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PRELIMINARY COMMUNICATION

DEOXYMETALLATION REACTIONS OF GROUP IV ORGANOMETALLICS

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The exceptional reactivity of organosilicon compounds having the structural feature of an electronegative group such as hydroxyl or halogen β to the silicon group has been recognized for better than twenty years[1].

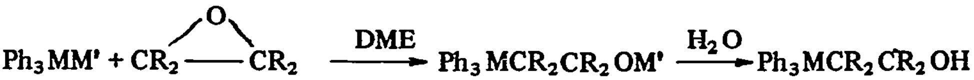
$$R_3SiCR_2CR_2X \rightarrow R_3SiX + CR_2{=}CR_2$$

Other elements in Group IV have shown similar reactivity, thus (3-chloro-2-hydroxypropyl)-triphenyllead yields elimination rather than substitution products upon treatment with HCl[2].

$$Ph_3Pb\,CH_2CH(OH)CH_2Cl + HCl \rightarrow CH_2{=}CHCH_2Cl + Ph_3PbCl + H_2O$$

These reactions are analogous to the well-known deoxymercuration reactions whose generally accepted mechanism[3] involves a metal-bridged ionic intermediate. We have investigated the mechanism of deoxymetallation of Group IV compounds with a hope toward further elucidating the structures and properties of bridged-metal ion species.

A series of substituted β-hydroxyalkyl triphenylmetal compounds was prepared by the reaction of triphenylmetal–alkali metal compounds with the appropriate epoxide[2] in dimethoxyethane (25°, 1 h):



$$Ph_3MM' + CR_2\overset{O}{—}CR_2 \xrightarrow{DME} Ph_3MCR_2CR_2OM' \xrightarrow{H_2O} Ph_3MCR_2CR_2OH$$

(M = Si, Ge, Sn, Pb; M' = Li, Na)

These products are air and water stable, however in either methanol/water or acetic acid/water mixtures containing catalytic amounts of perchloric acid, a rapid elimination reaction occurs to produce an alkene (95–100%) and a triphenylmetal salt (90–93% isolated yield).

$$Ph_3MCR_2CR_2OH + HOAc + H^+ \xrightarrow{HOAc/H_2O} Ph_3MOAc + H_2O + CR_2{=}CR_2 + H^+$$

$$Ph_3MCR_2CR_2OH + H_2O + H^+ \xrightarrow{MeOH/H_2O} Ph_3MOH + H_2O + CR_2{=}CR_2 + H^+$$

The kinetics of the elimination reaction were studied by a manometric technique and the rate of reaction was found to be first-order in organometallics and proportional to the Hammett acidity function. In acetic acid containing from 0–5% water, the rates are also proportional to the concentration of water[4].

$$\text{rate} = k\ [Ph_3MCR_2CR_2OH] \cdot h_0[H_2O]$$

In aqueous methanol solution water dependence was not noted, however, water was present in higher (27%) and constant concentration.

The relative rates of elimination as a function of both the metal and the structure of the alkyl group are given in Table 1.

TABLE 1

RATES OF THE ACID-CATALYZED ELIMINATION REACTIONS (73% AQUEOUS METHANOL, 25.0°)

Compound	$k_\psi \cdot M^{-1} \cdot \sec^{-1}$[a]	k_{rel}
$Ph_3SiCH_2CH_2OH$	No reaction	–
$Ph_3SiCH_2CH(OH)CH_3$	No reaction	–
$Ph_3GeCH_2CH(OH)CH_3$	No reaction	–
$Ph_3SnCH_2CH_2OH$	0.35	1.0
$Ph_3SnCH_2CH(OH)CH_3$	0.51	1.4
$Ph_2SnCH(CH_3)CH(CH_3)OH$	2.3	6.6
$Ph_3SnCH_2C(CH_3)_2OH$	4.4	12.4
$Ph_3PbCH_2CH_2OH$	0.77	2.2
$Ph_3PbCH_2CH(OH)CH_3$	1.9	5.4

[a] $k_\psi = k_{obs}/[H^+]$ The acid concentration is within the range 0.006 to 0.09 M and is essentially linearly related to h_0.

The effect of organometallic leaving group is particularily striking. Whereas the organotin and organolead compounds reacted rapidly at 25° in dilute acid solutions, no reaction was observable for the organogermanium or organosilicon compounds even at 60° and 8 M acid concentrations. This reactivity series ($Pb > Sn \gg Ge > Si$) parallels that observed in electrophilic aromatic demetallations[5]. Part of the lack of reactivity of the organosilicon and organogermanium compounds in this study is due to the electron-withdrawing effects of the phenyl substituents since 2-trimethylsilylethanol[6] undergoes the elimination reaction in 4 M sulfuric acid with k_{obs} equal to $4 \cdot 10^{-3}$ sec^{-1} at 25° in 50% methanol.

Alkyl substitution leads to an increase in the rate, however, the pattern of organotin and organolead compounds is compressed when compared to a similar series of deoxymercuration reactions[7] (Table 2). This implies that the transition state for deoxystannylation more nearly resembles the reactants.

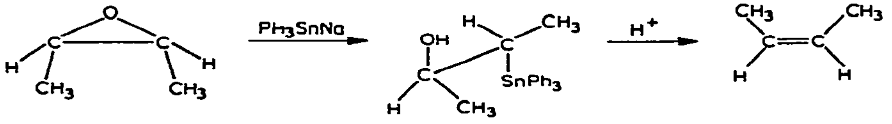
TABLE 2

RELATIVE RATES OF DEOXYMETALLATION REACTIONS

Compound	Deoxymercuration[a] (75% Aq. EtOH, 0°; M = HgCl, X = OEt)	Deoxystannylation[b] (73% Aq. MeOH, 25°; M = Ph_3Sn, X = OH)	Deoxyplumbylation[b] (73% Aq. MeOH; M = Ph_3Pb, X = OH)
$M{-}CH_2CH_2X$	1.0	1.0	1.0
$M{-}CH_2CH(X)CH_3$	14.4	1.4	2.5
$M{-}CH(CH_3)CH(CH_3)X$	86.6	6.6	–
$M{-}CH_2C(CH_3)_2X$	1560	12.4	–

[a] Ref. 7. [b] This work

The stereochemistry of the elimination reaction was studied by means of the *erythro*- and *threo*-3-(triphenylstannyl)-2-butanols. Reaction of *cis*-2,3-butylene oxide with triphenyltin sodium in dimethoxyethane gives a single product to which is assigned the *threo* configuration on the basis of two observations: first, unsymmetrical epoxides such as propylene oxide react with triphenyltin sodium to give the product in which the tin is attached to the least substituted carbon; and secondly, the reaction of triphenyltin sodium with alkyl halides proceeds with inversion of configuration[8]. Both observations point toward the nucleophilic character of triphenyltin sodium and hence, *trans* opening of the epoxide ring. When the *threo* compound was subjected to the elimination reaction conditions only (> 99.5% by vapor phase chromatography) *cis*-2-butene was formed. A 77:23 mixture of the *erythro* and *threo* alcohols prepared form the corresponding mixture of epoxides gave a 77:23 mixture of *trans*- and *cis*-2-butenes.



The overall stereochemistry is retention of the geometrical structure of the epoxide. Since the epoxide opening is very reasonably *trans*, the elimination reaction must also proceed in a *trans* manner. Moreover, both processes are highly stereospecific.

On the basis of the kinetic and stereochemical evidence accumulated thus far, we postulate that the deoxymetallation of Group IV organometallic alcohols proceeds in the following manner in aqueous acetic acid or aqueous methanol.

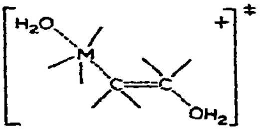
$$\mathrm{SH^+ + Ph_3MCR_2CR_2OH \rightleftharpoons Ph_3MCR_2CR_2OH^+}$$

$$\mathrm{Ph_3MCR_2CR_2OH_2{}^+ + H_2O \xrightarrow{slow} Ph_3MOH_2{}^+ + CR_2{=}CR_2 + H_2O}$$

$$\mathrm{Ph_3MOH_2{}^+ + SH \rightleftharpoons Ph_3MS + H_3O^+\ (in\ HOAc)}$$

or $$\mathrm{Ph_3MOH_2{}^+ + SH \rightleftharpoons Ph_3MOH + SH_2{}^+\ (in\ MeOH)}$$

A reasonable picture of the transition state for the slow step of the deoxymetallation is:



Although the transition state pictured above leads directly to the products, the available evidence is equally consistent with a transition state leading to the formation of an intermediate metal—olefin complex. Further work on this point is in progress.

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REFERENCES

1 (a) L.H. Sommer and F.C. Whitmore, *J. Amer. Chem. Soc.*, 68 (1946) 485
(b) L.H. Sommer, G.M. Goldberg, E. Dorfman and F.C. Whitmore, *ibid.*, 68 (1946) 1083.
(c) L.H. Sommer, D.L. Bailey and F.C. Whitmore, *ibid.*, 70 (1948) 2869
2 L.C. Willemsens and G.J.M. van der Kerk, *J. Organometal. Chem.*, 4 (1965) 34.
3 (a) J. Chatt, *Chem. Revs.*, 48 (1951) 7.
(b) N.S. Zefirov, *Russ. Chem. Revs.*, 34 (1965) 527.
4 F.J. Ludwig and K.H. Adams, *J. Amer. Chem. Soc.*, 76 (1954) 3853.
5 C. Eaborn and K.C. Pande, *J. Chem. Soc.*, (1960) 1566.
6 L.H. Sommer and R.A. Miller, unpublished work; cited in, L.H. Sommer, *Stereochemistry, Mechanism and Silicon*, McGraw-Hill, New York, 1965, p. 145.
7 K. Ichikawa, K. Nishimura and S. Takayama, *J. Org. Chem.*, 30 (1965) 1593.
8 D.D. Davis, Ph.D. Dissertation, Univ. of Calif., Berkeley, 1966.