tent of 61%. If the reaction was allowed to proceed further, the mixture began to separate into two phases and some decomposition set in.

To propiophenone (**1a**) (134 mg, 1 mmol) in 1 ml of dry CCl_4 in an nmr tube was added CSI (0.085 ml, 0.98 mmol). After 45 hr the mixture began separating into two phases. Nmr at 42 hr showed **1a** (43%), amide **2a**, (47%; τ 8.49 (d, J = 7 Hz, CH_3), 5.42 (q, J = 7 Hz, CH), and *ca.* −0.80 (NH)), and enol **2′a** (10%; τ 7.92 (s, CH_3), and −1.00 to −0.80 (OH and NH)). The enol form **2′a** was thus present to the extent of 18%.

Acknowledgment. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

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Unsaturated Carbenes from Primary Vinyl Triflates. II.[1] Spin Multiplicity via Stereochemistry of Addition to Olefins

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Received July 23, 1974

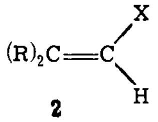
Abstract: The stereochemistry of addition of isopropylidenecarbene, generated from primary vinyl triflates, to olefins was investigated. Addition was found to be more than 98% stereoselective to *cis*- and *trans*-2-methoxy-2-butene and stereospecific to *cis*- and *trans*-2-butene indicating that the nascent carbene is a singlet. Dilution experiments with *trans*-2-butene and perfluorocyclobutane as the inert diluent strongly suggest that the singlet is also the ground state of such unsaturated carbenes.

It is well known[2] that carbenes can exist in both the singlet and triplet state depending upon both the nature of the particular carbene as well as its mode of generation. Methylene itself has been shown[3] to possess a triplet ground state in agreement with recent theoretical calculations.[4]

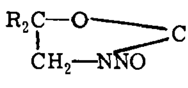
In recent years, besides continued developments in normal carbene chemistry,[2] there have been increasing reports and interest in unsaturated carbenes (**1**). Such species have been generated from primary vinyl halides[5] (**2**) and RLi, base decomposition of N-nitrosooxazolidones[6] (**3**), and most recently from primary vinyl triflates[1] (**4**) and *t*-BuOK. Despite this surgence of interest in unsaturated carbenes, very little is known about their spin multiplicity. Recent theoretical calculations by Dewar and coworkers[7] using the MINDO/2 procedure as well as earlier calculations by Gleiter and Hoffmann[8] predict the singlet to be the ground state for methylenecarbene itself (**1**; R = H). However, outside of a brief mention by Newman[6d] of the stereochemistry of addition of isopropylidenecarbene (**1**; R = CH_3) as generated from nitrosooxazolidone to *cis*- and *trans*-4-methyl-2-pentene, with little or no experimental detail given, there are no experimental data on the spin multiplicity of these species. Therefore, we undertook and report in this paper a detailed investigation of the spin multiplicity of unsaturated carbenes (**1**) as generated[1] from primary vinyl triflates (**4**) and determined by the stereospecificity of addition to olefins.

$(R)_2C{=}C:$

1


$(R)_2C{=}C(X)H$

2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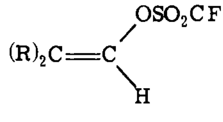
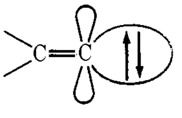

$(R)_2C{=}C(OSO_2CF_3)H$

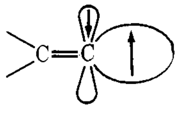
4

Results and Discussion

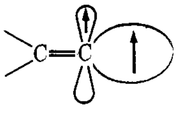
A priori any carbene, including unsaturated carbenes, may be in one of three low-energy states:[9] a singlet state (S_0) in which one carbon AO is empty and the second contains two unshared spin-paired electrons (**5**); a singlet (S_1) with two singly occupied orbitals (**6**); and the triplet state (T_1) in which two electrons with parallel spins singly occupy two carbon AO's (**7**). Perhaps the most direct and best experimental method for the determination of spin multiplicities is low-temperature ESR techniques. However, none of the presently available experimental procedures[1,5,6] for generating unsaturated carbenes is amenable to such techniques. Furthermore, this technique provides direct evidence only in the case of unpaired (i.e., triplet) electrons. Hence we chose the alternative and commonly employed technique[11] of the stereochemistry of carbene addition to cis and trans olefins.



5 (S_0)



6 (S_1)



7 (T_1)

The particular system studied was the reaction of isopropylidenecarbene (**1**; R = CH_3), as generated from the appropriate vinyl triflate (**4**; R = CH_3) and *t*-BuOK, with *cis*- and *trans*-2-butene and *cis*- and *trans*-2-methoxy-2-butene. The necessary vinyl triflate was prepared from isobutyraldehyde as previously described.[1]

Relative Reactivity of *cis*- and *trans*-2-Butene and *cis*- and *trans*-2-Methoxy-2-butene with Isopropylidenecarbene. In order to accurately assess the stereospecificity of reaction of the carbene with the "pure" isomeric olefins, it was first necessary to determine the relative reactivity of the cis and trans olefins. This was accomplished by reacting a large excess of a nearly 50:50 mixture of *cis*- and *trans*-2-butenes and *cis*- and *trans*-2-methoxy-2-butenes, respectively, with the carbene and careful analysis of the product ratios. Use of the well-established relationship[12] expressed in eq 1,

$$(k_x/k_y) = (P_xO_y/P_yO_x) \qquad (1)$$

where k_i is the rate constant for reactions of the carbene with the olefins, P_i is the mole fraction of adduct product, and O_i is the initial mole fraction of precursor olefin, allows calculation of the relative rates. The results are summarized in Table I.

It is interesting to note that, in the case of 2-butene, the cis isomer reacts considerably faster than the trans isomer, whereas the reverse is the case with the 2-methoxy-2-butenes. Although in normal carbene chemistry examples of relative reactivity with either faster trans reactivity or faster cis reactivity of 2-butene are known, the latter predominates.[2a] Since *trans*-2,3-dimethylmethylenecyclopropane is known[13] to be thermodynamically more stable than the corresponding cis isomer, the faster reaction of the cis olefin must be governed by factors other than thermodynamic and steric. A number of factors such as dispersion forces or secondary electrostatic interactions[14] and/or steric attraction[15] have been suggested as being responsible for such contrathermodynamic behavior.[16]

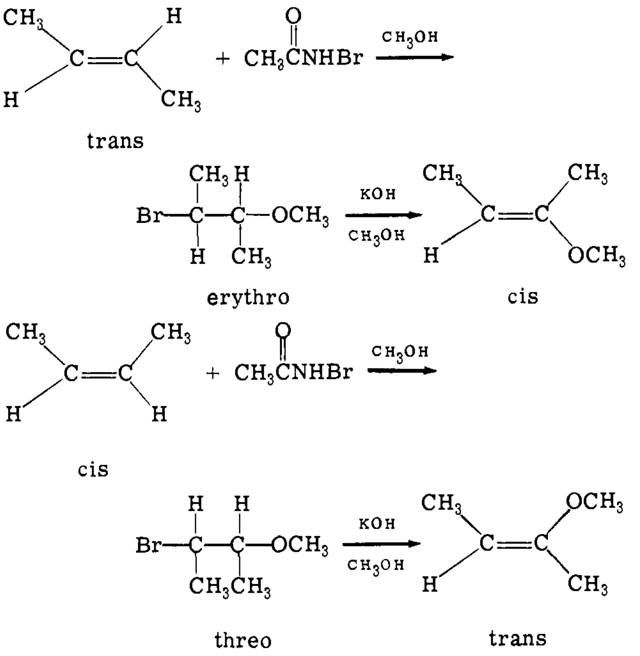
Reaction of Isopropylidenecarbene with *cis*- and *trans*-2-Butene. Phillips "pure grade" (99.0%) *cis*- and *trans*-2-butene were carefully analyzed by GC for exact amounts of each of the isomers. Each pure isomer was allowed to react in duplicate or triplicate with $(CH_3)_2C{=}CHOTf$ and *t*-BuOK at −20° for 48 hr, and the products were analyzed by GC equipped with a flame ionization detector. Since each of the "pure" isomeric olefins contained small amounts of the minor isomer, eq 1 and the experimentally observed relative rate of k_c/k_t = 3.85 from Table I were used to calculate the expected amount of the respective major methylenecyclopropane adduct. The results are summarized in Table II. The ratio of experimentally observed to calculated adduct corresponds to the stereospecificity of the carbene addition and is also given in Table II.

Table I. Relative Reactivity of Isopropylidenecarbene with 2-Butenes and 2-Methoxy-2-butenes at −20°

Reaction	Starting olefin % cis	% trans	Cyclopropane adduct % cis	% trans	k_c/k_t
			2-Butene		
1	42.3 ± 1.4	54.6 ± 1.1	72.9 ± 0.2	27.1 ± 0.2	3.47
2	42.3 ± 1.4	54.6 ± 1.1	76.4 ± 0.2	23.6 ± 0.2	4.18
3	42.3 ± 1.4	54.6 ± 1.1	75.1 ± 0.6	24.9 ± 0.6	3.89
				Av:	3.85 ± 0.25
			2-Methoxy-2-butene		
4	60.3 ± 1.1	39.7 ± 1.1	34.9 ± 1.2	65.1 ± 1.2	0.353 ± 0.033
5	60.3 ± 1.1	39.7 ± 1.1	35.0 ± 0.6	65.0 ± 0.6	0.355 ± 0.025
				Av:	0.354 ± 0.029

Reaction of Isopropylidenecarbene with *cis*- and *trans*-2-Methoxy-2-butene. *cis*- and *trans*-2-methoxy-2-butene were prepared from *trans*- and *cis*-2-butene, respectively,[17,18] as outlined in Scheme I. After careful analysis, each methoxybutene isomer was again allowed to react in duplicate or triplicate with $(CH_3)_2C{=}CHOTf$ and *t*-BuOK at −20° for 48 hr. The experimentally observed as well as the calculated amount of methylenecyclopropane adducts together with the stereospecificity of addition are given in Table II.

Scheme I



There is no doubt that the spectral data (given in the Experimental Section) are consistent with the assigned structures for the individual methylenecyclopropanes and with the fact that cis addition has taken place. Furthermore, control experiments show that the methylenecyclopropane products once formed are stable to the reaction conditions employed. Therefore as the data in Table II indicate the reaction of isopropylidenecarbene is highly stereoselective with each isomer of both olefins employed: reaction with *cis*-2-butene being >99.5% stereoselective, with *trans*-2-butene 100% stereospecific, and more than 98% stereoselec-

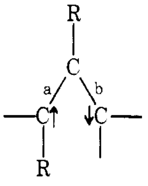
Table II. Stereospecificity of Reaction of Isopropylidenecarbene with *cis*- and *trans*-2-Butene and *cis*- and *trans*-2-Methoxy-2-butene at −20°

Reaction	Starting olefin % cis	Starting olefin % trans	Cyclopropane adduct Observed	% major isomer Calculated	Stereosp. Obsd/calcd
			2-Butene		
1	99.3 ± 0.1	0.6 ± 0.1[a]	99.42 ± 0.09	99.84 ± 0.05	99.6
2	99.3 ± 0.1	0.6 ± 0.1[a]	99.20 ± 0.06	99.84 ± 0.05	99.4
3	99.3 ± 0.1	0.6 ± 0.1[a]	99.24 ± 0.04	99.84 ± 0.05	99.4
4	0.40 ± 0.03	99.45 ± 0.05[a]	98.64 ± 0.12	98.48 ± 0.24	100.2
5	0.40 ± 0.03	99.45 ± 0.05[a]	98.42 ± 0.07	98.48 ± 0.24	99.9
6	0.40 ± 0.03	99.45 ± 0.05[a,b]	99.30 ± 0.06	98.48 ± 0.24	100.8
7	0.40 ± 0.03	99.45 ± 0.05[a,b]	99.09 ± 0.15	98.48 ± 0.24	100.6
8	0.40 ± 0.03	99.45 ± 0.05[a,c]	98.68 ± 0.30	98.48 ± 0.24	100.2
9	0.40 ± 0.03	99.45 ± 0.05[a,c]	98.38 ± 0.39	98.48 ± 0.29	99.9
			2-Methoxy-2-butene		
10	78.4 ± 1.5	2.3 ± 0.2[d]	96.42 ± 0.15	92.3 ± 1.3	104.5
11	78.4 ± 1.5	2.3 ± 0.2[d]	96.18 ± 0.08	92.3 ± 1.3	104.2
12	1.97 ± 0.03	93.3 ± 0.8[e]	97.6 ± 0.6	99.2 ± 0.2	98.4
13	1.97 ± 0.03	93.3 ± 0.8[e]	97.3 ± 0.5	99.2 ± 0.2	98.1
14	1.97 ± 0.03	93.3 ± 0.8[e]	97.5 ± 0.8	99.2 ± 0.2	98.2

[a] Also contains 0.1–0.2% of an unknown impurity. [b] 20.0 ± 1.0 mol % butene and 80.0 ± 1.0 mol % perfluorocyclobutane. [c] 5.0 ± 0.3 mol % butene and 95.5 ± 0.5 mol % perfluorocyclobutane. [d] Also contains 8.9% of $CH_3CH(OCH_3)CH{=}CH_2$ and 12.2% of other inert impurities. [e] Also contains 4.8% of $CH_3CH(OCH_3)CH{=}CH_2$.

tive with the 2-methoxy-2-butenes. But this high degree of stereoselectivity, although strongly suggestive, does not ipso facto prove a singlet as the ground state for isopropylidenecarbene, for such stereoselectivity could be due to a number of other factors. In particular, it is generally recognized[2b,11,19] that carbenoids react with a greater degree of stereoselectivity toward olefins and cyclopropanation than the corresponding "free" carbenes. However, there is reason to believe, coupled with experimental evidence,[1] that the unsaturated carbenes generated by *t*-BuOK decomposition of primary vinyl triflates are the "free" carbene[20] rather than carbenoids.

A further consideration is the expected degree of nonstereospecificity of a possible triplet unsaturated carbene addition to olefins. Triplet carbenes are generally considered to add to olefins via a two-step diradical process.[2a,b,11,23] For such a process to be nonstereospecific requires of course that spin relaxation and intersystem crossing of the diradical **11** be slow compared with rotamer equilibration. As the absolute lifetimes for such molecular processes in diradicals are not known, it is reasonable and generally assumed[2,11,23] that rotamer equilibration is fast compared with spin relaxation. Although this assumption is subject to criticism,[2b,11,24] a large amount of experimental data does indicate[2,11,22] that where triplet carbenes have been observed they do add nonstereospecifically to olefins both in the gas phase and the condensed phase. However, it is even more difficult to assess if such is still the case for an unsymmetrical methylene diradical **12** consisting of an alkyl and vinyl radical component. Although it seems reasonable to assume that the lifetime for intersystem crossing should be little affected by such a change, and since only rotation around bond a (essentially the same in both **11** and **12**) is significant for the stereochemical outcome, rotamer equilibration should also be little affected.



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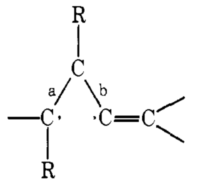

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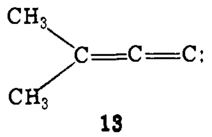
Finally there is the question of the spin multiplicity of the nascent unsaturated carbene and that of its true ground state. If the high degree of stereoselectivity, bordering on complete stereospecificity, observed in these unsaturated carbene additions to 2-butene and 2-methoxy-2-butene is indeed a result of a concerted cycloaddition, it strongly indicates that the reacting *nascent* carbene is a singlet. This, however, need not mean that the singlet is also the ground state of unsaturated carbenes, for it is not necessarily true that a carbene is generated and hence reacts in its ground state; in fact, the opposite is usually the case. Information concerning the ground state of a particular carbene may, however, be obtained by allowing the nascent carbene to energetically decay through collisions with an inert substrate prior to undergoing addition with olefin. In the gas phase, this is generally accomplished by means of a large excess of one of a number of inert carrier gases.[25] In the condensed phase, intersystem crossing is more difficult to promote by inert solvents because of the generally high reactivity of singlet carbenes in solution. However, a number of intersystem crossings have been successfully accomplished by means of dilution techniques usually with perfluoro compounds as inert diluents.[26] Therefore, we examined the stereochemistry of isopropylidenecarbene addition to *trans*-2-butene in the presence of excess perfluorocyclobutane. As the results in Table II (reactions 6–9) indicate, the stereospecificity is within experimental error identical with that observed in the absence (reaction 4 and 5) of diluent. To the extent that collision of the nascent carbene with perfluorocyclobutane would promote intersystem crossing and allow decay to the triplet, the absence of cis product and the retained stereospecificity are consistent with the idea that the singlet (presumably S_0) is the ground state as well for unsaturated carbenes,[27] in agreement with the aforementioned theoretical calculations.[7,8] Further support is provided for the singlet nature of unsaturated carbenes by the slower reactivity of butadiene relative to cyclohexene.[28]

Finally, it has been shown by Hartzler[29] that dimethylvinylidenecarbene (**13**) also adds stereospecifically to *cis*- and *trans*-2-butene indicating a singlet at least for the nascent, reacting carbene.



13

Summary

In this paper, we report the results of a careful examination of the stereochemistry of addition of unsaturated carbenes (**1**) as generated from primary vinyl triflates to olefins. Isopropylidenecarbene (**1**; R = CH_3) was found to add more than 98% stereoselectively to *cis*- and *trans*-2-methoxy-2-butene and stereospecifically to *cis*- and *trans*-2-butene, indicating that the nascent carbene is a singlet. Dilution experiments with perfluorocyclobutane and *trans*-2-butene further suggest that the singlet is also the ground state for such species.

Experimental Section

General. All boiling points are uncorrected. NMR spectra were recorded on a Varian Associates A-60 spectrometer, and data are given in δ (ppm) relative to internal or external tetramethylsilane (Me_4Si, δ 0) as indicated. All ir spectra were recorded on a Beckman IR5-A and are reported in wave numbers (cm^{-1}) calibrated to the 1603 cm^{-1} line of polystyrene. Mass spectra were recorded on a AEI-MS-30 spectrometer. Either a Varian-Aerograph 90P and 920 or a Varian Model 1200 Series flame ionization chromatograph was used for GLC analysis and preparative work, with the following columns: (A) 0.25 in. × 5 ft 10% SF-96 on 60-80 Chrom W; (B) 0.375 in. × 15 ft 15% SF-96 on 45-60 Chrom W; (C) 0.125 in. × 25 ft 5% SF-96 on 100-120 Chrom W; (D) 0.125 in. × 50 ft 5% SF-96 on 100-120 Chrom W; (E) 0.375 in. × 15 ft 15% Apiezon on 45-60 Chrom W; (F) 0.25 in. × 20 ft 15% Apiezon on 45-60 Chrom W; (G) 0.375 in. × 25 ft 20% SE-30 on 30-60 Chrom W; (H) 0.375 in. × 15 ft 15% QF-1 on 30-60 Chrom W.

Materials. 2-Methylpropenyl triflate was prepared from isobutyraldehyde as previously described.[1] Pure grade (99%) *cis*-2-butene and pure grade (99%) *trans*-2-butene were purchased from Phillips Petroleum Co. and analyzed for isomer purity on column G (vide infra). Perfluorocyclobutane was purchased from Pierce Chemical Co. and used without further purification. *N*-Bromoacetamide was purchased from Arapahoe Chemicals and used without further purification. Potassium *tert*-butoxide was prepared as previously described.[1]

Preparation of *erythro*-2-Bromo-3-methoxybutane.[17] To a 2-l. three-necked flask equipped with a magnetic stirrer, Dry Ice condenser, and a fritted-glass gas bubbler were added 1.5 l. of anhydrous methanol, 455 g (3.3 mol) of *N*-bromoacetamide, and 2 ml of concentrated H_2SO_4. After all the *N*-bromoacetamide had dissolved, the flask was cooled to about −60° and 168 g of 99% *trans*-2-butene slowly bubbled in over a period of 2 hr. At the end of this period, the solution was allowed to warm to room temperature and then stirred for 48 hr, after which it was diluted with 1 l. of saturated NaCl solution. The organic layer was separated, and the aqueous layer was extracted with three 300-ml portions of ether. The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent distilled through a short Vigreux column. The residue was distilled yielding 253 g (51%) of *erythro*-2-bromo-3-methoxybutane; bp 132–134° (650 mm) [lit.[17] 55.7–56.2° (40 mm)]; NMR (neat, int Me_4Si), δ 1.19 (d, $^3J = 6.1$ Hz, 3 H, CH_3), 1.63 (d, $^3J = 6.8$ Hz, 3 H, CH_3), 3.34 (d of q, $^3J = 6.1$, $^3J = 4.6$ Hz, 1 H), 3.36 (s, 3 H, OCH_3), 4.36 (d of q, $^3J = 6.8$, $^3J = 4.6$ Hz, 1 H); ir (neat) 1099 cm^{-1} (C—O).

Preparation of *threo*-2-Bromo-3-methoxybutane. This compound was prepared similar to that of the erythro isomer from 252 g (4.5 mol) of 99% *cis*-2-butene yielding 406 g (54%) of product: bp 135–138° (650 mm) [lit.[17] 55.6–55.7° (40 mm)]; NMR (neat, int Me_4Si) δ 1.14 (d, $^3J = 6.5$ Hz, 3 H, CH_3), 1.54 (d, $^3J = 7.0$ Hz, 3 H, CH_3), 3.30 (s, 3 H, OCH_3), 3.44 (d of q, $^3J = 6.5$ Hz, $^3J = 4.0$ Hz, 1 H), 4.16 (d of q, $^3J = 7.0$, $^3J = 4.0$ Hz, 1 H); ir (neat) 1093 cm^{-1} (C—O).

Preparation of *trans*-2-Methoxy-2-butene. To a solution of 112 g (2.0 mol) of KOH in 300 ml of methanol, in a 500-ml round-bottom flask, was added dropwise 167 g (1.0 mol) of the above threo-2-bromo-3-methoxybutane. The solution was refluxed for 18 hr forming a heavy white precipitate (KBr). The mixture was diluted with 300 ml of water and extracted with four 100-ml portions of pentane. The combined organic layer was dried over $CaCl_2$ and the solvent distilled through a Vigreux column. The residue upon distillation yielded 64 g (74%) of product contaminated with small amounts of the cis isomer and $CH_2{=}CHCH(CH_3)(OCH_3)$: bp 67–68.5° (650 mm) (lit.[18] 67–69°); NMR (neat, ext Me_4Si) δ 1.16 (q of d, $^3J = 6.6$, $^5J = 1.4$ Hz, 3 H, CH_3), 1.40 (m, 3 H, CH_3), 3.11 (s, 3 H, OCH_3), 4.04 (q of q, $^3J = 6.6$, $^4J = 1.0$ Hz, 1 H, HC=C); ir (neat) 1690 (C=C), 1079 (C—O), and 769 cm^{-1}.

Preparation of *cis*-2-Methoxy-2-butene. This compound was prepared in a similar manner to the trans isomer, 167 g (1.0 mol) of *erythro*-2-bromo-3-methoxybutane giving 66 g (77%) of product again contaminated with some of the trans isomer and $CH_2{=}CHCH(CH_3)(OCH_3)$: bp 69–71° (650 mm) (lit.[18] 73–74°); NMR (neat, ext Me_4Si) δ 1.42 (d, $^3J = 6.8$ Hz, 3 H, CH_3), 1.55 (bs, 3 H, CH_3), 3.22 (s, 3 H, OCH_3), 4.18 (q, $^3J = 6.8$ Hz, 1 H, HC=C); ir (neat) 1660 (C=C), 1001 (C—O), and 792 cm^{-1}.

Preparation of Addition Product with *cis*-2-Butene. Into a dry 15-ml round-bottom flask equipped with a magnetic stirrer and serum cap was weighed 6 mmol of *t*-BuOK, and then 10 ml of *cis*-2-butene was condensed. 2-Methylpropenyl triflate (5 mmol) was added to the mixture, and the reaction was allowed to proceed at −20° for 48 hr before it was worked up by adding 3 ml of pentane and allowing the *cis*-2-butene to evaporate. The adduct and *tert*-butyl isobutenyl ether were collected on column B at 105°. For *cis*-2-butene adduct: NMR (CCl_4, int Me_4Si) δ 0.90 (d, $J = 4.5$ Hz, 6 H, 2 CH_3), 1.26 (m, 2 H, cyclopropyl), 1.61 (t, $J = 1.0$ Hz, 6 H, 2 $CH_3C{=}C$); ir (neat) 1786 cm^{-1} (C=C); MS 110 (M^+, 31), 95 (54), 81 (25), 79 (22), 77 (17), 67 (65), 58 (34), 55 (42), 53 (28), 43 (100), 41 (52), 40 (19), 39 (42); Raman (neat, capiliary), 1778, 1640, 1448, and 745 cm^{-1}.

Preparation of Addition Product with *trans*-2-Butene. The addition product with *trans*-2-butene was prepared in a manner similar to that for *cis*-2-butene, and the adduct was collected on column B at 100°: NMR (CCl_4, int Me_4Si) δ 1.05 (bd s, 6 H, CH_3), 1.11 (m, 2 H, cyclopropyl), 1.75 (t, $J \simeq 0.7$ Hz, 6 H, 2 $CH_3C{=}C$); ir (neat 1774 cm^{-1} (C=C); MS 110 (M^+, 50), 95 (66), 93 (15), 82 (17), 81 (30), 79 (25), 77 (17), 68 (23), 67 (100), 65 (15), 56 (18), 55 (54), 54 (11), 53 (36), 51 (14), 43 (14), 42 (13), 41 (60), 40 (14), 39 (40); Raman (neat, capillary) 1786, 1457, 1371, 781, and 612 cm^{-1}.

Preparation of Addition Product with *cis*-2-Methoxy-2-butene. Into a dry 10-ml round-bottom flask equipped with a magnetic stirrer was weighed 6 mmol of *t*-BuOK, and 8 ml of *cis*-2-methoxy-2-butene was added. The mixture was cooled to −20° before adding 5 mmol of 2-methylpropenyl triflate. After the reaction proceeded for 72 hr at −20°, the mixture was worked up by washing with 1 ml of water followed by distillation to concentrate the organic layer for preparative GC work. The adduct and *tert*-butyl isobutenyl ether were collected on column A at 65°. For *cis*-2-methoxy-2-butene adduct: NMR ($CDCl_3$, int Me_4Si), δ 1.00–1.55 (m, 1 H, cyclopropyl), 1.05 (d, $J = 5.0$ Hz, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.81 (m, $J \simeq 2.0$ Hz, 6 H, 2 $CH_3C{=}C$), 3.25 (s, 3 H, OCH_3); ir (neat) 1761 (C=C) and 1055 cm^{-1} (C—O); MS 140 (M^+, 8), 125 (42), 93 (14), 91 (12), 79 (10), 77 (12), 67 (18), 57 (19), 55 (22), 53 (12), 43 (100), 41 (31), 39 (19); Raman (neat, capillary) 1773, 1652, 1468, 1370, 710, 638, and 300 cm^{-1}.

Preparation of Addition Product with *trans*-2-Methoxy-2-butene. The addition product with *trans*-2-methoxy-2-butene was prepared in a manner similar to that for *cis*-2-methoxy-2-butene, and the adduct was collected on column A at 65°: NMR ($CDCl_3$, int Me_4Si) δ 1.07–1.30 (m, 1 H, cyclopropyl), 1.14 (bd s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.76 (bd s, 3 H, $CH_3C{=}C$), 1.83 (d, $J \simeq 0.13$ Hz, 3 H, $CH_3C{=}C$), 3.30 (s, 3 H, OCH_3); ir (neat) 1773 (C=C) and 1058 cm^{-1} (C—O); MS 140 (M^+, 1), 125 (17), 77 (13), 67 (28), 55 (19), 53 (19), 51 (12), 43 (100), 41 (34), 40 (10), 39 (39); Raman (neat, capillary) 1775, 1653, 1445, 1374, 705, 652, and 190 cm^{-1}.

Relative Rate of Reaction of Isopropylidenecarbene with *cis*- and *trans*-2-Butene. Into a dry 15-ml round-bottom flask equipped with a magnetic stirrer and serum cap was weighed 0.75 mmol of *t*-BuOK, and 10 ml of mixed *cis*- and *trans*-2-butene (Phillips Petroleum) was condensed into the flask. The composition of the solvent mixture was found to be 54.6 ± 1.1% *trans*-2-butene, 42.3 ± 1.4% *cis*-2-butene, and 3.1 ± 5% impurity as determined by multiple GC analysis of a pentane solution of the olefin on column G at −23°. To the mixture of base and olefin, cooled to −20°, was added 0.5 mmol of 2-methylpropenyl triflate, and the reaction was allowed to proceed for 48 hr at −20°. At the end of this period, pentane was added, the 2-butene was allowed to evaporate, and the pentane solution was analyzed directly on a Varian Model 1200 Series flame ionization chromatograph on column D at 60°, using the above prepared and spectrally characterized authentic samples to determine retention times, and was found to contain 17.5% *tert*-

butyl isobutenyl ether and 82.5% adducts. The ratios of cis and trans adducts appear in Table I (reaction 1-3).

Relative Rate of Reaction of Isopropylidenecarbene with *cis*- and *trans*-2-Methoxy-2-butene. Into a dry 5-ml round-bottom flask equipped with a magnetic stirrer and a serum cap was weighed 0.5 mmol of *t*-BuOK, and 4 ml of mixed *cis*- and *trans*-2-methoxy-2-butene was added. The composition of olefin was found to be 60.3 ± 1.1% *cis*-2-methoxy-2-butene and 39.7 ± 1.1% *trans*-2-methoxy-2-butene as determined by multiple GC analysis on column F at 36°. The mixture of base and olefin was cooled to −20°, 0.25 mmol of 2-methylpropenyl triflate was added, and the reaction mixture was allowed to react at −20° for 48 hr. The reaction mixture was analyzed directly on a Varian Model 1200 Series flame ionization chromatograph on column C at 80°, using the above prepared authentic samples to determine retention time, and was found to contain 24.8% *tert*-butyl isobutenyl ether and 75.2% adducts. The ratios of cis and trans adduct appear in Table I (reactions 4 and 5).

Stereochemistry of Addition of Isopropylidenecarbene to 2-Butene. Into a dry 10-ml round-bottom flask equipped with a magnetic stirrer and serum cap was weighed 0.75 mmol of *t*-BuOK, and 8 ml of *cis*-2-butene (Phillips Petroleum, 99% pure) was condensed into the flask. The composition of the olefin was found to be 99.3 ± 0.1% *cis*-2-butene, 0.6 ± 0.1% *trans*-2-butene, and 0.1 ± 0.05% impurity as determined by multiple GC analysis of a pentane solution of the olefin on column G at −23°. To the mixture of base and olefin, cooled to −20°, was added 0.5 mmol of 2-methyl propenyl triflate, and the reaction was allowed to proceed for 48 hr at −20°. A pentane solution of the reaction was analyzed on a Varian Model 1200 Series flame ionization chromatograph on column D at 65°, with the aid of the above prepared authentic samples, and was found to contain 16.5% *tert*-butyl isobutenyl ether and 83.5% adducts. The ratios of cis and trans adducts appear in Table II (reactions 1-3).

The reaction with *trans*-2-butene was carried out as with *cis*-2-butene. The composition of the olefin was found to be 99.46 ± 0.02% *trans*-2-butene, 0.40 ± 0.03% *cis*-2-butene, and 0.14 ± 0.01% impurity as determined by multiple GC analysis of a pentane solution of the olefin on column G at −23°. The reaction was analyzed on Varian Model 1200 Series flame ionization chromatograph on column D at 65°, with the aid of the above prepared authentic smaples, and was found to contain 15.9% *tert*-butyl isobutenyl ether and 84.1% adducts. The ratios of cis and trans adducts appear in Table II (reactions 4-5).

Stereochemistry of Addition of Isopropylidenecarbene to 2-Methoxy-2-butene. Into a dry 10-ml round-bottom flask equipped with a magnetic stirrer and serum cap was weighed 0.75 mmol of *t*-BuOK, and 8 ml of *cis*-2-methoxy-2-butene was added. The composition of the olefin was found to be 78.4 ± 1.5% *cis*-2-methoxy-2-butene, 2.3 ± 0.2% *trans*-2-methoxy-2-butene, and 19.3 ± 0.5% inert impurities as determined by multiple GC analysis on column E at 35°. The mixture of base and olefin was cooled to −20°, 0.5 mmol of 2-methyl propenyl triflate was added, and the mixture was allowed to react for 48 hr at −20°. The reaction mixture was analyzed on a Varian Model 1200 Series flame ionization chromatograph on column C at 65°, with the aid of the above prepared authentic samples, and was found to contain 19.5% *tert*-butyl isobutenyl ether and 80,5% adducts. The ratios of cis and trans adducts appear in Table II (reaction 10 and 11). The reaction with *trans*-2-methoxy-2-butene was carried out as with *cis*-2-methoxy-2-butene, using 2.0 mmol of *t*-BuOK, 15 ml of *trans*-2-methoxy-2-butene, and 1.0 mmol of 2-methyl propenyl triflate. The composition of the olefin was found to be 93.26 ± 0.8% *trans*-2-methoxy-2-butene, 1.97 ± 0.03% *cis*-2-methoxy-2-butene, and 4.86 ± 0.11% inert impurities as determined by multiple GC analysis on column H at 80°. The reaction proceeded for 48 hr at −20° before being analyzed on Varian Model 1200 Series flame ionization chromatograph on column D at 80°, with the aid of the above prepared authentic samples, and was found to contain 29.1% *tert*-butyl isobutenyl ether and 70.9% adducts. The ratios of cis and trans adducts appear in Table II (reactions 12-14).

Stability of *cis*-2-Butene Adduct. Into a dry 5-ml round-bottom flask equipped with a magnetic stirrer was condensed 4 ml of *cis*-2-butene, and then 20 µl. of GC collected adduct with *cis*-2-butene was added. One milliliter of solution was removed and added to 1 ml of pentane and then sealed in a vial and maintained at −20° as a GC standard sample. To the remaining 3 ml of solution was added 0.175 mmol of *t*-BuOK, and the mixture was stirred for 72 hr at −20°. Pentane was added, the *cis*-2-butene was allowed to evaporate, and the pentane solution was analyzed by GC on column C at 65° and found to show no rearrangement to the trans isomer when compared with the control sample.

Stability of *trans*-2-Methoxy-2-butene Adduct. Into a dry 5-ml round-bottom flask equipped with a magnetic stirrer were added 4 ml of *trans*-2-methoxy-2-butene and 20 µl. of GC collected trans adduct. One milliliter of solution was removed, sealed in a vial, and maintained at −20°. To the remaining 3 ml of solution was added 0.2 mmol of *t*-BuOK, and the mixture was stirred for 60 hr at −20°. It was analyzed by GC, column H at 85°, and found to show no rearrangement to the cis isomer when compared with the control sample.

Addition of Isopropylidenecarbene to *trans*-2-Butene in the Presence of Octafluorocyclobutane. Into a 10-ml round-bottom flask equipped with a magnetic stirrer and serum cap was weighed 0.75 mmol of *t*-BuOK, and the appropriate amounts of *trans*-2-butene and octafluorocyclobutane were condensed. To this solution at −20° was added 0.5 mmol of 2-methylpropenyl triflate, and the mixture was allowed to react for 24-48 hr at −20°. Pentane was added, the solvents were allowed to evaporate, and the pentane solution was analyzed directly on a Varian Model 1200 Series flame ionization chromatograph on column C at 60° with the aid of authentic samples. The results are given in Table II (reactions 6-9).

Acknowledgments. This investigation was supported by Public Health Service Research Grant No. 1-RO-1-CA16903-01 from the National Cancer Institute. Helpful discussions with Professor J. P. Simons are gratefully acknowledged.

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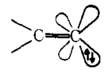
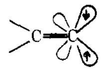
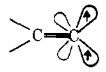


8 (S_0)



9 (S_1)



10 (T_1)

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Stereospecific Olefin-Forming Elimination Reactions of β-Hydroxyalkylsilanes

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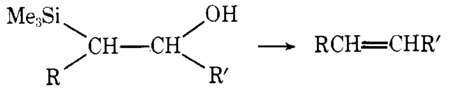
Received September 27, 1974

Abstract: In order to study the stereochemistry of elimination reactions of β-hydroxyalkylsilanes, 5-trimethylsilyl-4-octanol (**2**) was prepared by two routes, and the cis:trans ratios of the 4-octenes formed in the β-elimination reactions were examined. Addition of ethyllithium to vinyltrimethylsilane, followed by reaction with butyraldehyde, gave **2** as a 2:1 mixture of diastereomers. Reduction of 5-trimethylsilyl-4-octanone (**5**) with diisobutylaluminum hydride (DIBAL) at −120° gave predominantly one diastereomer of **2** (presumably threo); β-elimination reactions with sodium hydride or potassium hydride gave predominantly *trans*-4-octene, while β-elimination reactions under a variety of acidic conditions gave predominantly *cis*-4-octene. Thus, by a choice of conditions for the elimination reaction, either cis or trans olefin can be prepared from a single precursor.

The need for methods for the stereospecific synthesis of olefins has become increasingly apparent in recent years,[2] in part because of the discovery of many olefinic natural products, particularly the insect hormones and pheromones,[3] and in part because of the many recent advances in the use of polyolefins in nonenzymic biogenetic-like cyclizations to form polycyclic compounds.[4]

We have been interested in the possibility that the elimination reactions of β-hydroxyalkylsilanes could be used for the stereospecific synthesis of olefins.[5] These elimination



$$Me_3Si(R)CH{-}CH(OH)R' \longrightarrow RCH{=}CHR'$$

reactions have been known for almost 3 decades,[6] and have been shown to occur under both acidic[6] and basic[7-9] conditions. A number of synthetic applications have appeared recently,[8-15] beginning with the work of Peterson;[8] normally mixtures of cis and trans olefins have been obtained. Since the precursor β-hydroxysilanes in these reactions may have been mixtures of diastereomers, a definitive statement regarding the stereochemistry of the olefin-forming step was not possible.

We wish to report here the selective synthesis of one diastereomer of a β-hydroxyalkylsilane and the demonstration that the elimination reactions are stereospecific and can be controlled to proceed in either a syn or an anti manner; thus, either a cis or a trans olefin can be formed from a single β-hydroxysilane.

Results and Discussion

To determine the stereochemistry of the elimination reactions of β-hydroxyalkylsilanes, we have examined the cis: trans ratio of the 4-octenes produced by the elimination of 5-trimethylsilyl-4-octanol (**2**) prepared by two different routes. Compound **2** was first prepared by addition of ethyllithium to vinyltrimethylsilane, followed by reaction[16] with butyraldehyde. On treatment of **2** with acids, mixtures of *cis*- and *trans*-4-octene were formed. In one experiment, the absence of the isomeric 3-octenes in the product was demonstrated by ozonolysis.

Initially, we hoped to use an intermediate sulfonate derivative as a substrate for elimination reactions under mild conditions. Treatment of **2** with methanesulfonyl chloride and triethylamine[17] produced 4-octene directly in a 2:1 cis: trans ratio. Treatment of **2** with sodium hydride in hexamethylphosphoric triamide (HMPA) followed by *p*-toluenesulfonyl chloride and tetraethylammonium fluoride produced 4-octene in a 1:2 cis:trans ratio. Attempts to isolate the tosylate were unsuccessful; moreover, omission of the *p*-toluenesulfonyl chloride and the tetraethylammonium fluoride from the reaction mixture resulted in a similar mixture of octenes. The reversal of stereochemistry in these two reactions suggested that the β-hydroxyalkylsilane **2** had been formed as a mixture of diastereomers, and that the elimination reaction was syn under one set of conditions and anti under the other. We therefore sought to prepare one diastereomer of **2**.

Very few preparations of diastereomerically pure β-hy-