

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 C₇H₁₄O₂: C, 64.6; H, 10.8. Found: C, 64.3; H, 10.8.

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

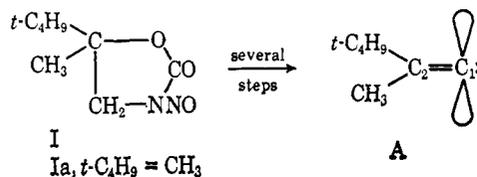
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Contribution from the Evans Chemistry Laboratory of the Ohio State University, Columbus, Ohio 43210. Received January 8, 1970

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-trimethylpropylidencarbene (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.

In earlier work the facts that alkylidencarbenes,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, R₂C=C:, were involved certain features regarding the stereochemistry of addition to unsymmetrical olefins could not be studied.

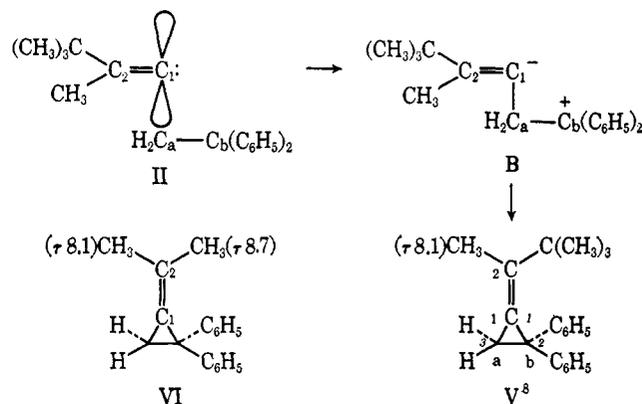
Accordingly we now report on the compounds resulting from treatment of 5-methyl-5-*t*-butyl-*N*-nitrosooxazolidone (I) with lithium ethoxide ethanolate³ in 1,1-diphenylethylene (II), tetramethylallene (III), and triethylsilane (in benzene) (IV). The structures of the compounds are explained by assuming the reactive intermediate to be 1,2,2-trimethylpropylidencarbene (A) (see ref 2 for the mechanism).



Assuming A to be a singlet unsaturated carbene,⁴ the vacant orbital of C₁ lies in the plane of the paper. When A approaches II (shown as viewed from the plane

of the double bond of the olefin) the axis of the vacant orbital is perpendicular to the plane of the double bond of II. C₁ 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-

Scheme I



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

(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 alkylidencarbene, R₂C=C:, root. Thus, H₂C=C: is methylenecarbene and (CH₃)₂C=C: is isopropylidencarbene, etc.

(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.

(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 C₁ and C₂ 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.

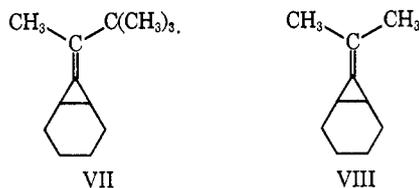
(7) Oxygenated compounds similar to those encountered before² are also obtained.

(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.

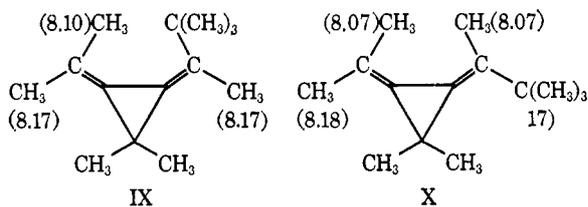
No effort was made to identify the minor component. The structure of the major component was established as V by elemental analyses, nmr, and mass spectral data. When isopropylidenecarbene was similarly generated from 5,5-dimethyl-N-nitrosooxazolidone (Ia) in 1,1-diphenylethylene a 16% yield⁷ of the corresponding isopropylidene cyclopropane, VI, was obtained. Comparison of the τ values for the methyl groups in V and VI establishes the stereochemistry of V as shown.

The fact that the main product, the *cis* isomer (V), is undoubtedly more strained than the *trans* isomer argues against a one-step mechanism because in a one-step process the less strained *trans* isomer would be predicted to be the major product.

Interestingly, the yield of V is comparable to that of VI and the yield of 7-(1,2,2-trimethylpropylidene)-bicyclo[4.1.0]heptane (VII) is comparable to that of 7-isopropylidenebicyclo[4.1.0]heptane (VIII), formed when the nitroso compounds I and Ia are treated with lithium ethoxide in cyclohexene. The above sets of facts are consistent with the stereochemistry of approach indicated in Scheme I as it is the methyl groups of the carbenes formed from I and Ia which provide the steric hindrance to addition.



Treatment of I with lithium ethoxide in tetramethylallene (III) yielded a mixture of products from which *cis*-1-isopropylidene-2-(1,2,2-trimethylpropylidene)-3,3-dimethylcyclopropane (IX), the *trans* isomer (X), and ethyl *trans*-2,3,3-trimethyl-1-butenyl ether (XI) were obtained in 15, 8, and 7% yields, respectively.

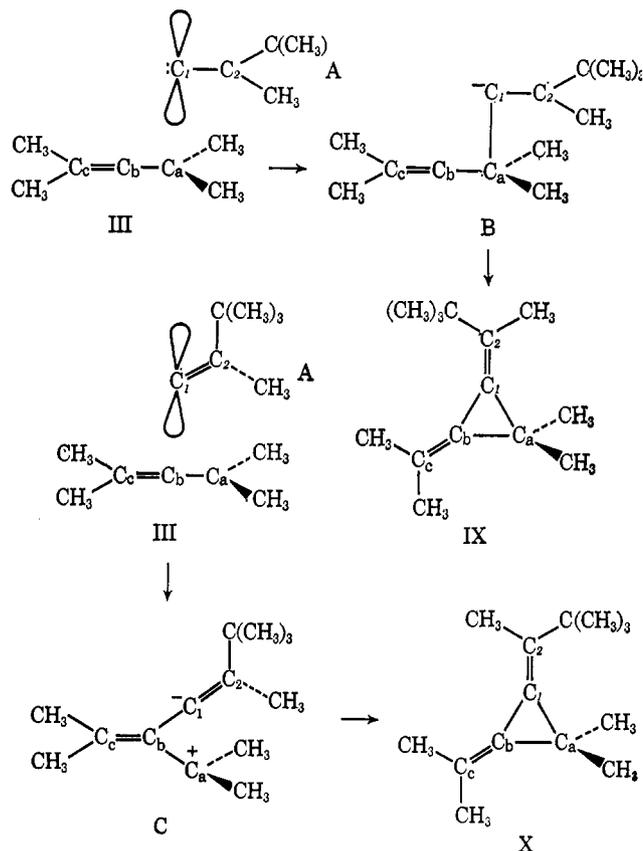


In assigning the structures to IX and X the assumption was followed that methyl groups on a double bond which are *cis* to the saturated *gem*-dimethyl group have slightly higher τ values than methyl groups *cis* to the exocyclic unsaturated groups.⁹

The hypothetical attacks of A on III leading to IX and X are shown in Scheme II. The three allenic carbons of III are lettered a, b, and c. The approach of A in which the attack is at C_a, with the methyl group as shown because of a smaller steric effect, leads to the dipolar ion B which cyclizes to the major product IX. The formation of the minor product X is rationalized by postulating that A attacks III at carbon b with the vacant orbital of C₁ in the plane of the paper but C₂ behind the paper. The line joining C₁ and C₂ of A is about perpendicular to the line joining C_a and C_b of III.

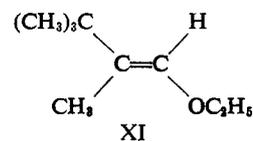
(9) G. Köbrich, H. Heinemann, and W. Zündorf, *Tetrahedron*, **23**, 565 (1967).

Scheme II



In the attack on C_b, A is shown in perspective. Such an attack leads to the dipolar ion C which cyclizes to the minor product, X. Examination of the cyclization of C with molecular models indicates that the twisting needed to yield X seems to be favored sterically over the twisting needed to yield IX. Admittedly the above arguments are not decisive. However, the main points we suggest are that IX is formed by attack of A at C_a of III whereas X is formed by attack at C_b.¹⁰

The structure of XI is based on the fact that no isomerization to an isomeric ether occurred on heating over 5% rhodium-on-alumina at 210° for 7 hr in a sealed tube. The formation of *trans* product in the reaction which leads to XI can be explained either by involvement of A or the corresponding unsaturated carbonium ion as each species is attacked from the less hindered side by the electrons on the oxygen of the alcohol. In formulas showing the reaction of A with III

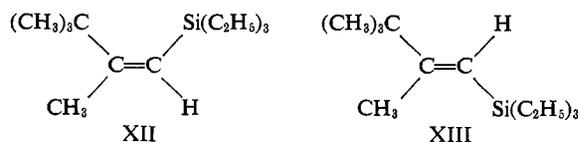


to form C, a slight perspective notation is used to show how the carbene portion is oriented.

Treatment of I in benzene containing triethylsilane with lithium ethoxide yielded 60% of a 10:1 mixture of the isomeric 1-methyl-1-*t*-butyl-2-(triethylsilyl)ethylenes (XII) and (XIII). The major product was assigned the

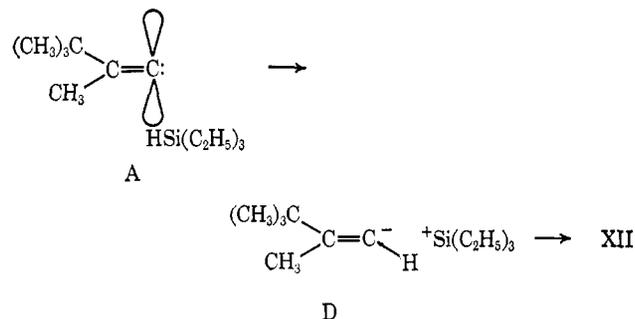
(10) Some IX may also be formed by attack at C_b. The attack of dichlorocarbene at the center carbon of an allene may account for the two isomers obtained by A. Bézauguet, *C. R. Acad. Sci., Paris*, **254**, 3371 (1962).

cis structure, XII, as on heating to 230° over rhodium-on-alumina catalyst, both XII and XIII yielded the same



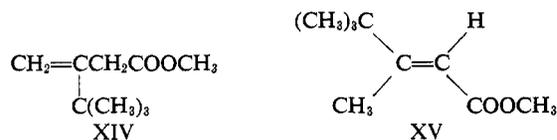
equilibrium mixture which contained about 95% XIII and 5% XII. We assume the more stable isomer to be *trans*.

Scheme III



The attack of A on triethylsilane removes a hydride ion to yield the ion pair D which immediately collapses to the major product XII, the *unstable* isomer. If a one step insertion of the carbene occurred as pictured in the case of a saturated carbene¹¹ the major product would be expected to be the stable isomer, XIII. Interestingly, if an unsaturated carbonium ion were involved, the expected product would be 2,3,3-trimethyl-1-butene as reactions of carbonium ions with trialkylsilanes result in hydride ion transfer.^{12,13}

During the preparation of I, the dehydration of methyl 3-hydroxy-3,4,4-trimethylpentanoate¹⁴ with thionyl chloride and pyridine was reexamined. The unsaturated esters were shown to consist of about equal amounts of methyl 3-*t*-butyl-3-butenoate (XIV) and methyl *trans*-3-*t*-butyl-2-butenoate (XV).



Experimental Section¹⁵

5-Methyl-5-*t*-butyl-2-oxazolidone. A mixture of 50.0 g (0.26 mol) of ethyl 3-hydroxy-3,4,4-trimethylpentanoate¹⁴ and 10.5 g (0.31 mol) of 95% hydrazine was heated at 90–100° while ethanol-water distilled (12 ml) during 30 min. The mixture on cooling furnished over 95% yield colorless hydrazide, mp 79.0–80.5°, which was converted directly to oxazolidone as follows.

A mixture of 100.0 g (0.57 mol) of the hydrazide in 800 ml of 6 *N* hydrochloric acid was treated at 5° with a solution of 69.0 g (1.0

mol) of sodium nitrite in 300 ml of water during 30 min. The resulting solution gave a positive nitrous acid test. Hexane (400 ml) was added and the mixture was heated to 60°. Gas evolution was rapid and quantitative after 2 hr. On cooling, 59.0 g (67%) of product, mp 129–129.5, crystallized. Recrystallization from benzene-hexane without significant loss yielded pure 5-methyl-5-*t*-butyl-2-oxazolidone: mp 129.5–130.5°; nmr (CDCl₃) τ 9.0 (s, 9 H, C(CH₃)₃), 8.57 (s, 3 H, CH₃), 6.33 and 6.89 (each center of doublets, 2 H, CH₂, $J = 8.5$ Hz) and 3.27 (broad, 1 H, NH).

Anal. Calcd for C₈H₁₅NO₂: C, 61.1; H, 9.6; N, 8.9. Found: C, 61.3; H, 9.6; N, 8.9.

5-Methyl-5-*t*-butyl-N-nitroso-2-oxazolidone (I). A solution of 50.0 g (0.32 mol) of oxazolidone in 250 ml of tetrahydrofuran and 100 ml of 12 *N* hydrochloric acid at 0° was treated with a solution of 50.0 g (0.75 mol) of sodium nitrite in 300 ml of water during 30 min. The organic layer which separated and an ether extract of the aqueous layer were combined and worked up as usual to yield a yellow solid which was recrystallized from cyclohexane to give 49.3 g (84%) of pure I in 3 crops, mp 87.5–88.5°.

Anal. Calcd for C₈H₁₄N₂O₃: C, 51.6; H, 7.6; N, 15.0. Found: C, 51.8; H, 7.8; N, 15.0.

***cis*-1-(1,2,2-Trimethylpropylidene)-2,2-diphenylcyclopropane (V).** A solution of 5.0 g (0.028 mol) of I in 90 g of 1,1-diphenylethylene¹⁶ was treated all at once at 60° with 4.5 g of lithium ethoxide ethanolate.³ The vigorous reaction was complete within 10 min. The mixture was poured into water and worked up as usual. Most of the diphenylethylene was removed by slow distillation at 145–148° (10 mm). The remaining yellow liquid contained some diphenylethylene and three products in a mole ratio of 1:2:18 (by glpc). The major component, V, amounted to 1.1 g (14%) and was the only product which could be obtained pure by preparative glpc on a 2 ft × 0.25 in. column of 10% SE-30 on Chromosorb W at 150° and with a helium flow of 150 ml/min, retention time, 13 min. On cooling a colorless solid, mp 62.5–65.0°, was obtained.

The nmr spectrum (CCl₄) showed bands at 2.88 (broad singlet, 10 H, aromatic), 8.05 (s, 3 H, CH₃), 8.5–9.5 (rounded multiplet, CH₂), and 8.80 (s, C(CH₃)₃). The CH₂ and C(CH₃)₃ signals totaled 11 protons. The mass spectrum (70 eV) showed the molecular ion at m/e 276 (15%) and the base peak at m/e 219 (M – C(CH₃)₃).

Anal. Calcd for C₂₁H₂₄: C, 91.3; H, 8.7. Found: C, 91.5; H, 8.5.

1-Isopropylidene-2,2-diphenylcyclopropane (VI). The procedure was the same as that used for the preparation of V, except that 5,5-dimethyl-N-nitroso-2-oxazolidone² was used instead of I. Diphenylethylene was removed by distillation at 75–88° (0.3 mm). Glpc analysis showed that 1.1 g (16%) of VI was present. Purification was accomplished by preparative glpc on a 5 ft × 0.25 in. column of 20% SE-30 on Chromosorb W at 160° with a helium flow of 90 ml/min, retention time 7 min. The product was slightly yellow.

Anal. Calcd for C₁₈H₁₈: C, 92.3; H, 7.7; mol wt, 234. Found: C, 92.5; H, 7.5; mol wt (mass spectrum), 234.

The nmr spectrum (CCl₄) showed bands at 8.7 (singlet with slight coupling, 3 H, CH₃ *cis* to phenyls), 8.3–9.3 (complex multiplet, 2 H, CH₂), 8.07 (singlet with slight coupling, 3 H, CH₃ *trans* to phenyls), 2.1–2.9 (multiplet with sharp peak at 2.8, 10 H, aromatic).

7-(1,2,2-Trimethylpropylidene)norcarane (VII). A solution of 10.0 g (0.057 mol) of I in 150 ml of pure cyclohexene at 40° was treated all at once with 6.0 g of lithium ethoxide ethanolate.³ Evolution of nitrogen occurred immediately and lasted 15 min. The cooled reaction mixture was poured into water and worked up as usual to yield 3.8 g (38%) of pure VII: bp 100–101° (10 mm); ir band at 5.65; nmr (CCl₄) 8.23 (s, 3 H, CH₃C), 8.90 (s, 9 H, C(CH₃)₃) and 8.0–9.2 (broad multiplet, 10 cyclohexyl protons).

Anal. Calcd for C₁₃H₂₂: C, 87.6; H, 12.4. Found: C, 87.5; H, 12.6.

***cis*- and *trans*-1-(1,2,2-Trimethylpropylidene)-2-(2-propylidene)-3,3-dimethylcyclopropane (IX) and (X).** A suspension of 5.0 g (0.027 mol) of I in 30 ml of tetramethylallene (Columbia Chemicals Co.) at 50° was treated with 3.5 g of lithium ethoxide ethanolate³ all at once. The reaction was complete within 5 min. The cooled mixture was worked up as usual. Distillation at 40–105° (10 mm) furnished 1.7 g of colorless products which by glpc (8 ft × 3/8 in. column of 20% Carbowax 20M on Chromosorb W, 110°, helium flow 100 cc/min) showed four components: A, 1 min, 0.23 g, tetramethylallene; B, 2 min, 0.27 g (7%), *trans*-2,3,3-tri-

(11) D. Seyferth, D. Damrauer, J. Y.-P. Mui, and R. F. Jula, *J. Amer. Chem. Soc.*, **91**, 2967 (1969).

(12) F. A. Carey and H. S. Tremper, *ibid.*, **90**, 2578 (1968).

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

(14) M. S. Newman and R. Rosher, *J. Org. Chem.*, **9**, 221 (1944).

(15) All melting points and boiling points are uncorrected. The term "worked up as usual" means that an ether-benzene layer containing the products was washed with dilute acid and/or base, with saturated salt solution, and then filtered through a cone of anhydrous magnesium sulfate. The solvents were removed by distillation (or on a rotary evaporator) and the residue was processed as indicated. Infrared absorption was reported in microns and nmr as τ relative to (CH₃)₄Si as 10.0 and were taken on a Varian A-60 instrument. Microanalyses were conducted by Galbraith Laboratories, Knoxville, Tenn.

(16) C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, H. Gilman, Ed., 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1932, p 226.

methyl-1-butenyl ethyl ether (XI); C, 3.6 min, 0.78 g (15%), IX; and D, 5.2 min, 0.42 g (8%), X. Pure materials were obtained by preparative glpc on the above column and showed the following properties.

XI: ir (neat) 5.95 (C=C), 8.85 (CO); nmr (CCl₄) 8.9 (s, 9 H, C(CH₃)₃), 8.6–8.9 (t, 3 H, CH₂CH₃, *J* = 7 Hz), 8.45 (d, 3 H, -CCH₃, *J* = 1.5 Hz), 6.25 (center of quartet 2 H, CH₂CH₃, *J* = 7 Hz) and 4.2 (m, 1 H, -CH), *n*^{25D} 1.4290.

Anal. Calcd for C₉H₁₈O: C, 76.0; H, 12.7. Found: C, 75.8; H, 12.8.

IX: ir (neat) 5.55 and 6.10 (C=C); nmr (CCl₄) 8.93 (s, 15 H, 2CH₃ at 3 position and C(CH₃)₃), 8.10 (s, 3 H, *cis*-CH₃), 8.17 (s, 6 H, *trans*-CH₃); (in benzene), 8.98 (s, 9 H, C(CH₃)₃), 8.92 (s, 6 H, 2 CH₃ at 3 position), 8.14 (s, 9 H, *cis*- and *trans*-CH₃); *n*^{25D} 1.4858.

Anal. Calcd for C₁₄H₂₄: C, 87.4; H, 12.6. Found: C, 87.3; H, 12.6.

X: ir (neat) 5.55 and 6.10 μ (C=C); nmr (CCl₄) 8.90 (s, 9 H, C(CH₃)₃), 8.83 (s, 6 H, CH₃ at 3 position), 8.18 (s, 3 H, *trans*-CH₃), 8.07 (s, 6 H, *cis*-CH₃); *n*^{25D} 1.4898.

Anal. Found: C, 87.3; H, 12.6.

cis- and *trans*-1-Methyl-1-*t*-butyl-2-(trimethylsilyl)ethylene (XII and XIV). A solution of 5.5 g (0.03 mol) of I in 50 ml of dry benzene and 20 g of triethylsilane (Pierce Chemical Co.) was treated all at once with 3.5 g of lithium ethoxide ethanolate.⁸ The reaction was complete within 5 min. After the usual work-up, a yellow liquid was obtained which showed two products by glpc (5 ft × 1/8 in. column, 7% Carbowax 20M on Chromosorb W, 80°) in a ratio of 10:1 with the major component eluting last. Distillation at 106–110° (10 mm) furnished 3.4 g (60%) of colorless material which had the same glpc as before distillation.

Preparative glpc (8 ft × 3/8 in. column, 20% Carbowax 20M on Chromosorb W at 95°, flow 80 ml/min) furnished pure samples of each component. The retention time of the major component was twice that of the minor component. The following properties were obtained.

XIII, minor (*trans*): ir (neat) showed strong bands at 3.3, 12.8, 13.5, 13.7, 13.9, weak bands at 6.2, 6.8, 8.0, 9.8, 11.9, medium bands at 7.0, 7.2, 9.0, 10.2, 11.6; nmr (CCl₄) 8.94 (s, 9 H, C(CH₃)₃), 8.20 (s, 3 H, CH₃), 4.81 (s, 1 H, =CH), 8.8–9.5 (m, 15 H, CH₂CH₃).

Anal. Calcd for C₁₃H₂₈Si: C, 73.5; H, 13.3; Si, 13.2; mol wt, 212. Found: C, 73.2; H, 13.1; mol wt, 212 (mass spectrum).

XII, minor (*cis*): ir (neat) strong bands at 3.3, 6.2, 9.8, 12.2, 12.8, 13.7, weak bands at 6.8, 7.3, 8.1, 9.1, medium bands at 8.3, 10.2, 11.6; nmr (CCl₄) 8.88 (s, 9 H, C(CH₃)₃), 8.05 (d, 3 H, CH₃, *J* = 1.5 Hz), 4.87 (m, 1 H, =CH), 8.9–9.7 (m, 15 H, CH₂CH₃).

Anal. Found: C, 73.3; H, 13.1; Si, 13.3; mol wt, 212 (mass spectrum).

A mixture of 0.6 g of the vinylsilanes (10 parts, XII + 1 part XIII) and 0.2 g of 5% rhodium on alumina was heated at 230°. Equilibration was obtained in about 8 hr in which the ratio of XIII to XII was 19.5:1.

Ethyl *trans*-2,3,3-Trimethyl-1-butenyl Ether (XI). A solution of 8.0 of I in 100 ml of absolute ethanol was treated dropwise with 13 *N* sodium ethoxide-ethanol solution until gas evolution stopped (20 min). The mixture was poured into water and worked up as usual. Distillation at 100° (150 mm) gave 4.5 g (75%) of XI, bp 150–151°. Analysis by glpc on several columns showed only one peak. A mixture of 50 mg of the vinyl ether and 10 mg of 5% rhodium on alumina heated in a sealed tube at 210° for 7 hr was unchanged as shown by glpc analysis. The *trans* configuration is assigned to the product on this basis. Spectral properties were identical with those obtained for XI from the tetramethylallene reaction.

Methyl 3-*t*-Butyl-3-butenate (XIV) and Methyl *trans*-3-*t*-Butyl-2-butenate (XV). Dehydration by thionyl chloride of methyl 3-hydroxy-3,4,4-trimethylpentanoate¹⁴ yielded a mixture of unsaturated methyl esters. By distillation and glpc analysis this mixture was shown to consist of about equal amounts of XIV (lower boiling, shorter retention time) and XV. The nmr spectra in CCl₄ were as follows: XIV, 8.92 (s, 9 H, C(CH₃)₃), 6.32 (s, 3 H, OCH₃), 5.27 (s with slight coupling, 2 H, CH₂), 5.06, 5.91 (broad, 1 H each, =CH₂); XV, 9.89 (s, 9 H, C(CH₃)₃), 7.82 (s, 3 H, CH₃), 6.32 (s, 3 H, OCH₃), 4.27 (broad, 1 H, =CH). The ir carbonyl bands of XIV and XV lie at 5.75 and 5.85 μ, respectively.

Photolysis of a solution of 4.0 g of XV in 150 ml of dry ether under nitrogen at 30° with a Hanovia 450-W lamp for 2.8 hr furnished 4.0 g of product consisting of 78% XV and 22% *cis* ester as analyzed by nmr. The products were not separated by vpc on several columns. In addition to the absorptions for the *trans* isomer, peaks at 8.79 (C(CH₃)₃), 8.13 (d, CH, *J* = 2 Hz) 6.32 (OCH₃), 4.2 (C=CH) for the *cis* isomer were present.

Isomerization of the 78:22 *trans*-*cis* mixture at 230° with 5% rhodium-on-alumina catalyst for 16 hr gave a mixture which was estimated by nmr to be 90:10 *trans*-*cis*.

Pure XV was shown to be identical with the product obtained from *trans*-1-bromo-2,3,3-trimethyl-1-butene via carbonation of the lithium derivative and esterification of the resulting acid with diazomethane.¹⁷

(17) See accompanying paper by M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, **92**, 4309 (1970).