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MERCURY IN ORGANIC CHEMISTRY. 19.
RHODIUM PROMOTED METHYLATION OF ORGANOMERCURIALS

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Summary: Alkenyl-, alkynyl- and arylmercurials are methylated in excellent yield upon treatment with stoichiometric amounts of $CH_3RhI_2(PPh_3)_2$ (**1**). Catalytic methylation of these organomercurials is possible using **1** and methyl iodide, but side reactions interfere.

Organomercurials are attractive synthetic organic intermediates due to their ready availability, stability, and ability to accommodate substantial organic functionality. A number of important synthetic applications of these compounds are now known.[1] Unfortunately, methods for the alkylation of organomercurials have proven quite limited and often proceed in low yield.[2-8] Our previous success using rhodium catalysts in the dimerization[9] and carbonylation[10] of alkenyl- and arylmercurials encouraged us to look at the cross-coupling of organomercurials and alkyl halides using rhodium reagents. Semmelhack[1] and Schwartz[12] have previously reported that methylorganorhodium(III) complexes undergo reductive elimination to afford cross-coupled methyl arenes and methyl olefins respectively (eq. 1). We reasoned that similar mixed diorganorhodium(III) species might be generated by transmetallation of organorhodium(III) halides and organomercurials (eq. 2). Subsequent reductive elimination should afford cross-coupled products. We wish at this time to report the success of this approach to the alkylation of organomercurials.

$$CH_3Rh(R)XL_n \longrightarrow R\text{-}CH_3 + XRhL_n \qquad (1)$$

$$RRhX_2L_n + R'HgX \xrightarrow{-HgX_2} RRh(R')XL_n \xrightarrow{-XRhL_n} R\text{-}R' \qquad (2)$$

Our initial efforts were devoted to studying the optimal conditions necessary for cross-coupling alkenylmercuric chlorides and readily available bis(triphenylphosphine)methyl-di-iodorhodium(III)[13] (**1**) (eqs. 3,4). Using thoroughly dried hexamethylphosphoramide

$$CH_3I \; + \; ClRh(PPh_3)_3 \longrightarrow \underset{1}{CH_3RhI_2(PPh_3)_2} \qquad (3)$$

$$RCH{=}CHHgCl \; + \; 1 \longrightarrow RCH{=}CHCH_3 \qquad (4)$$

(HMPA) as a solvent (1 ml per 0.1 mmol of 1 and organomercurial), adding excess lithium chloride (10 equiv) and heating to 70°C for ~24 hours under nitrogen, one is able to obtain excellent yields of the corresponding methyl olefin. Some representative yields are included in the Table (entries 1 and 2). Using these conditions, dialkynylmercurials can also be methylated in excellent yield (entry 3). However, in attempting to methylate arylmercurials this procedure afforded significant amounts of hydrogen substitution product as well as the desired methyl arene (eq. 5). This difficulty was traced to small amounts

$$ArHgCl \; + \; 1 \longrightarrow Ar{-}CH_3 \; + \; Ar{-}H \qquad (5)$$

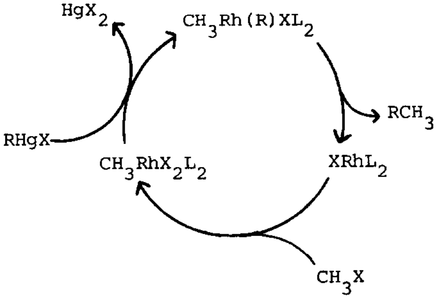
of water present in the lithium chloride and HMPA. By scrupulously drying the HMPA prior to each experiment and replacing the lithium chloride by methyl iodide (0.2 ml per 0.1 mmol of arylmercurial), this side product can be essentially eliminated and excellent yields of methyl arene can be obtained (entries 4-7). This reaction appears general for arylmercurials containing electron donating and electron withdrawing groups, as well as heterocyclic organomercurials. Unfortunately, alkylmercurials cannot be successfully methylated using either of the above procedures.

With the successful stoichiometric methylation of alkenyl-, alkynyl- and arylmercurials, we turned our attention to the catalytic cross-coupling of methyl iodide and these same organomercurials using 1 as a catalyst (eq. 6). In theory this approach should prove

$$RHgX \; + \; CH_3X \xrightarrow{\text{cat. } 1} R{-}CH_3 \; + \; HgX_2 \qquad (6)$$

catalytic in rhodium (Scheme). However, problems were envisioned since rhodium(I) and (III) salts are known to catalyze the dimerization of these same organomercurials.[9] In

SCHEME



practice alkenyl- and arylmercurials gave predominantly dimerization and only low yields of cross-coupled products (~20% yields). However, the reactions were catalytic (catalyst turnovers of 2-10). Using a dialkynylmercurial, substantially better results were obtained (eq. 7). Excellent results have also recently been obtained in the catalytic cross-coupling

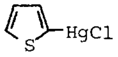
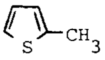
$$[(CH_3)_3CC{\equiv}C\text{-}]_2Hg \;+\; xs\ CH_3I \xrightarrow[\text{HMPA}]{2\%\ \underset{\sim}{1}} 2(CH_3)_3CC{\equiv}CCH_3 \qquad (7)$$
$$70°C\quad 24\ h \qquad\qquad 58\text{-}65\%$$

of arylmercurials and alkenyl halides (eq. 8). It appears likely that with the appropriate choice of organic halide, organomercurial and rhodium catalyst synthetically useful yields of cross-coupled products are feasible. This possibility is presently under examination.

$$ArHgCl \;+\; H_2C{=}CHBr \xrightarrow{\text{cat. }Rh^{I}} Ar\text{-}CH{=}CH_2 \qquad (8)$$

Table 1. Methylation of Organomercurials

$$RHgCl \;+\; \underset{\sim}{1} \xrightarrow[\text{HMPA}]{70°C\quad 24\ h} R\text{-}CH_3$$

entry	organomercurial	added reagent	product	% yield[a]
1	$C_6H_5CH{=}CHHgCl$	LiCl	$C_6H_5CH{=}CHCH_3$	97
2	$(CH_3)_3CCH{=}CHHgCl$		$(CH_3)_3CCH{=}CHCH_3$	92
3	$[(CH_3)_3CC{\equiv}C\text{-}]_2Hg$		$(CH_3)_3CC{\equiv}CCH_3$	99[b]
4	C_6H_5HgCl	CH_3I	$C_6H_5CH_3$	97
5	$\underline{p}\text{-}CH_3OC_6H_4HgCl$		$\underline{p}\text{-}CH_3OC_6H_4CH_3$	97
6	$\underline{m}\text{-}CH_3O_2CC_6H_4HgCl$		$\underline{m}\text{-}CH_3O_2CC_6H_4CH_3$	91
7				99

[a] Yield determined by gas liquid chromatography using an internal standard and appropriate correction factor.

[b] Yield based on alkylation of both organic groups of the dialkynylmercurial.

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REFERENCES

1. Larock, R. C. Angew. Chem., Int. Ed. Engl. 1978, 17, 27-37.
2. Kekulé, A.; Franchimont, A. Chem. Ber. 1872, 5, 906-8.
3. Whitmore, F. C.; Thurman, E. N. J. Am. Chem. Soc. 1929, 51, 1491-1503.
4. Schroeder, W. D.; Brewster, R. Q. J. Am. Chem. Soc. 1938, 60, 751-3.
5. Gilman, H.; Wright, G. F. J. Am. Chem. Soc. 1933, 55, 3302-14.
6. Beletskaya, I. P.; Vol'eva, V. B.; Reutov, O. A. Dokl. Akad. Nauk SSSR 1972, 204, 93-5; Proc. Acad. Sci. USSR, Chem. Sec. 1972, 204, 383-5.
7. Bergbreiter, D. E.; Whitesides, G. M. J. Am. Chem. Soc. 1974, 96, 4937-44.
8. Russell, G. A.; Hershberger, J.; Owens, K. J. Am. Chem. Soc. 1979, 101, 1312-3.
9. Larock, R. C.; Bernhardt, J. C. J. Org. Chem. 1977, 42, 1680-4.
10. Larock, R. C.; Hershberger, S. S. J. Org. Chem. 1980, 45, 3840-6.
11. Semmelhack, M. F.; Ryono, L. Tetrahedron Lett. 1973, 2967-70.
12. Schwartz, J.; Hart, D. W.; Holden, J. L. J. Am. Chem. Soc. 1972, 94, 9269-71.
13. Lawson, D. N.; Osborn, J. A.; Wilkinson, G. J. Chem. Soc., A, 1966, 1733-6.

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