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Reactions of Cyclopropylcarbinyl Halides with (Trimethylstannyl)alkalis. Evidence That Kinetically Free Intermediates Need Not Be Involved in Cyclopropylcarbinyl to 3-Butenyl Rearrangements

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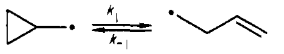
Studies on the reactions of cyclopropylcarbinyl bromide and iodide with trimethylstannyl anionoids have been made with emphasis on counterion, solvent, and addend (*tert*-butylamine and dicyclohexylphosphine) effects. Both halides yield cyclopropylcarbinyl- and 3-butenyltrimethylstannanes as major products. Depending upon reaction parameters much or all of the latter is shown to be formed by a mechanism or mechanisms which do not involve kinetically free radical or ionic intermediates. With cyclopropylcarbinyl bromide no electron transfer (ET) (free radical) component is observed in THF or in THF-containing 18-crown-6. However, in 20% THF-80% benzene a small extent of the ET mechanism is observed in the presence of DCPH. The iodide reacts in THF via S_N2 (or equivalent) and halogen-metal exchange (HME) mechanisms leading to the formation of both methylcyclopropane and 1-butene in the presence of the traps, indicating that the cyclopropylcarbinyl anion can undergo rearrangement to the 3-butenyl anion in competition with other processes. In the presence of 18-crown-6 and DCPH a small ET component is observed with the iodide.

In the area of reactive intermediates cyclopropylcarbinyl systems are generally considered to be among the most useful probes for the existence of carbocation and free-radical intermediates because of their rapid rearrangement into the 3-butenyl species (eq 1).[1] In general the equilibrium of eq 1 lies far to the right; e.g., for free radicals at 25 °C $k_1/k_{-1} = K = 3 \times 10^4$.[2] The value of k_1 is so large (10^8 s^{-1}) that the ring opening of the cyclopropylcarbinyl free radical to the 3-butenyl radical has been considered to be diagnostic in reactions such as peroxide decompositions and in chain reactions in which neutral molecules are the reactants.[2] It has also been applied recently by Wreford to establish an electron-transfer mechanism in reactions of alkali dialkylphosphines with cyclopropylcarbinyl bromide.[3] It was concluded that $KPMe_2$ reacts at least in part by an initial electron-transfer process leading to the cyclopropylcarbinyl free radical; emissive CIDNP signals were observed in the cyclopropylcarbinylphosphine product which constituted about half of the substitution product, the remainder being the rearranged 3-butenyldimethylphosphine.



(1)

In a later study involving the reaction of halides with anions Krusic and San Filippo observed appropriate ESR signals and rearranged product in the reaction of cyclopropylcarbinyl iodide with $CpFe(CO)_2Na$.[4] (Trimethylstannyl)alkalis also yielded rearranged products in reactions with cyclopropylcarbinyl bromide and iodide, leading to the suggestion by analogy that these species also reacted by electron-transfer and free-radical intermediates.[5-7] However, this has been challenged by Newcomb on the grounds that intramolecular trapping by cyclization of 5-hexenyl radicals should also be observable if free radicals were involved as significant intermediates. They observed none.[8a] Furthermore, observation of ESR signals was not reported for the (trimethylstannyl)alkali-halide reactions.[4]

Our own studies of the cyclopropylcarbinyl-(trimethylstannyl)alkali systems were under way when these reports appeared, but the results were so unusual that further careful examination appeared to be desirable. As suggested by Newcomb, and shown by Bergman[9] in reactions of $CpV(CO)_3H^-$, the cyclopropylcarbinyl system can show anomalous behavior. The results to be presented below support this view for the bromide and provide a reasonable interpretation of the reaction of the iodide with trimethylstannyl anionoids in THF.

Results and Discussion

The (trimethylstannyl)alkalis were prepared under argon usually by reaction of hexamethyldistannane with the metal at 0 °C. The preparations were centrifuged until the supernatant was crystal clear yellow-green before use. In order to insure maximum validity of the results replicate experiments were conducted by using separate preparations of the anionoids. An excess of the anionoid over that of the cyclopropylcarbinyl halide was used to insure complete consumption of the latter. Yields of products agreed to within ±2%, and mass balances of the C_4 moiety rarely fell below 90%. *tert*-Butylamine (TBA) was used to trap intermediate anions and dicyclohexylphosphine (DCPH) to trap free radicals. The latter also traps carbanions, but less efficiently than does TBA. Neither TBA nor DCPH reacted with (trimethylstannyl)sodium or the cyclopropylcarbinyl halides under the conditions of the experiments.

Cyclopropylcarbinyl Iodide. Results obtained with this halide are gathered in Table I. Entries 1, 4, and 7 represent control experiments with the three alkali metal counterions used. These show that the yields of the unrearranged product, (cyclopropylcarbinyl)trimethylstannane, depended upon counterion, increasing in the order K < Na < Li. The yields of the rearranged product, 3-butenyltrimethylstannane, increased in the opposite order. With Li^+ and Na^+ as counterions small, but sig-

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[4] Krusic, P. J.; Fagan, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250.

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[8] (a) Newcomb, M.; Courtney, A. R. *J. Org. Chem.* **1980**, *45*, 1707. (b) Newcomb, M.; Smith, M. G. *J. Organomet. Chem.* **1982**, *228*, 61.

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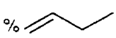
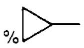
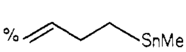
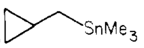
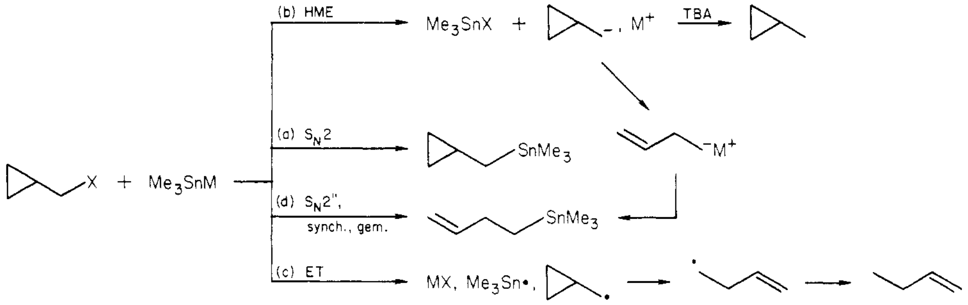
Table I. Effects of Counterion, TBA, and DCPH on Product Distribution from the Reaction of Me_3SnM with Cyclopropylcarbinyl Iodide in THF[a,b]

entry	M	addend (M)	%  [c]	% 	% 	% 
1	Li		1.8 (±0.1)	2.6 (±0.1)	33 (±0.5)	56 (±0.0)
2	Li	TBA (1.10)	2.6 (±0.1)	7.2 (±0.7)	31 (±2.0)	51 (±0.5)
3	Li	DCPH (1.0)	15 (±1.0)	4.9 (±0.2)	25 (±0.5)	55 (±1.0)
4	Na		10 (±0.5)	3.5 (±0.2)	59 (±0.5)	14 (±2.0)
5	Na	TBA (1.10)	2.6 (±0.2)	58 (±2.0)	23 (±0.5)	16 (±0.0)
6	Na	DCPH (1.10)	19 (±1.0)	24 (±0.5)	35 (±4.0)	18 (±2.0)
7	K				81 (±1.5)	7.2 (±0.3)
8	K	TBA (1.10)	+	29 (±1.0)	62 (±0.5)	7.2 (±0.6)
9	K	DCPH (1.10)	17 (±1.0)	10 (±0.0)	63 (±1.0)	10 (±1.5)

[a] Me_3SnM, prepared from $Me_3SnSnMe_3$ and the metal, added to cyclopropylcarbinyl iodide at 0 °C; yields based on the halide used. [b] Initial [] = 0.11 (±0.01) M; initial [Me_3SnM] = 0.22 (±0.02) M. [c] + indicates less than 0.5%.

Scheme I



nificant, amounts of both 1-butene and methylcyclopropane were also formed but were absent with K^+. No significant change in the yield of (cyclopropylcarbinyl)trimethylstannane was observed with any of the anionoids when TBA was used as an addend as seen by comparison of entries 1, 4, and 7 with 2, 5, and 8, respectively.

The effect of the presence of TBA on the yields of the other products was most pronounced with K^+ as the counterion. In the control experiment, entry 7, no hydrocarbon was observed. The presence of TBA, entry 8, caused a decrease from 81% to 62% in the yield of 3-butenyltrimethylstannane, while the hydrocarbon, exclusively methylcyclopropane, increased from essentially zero to 29%. These two changes in yields, 19% vs. 29%, do not compensate quantitatively. This is also true with Na^+ as the counterion and is apparently related to low C_4 mass balances (87–93%) in the control experiments. The fate of the missing C_4 was not established beyond verification that no C_8 hydrocarbon was observed. The effect of TBA on experiments with Me_3SnNa were similar to those with Me_3SnK, but Me_3Li showed much less hydrocarbon in the trapping experiments.

A complex pattern emerges when one compares the effects of DCPH as addend with those using TBA. With Me_3SnLi DCPH causes the total yield of hydrocarbon to increase from 10% to 20%, but 1-butene predominates; with Me_3SnNa it causes the total hydrocarbon yield to decrease but that of methylcyclopropane to predominate; with Me_3SnK the total hydrocarbon yield is not significantly changed and 1-butene predominates.

The general pattern of results can be discussed in terms of the mechanisms shown in Scheme I (X = I). Path (a), the S_N2 mechanism, occurs with each anionoid and its importance follows the probable extent of solvation of the counterion by THF: $Li^+ > Na^+ > K^+$.[10] Thus its distribution is counterion dependent but not affected by the presence of either TBA or DCPH. Path (b), the halogen–metal exchange mechanism (HME), was detected by the formation of hydrocarbons by trapping of intermediate carbanions with TBA.[11] The results indicate this to be the major source of rearranged substitution product with Me_3SnNa and a minor source with Me_3SnLi and Me_3SnK. It is important to note, however, that the major reduction product formed in each case is methylcyclopropane. This is a strong indication of the intermediacy of a carbanion. The cyclopropylcarbinyl free radical rearranges with a rate constant of about 10^8 s^{-1}.[2] The rate of rearrangement of the cyclopropylcarbinyl Grignard reagent is known to be many powers of ten smaller,[12] but that for (cyclopropylcarbinyl)alkalis is not known. The higher proportion of 1-butene in the hydrocarbon formed in the presence of DCPH is consistent with less efficient proton donation by this compound which is probably a weaker acid than TBA. Similar behavior was observed in our earlier study of 3-iodonortricyclene with Me_3SnNa. This hindered secondary cyclopropylcarbinyl iodide yielded nortricyclene in a preponderant excess over the rearranged 2-norbornene in the presence of TBA.[13] These observations suggest that the rearrangement of the (cyclopropylcarbinyl)alkalis in THF occurs rapidly enough to compete with proton abstraction from these weak acids. The higher total yield of hydrocarbon in the presence of DCPH as compared with TBA with Me_3SnLi, along with the 3-fold greater yield of 1-butene over methylcyclopropane (entry 3) may indicate a modest contribution from the ET mechanism. If this is real it suggests that both the S_N2 and ET mechanisms are facilitated by ion separation relative to the HME or other mechanisms which are occurring.

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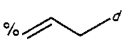
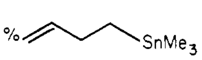
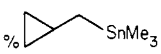
(13) Alnajjar, M. S.; Kuivila, H. G. *J. Org. Chem.* **1981**, *46*, 1053.

Table II. Effects of Counterion, TBA, and DCPH on Product Distributions from the Reaction of Me_3SnM with Cyclopropylcarbinyl Bromide[a, b]

entry	method[c]	M	addend (M)	%  [d]	% 	% 
			Solvent: THF			
1	A	Li		+	35 (±0.0)	64 (±1.5)
2	A	Li	TBA (1.10)	+	34 (±0.5)	66 (±1.5)
3	A	Li	DCPH (1.10)	7.2 (±0.15)	25 (±0.5)	67 (±1.5)
4	B	Li		2.0 (±0.2)	33 (±0.5)	58 (±0.5)
5	B	Li	TBA (1.0)	3.7 (±0.1)	37 (±1.5)	54 (±2.0)
6	B	Li	DCPH (1.10)	9.0 (±1.5)	19 (±0.0)	62 (±2.0)
7	A	Na		+	76 (±2.0)	19 (±0.5)
8	A	Na	TBA (1.25)	+	74 (±3.0)	20 (±1.0)
9	A	Na	DCPH (1.25)	13 (±1.0)	61 (±2.0)	24 (±0.5)
10	A	K		+	75 (±0.5)	23 (±0.0)
11	A	K	TBA (1.25)	+	76 (±2.0)	22 (±1.0)
12	A	K	DCPH (1.20)	4.4 (±0.2)	46 (±1.0)	45 (±1.5)
13	A	K	$(n\text{-Bu})_3P$ (1.15)	+	49 (±0.5)	47 (±0.5)
			Solvent: 20% THF–80% Benzene (v/v)			
14	A	Li		3.8 (±0.1)	64 (±0.5)	21 (±1.0)
15	A	Li	TBA (1.15)	6.5 (±0.5)	68 (±1.5)	20 (±0.5)
16	A	Li	DCPH (1.20)	41 (±2.0)	19 (±0.5)	32 (±0.5)
17	B	Li		4.0 (±0.1)	59 (±1.5)	17 (±1.0)
18	B	Li	TBA (1.15)	5.0 (±0.5)	66 (±2.0)	16 (±1.0)
19	B	Li	DCPH (1.15)	42 (±1.0)	18 (±0.5)	35 (±0.0)
20	A	Na		+	86 (±0.0)	3.0 (±1.0)
21	A	Na	TBA (1.10)	+	84 (±0.5)	5.0 (±0.15)
22	A	Na	DCPH (1.10)	19 (±0.0)	60 (±3.0)	5.0 (±0.5)
23	A	K		2.5 (±0.5)	76 (±1.0)	8.3 (±1.0)
24	A	K	TBA (1.0)	4.5 (±0.5)	78 (±1.0)	7.0 (0.5)
25	A	K	DCPH (1.0)	16 (±0.0)	64 (±0.5)	8.0 (0.0)

[a] Me_3SnM added to cyclopropylcarbinyl bromide at 0 °C; yields based on the halide used.

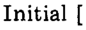
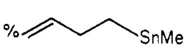
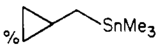
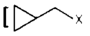
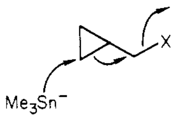
[b] Initial [] = 0.12 (±0.02) M; initial [Me_3SnM] = 0.24 (±0.04) M. [c] Method of preparation of Me_3SnM: A, from $Me_3SnSnMe_3$ and the metal; B, from $Me_3SnSnMe_3$ and methyllithium. [d] + indicates less than 0.5%.

Table III. Effects of 18-Crown-6 on Product Distribution from the Reaction of Me_3SnNa with Cyclopropylcarbinyl Halide in THF[a, b]

entry	halide	addend (M)	$\%C_4$[c]	% 	% 
1	Br	18-C-6 (0.80)	+	6.0 (±0.4)	92 (±1.5)
2	Br	18-C-6 (0.63), TBA (1.60)	+	2.0 (±0.1)	88 (±1.5)
3	Br	18-C-6 (0.60), DCPH (1.30)	+	3.0 (±0.2)	94 (±2.0)
4	I	18-C-6 (0.80)	+	30 (±1.0)	62 (±1.0)
5	I	18-C-6 (0.54), TBA (1.40)	2.0 (±0.2)[d]	21 (±1.0)	74 (±1.5)
6	I	18-C-6 (0.54), DCPH (1.0)	17 (±0.5)[d]	17 (±1.0)	64 (±1.0)

[a] Me_3SnNa, prepared from $Me_3SnSnMe_3$ and the metal, added to cyclopropylcarbinyl halides at 0 °C; yields based on the halide used. [b] Initial [] = 0.18 (±0.02) M; initial [Me_3SnNa] = 0.36 (±0.04) M. [c] + detected but less than 0.5%. [d] Total C_4 hydrocarbon, amounts of 1-butene and methylcyclopropane not determined.

The fact that substantial amounts of 3-butenyltrimethylstannane were formed in all experiments indicates that yet another mechanism must be involved or that the trapping of anions was quite inefficient.[15] The latter is unlikely because the cyclopropylcarbinyl anions are trapped before they can rearrange to the 3-butenyl anions (as best seen in entries 5 and 8), yet rearranged substitution product was formed. This leaves path d which is a substitution with synchronous rearrangement or a geminate process with rearrangement. This process shows a dependence upon counterion different from that of the S_N2 mechanism. This can be seen by comparing the results obtained in the presence of TBA. With Me_3SnLi the ratio of unrearranged to rearranged substitution product was 51/31; with Me_3SnNa it was 16/23; with Me_3SnK it was 7.2/62. Two reasonable possiblities for the synchronous substitution–rearrangement mechanisms are the S_N2'' and one involving a cyclic transition state, 1 and 2, respectively.



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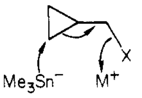

2

The latter seems to be particularly attractive here because

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(14) Newcomb in ref 8b reports that (tri-n-butylstannyl)lithium in THF at −20 °C is slowly consumed by reaction with dicyclohexylphosphine and that products of this reaction could lead to anamolous results. However, we have found no indication of reaction with (trimethylstannyl)sodium even at 0 °C over 24 h, a longer interval than any of our preparations were permitted to stand before use.

(15) In another ongoing study we have found that in 20% THF–80% benzene 6-bromo-1-hexene yields (cyclopentylmethyl)trimethylstannane as one product indicating the intermediacy of 5-hexenyl radicals. In the presence of DCPH 1-hexene was also formed. We earlier reported that 1-iodooctane yields significant amounts of octane in the presence of TBA.[11] Thus both primary radicals and anions can be trapped by these reagents in competition with other processes, coupling with trimethylstannyl species, in particular.

it occurs to the greatest extent relative to S_N2 with Me_3SnK which would exist to the greatest extent as contact ion pairs in THF. It is reasonable to conclude from these results that no substantial fraction of the rearranged substitution product is formed by way of kinetically free radicals, but that carbanions can be involved.

Cyclopropylcarbinyl Bromide. Experiments to parallel those with the iodide were conducted with the bromide. Results are presented in Table II. Entries 1–3 show the results obtained with Me_3SnLi prepared from hexamethyldistannane and lithium metal; entries 4–6 show results of additional experiments using the anionoid prepared by the reaction of methyllithium with hexamethyldistannane. Results obtained by using these two methods of preparation of the anionoid are only in fair agreement, but the same general pattern is evident in the two sets of data. The major product (58–64%) was (cyclopropylcarbinyl)trimethylstannane. No hydrocarbon was formed in the control experiments, or in the presence of TBA. In the presence of DCPH the only hydrocarbon found was 1-butene with a maximum yield of 9%. This sets a probable limit on the extent of reaction by a free radical mechanism. We conclude that path d of Scheme I is the major source of the rearranged substitution product. With Me_3SnNa (entries 7–9) and Me_3SnK (entries 10–12) the distribution of the two substitution products is approximately reversed from that observed with Me_3SnLi, 3-butenyltrimethylstannane amounting to more than three quarters of the product and (cyclopropylcarbinyltrimethyl)stannane the remainder. The presence of DCPH led to the formation of about 4% of 1-butene when Me_3SnK was the anionoid and 13% when it was Me^3SnNa. Thus, although there is a counterion effect on the distribution of rearranged and unrearranged substitution products the major pathways appear to be a and d, but the effect of counterion on the yield of (cyclopropylcarbinyl)stannane remains K < Na < Li.

One unexpected observation in the reactions with Me_3SnK appears in entry 12 which shows an increase in the yield of (cyclopropylcarbinyl)trimethylstannane in the presence of DCPH, along with the formation of some 1-butene. A similar increase in the yield of (cyclopropylcarbinyl)trimethylstannane was observed when tri-*n*-butylphosphine was used at the same concentration (entry 13), indicating that the hydrogen of the DCPH is not the cause of the effect. Thus the perturbation caused by the phosphines is toward a greater contribution from the S_N2 process.

It was of interest to establish what effect, if any, would result from a decrease in the coordinating capacity and polarity of the solvent from that of THF. This was determined by using a 20% THF–80% benzene mixed solvent. Results are displayed in the lower portion of Table II (entries 14–25). In the control experiment with Me_3SnLi (entry 14) one sees that the predominant product became 3-butenyltrimethylstannane, comprising about 75% of the substitution product in contrast with 37% found in THF. Furthermore 1-butene was formed in the control as well as in the experiments in the presence of TBA and DCPH (entries 15 and 16) amounting to 41% in the latter case. Here again one observes, as seen in entry 16, an increase in the yield of (cyclopropylcarbinyl)trimethylstannane, the 1-butene being formed entirely at the expense of the rearranged substitution product. The results using Me_3SnLi prepared by the alternative method B are in good agreement (entries 17–19) with these results.

When Me_3SnNa (entries 20–22) and Me_3SnK (entries 23–25) were used in the same solvent system the major substitution product was 3-butenyltrimethylstannane in each case, and the yields were very similar to those observed in THF as solvent. In the presence of DCPH no change in the yield of (cyclopropylcarbinyl)trimethylstannane was observed, but a decrease was seen in the yield of 3-butenyltrimethylstannane along with a concomitant increase in the yield of 1-butene. All of these observations lead to the suggestion that, although simple unhindered primary bromides react predominantly by the S_N2 mechanism in THF, a sufficient decrease in the ability of the solvent to coordinate cations can lead to the intrusion of the ET mechanism in the presence of DCPH.[15] The DCPH is considered to be a reliable trap for intermediate free radicals due to its ability to donate hydrogen atoms, but it may also act to alter the mechanistic competition. This effect is both counterion and solvent dependent, being observed with Me_3SnK in THF and with Me_3SnLi in 20% THF–80% benzene, but not unambiguously under the other conditions.

If shifting the dissociation equilibria of Me_3SnM toward greater aggregation introduces the possibility of observing the ET mechanism, what happens if the shift is toward greater ion pair separations? This was examined by using the reaction of Me_3SnNa with cyclopropylcarbinyl bromide and iodide in THF with 18-crown-6 as the coordinating species for the cation. Results are presented in Table III. With the bromide the overwhelming reaction course is presumably S_N2 as indicated by the formation of over 90% (cyclopropylcarbinyl)trimethylstannane. The presence of TBA or DCPH had no significant effect in producing hydrocarbon products. However, with the iodide about two-thirds of the reaction led to unrearranged substitution product and one-third to rearranged substitution product. About 2% of hydrocarbon was obtained in the presence of TBA and 17% in the presence of DCPH (compositions not determined). Comparison of these results with those obtained in 20% THF–80% benzene shows a complete reversal in the proportions of rearranged and unrearranged substitution products. In each case the hydrocarbon formed in the presence of DCPH appears at the expense of rearranged substitution product, consistent with some ET contributions in the control reactions.

Previous work[4,5] and our own unreported observations show that cyclopropylcarbinyl chloride reacts with trimethylstannyl anionoids in THF without rearrangement. The results presented here show that the bromide and the iodide react with rearrangement to a major degree by a mechanism or mechanisms involving no intermediates which can be trapped. With the iodide the HME mechanism competes effectively in THF in the presence of TBA. The ET mechanism can intrude with the bromide when the solvent is 20% THF–80% benzene and with the iodide in THF with 18-crown-6 and DCPH present. Counterion effects are quite evident in affecting the nature of the competition among mechanisms, but a complete interpretation must await the results of appropriately designed studies.

Our results are in agreement with previous reports[5,16] that trimethylstannyl anionoids react with cyclopropylcarbinyl bromide and iodide, to an extent depending on reaction parameters, to form rearranged substitution product. The agreement is not quantitative, but we believe that this is attributable to differences in reaction conditions because our own results, obtained under carefully duplicated conditions, showed very good reproducibility and satisfactory mass balances for the C_4 moieties. The im-

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[16] Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893.

portant difference is that we conclude, in agreement with Newcomb,[8b] that the major fraction of the rearranged substitution product need not be formed by way of free reactive intermediates. However, free radicals appear to be involved to a small degree with each halide, and anions are clearly involved with the iodide, the extent depending upon the reaction parameters.

Summary

Cyclopropylcarbinyl bromide and iodide react with trimethylstannyl anionoids to form rearranged and unrearranged substitution products in proportions depending on the solvent, counterion, and the presence, in some cases, of DCPH. The rearranged product is formed predominantly by a mechanism or mechanisms involving no intermediate that can be trapped by TBA or DCPH. Cyclopropylcarbinyl bromide reactions show little ET mechanism in THF in contrast to an earlier assumption.[4,5] But a modest contribution may be seen in 20% THF–80% benzene in the presence of DCPH. In the presence of 18-crown-6 ether no ET is observed. Cyclopropylcarbinyl iodide reacts mainly via S_N2, HME, and the mechanism(s) involving no trappable intermediates in THF. A substantial amount of HME may occur in the presence of TBA, and a small amount of ET is observed in the presence of DCPH when 18-crown-6 is present.

The cyclopropylcarbinyl anion formed in the HME mechanism may undergo rearrangement to the 3-butenyl anion before reacting further to form substitution product despite the "slowness" of the rearrangement. The results presented are consistent with the conclusion that formation of rearranged products in reactions of cyclopropylcarbinyl halides should not be taken as prima facie evidence for kinetically free-radical intermediates.

Experimental Section

General Procedures. Proton nuclear magnetic resonance spectra were obtained at 60 MHz by using a Varian EM360A instrument. Chemical shifts are reported in ppm downfield from internal tetramethylsilane followed in parentheses by multiplicity, coupling constants, number of protons, and assignment. ^{1}H–^{119}Sn coupling constants are reported as ${}^xJ$(Sn–H) with the superscript denoting the number of bonds intervening between the nuclei. Analytical gas chromatographic analyses were performed with a Hewlett Packard 5750 instrument with a thermal conductivity detector using a 16 ft × 0.25 in. stainless steel column packed with 15% SE-30 on chromosorb W AW-DMCS. Peak areas in the chromatogram were determined by digital integration with a Coloumbia Scientific Industries Supergrator-1, equipped with an angular base line correction. Yields were determined by the internal standard method.

All reactions with (trimethylstannyl)alkalis were conducted under argon. Tetrahydrofuran (THF) was dried by distillation from molten potassium. Benzene (Krackeler), dicyclohexylphosphine, tri-*n*-butylphosphine (Aldrich), and cyclopropylcarbinyl bromide (Alfa) were checked for purity and redistilled if necessary before use. *tert*-Butylamine (Aldrich) was distilled from calcium hydride under argon and stored over 3-Å molecular sieves. Cyclopropylcarbinyl iodide was prepared from the cyclopropylcarbinyl bromide and sodium iodide in acetone.[8a] Chlorotrimethylstannane and hexamethyldistannane were prepared as previously described.[11]

Preparation of (Trimethylstannyl)sodium and -potassium from Hexamethyldistannane and the Metal. A. Solvent: THF. In a typical reaction 3.33 g (10.0 mmol) of hexamethyldistannane was added to 25 mL of dry THF in a 3-neck flame-dried flask under argon. Finely cut metal (27.0 mmol) was added and the mixture stirred rapidly at 0 °C for 6–8 h. The black precipitate which formed was allowed to settle; the supernatant was removed and centrifuged to provide a clear light yellow-green solution. The concentration of stannylalkali was determined by the reaction of an aliquot with excess 1-bromobutane. The yield of butyltrimethylstannane obtained by GLPC using a 15% SE-30 on chromosorb W column (16 ft × 0.25 in.) was used to compute the concentration of stannylalkali.

B. Solvent: 20% THF/80% C_6H_6. To a 3-neck flame-dried flask containing 10 mL of dry THF was added 5.18 g (15.8 mmol) of hexamethyldistannane under argon. Finely cut metal (40 mmol) rinsed with petroleum ether was added and the mixture stirred vigorously at 0 °C for 6–8 h. The resulting solution was diluted with 40 mL of reagent grade benzene. The black precipitate which appeared was removed by centrifugation. The stannylalkali solution was stored at −10 °C before use (within 24 h) and its concentration was determined as described above.

Preparation of (Trimethylstannyl)lithium from Hexamethyldistannane and the Metal in either THF or 20% THF/80% C_6H_6. (Trimethylstannyl)lithium was prepared as above except that lithium ribbon was rinsed with methanol to remove the black coating and then rinsed several times with petroleum ether before use.

Preparation of (Trimethylstannyl)lithium from Hexamethyldistannane and Methyllithium. A flame-dried Schlenk tube equipped with a side arm was charged with 6.60 mmol of methyllithium/diethyl ether under argon. The tube was evacuated and maintained at 0.2 torr for 45 min at 0 °C to remove solvent. Hexamethyldistannane (2.25 g, 6.87 mmol) in 12 mL of dry THF (or 20% THF–80% C_6H_6, v/v) was added dropwise to the methyllithium with agitation to give (trimethylstannyl)lithium in quantitative yield as determined by the method described above.

Reactions of (Trimethylstannyl)alkalis with Cyclopropylcarbinyl Halides. In a typical reaction appropriate amounts of halide and TBA, DCPH, or $(n\text{-Bu})_3P$ were added to dry THF to form solutions of the desired concentrations. After cooling at 0 °C for 15 min under argon a solution of (trimethylstannyl)alkali was added in 100% excess by syringe. Reactions with both bromide and iodide were complete upon mixing. Yields of hydrocarbons and isomeric organostannanes were determined by GLC. It was observed that the same results were obtained whether the reaction mixture was analyzed directly or if it was quenched with H_2O, extracted with pentane, and then analyzed.

1-Butene, methylcyclopropane, 1-butenyltrimethylstannane, and (cyclopropylcarbinyl)trimethylstannane were isolated from the reactions of cyclopropylcarbinyl halides with (trimethylstannyl)sodium at 0 °C. 1-Butene: ^{1}H NMR ($CDCl_3$, −23 °C) δ 5.86 (m, 1 H, $H_2C{=}CH{-}CH_2$), 4.86 (m, 2 H, $H_2C{=}C{-}CH_2$), 2.20 (m, 2 H, $H_2C{=}CH{-}CH_2{-}CH_3$), 1.10 (t, 3 H, $H_2C{=}CH{-}CH_2{-}CH_3$). Methylcyclopropane: ^{1}H NMR ($CDCl_3$, −23 °C) δ 0.30–0.45 (m, C_3H_5), 0.90 (m, 3 H, $C_3H_5{-}CH_3$). 1-Butenyltrimethylstannane: ^{1}H NMR (CCl_4) δ 0.05 (m, 9 H $(CH_3)_3Sn$, ${}^2J$ ^{119}Sn–^{1}H = 53.0 Hz), 0.86 (t, 2 H, CH_2–Sn), 2.19 (s, 2 H, $H_2C{=}C{-}CH_2$), 4.19 (m, 2 H, $H_2C{=}C{-}CH_2$), 5.75 (m, 1 H, $H_2C{=}CH{-}CH_2$). (Cyclopropylcarbinyl)trimethylstannane: ^{1}H NMR (CCl_4) δ 0.07 (s, 9 H, $(CH_3)_3Sn$, ${}^2J$ ^{119}Sn–^{1}H = 53.0 Hz), 0.30–1.15 (br m, 7 H, C_4H_7).

Control Experiments. (A) Reaction of TBA, DCPH, and $(n\text{-Bu})_3P$ with Cyclopropylcarbinyl Halides. In a typical experiment 2.5 mmol of an addend under argon was added to 0.30 mmol of the halide in 1 mL of dry THF at 0 °C after cooling for 30 min. 1.0 mL of 0.60 M (0.60 mmol) (trimethylstannyl)sodium was added, and the yields of organostannanes and C_4 hydrocarbons were determined after standing at least 30 min. It was found that these yields were the same within ±3% of those obtained in the absence of the addend.

(B) Reaction of Me_3SnNa with TBA. To 1 mL of a 0.61 M solution of (trimethylstannyl)sodium in THF under argon was added 4.53 mmol of TBA at 0 °C. After 24 h at 0 °C *n*-butyl bromide (1.32 mmol) was added via syringe and the reaction mixture analyzed by GLC yielding 4.44 mmol (98%) of *n*-butyltrimethylstannane based on initial Me_3SnNa.

(C) Reaction of Me_3SnNa with DCPH. To 2.0 mmol of DCPH under argon was added 1 mL of a 0.50 M solution of (trimethylstannyl)sodium in THF at 0 °C. The reaction mixture was stored at 0 °C for 24 h followed by the addition of *n*-butyl bromide (1.30 mmol). The resulting *n*-butyltrimethylstannane was determined quantitatively by GLC; the calculated concentration of Me_3SnNa was 0.49 M indicating no significant reaction with DCPH. An occasional commercial sample of DCPH contained 6–8% of an acidic oxidation product which reacted rapidly with Me_3SnNa. These samples could be purified by simple vacuum distillation under argon.

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Registry No. TBA, 75-64-9; DCPH, 829-84-5; 18-crown-6, 17455-13-9; Me_3SnLi, 17946-71-3; Me_3SnNa, 16643-09-7; Me_3SnK, 72763-68-9; $(n\text{-}Bu)_3P$, 998-40-3; MeLi, 917-54-4; Na, 7440-23-5; K, 7440-09-7; $Me_3SnSnMe_3$, 661-69-8; $LSnMe_3$ (L = 3-butenyl), 17314-38-4; $LSnMe_3$ (L = cyclopropylmethyl), 51675-53-7; 1-butene, 106-98-9; methylcyclopropane, 594-11-6; cyclopropylcarbinyl bromide, 7051-34-5; cyclopropylcarbinyl iodide, 33574-02-6.

Interconversion between the Cation Radicals of Toluene and Cycloheptatriene: An Evaluation of the Difference between the Gas Phase and Solution

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The cation radicals of toluene and 1,3,5-cycloheptatriene may be prepared in solution by various means, and the literature in this area offers no evidence for the rearrangement that interconverts these materials in the gas phase. Thermodynamic calculation including estimates for solvation terms suggests a p*K*a of −12 for these cation radicals. This suggests rapid proton loss, which is consistent with existing measurements. Published theoretical calculations suggest an energy of activation of about 30 kcal mol^{-1} for rearrangement in the gas phase, and this is consistent with lifetime measurements long known in the photodissociation experiments. The information above leads to the conclusion that proton loss from the cation radicals in solution is preemptive of the arrangement. This is contrasted with the McLafferty rearrangement of ketones, which occurs both in the gas and in solution. In this case, proton loss is not a route to stabilization in the cation radicals for unrearranged aliphatic ketones.

In the gas phase, rearrangement attended by scrambling is long known to occur for the dissociating cation radicals of toluene and cycloheptatriene.[1]

In 1959, D. H. Geske electrochemically oxidized 1,3,5-cycloheptatriene in acetonitrile and spectrometrically demonstrated the sole production of tropylium cation.[2] In 1969, W. S. Trahanovsky and co-workers oxidized C-7 monodeuterio-1,3,5-cycloheptatriene with ceric ammonium nitrate in aqueous acetic acid and demonstrated that the deuterium had not scrambled among the six vinyl hydrogens of the cycloheptatriene prior to being lost.[3] These results, which are also consistent with the absence of any product evidence for rearrangement in the literature on oxidation of alkyl aromatics in solution,[4,5] stand in contrast to the gas-phase work.[1] This difference in chemical behavior in the gas phase and in solution is the subject of our current interest.

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(1) (a) The earliest work is reviewed in: H. M. Grubb and S. Meyerson, "Mass Spectroscopy of Organic Ions", F. W. McLafferty, Ed., Academic Press, New York, 1963, p 453 ff. Leading references to the extensive literature: (b) F. W. McLafferty and F. M. Bockhoff, *J. Am. Chem. Soc.*, **101**, 1783 (1979); (c) B. Jane Stapleton, R. D. Bowen, and D. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1219 (1979); (d) P. Ausloos, *J. Am. Chem. Soc.*, **104**, 5259 (1982); (e) R. C. Dunbar in "Gas Phase Ion Chemistry", M. T. Bowers, Ed., Academic Press, New York, 1979, p 181 ff and, in particular, p 198 ff. (f) The photochemical interconversion of these cation radicals in a frozen argon matrix has been claimed; see B. J. Kesall and L. Andrews, *J. Am. Chem. Soc.*, **105**, 1413 (1983).

(2) D. H. Geske, *J. Am. Chem. Soc.*, **81**, 4145 (1959).

(3) W. S. Trahanovsky, L. B. Young, and M. D. Robbins, *J. Am. Chem. Soc.*, **91**, 7084 (1969). This work shows, as required by the intermediacy of tropylium radical and/or cation, scrambling prior to the second proton (deuteron) loss. Assigning an unlikely isotope effect of unity for each loss yields a *minimum* value of $^3/_1$ d_1/d_0 benzaldehyde for scrambling prior to the first proton (deuteron loss). The experimental result was 1.5/1. We have repeated this experiment in dry HOAc with Co^{III} and obtained benzaldehyde as the major product with d_1/d_0 of 1.1 ± 0.05/1.

(4) There is strong evidence that both oxidizing systems[2,3] proceed via the intermediacy of the cation radical. See L. Eberson, *J. Am. Chem. Soc.*, **105**, 3192 (1983). There is a large literature in metal ion oxidation of toluene, cycloheptatriene, and structurally related materials. Although one-electron oxidations have sometimes been proposed, the evidence outside of Ce^{IV} is controversial. See also: L. Eberson, *Adv. Phys. Org. Chem.*, **18**, 79 (1982).

(5) Consistent with the conclusion on the absence of rearrangement (ref 2 and 3), the solution-phase literature cited below offers no chemical evidence of rearrangement nor, notably, any reference to the gas-phase work where the same cation radicals had exhibited the scrambling rearrangement. For a general review on cation radicals in solution, see, A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, **13**, 155 (1976). See also: W. S. Trahanovsky and L. B. Young, *J. Chem. Soc.*, **1965**, 5777; *J. Org. Chem.*, **31**, 2033 (1966); L. Syper, *Tetrahedron Lett.* 4493 (1966); K. Sakota, Y. Kamiya, and N. Ohta, *Can. J. Chem.*, **47**, 387 (1969); E. I. Heiba, R. M. Dessa, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 6830 (1969); P. Müller, E. Katten, and J. Rocek, *J. Am. Chem. Soc.*, **93**, 7114 (1971); R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J. Chem. Soc., Perkin Trans 1*, 325 (1973); J. K. Kochi, R. T. Tang, and T. Bernath, *J. Am. Chem. Soc.*, **95**, 7114 (1973); R. Tang and J. K. Kochi, *Inorg. Nucl. Chem.*, **35**, 3845 (1973); R. O. C. Norman, C. B. Thomas, and P. J. Ward, *J. Chem. Soc., Perkin Trans. 1*, 2914 (1973); P. Müller and J. Rocek, *J. Am. Chem. Soc.*, **96**, 2836 (1974); M. E. Kurz and G. W. Hage, *J. Org. Chem.*, **42**, 4080 (1977); E. Baciocchi, L. Mandolini, and C. Rol, *Tetrahedron Lett.* 3343 (1976); L. Eberson and L. Jönsson, *Liebigs Ann. Chem.*, 233 (1977); E. Baciocchi, C. Rol, and L. Mandolini, *J. Org. Chem.*, **42** 3682 (1977); A. Bewick, G. J. Edwards, J. M. Mellor, and S. Pons, *J. Chem. Soc., Perkin Trans. 2*, 1952 (1977); P. Müller and T. T. Khoi, *Tetrahedron Lett.* 1939 (1977); K. Nyberg and L.-G. Wistrand, *J. Org. Chem.*, **43**, 2613 (1978); E. Baciocchi, L. Eberson, and C. Rol, *Ibid.*, **47**, 5106 (1982).

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