

POLAR MECHANISMS IN GERMANIUM AND TIN HYDRIDE REDUCTIONS

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Owing to our recent interest in reactions involving transfer of hydride to carbonium ions from organosilicon hydrides (1,2) we were curious as to the relative effectiveness of germanium and tin hydrides in similar reactions. The possibility of observing polar mechanisms in tin hydride reactions appeared particularly significant since the free radical chain process has been established with certainty for many tin hydride reductions of alkyl halides (3). In the absence of evidence to the contrary, one becomes tempted to describe all tin hydride reductions of alkyl halides as following a homolytic pathway (4,5).

We now report that tin (and germanium) hydrides are very reactive toward hydride, as well as hydrogen atom, transfer and suggest that care be exercised in assuming that uncatalyzed reduction of reactive halides always occurs by a free radical process.

As in our previous work, carbonium ions were generated from alcohols in methylene chloride-trifluoroacetic acid at 25° with the appropriate hydride donor present, the solutions neutralized after 0.5 hr and analyzed by gas chromatography. Table I summarizes the product distribution observed for hydride transfer to the 4-t-butyl-1-phenylcyclohexyl cation (eq 1) and Table II pertains to hydride transfer to the diphenylcyclopropylmethyl cation (eq 2).

eq 1 R = Ph-

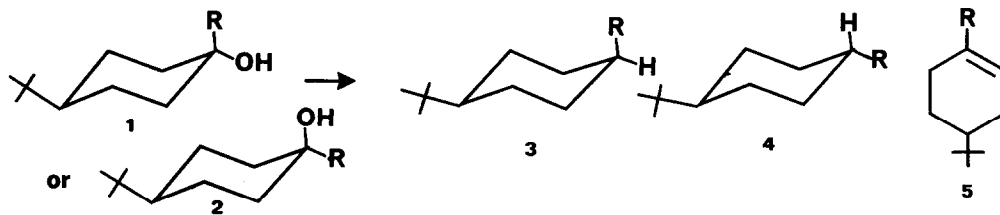


TABLE I

Alcohol	Hydride	Product Composition Percent		
		3	4	5
1	Ph ₃ SiH	10	18	72
1	Ph ₃ GeH	29	59	12
1	Ph ₃ SnH	36	52	12
1	Bu ₃ SnH	33	29	38
2	Ph ₃ SiH	20	29	51
2	Ph ₃ GeH	29	61	10
2	Ph ₃ SnH	38	52	10
2	Bu ₃ SnH	38	32	30

eq 2 R=Ph-

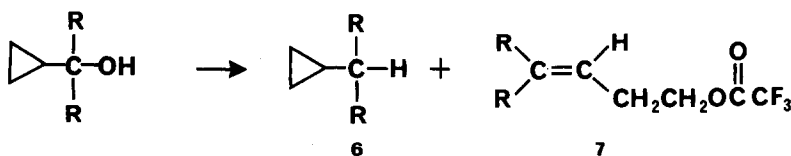
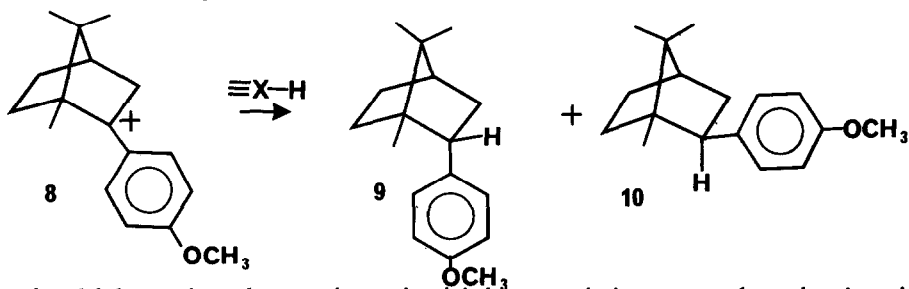


TABLE II

Hydride Source	6	7
Ph ₃ SiH	16	84
Ph ₃ GeH	45	55
Ph ₃ SnH	85	15
Bu ₃ SnH	78	22

It is evident from these data that not only are tin and germanium hydrides reactive toward hydride transfer, they are both better donors than silicon hydrides. This follows by comparing the relative amounts of hydride transfer to competing processes in the two reactions; elimination to **5** in eq 1 and ring opening to **7** in eq 2. Triphenyltin hydride especially, is clearly a very reactive hydride donor.

Cation **8** was generated from p-anisylisoborneol (**6**) in $\text{CH}_2\text{Cl}_2\text{-CF}_3\text{CO}_2\text{H}$ and using Ph_3SiH converted quantitatively to a mixture of 68% p-bornylanisole **9** and 32% p-isobornylanisole **10** (7,8). Triphenyltin hydride gave 98% **9** and 2% **10** while PhSiH_3 produced only **9**.



It should be pointed out that the high reactivity toward carbonium ions exhibited by tin and germanium hydrides is paralleled by their reactivity towards protonic acids, a factor which somewhat limits their usefulness in strongly acidic media. Under the conditions which the reactions in eq 1 and eq 2 were carried out the trifluoroacetic acid concentration was ~ 0.5 M. The stability of the hydrides could be determined by nmr in CDCl_3 by measuring the rate of disappearance of Si-H (5.55δ , Ph_3SiH), Ge-H (5.75δ , Ph_3GeH) or Sn-H (6.88δ , Ph_3SnH) versus the methyl peak of toluene as an internal standard. At a $\text{CF}_3\text{CO}_2\text{H}$ concentration of 6.7 M Ph_3SiH was 30% reacted after 12 hr, Ph_3GeH 50% reacted after 30 min and Ph_3SnH completely reacted within 1 min.

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- (8) Borohydride trapping of **8** gives 87% **9** and 13% **10**. H. M. Bell and H. C. Brown, J. Amer. Chem. Soc., 86, 5007 (1964).