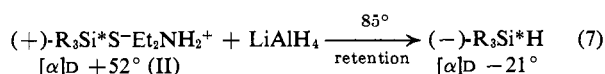


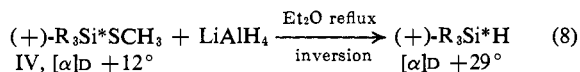
the former gives (+)-R<sub>3</sub>Si\*H by reduction and the latter gives (-)-R<sub>3</sub>Si\*H, it follows that opposite stereochemical paths obtain for formation of R<sub>3</sub>Si\*H in reactions 5a and 6. Use of leaving group reasoning (see below) clearly favors assignment of an inversion stereochemistry to the formation of (+)-R<sub>3</sub>Si\*H in reaction 5a and, in turn, reinforces assignment of the (+)-R<sub>3</sub>Si\*H configuration to the levorotatory enantiomers in Table I.

Thus, reaction 5a involves inversion and reaction 6 involves retention of configuration. The results for these two reactions were combined experimentally in a total reduction of the (+)-disilthiane, in which reaction 5a was directly followed by heating at 85°, and *racemic* R<sub>3</sub>Si\*H was obtained in 95% yield.

Reduction of the (+)-amine salt II was complicated by its low solubility in ether solvent, but when brought into contact with LiAlH<sub>4</sub> it went rapidly into solution, and upon heating at 85° yielded (-)-R<sub>3</sub>Si\*H, for which retention of configuration follows from the assigned configurational relationships.



Reaction of the (+)-methylthiosilane (IV) with LiAlH<sub>4</sub> in refluxing Et<sub>2</sub>O gave (+)-R<sub>3</sub>Si\*H, with inversion of configuration.



Methanolysis and hydrolysis of the disilthiane I (reactions 1c and 2) are complete in minutes at room temperature, in comparison to optically active R<sub>3</sub>Si\*-OSi\*R<sub>3</sub> which is unchanged after many hours under the same conditions. Reduction of the first silicon-sulfur bond in I (reaction 5a) is complete in 30 min at room temperature, whereas attempted reduction of R<sub>3</sub>Si\*OSi\*R<sub>3</sub> by heating with LiAlH<sub>4</sub> at 45° overnight gave only a trace of R<sub>3</sub>Si\*H.<sup>2a,5</sup> Thus it is clear that RS<sup>-</sup> is a better leaving group than its oxygen analog, RO<sup>-</sup>, with nucleophilic reagents.<sup>6</sup> Also, reactions 1c, 2, 5a, 6, and 7 reveal the (not unexpected) fact that RS<sup>-</sup> is a better leaving group than S<sup>2-</sup>.

The stereochemical consequences of the above leaving group relationships are of considerable interest. Thus, *inversion* in reaction 8 is in sharp contrast to the highly stereospecific reduction of R<sub>3</sub>Si\*OCH<sub>3</sub> with *retention* of configuration by LiAlH<sub>4</sub> in ether solvent.<sup>2a</sup> *Inversion* for the reduction of the first Si\*-S bond in the disilthiane is also in sharp contrast to reduction of both Si\*-O bonds with *retention* of configuration in the reaction of R<sub>3</sub>Si\*OSi\*R<sub>3</sub> with LiAlH<sub>4</sub> at elevated temperature.<sup>2a</sup> Furthermore, other reactions of R<sub>3</sub>Si\*OCH<sub>3</sub> and R<sub>3</sub>Si\*OSi\*R<sub>3</sub> are known to proceed with *retention* of configuration,<sup>2a</sup> unlike the situation for reactions of R<sub>3</sub>Si\*-SY which usually proceed with *inversion* of configuration. The present stereochemical studies of the silicon-sulfur bond provide additional evidence for the concept of inversion of configuration being favored

(5) Unpublished work of L. H. Sommer and C. L. Frye. Reduction of R<sub>3</sub>Si\*OSi\*R<sub>3</sub> to R<sub>3</sub>Si\*H was accomplished in 42% yield after heating at 110° for 3 days and at 143° for 8 hr. See ref 2a.

(6) Increased reactivity of the sulfur compounds with nucleophilic reagents, relative to the rates of their oxygen analogs, is in accord with previous conclusions of increased reactivity of R<sub>3</sub>SiX with smaller values of pK<sub>a</sub> for HX. See ref 4, Chapter 8.

by better leaving groups, whereas retention of configuration is common for poorer leaving groups in nonpolar solvents.<sup>7</sup> A clear case of operation of this principle is provided in the present work by *inversion* for reaction 5a (RS<sup>-</sup> leaving group) and retention in reaction 7 (S<sup>2-</sup> leaving group).<sup>8,9</sup>

**Acknowledgment.** We thank Dow Corning Corporation for continued generous support.

(7) See ref 4, Chapters 3 and 11. For example, the change from RCO<sub>2</sub><sup>-</sup> to RO<sup>-</sup> as a leaving group frequently results in a change from inversion to retention of configuration.

(8) The actual leaving group may approximate H<sub>3</sub>AlS<sup>-</sup>, but inductive electron release from aluminum to sulfur should still make this complex leaving group poorer than RS<sup>-</sup>.

(9) Formation of Et<sub>3</sub>SiSiEt<sub>3</sub> from Et<sub>3</sub>SiCl and H<sub>2</sub>S has been reported by G. Champetier, Y. Etienne, and R. Kullman, *Compt. Rend.*, **234**, 1985 (1952). Compound II is the first example of an amine salt of R<sub>3</sub>SiSH.

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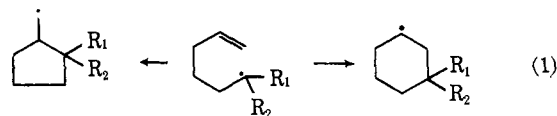
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Received August 29, 1966

## Radical Cyclizations in the Reaction of Trialkyltin Hydrides with Alkenyl Halides<sup>1</sup>

Sir:

The cyclization of 5-hexenyl radicals has been the subject of several recent papers and is of considerable interest since the direction of ring closure varies strikingly with changes in radical structure.



Thus with highly substituted radicals (R<sub>1</sub> = COOR, R<sub>2</sub> = CN) Julia<sup>2</sup> reports chiefly formation of cyclohexyl derivatives, while the simple 5-hexenyl radical cyclizes almost exclusively to the cyclopentylmethyl radical.<sup>3-5</sup> Five-membered-ring products are also preferred in intermediate cases, as in the addition of a number of radicals to 1,6-heptadiene, diallyl ether, and ethyl diallylacetate.<sup>6,7</sup>

The five-membered-ring closure is surprising since it is energetically unfavorable and contrary to the usual direction of radical addition, and we are investigating it in more detail. For this purpose we find that the reaction of organic halides with tributyltin hydride, developed by Kuivila,<sup>8</sup> provides a convenient means of generating a variety of radicals and that the cyclization in many cases competes favorably with reaction of the uncyclized radical with the hydride. Some preliminary

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

(2) M. Julia and Maumy, *Bull. Soc. Chim. France*, 434 (1966), gives a good summary of earlier work.

(3) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

(4) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

(5) R. G. Garwood, C. J. Scott, and B. C. L. Weedon, *Chem. Commun.*, **1**, 14 (1965).

(6) N. O. Brace, *J. Am. Chem. Soc.*, **86**, 523 (1964).

(7) J. I. G. Cadogan, *Chem. Ind. (London)*, 753 (1964).

(8) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

**Table I.** Ring Closures of Alkenyl Halides by Tributyltin Hydride

Halide	Products (%)
6-Bromo-1-hexene	1-Hexene (7) Methylcyclopentane (78) Cyclohexane (trace)
2-Bromoethyl allyl ether	Ethyl allyl ether (4) 3-Methyltetrahydrofuran (84)
6-Bromo-6-methyl-1-heptene	6-Methyl-1-heptene (35) Trimethylcyclopentane <sup>a</sup> (47) 1,1-Dimethylcyclohexane (0.6)
Allyl chloroacetate	Allyl acetate (89)
2-Bromoethyl crotonate	Ethyl crotonate (35) $\gamma$ -Lactone <sup>a</sup> (13)
5-Bromo-1-pentene	1-Pentene (90)
2-Chloroethyl vinyl ether	Ethyl vinyl ether (83)
3-Bromopropyl allyl ether	Propyl allyl ether (88)
Di(2-bromoethyl) maleate	$\gamma$ -Lactone <sup>a</sup>

<sup>a</sup> Presumably 1,1,3-trimethylcyclopentane,  $\alpha$ -ethyl- $\gamma$ -butyrolactone, and  $\alpha$ -carbethoxymethyl- $\gamma$ -butyrolactone, respectively, but not unequivocally identified.

results are listed in Table I. Experiments were run under some variety of conditions at 30–130°, using azobisisobutyronitrile (AIBN) or light as initiator at the lower temperatures, and exact conditions are not given since the table is only intended to indicate the occurrence or nonoccurrence of ring closure and its direction.

From the data in Table I, cyclization is observed only with radicals possessing unsaturation in the 5,6 position and also fails with allyl chloroacetate, presumably because of stabilization of the uncyclized radical. Five-membered-ring closure is the preferred reaction even in the case of the  $\alpha,\beta$ -unsaturated esters where the six-membered ring would be favored by formation of a highly resonance-stabilized radical.

We have examined the reaction of 6-bromo-1-hexene in more detail to see if yields of cyclized and uncyclized product show the expected dependence on hydride concentration. Results of experiments using excess halide and run to complete consumption of hydride are listed in Table II. In addition to the products shown, up to

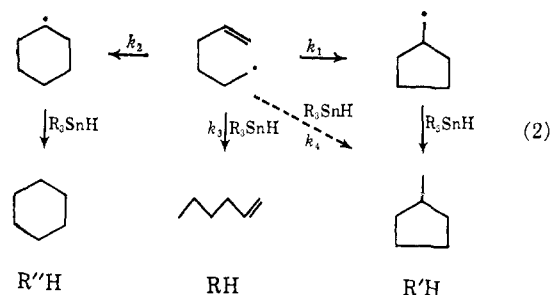
**Table II.** Reactions of 6-Bromo-1-hexene with Tributyltin Hydride<sup>a</sup>

[R <sub>3</sub> SnH], M	% yields	
	1-Hexene	Methylcyclopentane
	At 40°	
0.0160	7	78
0.0187	9	76
0.0407	16	66
0.0413	17	68
0.0824	24	61
0.0941	25	60
0.164	35	51
0.186	36	50
0.239	41	47
0.278	42	40
0.335	48	40
0.355	49	42
	At 130°	
0.0438	38	50
0.0657	36.5	48.5
0.132	37.5	49
0.263	38	46.5
0.526	45.5	36.5

<sup>a</sup> All experiments in sealed, degassed tubes, benzene solvent, 2–10-fold excess halide, AIBN initiator at 40°, di-*t*-butyl peroxide at 130°. Analyses by gas-liquid partition chromatography. Data at 130° are averages of duplicate runs.

1% cyclohexane is produced at 130°, but only traces at 40°, in accord with previous reports.<sup>4</sup>

The simplest kinetic scheme for analysis of the results involves reactions with rate constants  $k_1$ ,  $k_2$ , and  $k_3$  in eq 2



leading to the differential equation

$$-\frac{d[\text{R}_3\text{SnH}]}{d[\text{RH}]} = \frac{(k_1 + k_2) + k_3[\text{R}_3\text{SnH}]}{k_4[\text{R}_3\text{SnH}]} \quad (3)$$

Equation 3 may be integrated between  $[\text{R}_3\text{SnH}] = [\text{R}_3\text{SnH}]_0$  and zero and gives a reasonable fit to the results at 40° for  $k_3/k_1 = 10$  (since  $k_1/k_2 > 100$ ,  $k_2$  may be neglected).<sup>9</sup> The data at 130°, however, show too small a dependence on hydride concentration. They can be fitted if the cyclization corresponding to  $k_1$  is considered to be reversible, but such a result would predict significant formation of 1-hexene on the reduction of cyclopentylmethyl bromide (36% at  $[\text{R}_3\text{SnH}]_0 = 0.05 M$  on the basis of the fitting parameters). Careful examination of this reaction gave methylcyclopentane (77%) as the only C<sub>6</sub> hydrocarbon product, and under 0.1% 1-hexene, the limit of detection by gas-liquid partition chromatography. We conclude the cyclization is not significantly reversible under our conditions, in agreement with Lamb's peroxide studies.<sup>3</sup>

An alternative hypothesis is that cyclized product can arise directly from reaction of the uncyclized radical with tin hydride (perhaps by attack of tin on an internal radical- $\pi$  complex),<sup>10</sup> *i.e.*, to include the rate constant  $k_4$ . Neglecting the trace formation of cyclohexane, this yields

$$-\frac{d[\text{R}_3\text{SnH}]}{d[\text{RH}]} = \frac{k_1 + (k_3 + k_4)[\text{R}_2\text{SnH}]}{k_4[\text{R}_3\text{SnH}]} \quad (4)$$

Equation 4, on integration, fits the 130° data with the parameters  $k_3/(k_3 + k_4) = 0.6$ ,  $k_1/(k_3 + k_4) = 0.01$ . Both equations give similar fits to the 40° data, but (3) with  $k_2/k_1 = 10$  predicts that reaction of a small amount of bromide in pure tributyltin hydride (approximately 3 M) should give <3% methylcyclopentane. Experiments under these conditions actually yielded 8–17% methylcyclopentane and 63–79% 1-hexene, suggesting that the path corresponding to  $k_4$  occurs under these conditions as well.

Studies of these reactions are continuing to see if "concerted cyclization" is a reality and whether it

(9) Since yields of reduction products were not quite quantitative (presumably because of some hydride addition to the excess bromohexene), they were normalized to 100% for purposes of calculation. This treatment is valid if the side reaction is of the same order in hydride as the reduction, which is almost certainly true if they are competing chains.

(10) Interaction of polar radicals with  $\pi$ -electron systems is well established (*cf.* C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964)), but there is certainly less evidence of carbon radicals.

occurs in other systems and with other hydrogen donors as well.

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### Reactions of Aromatic Radical Anions. I. Coupling of Alkyl Free Radicals Generated by Electron Transfer to Alkyl Iodides<sup>1</sup>

Sir:

The reaction of sodium naphthalenide (I)<sup>2</sup> with alkyl iodides in 1,2-dimethoxyethane (DME) solution occurs predominantly by initial electron transfer to yield alkyl free radicals. By this process, radicals can be generated in sufficiently high concentration that radical combination competes favorably with either hydrogen abstraction from solvent or further reduction to primary carbanion.

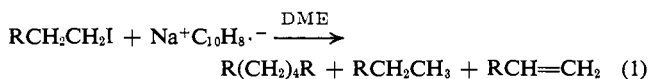
A DME solution approximately 1 *M*<sup>3</sup> in I was in-

**Table I.** Per Cent Yield of Aliphatic Hydrocarbons from the Reaction of Na<sup>+</sup>C<sub>10</sub>H<sub>8</sub><sup>-</sup> with RCH<sub>2</sub>CH<sub>2</sub>I<sup>a</sup>

R	R(CH <sub>2</sub> ) <sub>4</sub> R	RCH <sub>2</sub> CH <sub>3</sub>	RCH=CH <sup>2</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> <sup>-</sup>	50	22	6
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> <sup>-</sup>	55	17	4

<sup>a</sup> Values reported are the average of several independent determinations. Yields in general are reproducible to ±10% of the value reported.

jected rapidly into a DME solution approximately 1 *M* in alkyl iodide protected from atmospheric oxygen and moisture by means of a rubber serum cap. The reaction is macroscopically instantaneous and exothermic. Complete reaction of the alkyl iodide was ensured by continuing the injection of radical-anion solution until its dark green color persisted in the reaction vessel. The products of the reaction (1) were analyzed by vapor phase chromatography without further work-up. Quantitative results were obtained by including an inert internal standard of known concentration in the alkyl iodide solution. Reactions were carried out at both ambient temperature and with the vessel containing the alkyl iodide solution immersed in a Dry Ice-acetone bath. No significant temperature effects were discerned. The yields of aliphatic hydrocarbons from *n*-amyl iodide and *n*-heptyl iodide are presented in Table I.



(1) Presented in part at the 11th Conference on Reaction Mechanisms, McMaster University, Hamilton, Ontario, June 22–25, 1966, and at the 1st Middle Atlantic Regional Meeting, American Chemical Society, Philadelphia, Pa., Feb 3–4, 1966, Abstracts, p 120.

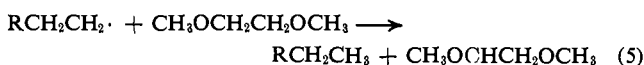
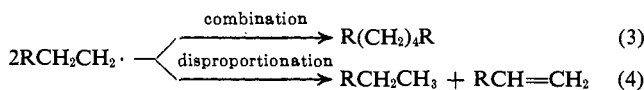
(2) N. D. Scott, J. F. Walker, and V. L. Hansely, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

(3) Solutions of I were prepared by adding 1 equiv of sodium to a DME solution 1 *M* in naphthalene. The virtually equal yield of naphthalene and dihydronaphthalene formed on quenching aliquots of these solutions in water indicated that essentially complete conversion of naphthalene to I had occurred.

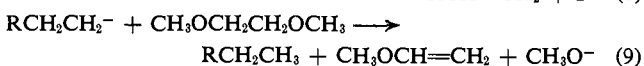
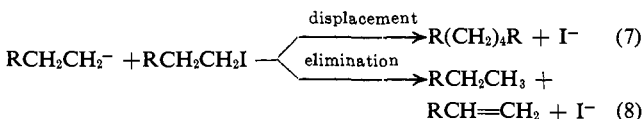
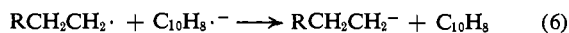
Either of two mechanisms, or a combination of both, can be postulated to explain these results.



Radical mechanism

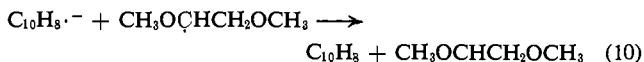


Carbanion mechanism

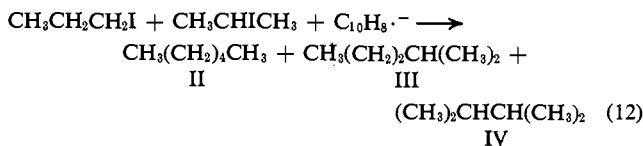


The alkene does not arise from a bimolecular elimination reaction of the alkyl iodide with I acting as a base, since the expected product of this reaction,<sup>2</sup> 1,4-dihydronaphthalene, is not formed in the reaction.

The final step (5, 9) in each mechanism is required to account for the fact that alkane is formed in excess of alkene. We have detected the presence of methyl vinyl ether in the product mixture, but this in no way serves to distinguish between the two mechanisms, since the fate of the radicals derived from solvent produced by the radical mechanism might well be further reduction (10) followed by fragmentation (11).



We have sought to differentiate between the radical and carbanion mechanisms by investigating the yield of coupled products in the reaction of I with an equimolar mixture of *n*-propyl iodide and isopropyl iodide. Potentially, three isomeric hexanes can be formed in this reaction.



If coupling occurs by combination (3), the three hexanes should be formed in a statistical ratio, [III] = 2([II][IV])<sup>1/2</sup>, which reflects only the concentration of the two isomeric propyl radicals.<sup>4,5</sup> This prediction, which has received extensive experimental verification, derives from the fact that radical coupling requires essentially no activation energy.<sup>4</sup> If coupling occurs by displacement (7), no such statistical product distribution would be expected. In a wide variety of nucleophilic displacement reactions which vary in absolute

(4) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 108 (1961); A. F. Trotman-Dickenson, *Ann. Rept. Chem. Soc.*, **55**, 41 (1958).

(5) The tacit but necessary assumption that both radicals are produced at the same rate is supported by data which suggest that the rate of reaction of both halides with I should be diffusion controlled [D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 1375 (1955)].