(5*S*)-5,6,6-Trimethylheptan-3-ol thus obtained was not isolated and was oxidized according to Brown[7] to the (−)(*S*)-5,6,6-trimethylheptan-3-one (VII), bp 128–130° (126 mm), $n^{25}\mathrm{D}$ 1.4277, $\alpha^{25}\mathrm{D}$ −7.00° (neat, $l = 1$) (*Anal.* Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 75.97; H, 12.44), which was purified through its semicarbazone, mp 159–160°.

VII was allowed to react with methylmagnesium bromide, and (−)(5*S*)-3,5,6,6-tetramethylheptan-3-ol (VIII), bp 89–92° (18 mm), $n^{25}\mathrm{D}$ 1.4435, $\alpha^{25}\mathrm{D}$ −7.00° (neat, $l = 1$) (*Anal.* Calcd for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.28; H, 13.89), was obtained.

VIII was dehydrated by distillation in the presence of I_2, and the olefins thus obtained were hydrogenated by H_2 at 120° in the presence of Raney nickel, yielding a mixture of (3*S*,5*R*)- and (3*S*,5*S*)-2,2,3,5-tetramethylheptane (IX and II, respectively), $n^{25}\mathrm{D}$ 1.4202, $[\alpha]^{25}\mathrm{D}$ −26.19° (*c* 20.58, *n*-pentane). *Anal.* Calcd for $C_{11}H_{24}$: C, 84.52; H, 15.48. Found: C, 84.24; H, 15.43.

Acid-catalyzed rearrangements in the dehydration and acid oxidation steps have to be considered improbable on the basis of published data[10,11] on similar compounds.

As I and II have optical activity of opposite sign, IX must have optical activity of the same sign as II; therefore II must have optical rotation of the same sign as the mixture of II and IX and possess therefore negative optical rotation. Consequently the diastereoisomer I, (3*R*,5*S*), has positive optical rotation.

The mixture of II and IX was analyzed by vpc, as in the case of the mixture of I and II; it contained 55 ± 3% II which has negative optical rotation and higher retention time; taking into account the optical purity of VI, a value of $[M]^{25}\mathrm{D}$ −108.28 ± 1.30° (*c* 20.58, *n*-pentane) can be calculated for the molar rotation of the mixture of IX and II. Comparing such a value with the one calculated for the same composition on the basis of the absolute value of the molar rotations of I and II ($[M]^{25}\mathrm{D}$ 115.6 ± 4°), a satisfactory agreement is obtained. This agreement can be taken as an indication that both in the synthesis of the mixtures of I and II and of II and IX no extensive racemization occurs at the two asymmetric centers.

Comparing the values found with the value calculated by the Brewster method,[5] a substantial agreement has been found both concerning the sign and the order of magnitude of the optical rotation of I and II, the discrepancy between the values calculated and found being larger in the case in which a single conformation is allowed (see Table I).

Table I

Compd	Max $[M]^{25}\mathrm{D}$ found (*c* 20.47, *n*-pentane)[a]	$[M]\mathrm{D}$ calcd by Brewster method[a]
I	+137.8 ± 3	+120
II	−97.5 ± 4	−180

[a] In degrees.

Our data confirm the previous hypothesis[4] that, in aliphatic hydrocarbons containing a hydrogen atom attached to the asymmetric carbon atoms,[12] when the presence of a few conformations having high optical rotation of the same sign can be foreseen by conformational analysis[5] a relatively high optical rotation can be found. This shows the substantial soundness but also the limits of conformational analysis in investigating the conformation of both low and high molecular weight hydrocarbons.

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(12) We thank one of the referees for calling our attention to the paper by H. Wynberg, G. L. Hekkert, J. P. M. Houbiers, and H. W. Bosch, *J. Am. Chem. Soc.*, 87, 2635 (1965).

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The Configuration of Vinyl Radicals. The Generation and Trapping of Each Member of a Configurationally Isomeric Pair of Vinyl Radicals

Sir:

We wish to report evidence that vinyl radicals derived from symmetrically disubstituted alkenes exist in a nonlinear configuration capable of facile isomeric interconversion. In addition we are pleased to communicate the results of the first successful attempt to trap the *cis* and *trans* isomers of a vinyl radical prior to their complete equilibration.

Several investigations bearing on the structure of vinyl radicals have been reported recently.[1–7] Under conditions of kinetic control, free-radical additions to terminal acetylenes yield predominantly the product of *trans* addition.[1–3] Skell and Allen[1] attribute this stereoselectivity to the configurational stability of the intermediate vinyl radical. Others[2,3] have suggested that the intermediate radical undergoes rapid *cis–trans* equilibration, but that the product-forming abstraction reaction involves stereoselective capture of one isomer of this pair.

Elegant electron spin resonance investigations have shown that at low temperatures in liquid ethylene–ethane[4] or in an argon matrix[5] the unsubstituted vinyl radical possesses a nonlinear configuration which undergoes facile inversion. The minimum activation energy for inversion is estimated to be approximately 2 kcal/mole.[4] The 1-methylvinyl radical generated by irradiation of allene in ethane at −172° is also nonlinear.[4] The inversion rate of the 1-methylvinyl radical is less than that for the unsubstituted vinyl radical. Since inversion of the vinyl radical presumably involves

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(1) P. S. Skell and R. G. Allen, *J. Am. Chem. Soc.*, 80, 5997 (1958); **86**, 1559 (1964).

(2) A. A. Oswald, K. Griesbaum, B. B. Hudson, Jr., and J. M. Bregman, *ibid.*, **86**, 2877 (1964).

(3) J. A. Kampmeier and G. Chen, *ibid.*, **87**, 2608 (1965).

(4) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(5) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964).

(6) R. M. Fantazier and J. A. Kampmeier, *J. Am. Chem. Soc.*, **88**, 1959, 5219 (1966).

(7) L. A. Singer and N. P. Kong, *ibid.*, **88**, 5213 (1966); *Tetrahedron Letters*, 2089 (1966).

Table I. Yield of Isomeric 3-Hexenes from Reaction of Sodium Naphthalenide with *cis*- and *trans*-3-Chloro-3-hexene[a]

		Product, % yield[b,c]			
		With *cis*-3-chloro-3-hexene[d]		With *trans*-3-chloro-3-hexene[e]	
Solvent[f]	Temp, °C	*trans*-Hexene	*cis*-Hexene	*trans*-Hexene	*cis*-Hexene
THF	0	69	31	85	15
THF	27	74	26	85	15
DME	0	56	44	82	18
DME	27	59	41	81	19

[a] The *cis*- and *trans*-3-chlorohexenes were prepared from isomerically pure *trans*- and *cis*-3-hexene, respectively, in the manner described by M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Am. Chem. Soc.*, **73**, 3329 (1951). [b] Reactions were carried out in the manner previously described.[10] Analysis was by vapor phase chromatography on an 8-ft column packed with a 30% $AgNO_3$–glycerine solution coated 20% by weight on Chromosorb P. Quantitative data were obtained by comparison of peak areas to that of an internal standard (pentane) of known concentration. [c] Each datum represents the average of at least three independent experiments. In general, yields were reproducible to ±6% of the value reported. Both 3-hexenes were shown to be configurationally stable under the reaction conditions. [d] Bp 119.5°; n^{20}D 1.4354. [e] Bp 114.6°; n^{20}D 1.4341. [f] THF = tetrahydrofuran; DME = 1,2-dimethoxyethane.

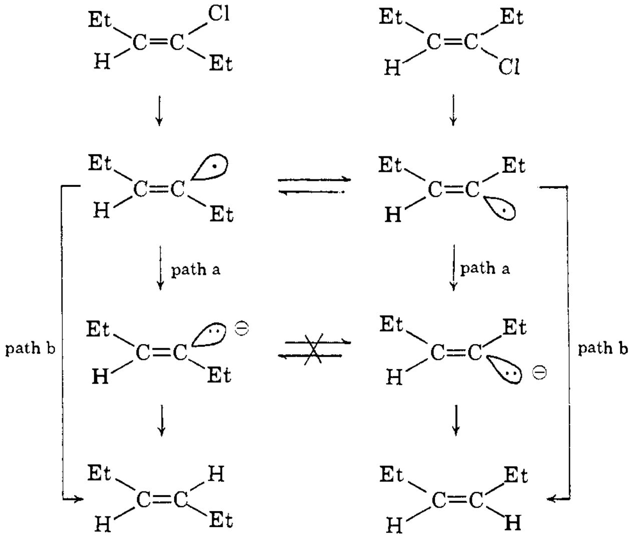
a tunneling process,[4,5] whereas inversion of the 1-methylvinyl radical does not,[4] no reliable estimate of the relative activation energies for inversion of these two species is possible. Thus one cannot employ the results of the esr studies to determine whether alkyl substitution at the 1 position stabilizes or destabilizes the linear configuration relative to the nonlinear configuration for the vinyl radical.

Both Fantazier and Kampmeier[6] and Singer and Kong[7] have studied the vinyl radical generating decomposition of *t*-butyl peresters of *cis–trans* pairs of α,β-unsaturated acids. Decompositions carried out in hydrogen-donating solvents led to mixtures of olefins whose relative concentration was independent of the configuration of the perester employed. Although both groups interpret these results in terms of rapid equilibration of the intermediate vinyl radicals, these data are equally well explained by postulating the intervention of a single, linear[8] vinyl radical as the intermediate in the decomposition of both the *cis* and *trans* peresters.[9]

Previous work has shown that the naphthalene radical anion undergoes an electron-transfer reaction with alkyl halides to yield halide ion and alkyl free radicals.[10–12] In an effort to generate isomeric vinyl free radicals, we have examined the reaction of sodium naphthalenide with *cis*- and *trans*-3-chloro-3-hexene. The sole detectable product derived from both chlorohexenes was a mixture of *cis*- and *trans*-3-hexene formed in at least 98% yield. The product analyses for several runs at two temperatures and in two solvent systems are presented in Table I.

In all instances, *trans*-3-hexene predominates in the product mixture, but the ratio of *cis*- to *trans*-3-hexene is decidedly a function of the configuration of the 3-chloro-3-hexene employed. This observation immediately excludes the possible intermediacy of either a single linear (sp) vinyl radical or two isomeric, configurationally stable, nonlinear (sp^2) vinyl free radicals. Use of sodium naphthalenide as the reducing agent precludes the possibility that a vinyl carbanion is generated directly by a two-electron reduction of 3-chloro-3-hexene.

We conclude that the initial charge-transfer reaction generates a nonlinear vinyl radical which is capable of facile inversion at the radical site, but that the radical is trapped before complete equilibration with its configurational isomer is achieved.[13]



The interconverting vinyl radicals might be trapped either by reduction to a configurationally stable carbanion[14,15] (path a) or by hydrogen abstraction from

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(8) For substituted vinyl radicals, the linear (sp) configuration would possess at least three inherent advantages relative to the nonlinear (sp^2) form: (1) decreased torsional strain, (2) decreased nonbonded strain, and (3) increased bond strengths resulting from sp hybridization at the radical site. The imprecision with which the relative stability of the linear and nonlinear configurations of the unsubstituted vinyl radical is known renders impossible an *a priori* estimate of the relative stabilities of the two forms for a substituted vinyl radical.

(9) Singer and Kong[7] were able to show that the temperature dependence of the ratio of *cis*- to *trans*-propenylbenzene derived from *t*-butyl α-methylpercinnamate could be interpreted logically in terms of rapidly equilibrating nonlinear vinyl radical intermediates. To explain these results on the basis of a single linear vinyl radical intermediate would require the seemingly unreasonable postulate that the stereoselectivity of hydrogen atom abstraction increases with temperature.

(10) G. D. Sargent, J. N. Cron, and S. Bank, *J. Am. Chem. Soc.*, **88**, 5363 (1966).

(11) J. F. Garst, W. Ayers, and R. C. Lamb, *ibid.*, **88**, 4260 (1966).

(12) S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4261 (1966).

(13) Inherent in the interpretation here presented is the assumption that initial electron transfer does not yield a hexenyl chloride radical anion as a discrete intermediate. Several lines of evidence point to the validity of this assumption. Perhaps the most compelling lies in the observation that the reaction cross section for the vapor-phase reaction of sodium atoms with vinyl chloride is on the order of 0.1 to 1.0 A^2. If vinyl chloride radical anions were viable species, one would expect this reaction to occur by a "stripping" mechanism. Such a mechanism, however, is known to lead to reaction cross sections on the order of 10^2 to 10^4 A^2. Low reaction cross sections are characteristic of the "rebound" mechanism, a path known to be followed in the vapor-phase reaction of alkali metal atoms with molecules, such as methyl iodide, which cannot form radical anions possessing even transient stability. For details, see: D. R. Herschbach, *Advan. Chem. Phys.*, 10, 319 (1966); K. R. Wilson and D. R. Herschbach, *Nature*, **208**, 183 (1965).

(14) For a summary of the evidence which indicates considerable configurational stability for vinyl carbanions, see D. J. Cram, "Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 133–135.

(15) Reduction of both *cis*- and *trans*-3-chloro-3-hexene with sodium in liquid ammonia, a reaction which presumably proceeds *via* the vinyl carbanion,[16,17] yields alkene with at least 96% retention of configuration. We have yet to establish conclusively that vinyl carbanion isomerization does not occur under the conditions of our investigation. Such isomerization, if it does occur, would not invalidate the present results as evidence for the nonlinearity of the 3-hex-3-enyl radical.

(16) See Hoff, *et al.*, footnote *a*, Table I.

(17) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 77.

solvent (path b). The fact that *trans*-3-hexene, the thermodynamically more stable isomer,[18] always predominates in the reaction mixture suggests that the former alternative (path a) is adopted. Vinyl free radicals generated by perester decomposition and trapped by reaction with hydrogen atom donors (*e.g.*, cumene) invariably lead to products which, relative to the equilibrium mixture, are markedly enriched in the thermodynamically less stable olefin.[6,7] This is readily explained in terms of increased steric interaction between the donor and acceptor molecules in the transition state for hydrogen atom donation to the *trans* radical as compared with the *cis* radical.[7] The transition state for electron transfer from radical anion to the vinyl radical presumably need not be so highly oriented or so intimate as that for hydrogen atom donation. Thus transfer should take place with equal ease to either the *cis*- or *trans*-vinyl radical.

Acknowledgment. We are pleased to thank the Mobil Oil Corporation for an unrestricted grant-in-aid employed in support of this research.

[18] $\Delta G_f{}^\circ{}_{298^\circ\mathrm{K}}$(*trans*-3-hexene(g)) = 18.86 kcal/mole; $\Delta G_f{}^\circ{}_{298^\circ\mathrm{K}}$(*cis*-3-hexene(g)) = 19.66 kcal/mole: F. D. Rossini, *et al.*, "Selected Values of the Properties of Hydrocarbons," National Bureau of Standards Circular C461, U. S. Government Printing Office, Washington, D. C., 1947.

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The Reaction of Phenyl(trihalomethyl)mercurials with Hexamethylditin. The First Case of Dihalocarbene Insertion into a Metal–Metal Bond to Give a Stable MCX_2M System

Sir:

In a recent communication[1] we described the reaction of phenyl(bromodichloromethyl)mercury with bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury. We proposed that an intermediate formed in these reactions was the product of dichlorocarbene insertion into the Si–Hg and Ge–Hg bonds, $Me_3MCCl_2HgMMe_3$ (M = Si and Ge), and that further reactions of this intermediate led to the observed products. This explanation in terms of dihalocarbene insertion into metal–metalloid bonds suggested to us that other such insertions into covalent metal–metal bonds should be possible and that in favorable cases the initial $M-CX_2-M$ systems could be both thermally stable and kinetically stable with respect to further attack by CX_2 and thus capable of isolation. We have found this to be the case with hexamethylditin in its reaction with phenyl(bromodichloromethyl)mercury and phenyl(dibromochloromethyl)mercury (eq 1).

$$C_6H_5HgCXClBr + (CH_3)_3Sn\text{–}Sn(CH_3)_3 \longrightarrow (CH_3)_3SnCXClSn(CH_3)_3 + C_6H_5HgBr \quad (1)$$
$$X = Cl \text{ or } Br$$

As an example, we describe the reaction between $PhHgCCl_2Br$ and hexamethylditin. A mixture of 0.10 mole each of the mercurial[2] and hexamethylditin in 250 ml of dry benzene was stirred and heated at reflux under nitrogen for 3.5 hr. The reaction mixture was filtered to remove 30.6 g of gray solid, mp 276–286° (phenylmercuric bromide contaminated with some metallic mercury). Concentration of the orange filtrate at 10 mm resulted in crystallization of 3.64 g of diphenylmercury. Trap-to-trap distillation at 0.8 mm (pot temperature to 100°) removed the remaining solvent and minor amounts of trimethyltin halides; further distillation at 2×10^{-4} mm at room temperature gave small amounts of trimethyltin halides and phenyltrimethyltin,[3] leaving a liquid identified as bis(trimethyltin)dichloromethane, $(CH_3)_3SnCCl_2Sn(CH_3)_3$, bp 48–50° ($2 \times 10^{-4}$ mm), $n^{25}D$ 1.5326, analysis for all elements satisfactory, in 53% yield. Its nmr spectrum (CS_2) showed a sharp singlet at 0.3 ppm downfield from internal tetramethylsilane, with the expected tin satellites ($J_{Sn^{119}-H^1}$ = 53.5 cps; $J_{Sn^{117}-H^1}$ = 51.5 cps), and the infrared spectrum (pure liquid) showed bands at 2980 (s), 2915 (s), 1191 (s), 770 (vs), 725 (s), 667 (m), 632 (s), 527 (s), and 507 (sh) cm^{-1}. The mass spectroscopically determined molecular weight was 410 (calculated 410); the major fragment was Me_3Sn^+.

A similar reaction using phenyl(dibromochloromethyl)mercury gave bis(trimethyltin)bromochloromethane, $(CH_3)_3SnCBrClSn(CH_3)_3$, bp 61° ($2 \times 10^{-4}$ mm), $n^{25}D$ 1.5502, in 39% yield. A satisfactory analysis and mass spectroscopic molecular weight were obtained. The trimethyltin resonance occurred at 0.3 ppm, and the infrared spectrum showed absorption at 2970 (m), 2900 (m), 1190 (m), 768 (vs), 720 (s), 674 (sh), 659 (s), 580 (s), and 526 (vs) cm^{-1}. It is of interest to note that the reaction of phenyl(bromodichloromethyl)mercury with hexamethylditin in benzene for 6 days at room temperature gave bis(trimethyltin)dichloromethane in 52% yield.

Attempts to utilize these bis(trimethyltin)dihalomethanes as sources of the carbene $(CH_3)_3SnCCl$[4] have thus far been unsuccessful, mostly because of the thermal stability of these compounds. Bis(trimethyltin)dichloromethane was not decomposed on being heated in a sealed tube at 145° for 40 hr. Attempted reaction with tetramethylethylene at 180° for 4 days gave trimethyltin chloride as the only identifiable organotin product. Similarly, bis(trimethyltin)bromochloromethane survived 20 hr of heating at 130° in the presence of tetramethylethylene without decomposition, but at 190–200° (24 hr) both trimethyltin bromide and chloride were formed.

We have found that nucleophilic attack by iodide ion at the metal in a trihalomethylmercury or -tin compound provides another procedure for the release of CX_2 from such reagents.[5] In the case of bis(trimethyl-

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[1] D. Seyferth, R. J. Cross, and B. Prokai, *J. Organometal. Chem.* (Amsterdam), 7, P20 (1967).

[2] D. Seyferth and J. M. Burlitch, *ibid.*, **4**, 127 (1965).

[3] By-product formation can be rationalized in terms of a reaction between phenylmercuric bromide and hexamethylditin to give trimethyltin bromide and $PhHgSnMe_3$. Decomposition of the latter then gives $PhSnMe_3$ and metallic mercury in one mode, diphenylmercury, metallic mercury, and hexamethylditin in another. This point is being examined.

[4] Note analogous release of CCl_2 from Me_3SnCCl_3 and Me_3SnCCl_2Br in this connection: D. Seyferth, F. M. Armbrecht, Jr., B. Prokai, and R. J. Cross, *J. Organometal. Chem.* (Amsterdam), **6**, 573 (1966).

[5] (a) D. Seyferth, J. Y.-P. Mui, M. E. Gordon, and J. M. Burlitch, *J. Am. Chem. Soc.*, **87**, 681 (1965); (b) D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *ibid.*, **89**, 959 (1967); (c) D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, in press.