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ORGANOELEMENTAL FRAGMENTATIONS

II*. A PROOF OF TAUTOMERIC ARENE INTERMEDIATES IN REACTIONS OF ORGANOMETALLIC BENZYL COMPOUNDS WITH ACIDS. AROMATISATIONAL MERCURATION OF 1-METHYLENE-2,4-CYCLOHEXADIENE

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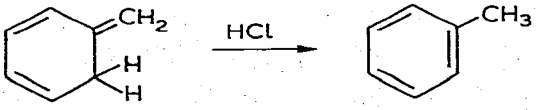
Summary

Soft Lewis acids of the $HgCl_2$ type are effective electrophilic traps for tautomeric arenes even in strongly acidic media which catalyse aromatisation of the arenes. Acid cleavage of $(PhCH_2)_3SnCl$ by the action of DCl and $HgCl_2$ has been studied, and it is shown that the organotin compound is protolysed via a fragmentation mechanism involving a 1-methylene-6-deuterio-2,4-cyclohexadiene intermediate that yields o-D-$C_6H_4CH_2HgCl$ under the action of $HgCl_2$.

Introduction

Tautomeric arenes [1] are known to undergo easy aromatisation under the action of protic acids [2,3].



We have found, however, that when similar trienes are treated with a threefold excess of mercury dichloride, the reaction results in the evolution of one equivalent of free acid per one mole of olefin converted, while a practically

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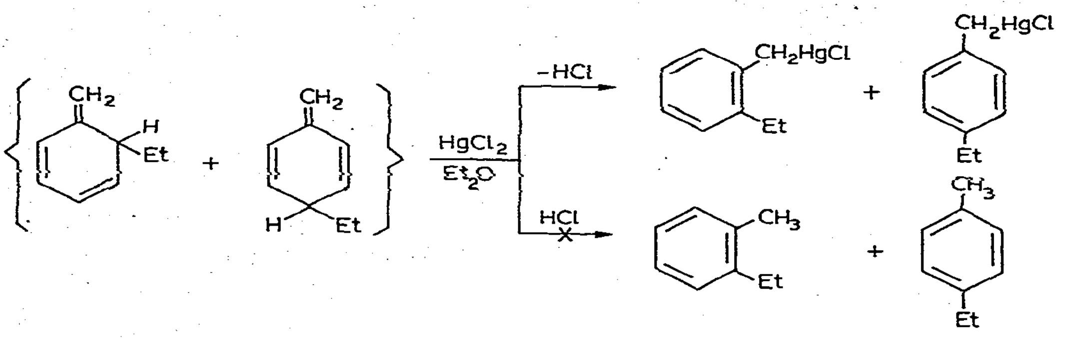
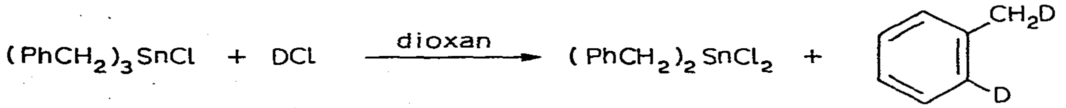
* For part I see ref. 1.

quantitative aromatisational mercuration takes place leading to an organomercury benzyl compound [1].

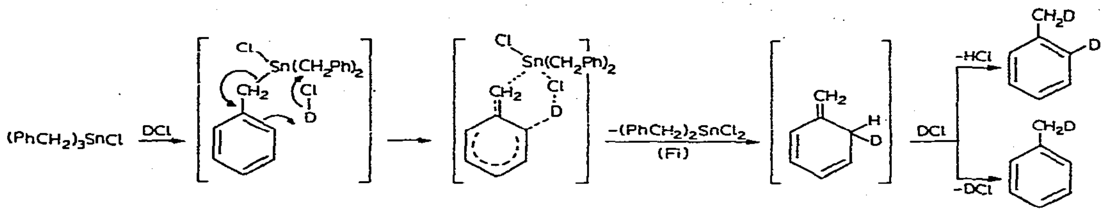


Consequently, the *exo*-methylene site may preferentially react with Lewis acids rather than with protic acids. If this is so, metal salts may be used as electrophilic traps for tautomeric arenes even in strongly acidic media.

For instance, we have shown that $(PhCH_2)_3SnCl$ cleaved by an excess of DCl in dioxan yields α,*o*-dideuteriotoluene [4].

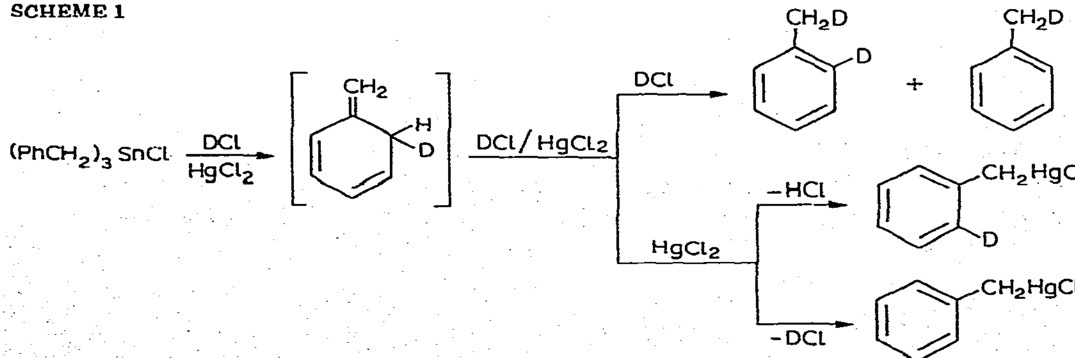


The mechanism of this and some other reactions of benzyl organometallics [1,5] implies the formation of a tautomeric toluene intermediate (1-methylene-2,4-cyclohexadiene) which, however, cannot be isolated since it rapidly isomerises under the action of an excess of acid.



We make the assumption that mercuric chloride added to the strongly acidic mixture could serve as an effective electrophilic trap for the triene intermediate.

SCHEME 1



If this assumption is valid, then the following experimental facts should be observed.

(i) The compound $(PhCH_2)_3SnCl$ when treated with HCl (DCl) in the presence of $HgCl_2$ should give $PhCH_2HgCl$.

(ii) The competing acidic aromatisation will be deprived of some substrate (1-methylenecyclohexadiene involved in the reaction with $HgCl_2$), hence the yield of demetallation product (toluene) should become lower.

(iii) The $PhCH_2HgCl$ formed should contain a deuterium label. The labelling intensity should correspond to the deuterium content in the ring of toluene, the labelled site should be the *ortho*-position exclusively (as in toluene).

Results and discussion

We have decomposed $(PhCH_2)_3SnCl$ by HCl in dioxan in the presence of mercuric chloride.

A solution of $(PhCH_2)_3SnCl$ (c_0 0.15 mole/l) in dioxan saturated with HCl (c_0 1.5 mole/l) was sealed in ampoules containing an exact amount of $HgCl_2$ (c_0 0.40 mole/l). The ampoules were kept at 100°C for 15 min, then the reaction was stopped by cooling the mixture down to 0°C. The solvent was removed under reduced pressure and the residue was studied by PMR methods using an XL-100 instrument (12% solution in dioxan).

The reaction mixture does contain a significant amount (Table 1) of $PhCH_2HgCl$ along with $(PhCH_2)_3SnCl$ and $(PhCH_2)_2SnCl_2$. The methylene proton chemical shifts and the coupling constants $J(\text{H—}^{199}\text{Hg})$, $J(\text{H—}^{117}\text{Sn})$, and $J(\text{H—}^{119}\text{Sn})$ were assigned by comparison with those in authentic samples.

The formation of $PhCH_2HgCl$ might be a result of a usual transmetallation of the organotin compound under the action of $HgCl_2$ [6]*. We have shown that, ceteris paribus, the organotin compound is not affected in the absence of acid even if a chloride anion donor (pyridine hydrochloride) is added to the reaction mixture.

$$(PhCH_2)_3SnCl + HCl + HgCl_2 \xrightarrow[100^\circ C,\ 15\ min]{dioxan} (PhCH_2)_2SnCl_2 + PhCH_3 + PhCH_2HgCl$$

The assumptions made above suggest that the formation of $PhCH_2HgCl$ in

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* The alkyl exchange (transmetallation) rate found [6] to be higher in benzylstannanes than in other organotin compounds may, in our opinion, be explained by assuming that a fragmentation operates in the reaction. Mercuric chloride may attack the benzene ring and the resulting tautomeric tolylmercury chloride may reorganise via two paths. The metal may migrate to a "less acidic", *exo*-cyclic position, and/or aromatisational mercuration may occur under the action of the second equivalent of mercuric chloride.

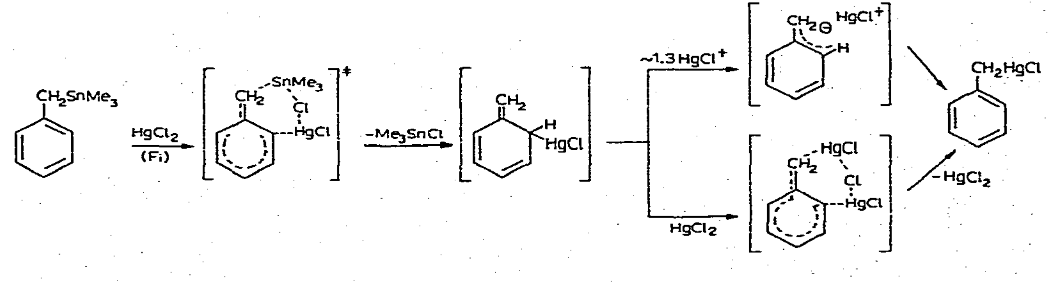


TABLE 1

REACTIONS OF $(PhCH_2)_3SnCl$, 100°C, 15 min, IN DIOXAN

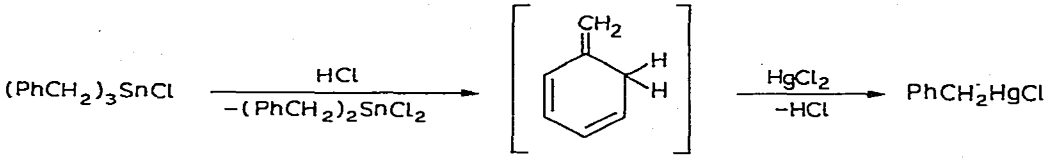
No.	Initial concentrations (mole/l)			$PhCH_3$ yield^a (%)	$PhCH_2HgCl$ yield^b (%)
	$(PhCH_2)_3SnCl$	HCl	$HgCl_2$		
1	0.15	1.5	none	60	none
2	0.15	1.5	0.40	22	30

^{a}GLC. ^{b}Isolated.

the system $(PhCH_2)_3SnCl/HCl/HgCl_2$ should diminish the toluene yield as compared with acidic cleavage in the absence of $HgCl_2$. Quantitative gas—liquid chromatographic (GLC) analyses demonstrate that this is indeed the case (Table 1).

These results are, in our opinion, especially interesting, if one considers them in terms of a formal trialkyl exchange. Indeed, a benzyl organotin species and mercuric chloride yield the respective organomercurial, but the process goes if and only if an acid is present!

We believe that this (formally speaking) transmetallation is a fragmentation, not a substitution, in other words it is a conjugate process of a new type necessarily implying participation of three species*. The mechanism is best presented as aromatisational mercuration of the 1-methylene-2,4-cyclohexadiene intermediate resulting from the organotin compound protolysed by HCl.



This mechanistic assumption has been verified by using an isotope method.

The compound $(PhCH_2)_3SnCl$ was protolysed by DCl in the presence of $HgCl_2$ under conditions identical to those described above.

The resulting organometallic compounds, previously detected by PMR, have been isolated, recrystallised, and sublimed. Their constants coincide with those described in the literature. A mixture of the $PhCH_2HgCl$ with an authentic sample gave no melting point depression, a mass spectrum of the compound confirmed its individuality.

The $PhCH_2HgCl$ isolated contains, in accord with our assumptions, a significant amount of deuterium [0.50 D/mole; the atomic percentage is 7.14% (method according to ref. 8), the gross percentage is 49.8% (mass spectroscopy)] in the benzene ring. Special experiments have shown that there are no secondary deuterium exchange processes which could have enriched the benzene rings of the organomercury and organotin compounds.

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* A similar process may be responsible for a significant accelerating effect of acids upon racemisation and one-alkyl exchange in ethyl α-bromomercuryphenylacetate acted upon by mercuric bromide [7]. Processes of this kind may have preparative significance for a great number of organometallic substrates, electrophilic agents, and traps.

The labelled $PhCH_2HgCl$ has its deuterium (IR) exclusively in the *ortho*-position of the ring (ν(C—D) = 635 cm^{-1} [9,10]; 8% solutions in $PhCH_3$ measured on a UR-20 instrument).

The fact that deuterium is exclusively in the *ortho*-position as is also the case with $(PhCH_2)_3SnCl$ decomposed by DCl in the absence of $HgCl_2$ [4], suggests that the presence of $HgCl_2$ does not alter the mode (concerted fragmentation) in which the isotope enters the ring, otherwise the deuterium *para*-attack would have made its contribution.

Thus, our experimental data agree exactly with the assumptions made above. Consequently, 1-methylene-6-deuterio-2,4-cyclohexadiene is a precursor of both α,*o*-dideuteriotoluene (the reaction with DCl [4]) and *o*-deuteriobenzylmercury chloride (the reaction in the presence of mercuric chloride, Scheme 1).

All these results are a direct proof in favour of the assumption that reactions of organomercury and organotin benzyl compounds with acids involve tautomeric arene intermediates [4,11]*.

The system studied in this paper is characteristic in that the 1-methylene-2,4-cyclohexadiene is subject to competing aromatisations exerted by electrophiles of two kinds, soft mercury dichloride and hard hydrogen chloride. The fact that despite the 3.5-fold excess of HCl over $HgCl_2$, the yield of $PhCH_2HgCl$ is 1.5 that of $PhCH_3$ suggests that in these competing aromatisation reactions the preference of the *exo*-methylene for the mercury salt is much higher than that of the proton**. Consequently, the aromatisation—metallation technique may be used as a tool for studying a wide range of organometallic benzyl compounds participating in the electrophilic fragmentations in which olefin intermediates of this type may be assumed to play a role.

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* Unsaturated hydrocarbons of this structure were isolated from $PhCH_2$—MgCl in 1960 by Raaen and, later, by Benkeser. The agents were cyanides [12] and alkylating species [13,14]. Naturally, the isolation is impossible in the case of electrophilic fragmentations in acidic media where the trienes are rapidly aromatised to form arenes.

** Unsaturated species of this type may be thought of as "super-soft" bases, to be discussed in one of our forthcoming papers.