is shown similarly in Chart II.[18-21] Purity of all final compounds was checked by glc and also nmr and ir spectra. **Stannanes** were prepared by $LiAlH_4$ reduction of the corresponding commercial chlorostannanes.[22] They were stored in benzene solution under argon at −20° until used.

Cyclizations were carried out in sealed, degassed tubes, using reagent concentrations indicated in Tables I–VI in benzene solvent containing AIBN (40 and 70°) or DTBP (100 or 130°) initiator and internal standard for subsequent analysis (*n*-hexane for C_6 compounds, *n*-heptane for C_7, and naphthalene for C_8 and C_9). Experiments were run to completion: 24 hr at 40°, 6 hr at 70°, and 3 hr at 100°.

Product analyses were carried out by glc using didecyl phthalate on 60–80 firebrick columns at 95–120°. In every system products were identified by collection and determination of physical properties as well as comparison of retention time with authentic standards. Cyclohexane and methylcyclohexane were obtained in such low yield that they were determined by retention time alone. Authentic materials were also used for calibration of the internal standards employed.

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Interconversion of 1-Phenyl-5-hexenyl, 2-Phenylcyclopentylmethyl, and 3-Phenylcyclohexyl Radicals[1]

Cheves Walling*[2] and Angela Cioffari

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received February 3, 1972*

Abstract: Reaction of either 6-bromo-6-phenyl-1-hexene or *trans*-2-phenylcyclopentylmethyl bromide with tributylstannane yields 6-phenyl-1-hexene (A), *trans*-1-methyl-2-phenylcyclopentane (B), and phenylcyclohexane (C) showing that the three corresponding radicals are interconvertible under these conditions. Further, the product ratio C/A is much higher in the second case indicating direct rearrangement of the 2-phenylcyclopentylmethyl radical to 3-phenylcyclohexyl without ring opening. Thus, this system provides the first clear-cut case of an intramolecular 1,2-alkyl shift in a monoradical rearrangement. The B → C rearrangement is also reversible since some B is formed starting with 3-bromo-1-phenylcyclohexane. *cis*-2-Phenylcyclopentylmethyl bromide similarly yields A, B, and C in addition to unrearranged hydrocarbon and the indan derivative arising from intramolecular radical attack on the aromatic ring. Here, product distributions indicate that A, B, and C arise solely by ring opening.

In our preceding paper[3] we examined the cyclization of a series of methyl-substituted 5-hexenyl radicals generated *via* the radical chain reaction between tributyl- or triphenylstannane and the appropriate alkenyl bromide[4] and concluded that, under our conditions, there was no evidence for reversibility of the cyclizations observed. This paper describes a similar study of the 1-phenyl-5-hexenyl radical where it was anticipated that resonance stabilization would increase the likelihood of observing reversibility of the cyclization process.[5]

Results

Experiments were carried out in sealed, degassed tubes using benzene as solvent, varying concentrations of tri-*n*-butylstannane, equivalent 6-bromo-6-phenyl-1-hexene, and azobisisobutyronitrile (AIBN) or di-*tert*-butyl peroxide (DTBP) as initiator. Reactions were run to complete consumption of stannane and gave 85–95% yields of olefin and cyclized products. Results (see Scheme I) appear in Table I with all yields normalized to 100%. During each run, stannane concentration varied from its initial value to zero. Since for later discussion product distributions over more limited

Table I. Reduction of 6-Bromo-6-phenyl-1-hexene by Tributylstannane

		Yield, %		
$[R_3SnH]$	*T*, °C	A	B	C
0.500	70	27.4	56.8	15.8
		(43.2)	(51.3)	(5.5)
0.250	70	11.6	62.3	26.1
		(15.7)	(65.6)	(18.7)
0.100	70	5.5	57.3	37.2
		(8.3)	(64.9)	(26.8)
0.050	70	2.7	49.7	47.6
		(3.3)	(53.5)	(43.2)
0.025	70	2.1	45.9	52.0
		(2.5)	(50.4)	(47.1)
0.010	70	1.5	39.2	59.3
0.500	100	17.4	53.8	28.8
		(26.3)	(56.7)	(17.0)
0.250	100	8.5	50.9	40.6
		(11.6)	(54.8)	(33.6)
0.100	100	3.8	45.0	51.2
		(5.1)	(53.0)	(41.9)
0.050	100	2.5	37.0	61.5
		(3.9)	(40.3)	(55.8)
0.025	100	1.1	33.7	66.2
		(1.4)	(34.6)	(64.0)
0.010	100	0.6	32.3	77.1

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(1) Taken from the Ph.D. thesis of A. Cioffari, Columbia University, 1971. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

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(3) C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, **94**, 6059 (1972).

(4) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, **88**, 5361 (1966).

(5) Since this work was completed, reversibility of this system under conditions of longer radical lifetime has been reported: M. Julia, *Accounts Chem. Res.*, **4**, 386 (1971).

ranges of stannane concentrations will be needed, they were computed as follows. In the first run of Table I, the final concentration of 6-phenyl-1-hexene (A) is 0.5 × 0.274 = 0.137 *M*, while in the second run (A) = 0.25 × 0.116 = 0.029 *M*. Since, once the concentration of stannane in run one drops from 0.5 to 0.25 *M*, it becomes a duplicate of run two, the concentration of olefin produced earlier equals 0.137 − 0.029 = 0.108 *M*, corresponding to a yield of 0.108/(0.5 − 0.25) = 43.2%. Values for all products computed in this way appear in parentheses between the concentrations of stannane involved and will be referred to as ΔA, ΔB, and ΔC.

Inspection of Table I shows that yields of cyclized products increase with decreasing stannane concentration and that both *trans*-1-methyl-2-phenylcyclopentane and phenylcyclohexane are produced (the behavior of the *cis*-2-phenylcyclopentylmethyl radical is considered later in this paper). More striking, ratios of six- to five-membered ring products increase steadily with decreasing stannane, suggesting that, at the least, closure to the five-membered ring is a reversible process.

Confirmation of interconversion of 2-phenylcyclopentylmethyl and 3-phenylcyclohexyl radicals was obtained by examining the reaction of 2-phenylcyclopentylmethyl bromide with tributylstannane and triethylsilane and 1-bromo-3-phenylcyclohexane with tributylstannane, Tables II–IV. Every bromide yields both five- and six-membered ring products, the amount of isomerization increasing with decreasing stannane or silane. The silane was selected because we anticipated that its lower reactivity would permit longer radical lives and increased rearrangement. Indeed, comparison of Tables II and III shows similar product ratios for 0.5–0.25 *M* silane and 0.025–0.010 *M* stannane indicating that the rate constants for tributylstannane reactions (k_a, k_b, and k_c in Scheme I) are some 20 times those for triethylsilane. Comparison of Tables I and II further shows that ratios of phenylcyclohexane (C) to 6-phenyl-1-hexene (A) are much larger starting with 2-phenylcyclopentylmethyl bro-

Table II. Reduction of *trans*-2-Phenylcyclopentylmethyl Bromide by Tributylstannane

[R_3SnH]	*T*, °C	Yield, % A	B	C
0.500	70	3.2	90.7	6.1
		(6.3)	(90.6)	(3.1)
0.250	70	1.5	89.4	9.1
		(2.0)	(92.4)	(5.6)
0.100	70	0.7	84.9	14.4
			(89.6)	(10.4)
0.050	70		81.5	18.5
			(88.3)	(11.7)
0.025	70		74.4	25.3
			(81.5)	(18.5)
0.010	70		64.5	35.5
0.500	100	1.0	90.3	8.7
		(1.5)	(93.8)	(4.7)
0.250	100	0.5	86.8	12.7
			(92.2)	(7.8)
0.100	100		79.9	20.1
			(84.3)	(15.7)
0.050	100		75.5	24.5
			(83.9)	(16.1)
0.025	100		67.9	33.1
			(74.9)	(25.1)
0.010	100		55.6	44.4

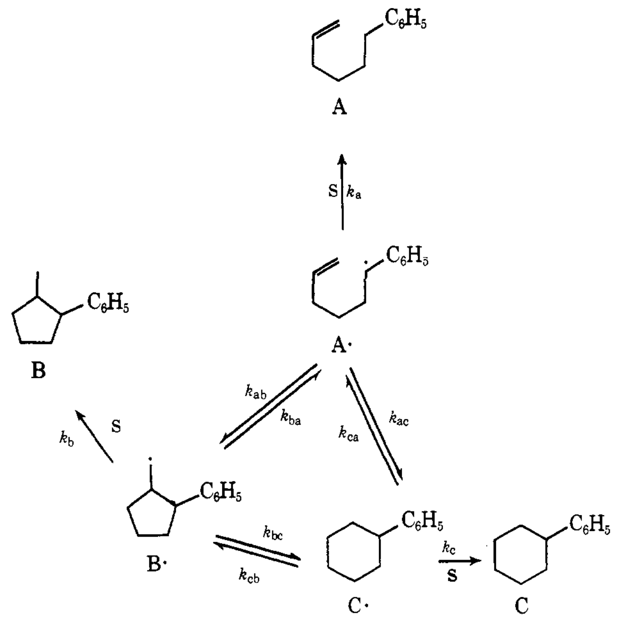
Table III. Reduction of *trans*-2-Phenylcyclopentylmethyl Bromide by Triethylsilane

[R_3SiH]	*T*, °C	Yield, % B	C
0.500	70	70.2	29.8
		(81.2)	(18.8)
0.250	70	59.2	40.8
		(68.7)	(31.3)
0.100	70	45.0	55.0
		(51.7)	(48.3)
0.050	70	38.3	61.7
		(45.2)	(54.8)
0.025	70	31.4	68.6
		(36.5)	(63.5)
0.010	70	23.8	76.2
0.500	100	62.6	37.4
		(73.3)	(26.7)
0.250	100	51.9	48.1
		(61.3)	(38.7)
0.100	100	37.8	62.2
		(44.0)	(56.0)
0.050	100	31.6	68.4
		(36.4)	(63.6)
0.025	100	26.8	73.2
		(33.7)	(66.3)
0.010	100	16.5	83.5

Table IV. Reduction of 3-Phenylcyclohexyl Bromide by Tributylstannane

[R_3SnH]	*T*, °C	Yield, % B	C
0.500	70		100
0.250	70		100
0.100	70	0.5	99.5
0.050	70	1.0	99.0
0.025	70	1.6	98.4
0.010	70	3.4	96.6
0.500	100	0.5	99.5
0.250	100	1.0	99.0
0.100	100	2.1	97.9
0.050	100	2.5	97.5
0.025	100	3.1	96.9
0.010	100	3.8	96.2

Scheme I



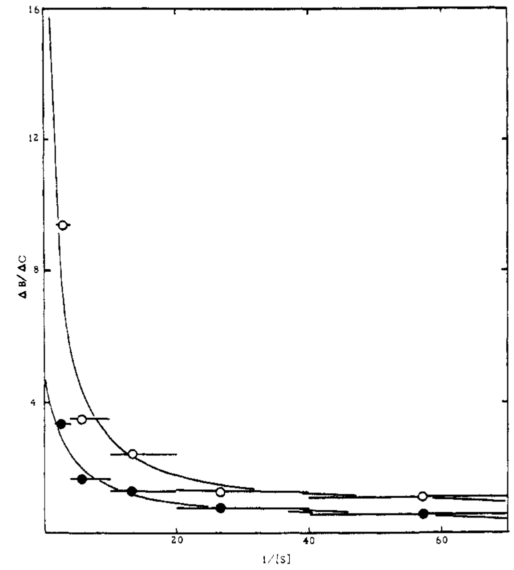


Figure 1. Estimation of k_{ab}/k_{ac} from eq 4: open circles 70°, solid circles 100°. Horizontal lines show ranges of concentration involved; circles represent average values.

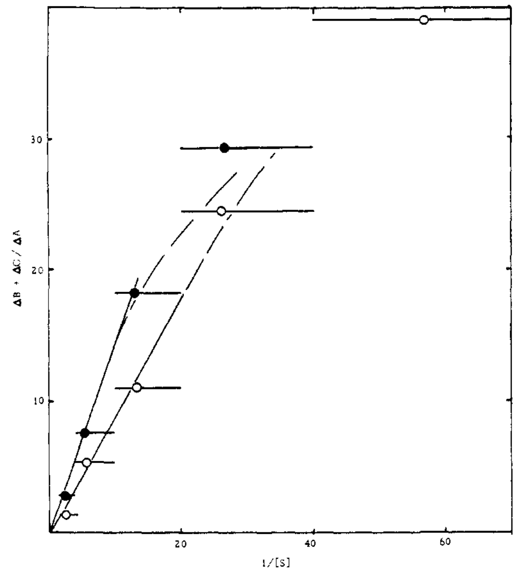


Figure 2. Estimation of $(r_{ab} + r_{ac})$ from eq 5: open circles 70°, solid circles 100°.

mide than with 6-bromo-6-phenyl-1-hexene. *This result requires that the 2-phenylcyclopentylmethyl radical have a path for rearrangement to 3-phenylcyclohexyl without going through a fully opened intermediate.* Accordingly, we must consider the fully reversible system shown in Scheme I. In the scheme, position of the radicals indicates their anticipated stability, C· > B· > A·. Relative rates of formation of products in Scheme I are given by the differential equations (*cf.* Appendix) where

$$r_{ca} + r_{cb} + [S] = r_{ac}d[A]/d[C] + r_{bc}d[B]/d[C] \quad (1)$$

$$r_{ba} + r_{bc} + [S] = r_{ab}d[A]/d[B] + r_{cb}d[C]/d[B] \quad (2)$$

$$r_{ab} + r_{ac} + [S] = r_{ba}d[B]/d[A] + r_{ca}d[C]/d[A] \quad (3)$$

$r_{ij} = k_{ij}/k_i$ and $[S] = [R_3SnH]$. Equation 1 applies to systems in which the initially generated radical is A· or B·, eq 2 to initial A· or C·, and eq 3 to initial B· or C·. In principle, all r's could be determined by linear regression analysis in six variables but attempts to do so using ΔA, ΔB, and ΔC's from Tables I–IV gave some negative values and poor correlation either because of experimental errors or incompleteness of the model.[6] Nevertheless, it proved possible to estimate several rate constant ratios by extrapolation procedures as follows.

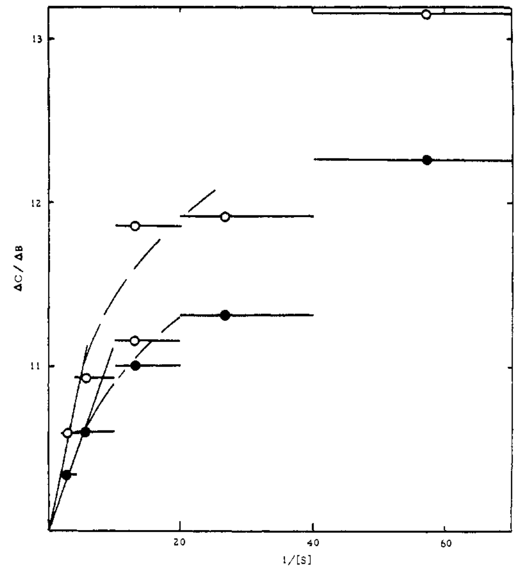


Figure 3. Estimation of r_{bc} from eq 6: open circles 70°, solid circles 100°.

Starting with A·, at increasing concentrations of stannane, isomerization to B· and C· becomes increasingly irreversible so that the product distributions approach

$$d[B]/d[C] = r_{ab}/r_{ac} = k_{ab}/k_{ac} \quad (4)$$

$$(d[B] + d[C])/d[A] = (r_{ab} + r_{ac})/[S] \quad (5)$$

Accordingly, if ΔB/ΔC is plotted *vs.* 1/[S], the intercept should yield k_{ab}/k_{ac}. Such plots are shown in Figure 1 with data fitted to hyperbolas since this is the form of the relation predicted by eq 1 and 2. At 100° the intercept indicates $k_{ab}/k_{ac} = 5 \pm 1$, but at 70° the slope of the plot is so steep that we can only conclude $k_{ab}/k_{ac} > 20$.

Similarly, from eq 5, the limiting slope of a plot of (ΔB + ΔC)/ΔA *vs.* 1/[S] as 1/[S] approaches zero should give $(r_{ab} + r_{ac})$. From Figure 2 values are 0.9 and 1.4 at 70 and 100°, respectively.

Next, since B· which opens to A· for the most part is either trapped as A or returns to B·, at high stannane concentrations reactions starting at B· should approach the product distribution

$$d[C]/d[B] = r_{bc}/[S] \quad (6)$$

with a limiting slope as 1/[S] = 0 of r_{bc}. A plot of data from Table II is given in Figure 3 and yields $r_{bc} = 0.012$ at 70° and 0.02 at 100°. We may also estimate r_{ba} by the following argument. From Table II, starting with B· at 70° in the presence of 0.5–0.25 M stan-

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[6] Errors in the original data are unfortunately magnified since use of (1–3) involves replacing differentials by Δ values and average concentrations, and further the former involves small differences between larger numbers.

nane (av 0.375 *M*) we obtain 6.3% A. However, from Table I, only 43.2% of A·'s are trapped as A under these conditions. Accordingly, 6.3/0.432 = 14.6% A· was actually formed. At the same time, 90.6% of B· was trapped as B. Accordingly, $r_{ba}/0.375 \cong 14.6/90.6$ and $r_{ba} \cong 0.06$. Similarly, at 100° $r_{ba} \cong 0.033$. Finally, at very low concentrations of S, all radicals are essentially in equilibrium so

$$d[C]/d[B] = r_{bc}/r_{cb} \tag{7}$$

The nearest approach to these conditions is probably in the silane experiments of Table III. Extrapolation of the data to zero silane concentration indicates a limiting value d[B]/d[C] of 0.1–0.2.

Discussion

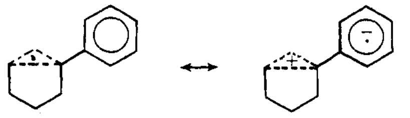
Rate constant ratios, obtained as described above, are summarized in Table V and give a revealing picture of the behavior of the system. Entering the system at A· (*i.e.*, in reactions of the unsaturated bromide) at high concentrations of stannane, the ratio of B to C formed is determined by r_{ab}/r_{ac} since little B· goes to C· before being trapped as B. Here ring closure gives chiefly a cyclopentylmethyl radical, as in all but the most hindered alkyl substituted 5-hexenyl radicals considered previously.[3] Also, compared with the alkyl cases, the competition between ring closure and reaction with stannane is more favorable for the former by a factor 4–10, presumably because of slower reaction of the benzylic radical with the stannane.

Table V. Summary of Rate Constant Ratios

	70°	100°
$(r_{ab} + r_{ac})$	0.9	1.4
$r_{ab}/r_{ac} = k_{ab}/k_{ac}$	>20	5
r_{ba}	0.06	0.033
r_{bc}	0.012	0.02
r_{cb}/r_{bc}	0.1–0.2	

At lower concentrations A· and B· approach equilibrium (at [S] = 0.1 *M* and 70°, A· is going to B· 100 times as fast as it is being trapped and B· is going to A· 6 times as fast); however, now significant amounts of B· leak directly and irreversibly to C·. At still lower concentrations equilibrium between B· and C· is approached so that the B/C ratio is determined by r_{cb}/r_{bc} and C is favored. The approach to this equilibrium is slower because of the very small value of r_{cb} (0.0012–0.0024 at 70°). If we assume $k_c \cong k_b$[7] the equilibrium constant for C· and B·, $k_{cb}/k_{bc} \cong 0.1–0.2$. Similarly, since at 70° $r_{ab}/r_{ba} = 15$ and presumably $k_a \leq k_b$, the equilibrium constant for B· and A· is $k_{ab}/k_{ba} \geq 15$.

The most important conclusion from this study is that our data require a direct rearrangement of a cyclopentylmethyl radical B· to a cyclohexyl radical C· without going through an open chain intermediate A· and accordingly provide the first clear-cut case of a simple radical rearrangement involving an intramolecular 1,2-alkyl migration.[8] Evidently, our system provides a particularly favorable case since the fragments from the competing β scission (to A·) are kept together and can recyclize, and the neighboring phenyl group can facilitate both processes through contribution of benzylic resonance to the transition states so that they compete with trapping by stannane. Actually, from Table V, $k_{ba}/k_{bc} = 5$ at 70° and 1.6 at 100°. Ring opening is the faster process, but the change in the ratio with temperature shows that the rearrangement has a lower enthalpy and a more negative entropy of activation anticipated for a tighter transition state. Finally, it is possible that since rearrangement occurs here, but not in the several alkyl substituted systems we have studied, we are dealing with a transition state with considerable carbonium ion character, *i.e.*



(8)

which lowers its energy.[9] In this regard, other systems in which Julia has observed facile methylcyclopentyl → cyclohexyl radical rearrangements[5] all contain –CN, –COOMe, and similar groups which could accommodate a comparable charge separation, although here open chain intermediates have not been unequivocally excluded.

Reduction of *cis*-2-Phenylcyclopentylmethyl Bromide. Generation of the *cis*-2-phenylcyclopentylmethyl radical from the corresponding bromide by reaction with tributylstannane or triethylsilane (Tables VI and VII) produces two additional products besides those shown in Scheme I. Product D, *cis*-1-methyl-2-phenylcyclopentane, is simply the consequence of trapping the unrearranged cis radical, while E, 1,2,3,3a,8a-hexahydrocyclopent[*a*]indene, must arise from radical attack on the aromatic ring facilitated by the cis stereochemistry of D· about the relatively rigid cyclopentane ring.[10]

Table VI. Reduction of *cis*-2-Phenylcyclopentylmethyl Bromide by Tributylstannane

		Products, %				
$[R_2SnH]$	*T*, °C	A	B	C	D	E
0.500	70	2.3	4.8	1.3	85.6	6.0
0.250	70	1.4	7.9	3.1	78.0	9.6
0.100	70	1.1	12.8	7.5	64.3	14.3
0.050	70	0.6	14.4	14.1	53.7	17.2
0.025	70		15.1	18.7	46.9	19.3
0.010	70		15.4	22.4	42.1	20.1
0.500	100	1.8	6.5	3.3	79.6	8.8
0.250	100	1.5	9.4	7.2	69.2	12.7
0.100	100	Trace	12.9	14.5	55.1	17.5
0.050	100		13.2	22.0	45.2	19.6
0.025	100		14.6	24.3	39.7	21.4
0.010	100		14.0	33.3	30.9	21.8

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(7) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 90, 7047 (1968), report the rate constants for primary alkyl and cyclohexyl radicals with tributylstannane are the same within experimental error (1×10^6).

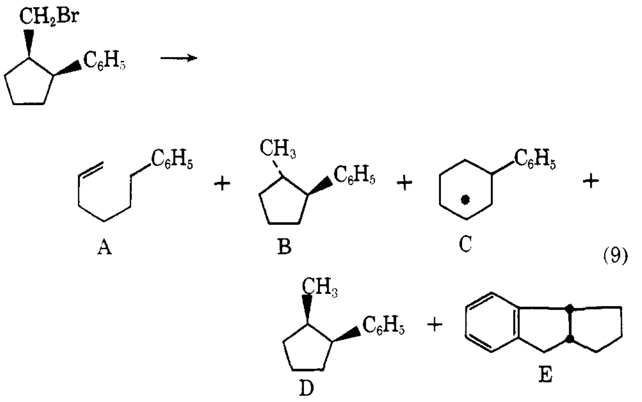
(8) For discussion, *cf.* C. Walling, "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963. 1,2-Hydrogen and alkyl rearrangements in biradicals are well established.

(9) Simple quantum mechanical arguments indicate that adding a third electron to a triangular transition state as in (8) raises its energy,[8] and charge-separated structures similar to (8) may also be invoked to account for facile rearrangements observed in diradicals: *cf.* C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *J. Amer. Chem. Soc.*, 92, 4927 (1970).

(10) Such cyclizations to yield, eventually, indan and tetralin derivatives are well known and reviewed by Julia.[5]

Table VII. Reduction of *cis*-2-Phenylcyclopentylmethyl Bromide by Triethylsilane

[R_3SiH]	T, °C	Products, %: B	C	D	E
0.500	70	24.1	8.9	54.5	2.5
0.250	70	26.8	14.2	45.2	5.8
0.100	70	28.9	23.0	34.1	7.9
0.050	70	26.6	34.6	22.6	8.2
0.025	70	25.8	42.5	20.3	8.4
0.010	70	26.5	53.2	15.1	8.2
0.500	100	18.4	12.5	48.6	1.5
0.250	100	22.3	23.8	39.7	3.2
0.100	100	21.6	25.6	30.2	5.6
0.050	100	21.3	45.5	23.1	7.1
0.025	100	21.6	52.0	16.5	6.9
0.010	100	23.1	66.1	10.2	7.2



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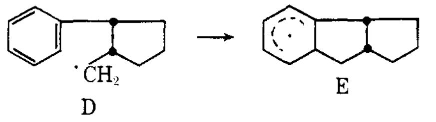
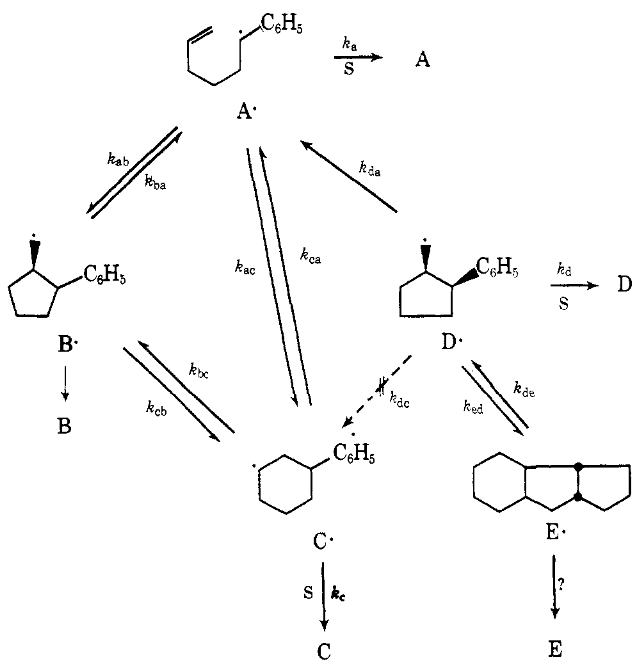


(10)

Just how E· is converted to E is not clear. Reaction with stannane to yield a dihydro compound which is subsequently oxidized on work-up is possible, but the most obvious direct path, disproportionation with another radical, seems unlikely since this would be a chain termination step and yields as high as 20% are observed in the presence of only 5% initiator.

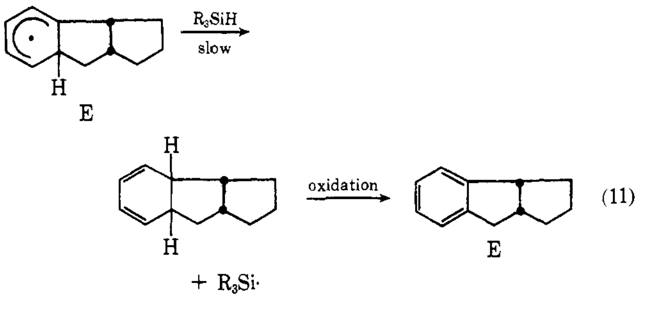
The product distributions shown in Table VI appear consistent with Scheme II and allow us to draw some conclusions about relative rates. First, since neither D nor E were ever detected in systems starting with A·, B·, or C·, conversion of D· to A· must be effectively irreversible under our conditions.[11] Second, the ratios of C/(A + B + C) at each stannane concentration in Table VI agree very well with yields of C in Table I. Accordingly, the data give no evidence for any direct rearrangement of D· to C· analogous to the B· → C· process; presumably, the *cis*-phenyl group provides enough steric hindrance to a transition state analogous to (8) so that the reaction is not observed. Third, the ratio E/(A + B + C) decreases with decreasing stannane concentration (from 0.72 to 0.52 at 70° and from 0.77 to 0.45 at 100°) implying that the conversion D· → E· is reversible as indicated.

Scheme II



Fourth, calculation of ΔD and Δ(A + B + C) between 0.5 and 0.25 M stannane at 70° as in Tables I–IV gives 93.2 and 4.4%, respectively, from which $r_{da} = k_{da}/k_d = 0.375 \times 4.4/93.2 = 0.018$. A similar calculation using 100° data gives $r_{da} = 0.021$. These numbers are slightly smaller than those for r_{ba} given in Table V, so steric repulsion does not appear to facilitate ring opening of D·.

Finally, the data of Table VII show results obtained using triethylsilane and reflect conditions where radicals have longer lives, most yields at any silane concentration being comparable to those at stannane concentrations one-tenth as large. Actually, these reactions ran rather poorly, showing 2–13% unreacted bromide, and lower yields of E than in the comparable stannane runs. This would be consistent with a reaction path for E formation *via* a dihydro derivative in which the unreactive silane fails to propagate the chain efficiently so that E· builds up and terminates chains.



(11)

Experimental Section

Materials. All reactants, solvents, and reference materials were either commercial materials purified by conventional methods and physical constants and purity checked before use or were synthesized by straightforward methods. The indan derivative E was identified by comparison with an authentic sample kindly supplied by Professor Pines.[11]

Cyclizations and analyses were carried out as described in the preceding paper.[3] Analyses by glc were done on didecyl phthalate columns using naphthalene as an internal standard.

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(11) However, H. Pines, N. C. Sih, and D. B. Rosenfield, *J. Org. Chem.*, 31, 2255 (1966), have reported B, C, D, and E as products when 6-phenyl-1-hexene is heated with peroxides at 85–150°. Here radical lives would be much longer than in our systems, and since product formation depends on R· + R′H ⟶ RH + R′· reactions, there should be a strong selectivity for five-membered ring products derived from primary radicals.

Appendix

The differential eq 1–3 were derived as follows. From Scheme I and entering the cycle at A· or B·

$$d[C]/d[A] = k_c[C\cdot]/k_a[A\cdot] \qquad (12)$$

$$d[B]/d[A] = k_b[B\cdot]/k_a[A\cdot] \qquad (13)$$

However, from the usual steady-state assumption

$$d[C\cdot]/dt = 0$$

$$k_{ac}[A\cdot] + k_{bc}[B\cdot] = k_{ca}[C\cdot] + k_{cb}[C\cdot] + k_c[S][C\cdot] \qquad (14)$$

Eliminating radical concentrations by combination of eq 12–14 yields eq 1, and eq 2 and 3 follow by virtue of the symmetry of the system when it is entered at A· or C· or at B· or C·, respectively.

Pentachlorocyclopentadienide Anion[1]

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Abstract: Salts of the aromatic pentachlorocyclopentadienide anion, $C_5Cl_5^-$, with the large cations Tl^+, $Tl^+\cdot 2C_6H_5CH_3$, $(C_2H_5)_3NH^+$, 1-methylpyridinium, $(C_4H_9)_4P^+$, and quaternary ammonium, have been isolated and characterized spectroscopically. The results are consistent with a delocalized, fivefold symmetric structure. The anion shows only two absorptions in the near infrared at about 1415 and 679 cm^{-1}. The electronic spectrum of $C_5Cl_5^-$ shows a principal absorption at approximately 201 nm with several shoulders. The nqr spectra of the salts (except for the $Tl^+\cdot 2C_6H_5CH_3$ salt) show frequencies in the range 35.0–35.7 MHz. Charge distributions in $C_5Cl_5^-$, C_6Cl_6, and $C_3Cl_3^+$ are estimated from nqr data and compared with distributions in their hydrocarbon analogs. $Tl^+C_5Cl_5^-\cdot 2C_6H_5CH_3$ appears to be a ground-state charge transfer complex; the 1-methylpyridinium salt is an excited-state charge transfer complex. Nqr spectra are presented for decachlororuthenocene and 1,1′-dichloroferrocene and are interpreted in terms of repulsions between lone pairs on chlorine and electrons located on the metal atom. The salts of $C_5Cl_5^-$ are all unstable at room temperature. The $C_5Cl_5^-$ anion is weakly basic, easily oxidized, and appears to decompose *via* the pentachlorocyclopentadienyl radical, $C_5Cl_5\cdot$. A simple preparation of 5-bromopentachlorocyclopentadiene is reported. All attempts to date to react $C_5Cl_5^-$ with transition metal salts to give perchlorometallocenes have failed.

Four members of the family of monocyclic conjugated chlorocarbons[2] $(CCl)_n{}^{m\pm}$ have been well characterized: $C_3Cl_3^+$, C_6Cl_6, $C_7Cl_7^+$, and C_8Cl_8. There is evidence for the existence of C_4Cl_4, $C_5Cl_5^+$, $C_5Cl_5\cdot$,[3] and $C_5Cl_5^-$. Our interest in the chemistry of the members of this family led us to study more thoroughly the chemistry of the pentachlorocyclopentadienide anion, $C_5Cl_5^-$. Neglecting the chlorine atoms, this anion has six π electrons, and so should be aromatic.

Lithium pentachlorocyclopentadienide was first mentioned in 1955 as the probable product of $LiAlH_4$ reduction of hexachlorocyclopentadiene (C_5Cl_6) at low temperature.[4] This reaction produced, after hydrolysis, 1,2,3,4,5-pentachlorocyclopentadiene, C_5Cl_5H. The chemistry of LiC_5Cl_5 has been further investigated by McBee, Halling, and Morton,[5] who found that LiC_5Cl_5 solutions can also be prepared from C_5Cl_6 and lithium metal at low temperature. The anion has been generated by electroreduction of C_5Cl_6 or octachlorocyclopentene,[6] and mentioned as a possible intermediate in the reaction of trialkyl phosphites with C_5Cl_6.[7]

Despite its frequent mention, no salts of the $C_5Cl_5^-$ anion have been isolated, nor has the ion been characterized spectroscopically. We wish to report the preparation and characterization of a series of solid salts: $Tl^+C_5Cl_5^-$ (**1**), $Tl^+C_5Cl_5^-\cdot 2C_6H_5CH_3$ (**2**); $R_4N^+C_5Cl_5^-$, where R = n-C_3H_7 (**3a**), n-C_4H_9 (**3b**), or n-C_7H_{15} (**3c**); $(C_2H_5)_3NH^+C_5Cl_5^-$ (**4**); $(n\text{-}C_4H_9)_4P^+C_5Cl_5^-$ (**5**); and $C_5H_5NCH_3^+C_5Cl_5^-$ (**6**).

Preparation. The thallium(I) salt (**1**) may be prepared by the reduction of C_5Cl_6 in ether at −25° with thallium amalgam. However, this reaction is slow and decomposition of **1** reduces the yield. The preferred method is addition of thallium(I) ethoxide $(TlOC_2H_5)_4$ to C_5Cl_5H in pentane at −78°. If this reaction is carried out in toluene solution, the adduct **2** crystallizes rather than **1**.

The salts **3a**, **3b**, and **3c** may be precipitated at −78° from methanol by (a) adding a solution of the quaternary ammonium hydroxide to C_5Cl_5H or (b) adding lithium methoxide to a solution of the quaternary ammonium halide and C_5Cl_5H. **5** and **6** are prepared analogously. **4** may be precipitated from ether by adding triethylamine to C_5Cl_5H at −78°.

All of the compounds may be stored indefinitely at −80°, but none are thermally stable above −15°. Their rates of decomposition vary. **1** ignites spontaneously at −15° in air or in a nitrogen atmosphere with emission of orange light but without violence, yielding a deep blue ash. **4** also decomposes rapidly, but without light emission. **2**, **5**, and **6** can be handled

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(1) Some of this work has appeared in preliminary form; G. Wulfsberg and R. West, *J. Amer. Chem. Soc.*, **93**, 4085 (1971).

(2) Review by R. West, *Accounts Chem. Res.*, **3**, 130 (1970).

(3) F. Graf and Hs. H. Gunthard, *Chem. Phys. Lett.*, **7**, 25 (1970).

(4) E. T. McBee and D. K. Smith, *J. Amer. Chem. Soc.*, **77**, 389 (1955).

(5) E. T. McBee, R. A. Halling, and C. J. Morton, unpublished studies. R. A. Halling, Ph.D. Thesis, Purdue University, 1965; *Diss. Abstr. B*, **27** (2), 409 (1966).

(6) L. G. Feoktistov and A. S. Solonar, *J. Gen. Chem. USSR*, **37**, 931 (1967).

(7) V. Mark, *Tetrahedron Lett.*, 295 (1961).