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A SIMPLE METHOD FOR PREPARING SOME CYCLOPROPYLCARBINYL COMPOUNDS

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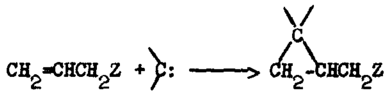
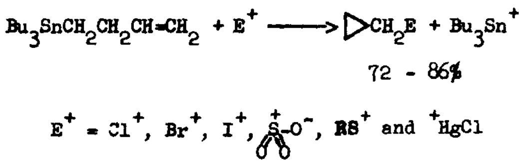
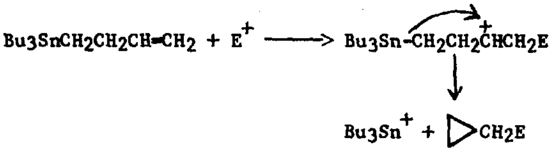
During the relatively recent past several cyclopropylcarbinyl derivatives have been prepared by a variety of procedures. The common basis for the most widely used of these methods formally involves additions of divalent carbon fragments from precursors such as RHgCBr, $\mathrm{IZnCH_2I}$, $\mathrm{\overset{+}{S}CH_2^-}$, and $\mathrm{RCHN_2}$ to allyl compounds. Although these methods have considerable utility, none of them, for one reason or another, can be regarded as the ultimate synthetic tool.[1] Consequently, we now describe a method which fills some of the need that currently exists for improved and more versatile cyclopropylcarbinyl compound syntheses.



Our unique method very simply involves additions of electrophilic reagents (Cl_2, Br_2, I_2, SO_3, RSCl and $HgCl_2$) to 3-butenyltributyltin to give directly in moderate to high yields the corresponding cyclopropylcarbinyl compounds.



Three modes of electrophilic attack on the organotin compound are possible: (1) cleavage of a butyl-tin bond;[2] (2) cleavage of the butenyl-tin bond; or (3) addition to the carbon-carbon double bond. With the exception of the reactions of 3-butenyltributyltin with iodine and mercuric chloride, the electrophiles almost exclusively added to the terminal carbon of the double bond to initiate cyclopropane formation (see Table I). Presumably, the potential competing cleavage reactions are rendered relatively non-competitive to the addition reaction owing to the ability of the carbon-tin sigma bond to stabilize a gamma carbonium ion.[3,4]



The starting compound, 3-butenyltributyltin,[5] was readily obtained from reactions of tributyltin halides with 3-butenylmagnesium halides. Since the tributyltin moiety resulting from all of the electrophilic cyclo-destannylation reactions of 3-butenyltributyltin was ultimately recovered as tributyltin halide, the overall reactions formally represent conversions of 3-butenyl halides to cyclopropylcarbinyl derivatives.

Interestingly, triphenylcarbonium ion (from triphenylmethyl bromide) did not add to the double bond of the butenyl group of the organotin compound, but apparently abstracted a hydride from the beta carbon atom as evidenced by the rapid formation of triphenylmethane and tributyltin bromide. This finding is not difficult to rationalize since the carbonium ion which results from hydride loss is stabilized both by the double bond and the beta tin-carbon sigma bond.[6]

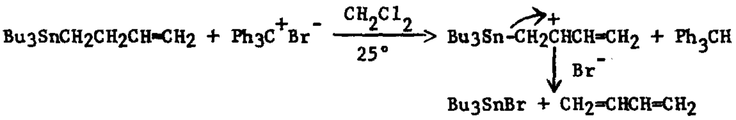


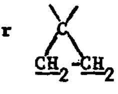
TABLE I

REACTIONS OF ELECTROPHILES WITH $Bu_3SnCH_2CH_2CH{=}CH_2$

Electrophile[a]	Solvent	Temperature	$\triangleright CH_2E$(%)	BuE(%)	C_4H_7E(%)
Cl_2	CH_2Cl_2	-65°	72[b]	trace	0
Br_2	CH_2Cl_2	-65°	86[b]	0	0
I_2	CH_2Cl_2	0°	82[b]	10	trace
SO_3	CH_2Cl_2	-65°	84[c]	trace	0
$HgCl_2$	CH_3CN	35°	73[d]	6	6
2,4-$(NO_2)C_6H_3SCl$	CH_3CO_2H	100°	80[e]	0	0

a. The halogens, sulfur trioxide, and the sulfenyl chloride were added at rapid drop rates to 3-butenyltributyltin which resulted in instantaneous reactions. Mercuric chloride and 3-butenyltributyltin were allowed to react one hour.

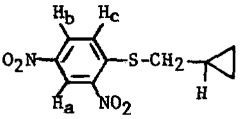
b. To realize complete recovery of the cyclopropylcarbinyl halides from the corresponding tributyltin halides subsequent to removal of the solvent, it was necessary to carry out the distillations under reduced pressure (~ 20 mm). The cyclopropylcarbinyl halides were characterized by comparisons of their bp's, ir and ^{1}H nmr spectra with those of authentic compounds.

c. Tributylstannyl cyclopropylcarbinylsulfonate was not isolated directly, but was treated with water and subsequently esterified with diazomethane to give methyl cyclopropylcarbinylsulfonate, bp 68-72° ~ 0.2 mm. The ^{1}H nmr spectrum of the sulfonate exhibited the very characteristic complex high field splitting pattern for 

between 0.3 - 0.8 ppm and the methine proton centered at 1.3 ppm, a doublet (J = 6.5 Hz) for the carbinyl protons at 3.0 ppm, and a singlet for the methyl protons at 3.9 ppm.

d. Cyclopropylcarbinylmercuric chloride, accompanied by small amounts of the other two cleavage products,[7] was separated from excess mercuric chloride in the reaction concentrate by extraction into chloroform. A ^{1}H nmr spectrum of the mixture in $CDCl_3$ confirmed the presence of the three mercury compounds; peaks centered at 2.1 ppm (carbinyl protons, d, J = 6.5 Hz), 6.0 - 5.0 ppm (vinyl protons, m), and 1.8 ppm ($-CH_2HgCl$, m). Attempts to resolve the mixture by crystallization and chromatographic techniques failed. Raman, ^{13}C nmr, and ir spectral analyses also were in accord with the structure assignments.

e.

The , mp 80 - 81°, was positively identified by ^{1}H nmr spectral analysis in $CDCl_3$ with peaks centered at 9.1 ppm (d, J_{ab} = 2 Hz), 8.3 ppm (H_b, two d's), 7.5 ppm (d, J_{bc} = 8 Hz), 3.1 ppm (carbinyl H's, d, J = 7 Hz) and 1.5 - 0.3 ppm for the cyclopropyl protons. An elemental analysis was in agreement with the structure assignment.

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2. W. P. Neuman in D. Seyferth (Ed.), "The Organic Chemistry of Tin", Interscience Publishers, New York, N.Y., 1970, pp. 36-38.
3. H. G. Kuivila and N. M. Scarpa, *J. Am. Chem. Soc.*, **92**, 6990 (1970).
4. D. D. Davis, R. L. Chambers, and H. T. Johnson, *J. Organometal. Chem.*, **25**, C13 (1970).
5. D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **84**, 361 (1962).
6. J. M. Jerkunica and T. G. Traylor, *ibid.*, **93**, 6278 (1971) have demonstrated that hydride losses from carbon atoms beta to a trimethyltin group occur rapidly and quantitatively.
7. At this time it is not known whether the 3-butenylmercuric chloride results directly from a mercuro-destannylation reaction or indirectly from a ring opening-isomerization of cyclopropylcarbinyl mercuric chloride. See, for example, D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, Inc., 1965, pp. 215-222.