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Preliminary communication

REACTIONS OF ORGANIC HALIDES WITH R_3MMR_3 COMPOUNDS (M = Si, Ge, Sn) IN THE PRESENCE OF TETRAKIS(TRIARYLPHOS- PHINE) PALLADIUM

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Summary

Compounds of the type $ArSnR_3$ (R = Me or Bu), $ArGeEt_3$ and $XC_6H_4CH_2SiMe_3$ are formed, though sometimes in poor yield, by interaction of $ArHal$ or $XC_6H_4CH_2Hal$ with the appropriate R_3MMR_3 compounds in the presence of $[Pd(PAr_3)_4]$.

In 1973, Atwell and Bokerman showed that certain organic halides, RX , reacted with disilane derivatives in the presence of some transition metal complexes to give $R-Si$ compounds, the reaction being especially effective with allyl halides [1]. More recently, Matsumoto and his colleagues observed that aryl bromides (and some chlorides) react with hexamethyldisilane in the presence of $[Pd(PPh_3)_4]$ to give aryl $SiMe_3$ compounds [2], thus providing an important new route to such compounds, especially those in which the aryl group bears reactive functional substituents (e.g. NO_2) and so could not be attached to silicon by established methods involving Grignard or organolithium reagents**. We have made a preliminary survey of extensions of this reaction to use of (a) distannane and digermane derivatives, (b) benzyl halides, and (c) other $[Pd(PAr_3)_4]$ complexes.

The results are presented in Table 1, and the significant features are: (1) Hexabutyl- and hexamethyl-distannane ($R'_3SnSnR'_3$) react with some $ArBr$ compounds to give $ArSnR'_3$, but the yields are much smaller than those from hexamethyldisilane, and substantial amounts of the diphenyl, $ArAr$, are

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** The preparation of $p-NO_2C_6H_4SiMe_3$ by this route is not in fact as useful as Matsumoto et al. supposed [2], since this compound can be obtained easily (if indirectly) in good yield by nitrodesilylation of $(p-Me_3Si)_2C_6H_4$ [3]. However, we have used their method to obtain 2,4-(NO_2)- $C_6H_4SiMe_3$, which is not available by other routes.

- formed. The extent of the diphenyl formation is apparently decreased by electron-releasing substituents and increased by electron-withdrawing substituents, so that no *p*-nitrophenyltin compounds were obtained. Use of the mixed $\text{Me}_3\text{SiSnMe}_3$ gave *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{SiMe}_3$ but no *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{SnMe}_3$.
- (2) In the very small number of experiments in which it was used, hexaethyl-digermane gave some ArGeEt_3 products, but diaryl formation was again substantial.
- (3) Benzyl halides $\text{YC}_6\text{H}_4\text{CH}_2\text{X}$ react with hexamethyldisilane to give dibenzyl along with $\text{YC}_6\text{H}_4\text{CH}_2\text{SiMe}_3$ compounds in yields which are low for $\text{X} = \text{H}, \text{Me}$ or Cl , but large when X is strongly electron-withdrawing, especially for $\text{X} = p\text{-CN}$. The relatively low yields for $\text{X} = m\text{-}$ or $p\text{-NO}_2$ may be due to secondary reactions, the formation of *m*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_3$ even in very low yield, is significant, however, since this compound has not been accessible in the past.
- (4) Variation of aryl group in the palladium complex seems to have a significant influence, so that a virtually quantitative yield of *p*- $\text{NCC}_6\text{H}_4\text{CH}_2\text{-SiMe}_3$ was obtained by use of $[(p\text{-MeOC}_6\text{H}_4)_3\text{P}]_4\text{Pd}$. However, we are not yet certain that the variation reflects real differences in catalytic ability, rather than, for example, the presence of inhibiting or enhancing impurities.

TABLE 1

INTERACTION OF RHal AND $\text{R}'_3\text{MMR}'_3$ IN THE PRESENCE OF $[\text{Pd}(\text{PAR}_3)_4]$.

RHal	$\text{R}'_3\text{MMR}'_3$	Conditions ^a		Products ^b and yields (%) ^c
		Temp (°C)	Time (h)	
$\text{C}_6\text{H}_5\text{Br}$	$\text{Bu}_3\text{SnSnBu}_3$	120	40	RSnBu_3 (28); R_2 (31)
<i>p</i> - $\text{MeOC}_6\text{H}_4\text{Br}$	$\text{Bu}_3\text{SnSnBu}_3$	120	40	RSnBu_3 (55); R_2 (8)
<i>p</i> - $\text{MeOC}_6\text{H}_4\text{Br}$	$\text{Me}_3\text{SnSnMe}_3$	120	40	RSnMe_3 (52); R_2 (7)
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{Br}$	$\text{Bu}_3\text{SnSnBu}_3$	120	40	R_2 (38)
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{Cl}$	$\text{Bu}_3\text{SnSnBu}_3$	120	40	R_2 (26)
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{Br}$	$\text{Me}_3\text{SnSnMe}_3$	120	40	R_2 (58)
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{Br}$	$\text{Et}_3\text{SnSnMe}_3$	120	40	R_2 (53)
$\text{C}_6\text{H}_5\text{Br}$	$\text{Et}_3\text{GeGeEt}_3$	180	90 ^d	RGeEt_3 (28); R_2
<i>p</i> - $\text{MeC}_6\text{H}_4\text{Br}$	$\text{Et}_3\text{GeGeEt}_3$	140	90	RGeEt_3 (35); R_2 (60)
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$\text{Me}_3\text{SiSiMe}_3$	140	60	RSiMe_3 (25); R_2
$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$		140	65	RSiMe_3 (11); R_2
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$		120	90	RSiMe_3 (12); R_2
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$		120	90	RSiMe_3 (19); R_2
<i>m</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$		140	60	RSiMe_3 (6); R_2
<i>p</i> - $\text{MeC}_6\text{H}_4\text{CH}_2\text{Br}$		120	20	RSiMe_3 (5); R_2
<i>m</i> - $\text{MeC}_6\text{H}_4\text{CH}_2\text{Br}$		120	20	RSiMe_3 (8); R_2
<i>p</i> - $\text{NCC}_6\text{H}_4\text{CH}_2\text{Br}$		140	20	RSiMe_3 (57); R_2
<i>p</i> - $\text{NCC}_6\text{H}_4\text{CH}_2\text{Br}$		140	20 ^e	RSiMe_3 (87); R_2
<i>p</i> - $\text{NCC}_6\text{H}_4\text{CH}_2\text{Br}$		140	10 ^f	RSiMe_3 (98); R_2
<i>m</i> - $\text{NCC}_6\text{H}_4\text{CH}_2\text{Br}$		140	20	RSiMe_3 (29); R_2
2,4-(NO_2) $_2\text{C}_6\text{H}_3\text{Cl}$		140	90 ^g	RSiMe_3 (40) ^h

^aUnless otherwise specified toluene (6–10 ml) was used as solvent and $[\text{Pd}(\text{PPh}_3)_4]$ as catalyst. The RHal , $\text{R}'_3\text{MMR}'_3$, and $[\text{Pd}(\text{PAR}_3)_4]$ were used in 7.7 and 0.05 mmol amounts, respectively, and reactions were carried out in sealed ampoules. ^b $\text{R}'_3\text{MHal}$ compounds were always produced. ^cUnless otherwise specified, yields were determined by GLC (with the aid of authentic samples, except for *m*- $\text{NO}_2\text{C}_6\text{H}_4\text{-CH}_2\text{-SiMe}_3$, which is assumed to give the same detector response as its *p*-isomer). ^dMesitylene was used as solvent. ^e $[\text{Pd}[\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3]_4]$ used as catalyst. ^f $[\text{Pd}[\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3]_4]$ used as catalyst. ^gBenzene was used as solvent. ^hYield of purified (distilled, recrystallized from MeOH) material, m.p. 61°C, from aryl chloride (10 mmol) and $\text{Me}_3\text{SiSiMe}_3$ (30 mmol).

It is clear that the method developed by Matsumoto and his colleagues has considerable scope for extension. No attempt was made in our survey to optimize yields, and it seems likely that systematic study will lead to substantial improvements.

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References

- 1 W. Atwell and G.N. Bokerman, U.S. Patent 3, 772, 347, 1973.
- 2 H. Matsumoto, S. Nagashima, K. Yoshihiro and Y. Nagai, *J. Organometal. Chem.*, 85 (1975) C1.
- 3 F.B. Deans and C. Eaborn, *J. Chem. Soc.*, (1955) 498.