Journal of Organometallic Chemistry, 225 (1982) 31—41
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MERCURY IN ORGANIC CHEMISTRY

XXI *. METHYLATION OF ORGANOMERCURIALS VIA ORGANORHODIUM SPECIES **

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(Received March 31st, 1981)

Summary

Alkenyl-, alkynyl- and arylmercurials are methylated in excellent yield upon treatment with stoichiometric amounts of $CH_3RhI_2(PPh_3)_2$ (I) at 70°C in hexamethylphosphoramide with added lithium chloride or methyl iodide. While the reactions can be made catalytic in rhodium using methyl iodide and I as a catalyst, the overall yields and catalyst turnover are low due to competing dimerization of the organomercurials. Organomethylrhodium(III) species are presumed intermediates in these reactions.

Introduction

Organomercuric halides are attractive synthetic organic intermediates due to their ready availability, ease of handling, high chemical and thermal stability, and ability to accommodate a wide range of organic functionality. Numerous synthetic applications of these compounds are now known, many involving reactions with transition metal reagents [1]. Unfortunately, no general method for the direct alkylation of a wide range of organomercurials has yet been reported. Alkyl halides react with organomercurials only under forcing conditions [2—5] or in the presence of aluminum bromide [6] to give low to modest yields of cross-coupled products. Primary and secondary alkylmercurials, but not arylmercurials, react with iodo(tri-n-butylphosphine)copper(I) and 3 equiv. of tert-butyl lithium to generate a complex of unknown structure which will alkylate primary alkyl iodides [7]. More recently, alkylmercurials have been

* For part XX see ref. 33.

** In honor of Professor Henry Gilman for his years of outstanding teaching and research in organometallic chemistry and his personal kindness and encouragement to the senior author.

0022-328X/82/0000—0000/$02.75

reported to undergo alkylation by nitronate anions by a radical anion chain mechanism [8].

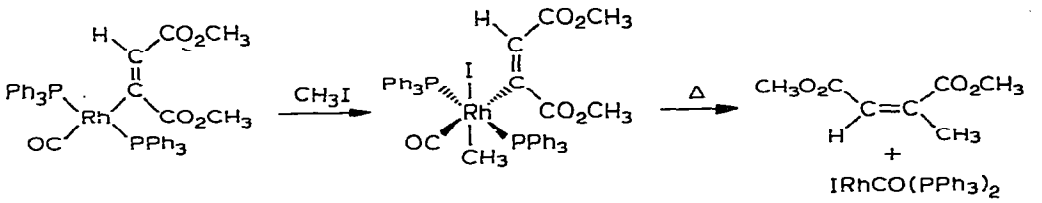
Our previous success using rhodium catalysts in the dimerization [9] and carbonylation [10] of alkenyl- and arylmercurials (eq. 1) encouraged us to look at the cross-coupling of organomercurials and alkyl halides using rhodium

$$R{-}R \xleftarrow[0.5\%[ClRh(CO)_2]_2]{} RHgCl \xrightarrow[0.5\%[ClRh(CO)_2]_2]{CO} R{-}\overset{\overset{O}{\|}}{C}{-}R \qquad (1)$$

reagents. Semmelhack and Ryono have previously reported that tris(triphenylphosphine)methylrhodium(I) readily methylates aryl iodides, presumably via arylmethylrhodium(III) intermediates (eq. 2) [11]. Schwartz and coworkers have

$$CH_3Rh(PPh_3)_3 \xrightarrow{ArI} CH_3Rh(Ar)I(PPh_3)_3 \rightarrow Ar{-}CH_3 + IRh(PPh_3)_3 \qquad (2)$$

observed a similar cross-coupling reaction upon thermolysis of an alkenylmethylrhodium(III) complex (eq. 3) [12]. While the rhodium in these reactions cannot be used catalytically, it can in theory be recycled quite easily. We reasoned that



(3)

similar organomethylrhodium(III) complexes could be generated via transmetallation between organomercurials and readily available diiodomethylbis(triphenylphosphine)rhodium(III) (I) (eq. 4). Subsequent reductive elimination should

$$ClRh(PPh_3)_3 \xrightarrow{CH_3I} \underset{(I)}{CH_3RhI_2(PPh_3)_2} \xrightarrow{RHgCl} CH_3Rh(R)I(PPh_3)_2 \qquad (4)$$

afford the desired cross-coupled product and regenerate a rhodium(I) complex theoretically capable of reacting further with methyl iodide to provide a means of catalytically cross-coupling alkyl halides and organomercurials (eq. 5). At this time we wish to report the successful methylation of organomercurials via organorhodium intermediates.

$$CH_3Rh(R)I(PPh_3)_2 \rightarrow R{-}CH_3 + IRh(PPh_3)_2 \qquad (5)$$

Results and discussion

Methylation of alkenyl-, alkynyl- and alkylmercurials

Before examining the catalytic cross-coupling of organomercurials and alkyl halides, we elected to study the stoichiometric cross-coupling of organomercurials and an isolable organorhodium(III) complex in the hope of optimizing reaction conditions for cross-coupling. The readily available, easily isolable methylrho-

dium(III) complex I, prepared by reacting methyl iodide and Wilkinson's catalyst [13], was chosen for initial studies (eq. 6). This complex was originally designated as $CH_3RhCl(PPh_3)_2 \cdot CH_3I$ [13], but a subsequent crystal structure determination indicated that the compound was more correctly formulated as I

$$CH_3I + ClRh(PPh_3)_3 \rightarrow CH_3RhI_2(PPh_3)_2 \quad (6)$$

(I)

[14]. Initial attempts to prepare I in situ in either methylene chloride or hexamethylphosphoramide (HMPA) and subsequently to cross-couple it with styrylmercuric chloride afforded only small amounts of propenylbenzene in HMPA and none in methylene chloride. Since the methylrhodium(III) intermediate in these in situ preparations never developed its characteristic green color, isolated and purified I was used in subsequent investigations. The optimal reaction conditions for the stoichiometric cross-coupling of I and styrylmercuric chloride were then established (eq. 7). The results are summarized in Table 1. The

$$C_6H_5CH{=}CHHgCl + I \rightarrow C_6H_5CH{=}CHCH_3 \quad (7)$$

optimum conditions include the addition of excess lithium chloride, HMPA as the solvent, and a reaction temperature of ~70°C for 24 h. In the absence of I, styrylmercuric chloride and methyl iodide do not form propenylbenzene.

The generality of this cross-coupling reaction was then examined on a variety of alkenyl- and alkynylmercurials (Table 2). All yields were determined by gas liquid chromatographic analysis due to the expense of running rhodium reactions on a preparative scale. This prevented a determination of the stereochemistry of these reactions since the gas chromatographic equipment available at the time of these studies was unable to separate the *cis* and *trans* isomers. One further complication only realized much later was that alkenylmercurial reactions worked up by adding water gave drastically reduced yields. Either acid produced on hydrolysis or the mercury and/or rhodium salts in the presence of water appear to destroy the olefin product. This is apparently not true for alkynes, however, as evidenced by the excellent yield in entry 6. The results reported in Table 2 indicate that a variety of alkenylmercurials undergo methyla-

TABLE 1

METHYLATION OF STYRYLMERCURIC CHLORIDE

$C_6H_5CH{=}CHHgCl + I \xrightarrow[24\ h]{N_2} C_6H_5CH{=}CHCH_3$

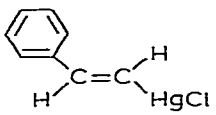
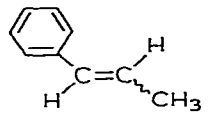
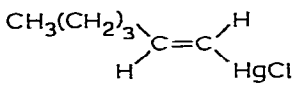
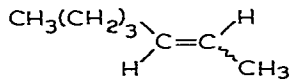
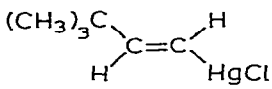
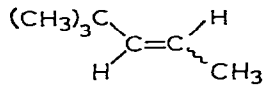
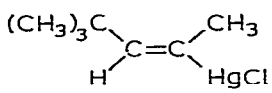
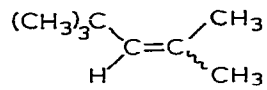
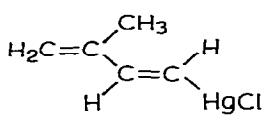
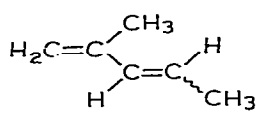
Added reagents	Solvent	Temp. (°C)	Yield [a] (%)
—	HMPA	25	18
10 LiCl			48
		70	95
	THF	−78 to 25	8
		65	16 [b], 11

[a] Yield determined by gas liquid chromatography using an internal standard. [b] Yield after 1 h.

TABLE 2

METHYLATION OF ALKENYL- AND ALKYNYLMERCURIALS

$$RHgCl + I \xrightarrow[HMPA,\ 70^{\circ}C,\ 24\ h]{10\ LiCl} R{-}CH_3$$

Entry	Organomercurial	Product	Yield (%) [a]
1			97 [b]
2			94 [b]
3			92 [b]
4			90, 17 [c]
5			93, 10 [c]
6	$[(CH_3)_3C{-}C{\equiv}C{-}]_2Hg$	$(CH_3)_3C{-}C{\equiv}C{-}CH_3$	99 [c, d]

[a] Yield determined by gas liquid chromatography using an internal standard and appropriate correction factors. [b] Ether added prior to GLC analysis. [c] Pentane and water added prior to GLC analysis. Note: this generally results in sharply reduced yields with alkenylmercurials. [d] Yield based on methylation of both alkynyl groups of the organomercurial.

tion in excellent yield. Dialkynylmercury compounds react with complete methylation of both organic groups.

The attempted methylation of n-decylmercuric chloride afforded only n-decane, 1-decene and other isomeric decenes which were not further identified. The observed products are consistent with formation of a n-decylrhodium species which preferentially undergoes beta hydride elimination to form 1-decene and a rhodium hydride. The rhodium hydride presumably reduces the starting organomercurial to give n-decane and also isomerizes the initially formed 1-decene to generate a mixture of isomeric decenes. The methylation of benzylmercuric chloride and α-chloromercuriacetophenone, both incapable of beta hydride elimination, also failed for unexplained reasons.

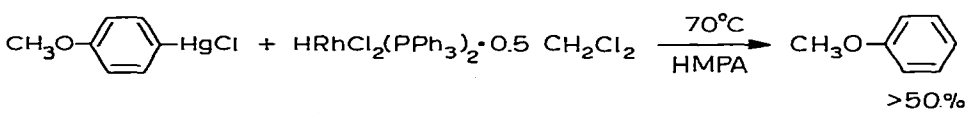
Methylation of arylmercurials

The ready availability of a vast array of functionally substituted, isomerically

pure arylmercurials via direct electrophilic mercuration of simple arenes makes the alkylation of these compounds a potentially valuable synthetic procedure. In examining optimum reaction conditions, HMPA was once again found to be vastly superior to diethyl ether or tetrahydrofuran (THF) as a solvent. However, under the previously established optimum reaction conditions (excess LiCl, HMPA, 70°C, 24 h) arylmercurials were found to react with I to give not only the methyl-substituted arene, but also varying amounts of hydrogen substitution product as well (eq. 8). With *m*-nitrophenylmercuric chloride, *m*-carbo-

$$ArHgCl + I \rightarrow Ar{-}CH_3 + Ar{-}H \qquad (8)$$

methoxyphenylmercuric chloride, 3-chloromercuripyridine and 2-chloromercurinaphthalene the two products were observed in approximately a 4 to 1 ratio, with the methyl product predominating. Substitution of LiI, NaI, NaOAc or $NaOCH_3$ for LiCl resulted in lower yields of methyl arene, although certain other bases appeared to reduce the amount of hydrogen substitution product. Lower reaction temperatures reduced the amount of reduction product, but methylation proved inconveniently slow. It was subsequently observed that substitution of LiCl by excess methyl iodide reduced the amount of hydrogen-substituted arene, and if the HMPA was scrupulously dried this side product was essentially eliminated. Apparently traces of water present in the HMPA or lithium chloride in the presence of I or methyl iodide generate sufficient acid to protonate the arylmercurial. The production of an acid was crudely verified by pH measurements. The pH of a 50/50 HMPA/H_2O mixture is 8.2, while prior addition of methyl iodide to the HMPA resulted in a solution of pH 2.2. HMPA and methyl iodide were found to react at 70°C to precipitate tetramethylammonium iodide. Finally, the addition of D_2O to a solution containing *p*-anisylmercuric chloride, methyl iodide and HMPA gave a 74% yield of anisole which was highly (~88%) deuterated. While it is reasonable that the hydrogen substitution product can arise by simple protonolysis of the arylmercurial, a well known reaction of arylmercurials and one verified by us with *p*-anisylmercuric chloride and HI in HMPA, it is also possible that the acid generated is undergoing oxidative addition to a rhodium(I) species to give a rhodium(III) hydride capable of reducing the arylmercurial. This possibility has been confirmed on a model system (eq. 9).



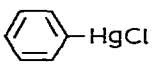
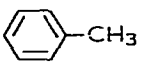
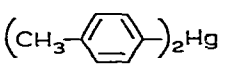
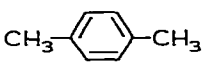
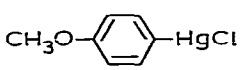
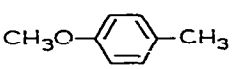
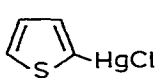
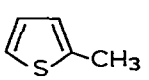
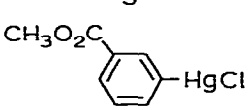
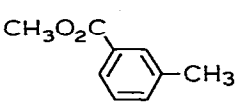
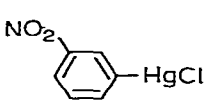
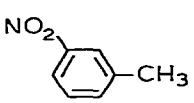
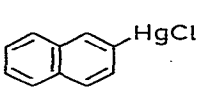
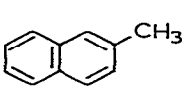
(9)

By using freshly distilled HMPA prior to each reaction and substituting methyl iodide for LiCl, one can obtain excellent yields of methyl arenes containing only very minor amounts of hydrogen-substituted product (Table 3). The reaction appears general for a wide variety of substituted arenes, including those too reactive for typical Friedel-Crafts alkylation, such as thiophene, or those too deactivated, such as the *m*-nitro- and *m*-carboxymethoxy-substituted arenes. The reaction appears limited only by the conditions required to effect the reaction. For example, no 3-methylpyridine was observed in the methylation of 3-chloromercuripyridine, possibly due to methylation of the product by the excess methyl iodide present in the reaction mixture. *p*-Chloromercuri-

TABLE 3

METHYLATION OF ARYLMERCURIALS

$$ArHgCl + I \xrightarrow[HMPA,\ 70°C,\ 24\ h]{xs\ CH_3I} Ar{-}CH_3$$

Arylmercurial	Product	Yield (%) [a]
		97 (–[b])
		95 (4)[c]
		97 (3)
		99 (<2)
		91 (2)
		82 (6) 75 (4) 69 (2) 66 (3)
		51 (<2)[d]

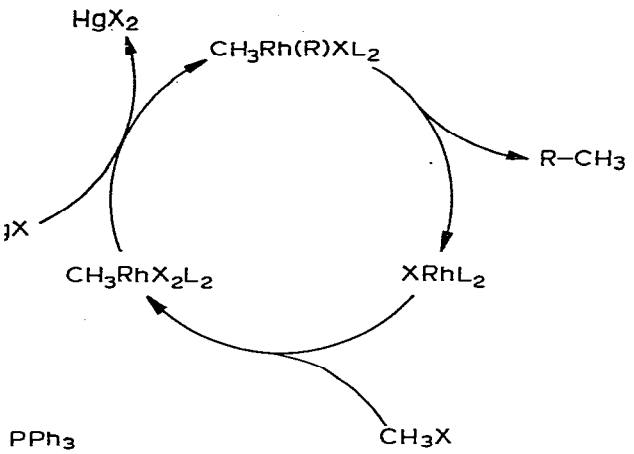
[a] Yield determined by gas liquid chromatography using an internal standard and appropriate correction factors. Yield of hydrogen substitution product in parentheses. [b] Yield not determined. [c] Yield based upon alkylation of both aryl groups of the arylmercurial. [d] Low yield due to extraction difficulties.

phenol also failed to undergo methylation. It is not clear if this is due to the acidity of the phenol, the fact that phenols form complexes with HMPA, or some other reason. An hydroxyl group per se does not interfere in the reaction since phenylmercuric chloride can be methylated by I in the presence of ethylene glycol. Other than these experimental difficulties, the methylation of arylmercurials appears quite general.

Catalytic methylation of organomercurials

Since the rhodium(I) complex presumably formed upon reductive coupling of the intermediate organomethylrhodium(III) complex (eq. 5) should undergo oxidative addition in the presence of methyl iodide to regenerate a methylrhodium(III) complex, these methylation reactions should in theory be catalyzed by either rhodium(I) or rhodium(III) complexes (Scheme 1). The successful catalytic methylation of organomercurials depends ultimately on three specific

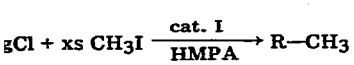
IEME 1

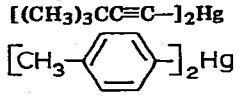
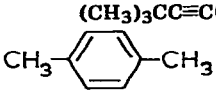


ction requirements. First, methyl iodide should be the only species to oxida-ely add to the rhodium(I) species. Second, the organomercurial should ticipate by transmetallation only and, third, reductive elimination of the thyl product from the intermediate derived from the two previous reactions uld be facile. While our stoichiometric cross-coupling reactions have ablished the validity of the third point, the first two requirements present ious difficulties. In our earlier work we have reported that both rhodium(I) d (III) salts catalyze the dimerization of alkenyl- and arylmercurials, presum-y through oxidative addition of the organomercurials to rhodium(I) species . Others have suggested similar reactions [15—17]. In several instances, npounds containing a rhodium(III)—mercury bond have actually been lated and characterized [18—21]. The question then remained as to whether methyl iodide would compete successfully for the rhodium(I) intermediate

BLE 4

TALYTIC METHYLATION OF ORGANOMERCURIALS



alyst (I)	Organomercurial	Product	Yield (%) [a]	Catalyst turnover
	$C_6H_5CH{=}CHHgCl$	$C_6H_5CH{=}CHCH_3$	19	10
	$[(CH_3)_3CC{\equiv}C{-}]_2Hg$	$(CH_3)_3CC{\equiv}CCH_3$	58, 65 [c]	30
			18, 19, 22 [d]	2
			39 [e]	2

ield determined by gas liquid chromatography using an internal standard and appropriate correction ors. [b] Excess LiCl added. [c] Yield based on methylation of both alkynyl groups of the dialkynyl-curial. [d] Toluene formed in 8% yield. [e] Toluene formed in 11% yield.

or substantial dimerization of the organomercurial would result.

Our attempts to catalytically methylate a variety of organomercurials are summarized in Table 4. While the reaction is catalytic in rhodium, as predicted, the overall yield of methyl product and the catalyst turnover is low when alkenyl- and arylmercurials are employed. In the reaction of styrylmercuric chloride the major product formed is 1,4-diphenyl-1,3-butadiene. Propenylbenzene is formed in only 19% yield. It is noteworthy, however, that this reaction was analyzed after an aqueous work-up, which as noted earlier tends to markedly lower the yield of olefin. To evaluate the catalytic coupling by the turnover number for methylation is really not accurate, since the rhodium species present remains catalytically active. Unfortunately, oxidative addition of the alkenylmercurial which produces the symmetrical diene [9] competes with oxidative addition of methyl iodide which affords the methyl olefin. Thus, this methylation fails catalytically due to a side reaction consuming one of the reactants, and not because the catalyst is ineffective. With the dialkynylmercurial the yield of methyl alkyne based on organomercurial, and the catalyst turnover number are noticeably higher, high enough that the reaction begins to be synthetically significant. The enhanced methyl—alkynyl coupling is apparently due primarily to the alkynyl moiety and not the fact that we are now dealing with a diorganomercurial as opposed to an organomercuric chloride, since another diorganomercurial, di-*p*-tolylmercury, gives a disappointingly low yield of *p*-xylene. Biaryl is also evident in this reaction. While the results on the rhodium-catalyzed cross-coupling of methyl iodide and organomercurials are certainly disappointing, it seems likely that other catalysts, or combinations of organomercurial and organic halide may prove more effective. Indeed, we have recently observed that arylmercurials and alkenyl halides can be efficiently cross-coupled using a rhodium catalyst. We hope to report on this reaction before long.

Conclusion

The methylrhodium compound I stoichiometrically reacts with alkenyl- and alkynylmercurials forming methyl-substituted alkenes and alkynes in high yield in HMPA with added lithium chloride at 70° C. Methyl-substituted arenes are similarly formed from I and arylmercurials in HMPA with added methyl iodide at 70° C. Although this methylation sequence is catalytic with respect to rhodium, rhodium-catalyzed diene and biaryl formation interfers with these catalytic cross-coupling reactions. It is noteworthy, however, that methyl—alkynyl cross-coupling is synthetically significant using only catalytic amounts of I. Although the immediate synthetic importance of this catalytic methylation of organomercurials is limited, the methylation of organomercurials via a methylrhodium(III) compound has been demonstrated. Further modification in either the organomercurial or the organorhodium compound may improve the synthetic feasibility of these carbon—carbon bond-forming reactions.

Experimental

Reagents

All chemicals were used directly as obtained commercially unless otherwise

indicated. Ether and THF were distilled from lithium aluminum hydride. HMPA was distilled from calcium hydride at reduced pressure. Pentane was stirred over fuming sulfuric acid, washed with water, dried over anhydrous $MgSO_4$ and distilled from calcium hydride.

The alkenylmercurials were prepared by a hydroboration-mercuration sequence and have been previously described [22—24]. Bis(3,3-dimethyl-1-butynyl)mercury was prepared as described in the literature [25]. Phenylmercuric chloride (Aldrich), di-*p*-tolylmercury and *p*-chloromercuriphenol (Eastman) were used directly as obtained commercially. *p*-Anisylmercuric chloride [26], 2-chloromercurithiophene [27], *m*-carbomethoxyphenylmercuric chloride [28], *m*-nitrophenylmercuric chloride [29], 2-chloromercurinaphthalene [29] and 3-chloromercuripyridine [30] were prepared using literature procedures.

$ClRh(PPh_3)_3$ [31] was prepared from $RhCl_3 \cdot 3\ H_2O$, and $CH_3RhI_2(PPh_3)_2$ [13,14] and $HRhCl_2(PPh_3)_2 \cdot 0.5\ CH_2Cl_2$ [32] were prepared from $ClRh(PPh_3)_3$ according to the literature. Neither $CH_3RhI_2(PPh_3)_2$ nor $HRhCl_2(PPh_3)_2 \cdot 0.5\ CH_2Cl_2$ were recrystallized. These adducts are fairly air-stable as solids, but are rapidly air-oxidized in solution.

Equipment

All gas chromatography was carried out on Varian Model 920 or Series 2700 Aerograph instruments with thermal conductivity detectors. The retention times of authentic samples of products on various columns under a variety of column conditions were used to identify products. In addition, a Finnegan 4023 gas chromatograph-mass spectrometer was employed to verify the identity of products. All gas chromatography yields were determined by using hydrocarbon internal standards and appropriate correction factors.

Methylation of alkenyl-, alkynyl- and alkylmercurials

The following procedure for the formation of propenylbenzene from *trans*-styrylmercuric chloride and I is representative of the procedure used for the methylation of all alkenyl-, alkynyl- and alkylmercurials mentioned in the text and summarized in Table 2. With appropriate changes in solvent and temperature the results of Table 1 were obtained similarly.

A 47.3 mg (0.05 mmol) sample of I, 17.0 mg (0.05 mmol) *trans*-styrylmercuric chloride and at least 21.3 mg (0.5 mmol) anhydrous lithium chloride were weighed into a 5 ml round-bottom flask equipped with a septum inlet, a condenser with a gas inlet tube and a magnetic stirring bar. After flushing with nitrogen, 8.5 mg (0.05 mmol) n-dodecane and 0.5 ml HMPA were added by syringe. The reaction was allowed to stir in a 70°C oil bath. After 24 h, 0.5 ml ether was added rinsing down the interior of the condenser and the reaction mixture was analyzed by gas chromatography. Other methyl olefins and alkynes were synthesized analogously using other organomercurials, internal standards and GLC analysis conditions.

Reaction of p-anisylmercuric chloride, methyl iodide and HMPA after initial deuterium oxide addition

A 171.6 mg (0.5 mmol) sample of *p*-anisylmercuric chloride was weighed

into a 25 ml round-bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, 5 ml HMPA and 1 ml methyl iodide were added by syringe. After stirring 6 h at 70°C, the reaction mixture was poured into pentane and water. The pentane layer was separated and the water layer re-extracted with pentane. The pentane layers were combined, dried over anhydrous Na_2SO_4 and concentrated, and the arene was isolated by preparative gas chromatography and submitted to mass spectral analysis.

Methylation of arylmercurials

The following procedure is representative of that used to obtain the results reported in Table 3. 47.3 mg of I (0.05 mmol) and 17.2 mg (0.05 mmol) *p*-anisylmercuric chloride were weighed into a 5 ml round-bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing with nitrogen, 7.8 mg (0.05 mmol) n-undecane, 0.1 ml (excess) methyl iodide and 0.5 ml HMPA were added by syringe. After stirring for 24 h at 70°C, 0.5 ml benzene and 0.5 ml water were added and the benzene layer analyzed by gas chromatography. Other arylmercurials were treated similarly and analyzed using appropriate internal standards and GLC conditions.

Catalytic methylation of organomercurials

The following three procedures were employed in obtaining the results reported in Table 4.

A 17.0 mg (0.05 mmol) sample of *trans*-styrylmercuric chloride, 21.3 mg (0.5 mmol) lithium chloride and 1.0 mg (0.001 mmol) of I were weighed into a 5 ml round-bottom flask equipped with a septum inlet, a condenser attached to a gas inlet tube and a magnetic stirring bar. After flushing with nitrogen, 8.5 mg (0.05 mmol) n-dodecane, 1.0 ml HMPA and 0.1 ml (excess) methyl iodide were added by syringe. The extra HMPA was required to prevent the solution from becoming too viscous and impeding stirring. The solution was stirred under nitrogen in a 70°C oil bath. After 24 h, 0.5 to 1.0 ml water and 0.5 ml benzene were added and the organic layer subjected to gas chromatographic analysis.

A 9.1 mg (0.025 mmol) sample of bis(3,3-dimethyl-1-butynyl)mercury and 1.0 mg (0.001 mmol) of I were weighed into a 5 ml round-bottom flask equipped with a septum inlet, a condenser attached to a gas inlet tube and a magnetic stirring bar. 2.13 mg (0.5 mmol) lithium chloride was added. After flushing with nitrogen, 5.0 mg (0.05 mmol) n-heptane, 1.0 ml HMPA and 1 ml methyl iodide were added by syringe. The solution was stirred under nitrogen in a 70°C oil bath. After 24 h, 0.5 to 1.0 ml water and 0.5 ml pentane were added and the pentane layer subjected to GLC analysis.

The following reaction was performed using the previously described measures to exclude moisture. A 4.7 or 9.4 mg (0.005 or 0.01 mmol) sample of I and 7.3 mg (0.025 mmol) di-*p*-tolylmercury were weighed into a 5 ml round-bottom flask equipped with a septum inlet, condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing with nitrogen 6.4 mg (0.05 mmol) n-nonane, 0.1 ml (excess) methyl iodide and 0.5 ml HMPA were added by syringe. After stirring at 70°C for 24 h, 0.5 ml benzene and 0.5 ml water were added and the benzene layer analyzed by gas chromatography.

Acknowledgement

The authors gratefully acknowledge the National Science Foundation for funds used to purchase the Finnegan 4023 gas chromatograph-mass spectrometer used in this work and Johnson Mathey Inc. for generous loans of rhodium trichloride. S.S. Hershberger wishes to thank the Department of Health. Education and Welfare and Iowa State University for a graduate fellowship. We also gratefully acknowledge Mr. D.R. Leach who ran several final experiments.

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