾ This work was supported by Special Fund 178107 from The Ohio State University and by National Science Foundation Grant 5552.

⁽²⁾ M. S. Newman and A. Kutner, J. Amer. Chem. Soc., 73, 4199 (1951).

 ^{(3) (}a) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 89-90; (b) M. S. Newman and A. O. M. Okorodudu, J. Org. Chem., 34, 1220 (1969).

⁽⁴⁾ For the preliminary account of these reactions, see M. S. Newman and C. D. Beard, J. Amer. Chem. Soc., 91, 5677 (1969).

⁽⁵⁾ For an example of other vinyl cations which react with iodide ion in preference to water, see L. L. Miller and D. A. Kaufman, J. Amer. Chem. Soc., 90, 7282 (1968).

VIa, X = I

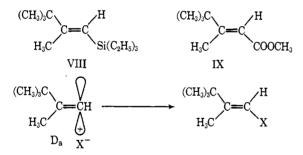
VIIa, X = Br

VIb, X = I

VIIb, X = Br

the isomeric iodides, VIa,b, had the same stereochemistry as the major component of the bromides, VIIa,b. Although the isomeric bromides, VIIa,b (93:7 ratio), could not be separated, treatment of the mixture with lithium followed by reaction of the resulting vinyllithium compounds with triethylsilyl chloride^{6,7} and with carbon dioxide (followed by esterification with diazomethane) yielded the known trans compounds VIII⁸ and IX⁸ which were mixed with small amounts (2-3%)of the isomeric cis impurities. As alkyl vinyllithium compounds have been shown to maintain their structure⁷ the above results establish the stereochemistry of the vinyl bromides VIIa,b. An attempt to treat the vinyl iodides, VIa,b, with lithium failed to yield definitive results.9

Thus, the unsaturated carbonium ion D formed from V reacts from the unhindered side, as shown below, much as does the corresponding unsaturated carbene.8 The vacant orbital at the terminal carbon of D lies in the plane of the paper and the approach of the halide ion is mainly from the side nearer the methyl group.¹⁰



In repeating earlier experiments in which Ia was treated with aqueous sodium hydroxide the product, formerly reported to be hexahydrobenzaldehyde (X),^{2,11} was shown to consist of a mixture of X (89%) and cycloheptanone (XI) (11%). This type of experiment was then repeated in water-glyme (5:1) in the presence of added lithium bromide. Since no 1-bromocycloheptene was formed it is concluded that the cycloheptanone does not arise from a cyclopheptenyl carbonium ion. The products (obtained in high yield)

(6) D. Seyferth and L. G. Vaughan, J. Amer. Chem. Soc., 86, 883

(1964). (7) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 130 ff. (8) M. S. Newman and T. B. Patrick, J. Amer. Chem. Soc., 92, 4312

(1970).

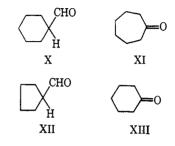
(9) Since this work was done, the structure of VIa has been established as trans by nmr studies. A Communication to the Editor concerning this and other work has been submitted to J. Amer. Chem. Soc. by C. Y. Meyers, I. Sataty, and U. Folli of Southern Illinois University, Carbondale, Ill.

(10) In related work treatment of V with sodium ethoxide in ethanol

afforded the trans-vinyl ethyl ether (VI, $X = OC_3H_5$). See ref 8. (11) M. S. Newman, J. Amer. Chem. Soc., 71, 378 (1949). In this paper and in ref 2 the presence of a small amount of cycloheptanone was not detected.

consisted of 3% hexahydrobenzaldehyde (X), 49% bromomethylenecyclohexane (IIb), and 48% cycloheptanone.

The increase in the amount of cycloheptanone (XI) caused by the addition of lithium bromide led to experiments in which other inorganic salts were added. The best of these, in terms of increasing the amount of carbon skeletal rearrangement, was lithium nitrate. which caused much more rearrangement than sodium nitrate. Similar experiments showed that the proportions of cyclopentylformaldehyde (XII) and cyclohexanone (XIII) formed from Ib were responsive to



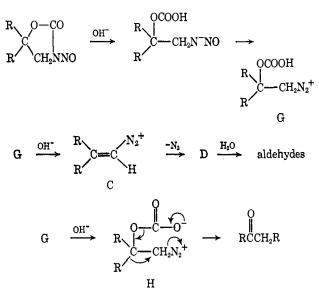
salt effects as were the proportions of isobutyraldehyde and 2-butanone formed from Ic. Some results are summarized in Table I.

Table I. Decomposition of Nitrosooxazolidones in Aqueous Glyme^a

R C CH ₂ -NNO			
RR	Added salt	(R)₂CHCHO	[%] RCOCH₂R [₺]
-(CH ₂) ₅ -	None	89	11
	LiNO ₃ ^d	33	67
$-(CH_2)_4-$	None	50	50
	LiNO ₃	4	96
2CH ₃ -	None	94	6
·	LiNO ₃	41	59

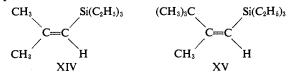
^a In all cases the combined yields of aldehyde and ketone were 90-95%. ^b The percentages reported were determined by glpc analyses of once distilled reaction product. ^c Reactions were run in 5:1 water-glyme (see Experimental Section for details). ^d Concentrated solutions (50-54 g/100 ml of water) were used.

In explanation of the above results (see Scheme II) we believe that the starting nitrosooxazolidones, Ia,b,c, are attacked by hydroxide ion as described² to yield the corresponding cations G. Attack by hydroxide ion at the hydrogen adjacent to the diazo group leads to elimination and formation of the ion C. Decomposition of C via the vinyl cation D yields the aldehydes, X, XII, and isobutyraldehyde and (in the experiment involving lithium bromide) the vinyl bromide IIb. Alternately, G is attacked by hydroxide ion to yield the dipolar ion, H, which by a concerted mechanism as shown yields carbon dioxide, nitrogen, and rearranged ketones, XI, XIII, and 2-butanone. The role of lithium nitrate (and other salts) in promoting the path leading to skeletal rearrangement, or in preventing the other path, is not clear and needs further study. Since lithium nitrate is much more effective than sodium nitrate, the inorganic cation must play a role.



2. Reactions Involving Unsaturated Carbenes. When a solution of Ic in benzene containing excess triethylsilane was treated with lithium ethoxide, a 61%yield of 2-methylpropenyltriethylsilane (XIV)12 was obtained. Thus a new synthesis of vinylsilanes has been effected. Since carbonium ions have been shown to abstract hydride ion from trialkylsilanes¹³ whereas carbenes insert into the SiH bond¹⁴ the formation of XIII indicates that the unsaturated carbene F derived from Ic is involved.

In a similar experiment except that V was used instead of Ic, cis-2,3,3-trimethyl-1-butenyltriethylsilane (XV) was obtained. The formation of the less stable vinylsilane XV is discussed in the accompanying paper.8



Experimental Section¹⁵

Alkaline Treatment of 5,5-Dialkyl-N-nitrosooxazolidones in 2-Methoxyethanol Containing Inorganic Halide Salts. A 20% solution of lithium 2-methoxyethanolate in 2-methoxyethanol was added dropwise during 15 min to a well-stirred solution of 0.05 mol of Ia in 120 ml of 2-methoxyethanol saturated with lithium bromide (ca. 22 g/100 ml at room temperature) until the theoretical amount of nitrogen had been evolved (usually 15 min). The temperature was maintained at or below 40° by cooling. The mixture was then diluted with ice water and worked up in the usual way15 to yield 73% of IIb, bp 78-80° (20 mm), having ir and nmr spectra as described.¹⁶ In similar reactions except that the solvent was saturated with sodium iodide (ca. 27 g/100 ml at room temperature) or lithium chloride (ca. 13 g/100 ml at room temperature) there were obtained iodomethylenecyclohexane (IIa), bp 45-47° (0.2 mm), nmr δ 5.77 (m, 1 H, =CH), 2.28 (m, 4 H, CH₂C=), 1.57 (m, 6 H, -CH₂-) in 82% yield, and chloromethylenecyclohexane (IIc), 1^{7} bp 160-161°, in 78% yield, respectively.

Anal. Calcd for C7H11I: C, 37.8; H, 5.0; I, 57.2. Found: C, 38.0; H, 4.9; I, 57.3.

Similar treatment of Ib and Ic in the presence of sodium iodide afforded iodomethylenecyclopentene (III) [bp 83-85° (15 mm); nmr δ 5.85 (m, 1 H, =CH), 2.28 (m, 4 H, CH₂C==), 1.80 (m, 4 H, CH2) in 81 % yield] and 1-iodo-2-methylpropene (IV) [bp 126-127° nmr δ 5.82 (m, 1 H, ==CH), 1.90 (d, 3 H, CH₃), 1.83 (s, 3 H, CH₃) in 80% yield] respectively.

Anal. Calcd for C_8H_9I : I, 61.0. Found: I, 61.1. Calcd for C_4H_7I : I, 69.7. Found: I, 69.5.

Similar treatment of V⁸ in the presence of added sodium iodide afforded the isomeric iodides, trans-1-iodo-2,3,3-trimethyl-1-butene (VIa) and cis-1-iodo-2,3,3-trimethyl-1-butene (VIb) as a mixture, bp 76-78° (20 mm), which consisted of about 94% VIa and 6% VIb. By preparative glpc pure samples of VIa⁹ (eluted first) [nmi δ 6.00 (m, 1 H, =CH), 1.85 (d, $J \cong 1.5$ Hz, 3 H, CH₃C=), 1.10 (s, 9 H, CH₃C), and VIb; nmr δ 6.00 (m, 1 H, =CH), 1.93 (d, $J \cong 1.5$ Hz, 3 H, CH₃C==), 1.30 (s, 9 H, CH₃C)] were obtained.

Anal. Calcd for $C_7H_{13}I$: C, 37.5; H, 5.8; I, 56.7. Found: (for VIa, C, 37.7; H, 6.0; I, 56.5; for VIb, I, 56.5).

Pure VIa and VIb were recovered unchanged when subjected to the reaction conditions and on distillation at about 90°. No isomerization of either VIa or VIb took place on exposure to ordinary light in the laboratory. All attempts to prepare vinyllithium derivatives by treatment with lithium metal in ether failed to give clean-cut products.

The isomeric bromides, VIIa and VIIb, prepared as above, were obtained in 76% yield as a liquid, bp 64-68° (18 mm). These were not completely separated by glpc on any of four columns. The isomer VIIb appeared as a shoulder on the long time side in all columns and was estimated to constitute about 8% of the mixture. The mixture of VIIa and VIIb was converted as described⁸ into the lithium derivatives which on reaction with triethylsilyl chloride yielded the corresponding triethylsilyl compounds in 45% yields.

In another experiment, the lithium derivative formed from the mixture of VIIa and VIIb was added to a Dry Ice-ether suspension. The acid formed was esterified with diazomethane to yield (10%) a mixture of unsaturated esters, the major (98%) component of which was identical with methyl trans-2,3,3-trimethyl-2butenoate (IX) as shown by glpc analysis and comparison with an authentic sample.8

Alkaline Treatment of 5,5-Disubstituted N-Nitrosooxazolidones in Aqueous Glyme. In a typical experiment an equivalent of 50% sodium hydroxide was added dropwise with stirring to 5.0 g (0.029 mol) of Ia partly dissolved in 100 ml of 5:1 water-glyme, the temperature being held below 40° by cooling. After the evolution of nitrogen (quantitative in 1 hr) the mixture was worked up as usual. The residue was distilled from a small flask into a weighed receiver. The yields of a mixture of cyclohexanecarboxaldehyde (X) and cycloheptanone (XI) were in the 90–95% range and the ratio of X to XI was about 89/11 as determined by glpc. Comparison of the minor product with authentic cycloheptanone proved the identity.

Repetition of the above experiment when the aqueous medium was saturated with lithium bromide produced a mixture of products in high yield which was shown by glpc to contain 3% X, 49% IIb, and 48% XI. A sample of pure 1-bromocycloheptene was prepared as described¹⁸ in 40% yield. The vinyl hydrogen in the nmr was a triplet at δ 6.13 (J = 7 Hz). The nmr spectrum of IIb (=CH at 5.80)18 showed that no 1-bromocycloheptene was present.

2-Methylpropenyltriethylsilane (XIV). To a solution of 5 g of Ic in 25 ml of benzene and 25 g of triethylsilane was added a small excess of lithium ethoxide ethanolate19 in four portions. The theoretical amount of nitrogen was soon evolved and after the usual work-up distillation afforded 3.61 g (61%) of XIV: bp 77-79° (16 mm), 186-188° (755 mm) (lit.¹² bp 185-186° (740 mm)); nmr δ 5.17 (m, 1 H, =CH), 1.85 (d, 3 H, CH₃C=), 1.77 (s, 3 H, CH₃C=),

⁽¹²⁾ A. D. Petrov and G. I. Nikishin, Zh. Obshch. Khim., 26, 1233 (1956).

⁽¹³⁾ F. A. Carey and H. S. Tremper, J. Amer. Chem. Soc., 90, 2578 (1968); 91, 2967 (1969).

⁽¹⁴⁾ D. Seyferth, R. Damrauer, J. Y-P. Mui, and T. F. Jula, ibid., 91, 2944 (1969).

⁽¹⁵⁾ For analytical glpc a 6 ft \times $\frac{1}{8}$ in. aluminum column packed with 7% Carbowax 20M on 60-80 mesh Chromosorb W was used in the 130-150° range. For preparative glpc an 8 ft \times $^{3}/_{8}$ in. aluminum column packed with 12% Carbowax 20M on 40/60 mesh Chromosorb W was used at 140° with a helium flow of 120 ml/min. All experiments in which yields are reported were done at least twice. Nmr spectra were taken in CCl_4 using $(CH_3)_4Si$ as internal standard on a Varian A-60. All microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The term "worked up as usual" means that the reaction mixture was diluted with ice water and the products extracted into etherbenzene. The ether-benzene extracts were washed with saturated salt solution and filtered through a cone of anhydrous MgSO4. The solvents were then removed under vacuum.

⁽¹⁶⁾ J. Wolinsky and K. L. Erickson, J. Org. Chem., 30, 2208 (1965). (17) D. Seyferth, J. K. Heeren, G. Singh, S. O. Grim, and W. B.
 Hughes, J. Organometal. Chem., 5, 267 (1966).
 (18) P. Cresson, Bull. Soc. Chim. Fr., 2629 (1964).
 (19) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., J. Amer. Chem.

Soc., 85, 2754 (1963).

1.25–0.30 (m, 15 H, CH₂CH₃). A sample of XIV was prepared in 40% yield by forming the lithium derivative from 2-methyl-1-propenyl bromide and treating with triethylsilyl chloride as described.¹² The two samples of XIV were identical.

2-Methoxyethyl 2-Methylpropenyl Ether (IVa). By a procedure similar to that described 3b Ic was converted into IVa, bp 151–155°,

in 71% yield. The analytical sample was collected by preparative glpc and readily formed a yellow 2,4-dinitrophenylhydrazine derivative, mp 181–182°, alone and mixed with the 2,4-DNPH derivative of isobutyraldehyde.

Anal. Calcd for $C_7H_{14}O_2$: C, 64.6; H, 10.8. Found: C, 64.3; H, 10.8.

Stereoselective Reactions of 1,2,2-Trimethylpropylidenecarbene with 1,1-Diphenylethylene, Tetramethylallene, and Triethylsilane

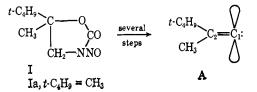
Melvin S. Newman and Timothy B. Patrick¹

Contribution from the Evans Chemistry Laboratory of the Ohio State University, Columbus, Ohio 43210. Received January 8, 1970

Abstract: Treatment of 5-methyl-5-t-butyl-N-nitrosooxazolidone (I) with lithium ethoxide ethanolate in the presence of 1,1-diphenylethylene (II), tetramethylallene (III), and triethylsilane (IV), respectively, yielded the following major products: cis-1-(1,2,2-trimethylpropylidene)-2,2-diphenylcyclopropane (V); cis-1-isopropylidene-2-(1,2,2-trimethylpropylidene)-3,3-dimethylcyclopropane (X) (also lesser amounts of the *trans* isomer, XI); and cis-1-methyl-1-t-butyl-2(triethylsilyl)ethylene (XIV). The stereochemistry of the products is explained by assuming that 1,2,2-trimethylpropylidenecarbene (A) is the intermediate formed from I and that the approach of A toward the various reactants takes place so that the smaller group is near the reactant.

I n earlier work the facts that alkylidenecarbenes,² produced on treatment of 5,5-dialkyl-N-nitrosooxazolidones with lithium alkoxides in aprotic solvents, are electrophilic species yet react more slowly with tetramethylethylene than with cyclohexene were explained by assuming that a steric effect is operative.² As only symmetrically substituted unsaturated carbenes, $R_2C=-C$; were involved certain features regarding the stereochemistry of addition to unsymmetrical olefins could not be studied.

Accordingly we now report on the compounds resulting from treatment of 5-methyl-5-*t*-butyl-N-nitrosooxazolidone (I) with lithium ethoxide ethanolate⁸ in 1,1-diphenylethylene (II), tetramethylallene (III), and triethylsilane (in benzene) (IV). The structures of the compounds are explained by assuming the reactive intermediate to be 1,2,2-trimethylpropylidenecarbene (A) (see ref 2 for the mechanism).

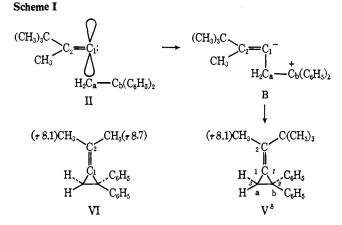


Assuming A to be a singlet unsaturated carbene,⁴ the vacant orbital of C_1 lies in the plane of the paper. When A approaches II (shown as viewed from the plane

(3) W. M. Jones, M. H. Grasley, and N. S. Brey, *ibid.*, 85, 2754 (1963).
(4) R. Gleiter and R. Hoffman [*ibid.*, 90, 5457 (1968)] give calculations which support the concept that singlet carbenes at an unsaturated

carbon may be preferred to triplet.

of the double bond of the olefin) the axis of the vacant orbital is perpendicular to the plane of the double bond of II. C_1 approaches C_a of II so that the methyl (smaller) group of A is pointed toward II as shown in Scheme I.⁵ The reaction proceeds through a dipolar ion, B,⁶ which rapidly yields V. This hypothetical reaction path predicts that V should be formed. Experiment shows that a mixture of olefins is obtained in 15% yield.⁷ The olefin mixture is composed of ten parts of *cis*-1-(1,2,2-trimethylpropylidene)-2,2-diphen-



ylcyclopropane (V) to one part of an unidentified product which has a slightly higher retention time (glpc).

(5) As long as the axis of the vacant orbital of A is perpendicular to the plane of II the projected angle described by the line joining C_1 and C_2 with the line joining C_a and C_b can have any angle (0-180°). We prefer an angle of 180° as shown because less movement is required to reach the final structure if this angle is involved.

(6) If a triplet carbene were involved, the intermediate, B, would be a diradical. However, the stereochemistry of the product would probably be the same.

(7) Oxygenated compounds similar to those encountered before² are also obtained.

(8) The heavy numbers refer to the numbering system of the alkylidene cyclopropane molecule. The numbers and letters in italics refer to the origin of the carbons in A and II, respectively.

⁽¹⁾ Postdoctoral Research Associate supported by Grant 5552 of the National Science Foundation.

⁽²⁾ We have been informed by Dr. K. Loening of Chemical Abstracts, Columbus, Ohio, that the nomenclature system for unsaturated carbenes recommended in M. S. Newman and T. B. Patrick, [J. Amer. Chem. Soc., 91, 6461 (1969)] is incorrect. A correct system is based on the alkylidenecarbene, $R_2C=C$; root. Thus, $H_2C=C$: is methylenecarbene and $(CH_4)_2C=C$: is isopropylidenecarbene, etc.