

The following table shows the percentage of ligand displacement obtained during the present investigation.

Table - 1

Reaction	Products	% of conversion
1. $\text{Ph}_3\text{SnOX} + \text{H}_2\text{DZ} \longrightarrow$	$\text{Ph}_3\text{Sn}(\text{HDZ}) + \text{H.OX}$	90.0
2. $\text{Ph}_2\text{Sn}(\text{OX})_2 + 2\text{H}_2\text{DZ} \longrightarrow$	$\text{Ph}_2\text{Sn}(\text{HDZ})_2 + 2\text{HOX}$	89.0
3. $\text{Ph}_2\text{Sn}(\text{HDPC})_2 + 2\text{H}_2\text{DZ} \longrightarrow$	$\text{Ph}_2\text{Sn}(\text{HDZ})_2 + 2\text{H}_2\text{DPC}$	94.0
4. $\text{Me}_2\text{SnCl}(\text{HDPC}) + \text{H}_2\text{DZ} \longrightarrow$	$\text{Me}_2\text{SnCl}(\text{HDZ}) + \text{H}_2\text{DPC}$	91.0
5. $\text{Ph}_2\text{Sn}(\text{PBHA})_2 + 2\text{H}_2\text{DZ} \longrightarrow$	$\text{Ph}_2\text{Sn}(\text{HDZ})_2 + 2\text{HPBHA}$	83.0
6. $\text{Ph}_3\text{Sn}(\text{PBHA}) + \text{H}_2\text{DZ} \longrightarrow$	$\text{Ph}_3\text{Sn}(\text{HDZ}) + \text{HPBHA}$	75.0
7. $\text{Ph}_3\text{Sn}(\text{HDZ}) + \text{H}_2\text{DPC} \longrightarrow$	no reaction	-
8. $\text{Ph}_2\text{Sn}(\text{HDZ})_2 + 2\text{H}_2\text{DPC} \longrightarrow$	no reaction	-
9. $\text{Ph}_2\text{Sn}(\text{HDPC})_2 + 2\text{HOX} \longrightarrow$	$\text{Ph}_2\text{Sn}(\text{OX})_2 + 2\text{H}_2\text{DPC}$	92.3
10. $\text{Bu}_2\text{Sn}(\text{HDPC})_2 + 2\text{HOX} \longrightarrow$	$\text{Bu}_2\text{Sn}(\text{OX})_2 + 2\text{H}_2\text{DPC}$	~100.0
11. $\text{Ph}_3\text{SnOX} + \text{H}_2\text{DPC} \longrightarrow$	no reaction	-
12. $\text{Me}_2\text{Sn}(\text{nitro PBHA})_2 + 2\text{HOX} \longrightarrow$	$\text{Me}_2\text{Sn}(\text{OX})_2 + 2\text{nitro PBHA}$	84.0
13. $\text{Me}_2\text{Sn}(\text{nitro PBHA})_2 + 2\text{H}_2\text{DPC} \longrightarrow$	$\text{Me}_2\text{Sn}(\text{HDPC})_2 + 2\text{nitro PBHA}$	8.0
14. $\text{Me}_2\text{Sn}(\text{HDPC})_2 + 2 \text{ nitro PBHA} \longrightarrow$	no reaction	-

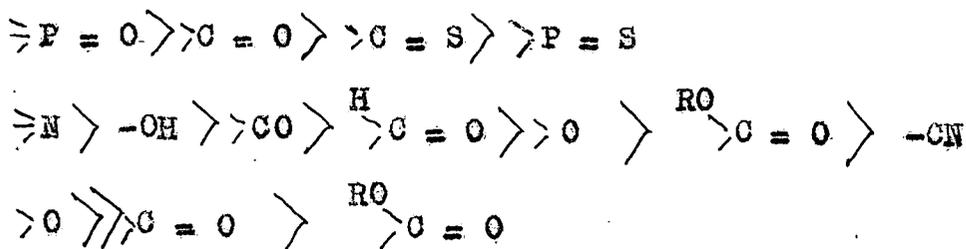
Here the following abbreviations have been used:

HOX = oxine or 8-hydroxy quinoline; H_2DZ = Dithizone; H_2DPC = diphenyl carbazone; HPBHA = N-phenyl benzohydroxamic acid and nitro PBHA = N-phenyl-p-nitro benzohydroxamic acid.

From the above table it is apparent that of the bidentate chelate ligands diphenyl thiocarbazono has highest donor strength for different organotin moieties. The order of donor abilities of these ligands used in the following study are as follows:

Diphenyl thiocarbazono Oxine Diphenyl carbazono
Hydroxamic acid.

This order of reactivity can be expected if we consider the organotin moieties as relatively soft acid according to HSAB concept. T.L.Ho (21) has observed that it is now established that thiols, thioethers and phosphines (soft donors) form much weaker complexes with the metal ions in reagents which happen to be hard Lewis acids than do ethers and amines (hard donors) by co-ordination with the magnitude of proton resonance shifts in the proximal methylene or methyl groups. The relative abilities of various groups for hard acids are listed as follows:



Thus, though it is expected that the proximal methyl groups in Me_2SnCh_2 (Ch = chelate) should undergo considerable shielding compared to Me_2SnCl_2 and consequently might have different $^{119}\text{Sn-C-H}$ coupling constant values. $\text{Me}_2\text{Sn}(\text{OX})_2$ have very similar coupling

constant values to Me_2SnCl_2 . The close similarity of these values has been ascribed due to structural features of the complex. We also observed anomaly in the shielding of $\text{Me}_2\text{Sn}(\text{HDZ})_2$ and $\text{Bu}_2\text{Sn}(\text{HDZ})_2$. In $\text{Me}_2\text{Sn}(\text{HDZ})_2$ the methyl group absorbs at δ 1.28 ppm where as the triplets (δ -0.58, 0.66, 0.74 ppm) associated with the methyl groups have been observed for $\text{Bu}_2\text{Sn}(\text{HDZ})_2$, possibly for structure features of these compounds. The position of the methyl groups in p.m.r. spectra is given in the following table.

Table - 2

Compound	Position of CH_3 proton (in δ -ppm)
$\text{Me}_2\text{Sn}(\text{HDZ})_2$	1.28 (15)
$\text{Me}_2\text{Sn}(\text{OX})_2$	0.44 (20)
$\text{Me}_2\text{Sn}(\text{HDPC})_2$	0.80
$\text{Me}_2\text{Sn}(\text{nitro PBHA})_2$	0.80 (17)
Me_2SnCl_2	1.22 (20)

In $\text{Me}_2\text{Sn}(\text{HDZ})_2$, the methyl group suffers deshielding instead of usual shielding expected for such co-ordination compounds. Apart from this compound, the nature of displacement of ligands observed during the present investigation closely resemble the shielding

observed in these compounds. Thus oxine can replace both diphenyl carbazone and nitro PBHA quite easily, whereas the diphenyl carbazone can only marginally displace nitro PBHA from its complexes. The diphenyl thiocarbazone can replace all these ligands from their complexes quite easily. Hence we may assume where the structural features do not affect the ρ position of CH_3 protons, the magnitude of shielding can possibly give some idea about the relative donor strength of the ligands.

Drago and Wayland (22) observed that every acid and base has both class A and B character but generally one type of behaviour predominates. The rates of bimolecular nucleophilic substitution reactions are determined by several factors relative to the nature of substrate and reagent and to the conditions (solvent, temperature, etc.) (23). By measuring under the same experimental conditions the rate of displacement of the ligand from a substrate $\text{M} - \text{X}$ by various reagents Y , a quantitative sequence of relative reactivity can be obtained.

In view of the number of variables that can affect the nucleophilicity, it is desirable to limit the range of the nucleophiles studied in order to eliminate certain structural factors such as steric hindrance etc. Following Pearson's classification of soft and hard acids and bases, it appears that in substitution reactions at soft reaction centres, the micropolarizability or softness of Y is most important factor in determining nucleophilicity, whereas the basicity of Y play only a minor role.

Unfortunately, from a practical point of view, Drago et al observed that, "softness is not a property that can be quantitatively measured by a direct physical experiment. It should be borne in mind that the HSAB concept represents an empirical approach which is often invalidated by the fact that there is no clear boundary between the two different types of acids and bases. The exact softness scale is neither available nor advisable empirical systematization of various acids and bases is essential for correlating experimental observations. The best compromise would be to establish guide lines for the rough estimation of softness in a comparative sense" (24).

It is interesting to note that of the two ligands viz. oxine and diphenyl carbazone, the former produces complexes with organotin moieties displacing diphenyl carbazone. In oxine complexes, the formation of co-ordination bond is effected through nitrogen, whereas in diphenyl carbazone, it is through oxygen. Since, nitrogen is a better donor than oxygen, the stability of oxine compound is expected to be higher than diphenyl carbazone.

The assumption of organotin compounds as a hard acid is, therefore, should be under some scrutiny, since the experimental observations obtained during the present investigation clearly show the opposite character, i.e., these are at least borderline between hard and soft acid, if not definitely soft acids, since N-S donor apparently forming strongest complex, followed by N-O donors and the O-O donors form weakest complexes.