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Carbonylation of Organomercury Compounds: A General Synthesis of Carboxylic Acids and Esters[1]

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Organomercury compounds react with carbon monoxide in aqueous or alcoholic media to give good yields of carboxylic acids or esters. The carboxyl group is introduced selectively at the site of the carbon–mercury bond. Homogeneous group 9 and 10 metal complexes catalyze this carbonylation reaction, which yields mercury(0) as the inorganic byproduct. The mercuration–carbonylation sequence represents a general synthesis of carboxylic acids and esters.

The simple preparation of organomercury compounds by the solvomercuration of olefins,[3-7] mercuration of aromatics,[3,8] and mercury–metal exchange reactions[9,10] makes organomercurials attractive for the selective functionalization of hydrocarbons.[11] In a previous paper two new reactions of the carbon–mercury bond catalyzed by group 9 and 10[31] metal complexes were introduced: hydrogenation and carbonylation.[12] The latter represents a new, general synthesis of carboxylic acids and esters. This paper presents the details of this chemistry and highlights its synthetic utility.

Direct carbonylation of organomercurials at high temperatures and pressures provides generally low yields of mixtures of carboxylic acids, esters, keto acids, alcohols, and dimerization products.[13] Palladium(II) salts promote the carbonylation of organomercurials to carboxylic acids/esters admixed with carbonyl compounds and dimers.[14] The reaction is stoichiometric in palladium but becomes catalytic in palladium if a stoichiometric quantity of an oxidant (copper(II) chloride) is present to regenerate the active palladium salt.

The carbonylation reaction discussed here is generally catalyzed by a group 9 and 10 metal complex, proceeds rapidly at mild conditions, and gives moderate to excellent yields of carboxylated product. Metallic mercury released by the reaction collects as a shiny pool easily separated from the product. Direct air oxidation in carboxylic acid media of the mercury regenerates a mercury(II) carboxylate suitable for the synthesis of organomercurials.

Table I. Carbonylation of Organomercurials as a General Reaction[a]

$$\mathrm{RHgX} + \mathrm{CO} + \mathrm{R'OH} \xrightarrow{\text{catalyst}} \mathrm{RCOOR'} + \mathrm{Hg} + \mathrm{HX}$$

R	R'OH	catalysts
aryl	water	L_2PdCl_2
alkyl	alcohols	L_4Pd
allyl	phenols	Pd + L
vinyl	polyols	L_3RhCl
β-Oxyalkyl	acids	L_4Pt

[a] L = Triphenylphosphine. Conditions: 50–150 °C; 1–50 atm; 0.5–24 h. RHgX/catalyst mole ratio: 100–250. Catalyst efficiency: 4700–5000 g of product/g of metal/h. Insensitive to H_2, CO_2, O_2, and H_2O. Hg recovered as Hg pool.

General Scope of the Reaction. The overall scope of this chemistry is summarized by Table I from which it is apparent that the reaction is capable of broad application in terms of its components, whose combination may be varied as described. Most organomercurials convert in high yield at <100 °C and <100 psig in 30–60 min; in the case of refractory organomercurials, extended reaction periods are preferred over more forcing conditions, especially temperature, to maintain selectivity. While the mercurial/catalyst mole ratio normally fell in the 100–250 range, reactions have been performed using palladium-based catalysts where this value ranged from 5000–7000. Consistent with these values is the high catalyst efficiency. Operability over the range of 0.1–100 g of starting organomercurial has been demonstrated. In one case, kilogram lots of pseudocumylmercuric acetate were converted in >80% yield to methyl durylate, indicating the ease of reaction scaleup. The reaction is insensitive to the presence of hydrogen, oxygen, carbon dioxide, or water in the carbon monoxide. While not investigated here, poisoning of the catalyst by sulfur types, especially hydrogen sulfide, would dictate the use of sulfur-free gas streams. With this exception the use of high purity carbon monoxide is not required.

In the succeeding sections the influence of the following variables on this reaction will be reviewed: the organomercurial anion; the catalyst; the organic radical; the alcohol/solvent system. These topics focus initially only on the conversion of the organomercurials to ester products. The results show that the yields of ester are not quantitative. Both hydrocarbon byproduct and free carboxylic acid are sometimes present in appreciable yields; these aspects of the chemistry will be addressed subsequently. In addition, conversion of a mercurial was not complete

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Table II. Carbonylation Reactions Insensitive to Mercury Anion

organomercurial	catalyst	*T*, °C	*P*, psig	*t*, h	methyl ester (yield, %)
n-hexylmercuric acetate	*a*	65	100	6	heptanoate (63)
n-hexylmercuric bromide	*a*	75	70	72	heptanoate (72)
(2-methoxy-2-phenylethyl)mercuric iodide	*a*	65	50	100	3-methoxy-3-phenylpropanate (44)
phenylmercuric trifluoroacetate	*b*	95	70	1	benzoate (69)
phenylmercuric nitrate	*b*	75	100	0.5	benzoate (56)
phenylmercuric chloride	*b*	75	100	0.5	benzoate (26)
mesitylmercuric pivalate	*b*	75	100	5	isodurylate (20)

[a] Tris(triphenylphosphine)chlororhodium(I). [b] Bis(triphenylphosphine)dichloropalladium(II).

Table III. Group 9 and 10 Complex Catalyzed Carbonylations of Phenylmercuric Trifluoroacetate to Methyl Benzoate[a]

catalyst	yield, wt %
disodium tetrachloropalladium(IV)	7
palladium(II) chloride	24
palladium(II) chloride + triphenylphosphine	72
palladium(II) chloride + bis(1,2-diphenylphosphino)ethane	21
palladium(II) chloride + triisopropylphosphite	60
bis(tri-*n*-butylphosphine)dichloropalladium(II)	69
bis(triphenylphosphine)dichloropalladium(II)	69
bis(triphenylphosphine)dichloroplatinum(II)	35
bis(triphenylphosphine)chlororhodium(I)	56
tetrakis(triphenylphosphine)palladium(0)	50
tetrakis(triphenylphosphine)platinum(0)	34

[a] Conditions: 75–150 °C; 100–300 psig; 0.4–6 h; PhHgTFAc/catalyst = 50–100.

in every case since the scoping phase of this study did not define optimal reaction conditions for each substrate. Where reactions have been analyzed in detail, conversion of the organomercurial was virtually quantitative with ester, acid, and hydrocarbon accounting for all of the reacted mercurial.

The Organomercurial Anion. The majority of the organomercurials employed in this study were synthesized by using mercury(II) acetate or trifluoroacetate, whose reactivity afforded high yields of mono- and dimercurated products simply and selectively. Limited experiments examined the influence of other mercury anions, and the results are summarized in Table II. In general, all organomercurials convert. The acetates and nitrate are most reactive followed by the halides. The pivalate is the most refractory in this series, but its reactivity is influenced by steric factors arising from the mesityl radical and the bulky structure of the anion itself. On balance, Table II illustrates the general applicability of the carbonylation reaction with various anions and supports the preferential use of the acetate or trifluoroacetate series.

The Catalyst. Tables I and II illustrate the phosphine complexes of palladium and rhodium as catalysts for this reaction. However, other group 9 and 10 metal complexes are effective, and these are compared in Table III. The catalysts may either be preformed or generated in situ through the combination of the metal salt with the appropriate quantity of phosphorus ligand. The catalysis afforded by the use of a group 9 and 10 metal complex is evident from the tripling of yield when triphenylphosphine was added to palladium(II) chloride. The choice of phosphorus ligand appears arbitrary although the bidentate phosphinoethane is adverse. Little difference is noted between reactions catalyzed by Pd(II) and Pd(0) complexes; this fact indicates that the low valence state of the metal is the active catalyst with Pd(II) being reduced by carbon monoxide to Pd(0) in these reactions. The Pt complexes also reveal an insensitivity to Pt oxidation state; however, the Pt complexes exhibit poorer ester yields relative to their Pd and Rh analogues. These distinctions will be further considered in the subsequent discussion of the reaction mechanism.

The Organic Radical. The variation in the structure and nature of the organic radical bonded to mercury is broad. Alkyl, vinyl, allyl (Table IV), and aryl (Table V) mercurials all convert to methyl esters when carbonylated in methanol in the presence of a catalyst. Standard reaction conditions were employed, and the yield reported for a specific organomercurial does not represent the maximum achievable at conditions optimal for that substrate. In all cases the introduction of the carbomethoxy group occurred at the site of the carbon–mercury bond to yield a specific product. No isomerization or rearrangement reactions were detected. Table IV includes the conversion of 2-substituted alkylmercurials prepared by solvomercuration in methanol and acetic acid. Yields tend to be diminished in these cases due to reversible dissociation of the substrate under reaction conditions. Since alkyl, vinyl, and allyl mercurials may not be synthesized directly from hydrocarbons, the mercuration/carbonylation sequence offers only one advantage over the carboxylation of Grignard and lithium compounds: the presence of functional groups normally reactive toward these metals.

The synthetic potential of this reaction is most evident in the carbonylation of aryl mercurials (Table V). Direct synthesis of the arylmercury salts by mercuration followed by carbonylation is an effective route to methyl benzoates or phthalates in the case of dimercurated adducts. Selectivities in the aromatic series are established in the

Table IV. Conversion of Alkyl, Vinyl, and Allyl Mercurials to Methyl Esters by Carbonylation in Methanol

organomercurial	conditions	ester (yield, %)
ethylmercuric acetate	*a*	methyl propionate (66)
hexylmercuric acetate	*a*	methyl heptanoate (63)
n-dodecylmercuric acetate	*a*	methyl tridecanoate (48)
1-(acetoxymercurio)-2-methoxyhexane	*a*	methyl β-methoxyheptanoate (28)
1-(acetoxymercurio)-2-methoxycyclohexane	*a*	1-carbomethoxy-2-methoxycyclohexane (21)
1-(acetoxymercurio)-2-acetoxyethane	*a*	methyl β-acetoxypropionate (31)
(2-Methoxy-2-phenylethyl)mercuric iodide	*a*	methyl 3-methoxy-3-phenylpropionate (44)
vinylmercuric acetate	*b*	methyl acrylate (74)
isopropenylmercuric acetate	*b*	methyl methacrylate (31)
(2,2-diphenylvinyl)mercuric acetate	*b*	methyl 2,2-diphenylacrylate (36)
allylmercuric acetate	*a*	methyl 3-butenoate (35)

[a] 65–100 °C; 100–500 psig; 0.5–40 h; L_3RhCl; RHgOAc/Rh = 100–250. [b] 75–100 °C; 50–100 psig; 1–3 h; L_2PdCl_2; RHgOAc/Pd = 100–200.

Table V. Conversion of Aromatics to Methyl Esters by the Mercuration/Carbonylation Sequence[a]

			isomer distribution, % (locant)		
aromatic	X	yield, %	ortho	meta	para
		Monomercuration			
benzene	OAc	83			
toluene	TFA	88	47	25	28
ethylbenzene	TFA	89	35	8	57
tert-butylbenzene	TFA	75	0	28	72
o-xylene	OAc	85	15 (3)	0	85 (4)
m-xylene	OAc	64	80 (4)	0	20 (5)
p-xylene	OAc	84			
mesitylene	TFA	30			
pseudocumene	OAc	69	92% 2,4,5-, 6% 2,3,5-, 2% 2,3,6-trimethyl		
biphenyl	TFA	60			100 (4)
naphthalene	TFA	60	30 (α)	70 (β)	
chlorobenzene	TFA	75	14	0	86
anisole	OAc	70	16	0	84
anisole	TFA	79	86	0	14
methyl benzoate	TFA	68	70	30	0
dimethyl terephthalate	TFA	30	100 (3)	0	0
aniline	OAc	10	2	0	98
N,N-dimethylaniline	OAc	47	0	0	>98
acetanilide	OAc	78	0	0	>98
		Dimercuration			
biphenyl	TFA	67	0	0	100 (4,4′)
o-xylene	TFA	67	dimethyl 4,5-dimethylphthalate, 94		
m-xylene	TFA	30	dimethyl 4,6-dimethylisophthalate, 72		
p-xylene	TFA	33	dimethyl 2,5-dimethylterephthalate, 30		

[a] Conditions: 75–100 °C; 50–100 psig; 1–3 h; L_2PdCl_2; ArHgX/Pd = 100–200.

mercuration reaction and are reflected in the isomer distributions listed in Table V. The isomer distributions for toluene and ethyl benzene reflect mercuration at equilibrating conditions; mercuration at brief reaction periods gives the following isomer distribution: 22% ortho, 10% meta, and 68% para.[15] Not surprisingly, *tert*-butyl benzene yields no ortho ester due to the steric influence of the *tert*-butyl radical on both the mercuration and carbonylation reactions; steric factors are also responsible for the low yield of ester from mesitylene. Pseudocumene is converted in good yield and in high selectivity to methyl durylate, whose oxidation leads to pyromellitic acid. Monomercuration and carbonylation of biphenyl gives methyl 4-phenylbenzoate selectively. Dimercuration/carbonylation is equally selective to 4,4′-dicarbomethoxybiphenyl. There exists an interesting reversal in the product selectivities for anisole depending upon the choice of mercurating agent. The high ortho substitution in the trifluoroacetate case is ascribed to the contribution of methoxy oxygen coordination with the more electrophilic $[HgOOCCF_3]^+$ cation. Methyl benzoate, normally a meta director, also experiences a high degree of ortho substitution during mercuration for similar reasons.[16] The trimethyl ester of trimellitic acid arose from the reaction of dimethyl terephthalate; the ester yield was depressed by substantial byproduct formation, but the reaction demonstrates the synthesis of aromatic polycarboxylic acids by this procedure. The synthesis of *p*-aminobenzoic acid from aniline was of special interest due to the utility of this amino acid as a monomer and in pharmaceuticals. The required para-mercurated aniline separates quantitatively from aqueous mercury(II) acetate. Carbonylation in methanol reproducibly gave <20% methyl *p*-aminobenzoate and 40–50% aniline with the balance being uncharacterized polymeric amides. Carbonylation of the mercurials derived from *N,N*-dimethylaniline and acetanilide proceeded normally, indicating that blocking the reactive amino group inhibits those side reactions occurring in the case of aniline.

Table VI. Solvent-Determined Selectivity to Ester and Carboxylic Acid during Carbonylation[a]

	yield,[b] %	
	PhCOOR	PhCOOH
alcohol		
methanol	83	5
methanol[c]	38	50
ethanol	84	
isopropyl alcohol	45	24
sec-butyl alcohol	41	25
isobutyl alcohol	70	20
tert-butyl alcohol	2	84
1,2-ethanediol	70	
70% phenol–30% THF	72	
1-octanol	99	
allyl alcohol	55	
acid		
acetic		53
trifluoroacetic		35
aqueous		
20% water–80% THF		58
20% water–80% acetone		61

[a] Conditions: phenylmercuric acetate; 90–100 °C; 60–100 psig; 1 h; L_2PdCl_2. [b] Based on phenylmercuric acetate. [c] Tris(triphenylphosphine)chlororhodium(I).

Dimercuration and carbonylation of the isomeric xylenes yielded the various phthalate esters shown in Table V. Selectivity to the dimethyl phthalates declined due to the increasing formation of free xylene and monoester, which were isolated by fractionation. Analysis of the dimercurials confirmed that the monoester was produced by hydrogenolysis of the dimercurial during carbonylation and not from any monomercurated impurity present after the mercuration.

The Solvent. The effects of a variety of solvents were determined by the carbonylation of phenylmercuric acetate or trifluoroacetate catalyzed by bis(triphenylphosphine)dichloropalladium(II). Table VI presents the results of these reactions. In anhydrous alcohols both ester and free

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Table VII. Hydrocarbon Yield as a Function of Steric and Electronic Factors[a]

arylmercuric acetate	hydrocarbon yield, %
phenyl	5
pseudocumyl (2,4,5-trimethyl)	10
mesityl (2,4,6-trimethyl)	40
phenyl	5
chlorophenyl	23
methoxyphenyl	29
4-aminophenyl	40
4-(*N*,*N*-dimethylamino)phenyl	45
4-(acetamido)phenyl	<22
pseudocumyl acetate	10
pseudocumyl trifluoroacetate	20

[a] Conditions: methanol; 70–100 °C; 60–100 psig; L_2PdCl_2.

carboxylic acid are observed as products of the carbonylation reaction.[17] The selectivity to these two carboxylated products was a function of the alcohol and the catalyst used. The rhodium catalyst yielded more carboxylic acid than the palladium catalyst as the comparative reactions in methanol illustrate. Table VI also demonstrates the trend toward more free acid for the C_1–C_4 alcohols in the sequence tertiary > secondary > primary. These results are rationalized by the intermediate formation of a mixed acid anhydride during the reaction, which will be discussed subsequently in the consideration of the reaction mechanism. Complete product selectivities were not determined for the remaining alcohols in Table VI, and these entries serve primarily to demonstrate the scope of this reaction variable.

In carboxylic acid and aqueous media, benzoic acid is the sole carbonylation product consistent with expectations. Yields in these cases tend to be reduced by the formation of free hydrocarbon byproduct.

Reaction Mechanisms. This section will address the various mechanisms giving rise to the three principal products observed in the carbonylation of organomercurials.

In nearly all carbonylations the formation of a hydrocarbon byproduct occurs which formally results from the replacement of the C–Hg bond with a C–H bond. This hydrogenolysis reaction can take place in the absence of a catalyst but fails to occur in the absence of carbon monoxide. This side reaction is rationalized by eq 1–4. All

$$2RHgX \rightarrow RHgR + HgX_2 \quad (1)$$

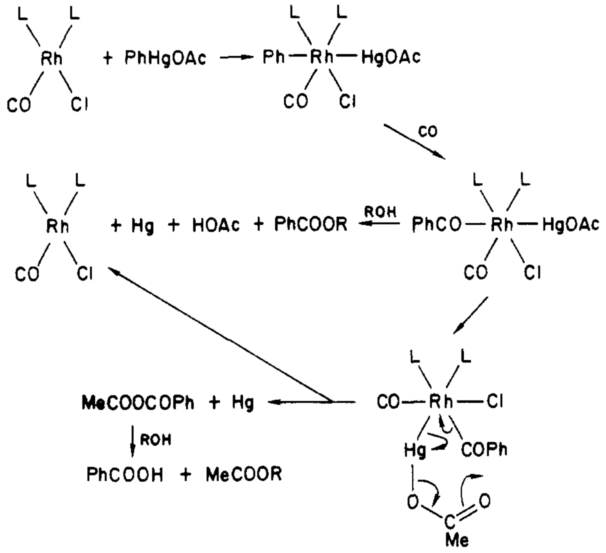
$$HgX_2 + CO + 2CH_3OH \rightarrow (CH_3O)_2CO + Hg + 2\,HX \quad (2)$$

$$RHgR + HX \rightarrow RH + RHgX \quad (3)$$

$$RHgX + HX \rightarrow RH + HgX_2 \quad (4)$$

four reactions are well-known in mercury chemistry[18,19] but have not been reported in combination previously. The ratio of hydrocarbon to carbonylated products tends to increase with (1) increasing steric hindrance around the C–Hg bond, (2) increasing electron donor ability of the aromatic substituents, and (3) decreasing basicity of the mercury anion. These relationships are illustrated in Table VII and help account for low yields of carbonylated products in those cases where the C–Hg bond is subject to steric hindrance and the mercury anion is trifluoroacetate.

Scheme I



The reaction paths leading to the formation of ester and acid products are depicted in Scheme I. The initial step is the oxidative addition of the organomercurial to the low-valent group 9 or 10 metal complex; such an addition to generate a Rh–Hg bimetallic complex containing a C–Rh bond has been described.[20] Insertion of carbon monoxide and alcoholysis of the phenylacyl–rhodium complex leads directly to ester, metallic mercury, and the regenerated catalyst.[21] Internal acetate transfer, or the attack of external acetate on the phenacyl–Rh bond, releases the mixed methyl phenyl anhydride, which is known to react with alcohols to yield principally benzoic acid and the corresponding methyl acetate.[22] Competition between alcohol and acetate for the acyl–metal species accounts for the different ester/acid selectivities seen in Table VI. As the alcohol becomes more sterically encumbered, acetate attack dominates, leading to increasingly higher yields of free acid. Relative stability of the acyl–metal complexes is also a factor in product selectivity since the rhodium complex favors carboxylic acid formation over that of ester. This distinction suggests greater stability for the rhodium adduct,[23] while the more labile palladium complex undergoes facile alcoholysis to produce ester. While not examined in this work, a similar mechanism is suggested to account for the low yields of ester in the case of platinum-based catalysts (Table III). In aqueous media carboxylic acid and hydrocarbon are the only products consistent with these processes.

Mercury Metal Oxidation. If desired, the mercury(0) released in this reaction may be oxidized to mercury(II) carboxylates suitable for the mercuration reaction. While the oxidation of mercury in inorganic acids to prepare inorganic mercury salts was known,[24] the synthesis of mercury(II) carboxylates by oxidation was not. Mercury metal is quantitatively converted to mercury(II) trifluoroacetate in 3 h at room temperature under 60 psig of oxygen by simple agitation in trifluoroacetic acid containing a catalytic quantity of concentrated nitric acid. Nitrate and nitrite salts, or any gaseous nitrogen oxide,

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[17] In no case were ketones observed in these reactions.

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[22] Bailey, P. S.; Chang, Y.-G. *J. Org. Chem.* **1962**, *27*, 1192.

[23] A stable adduct between phenylmercuric acetate and the rhodium catalyst has been isolated and characterized.[12]

[24] Reid, H. S.; Maude, A. H. U.S. Patent 1 721 188, 1929; U.S. Patent 1 808 253, 1931.

may be substituted for the nitric acid; the true oxidizing agent is nitric oxide, which is regenerated by oxidation with oxygen. The procedure may be modified to produce mercury(II) sulfonates.[25]

The extent of mercury oxidation in organic acids is dependent on the choice of acid. In acetic acid the nitric oxide catalyzed reaction requires 65 °C, where it proceeds quantitatively to mercury(I) acetate. Attempts to drive the oxidation to completion at high temperatures approaching 100 °C are frustrated by the reaction of mercury(II) acetate with acetic acid to give a polymeric mercury acetoxy species. However, *the addition of certain cocatalysts, especially palladium(II) salts, silica gel, or activated carbon (Norite A), allows quantitative conversion to mercury(II) acetate at 65 °C.* The role of these agents in promoting the mercury(I) to -(II) oxidation is obscure.

Summary. Good to excellent yields of methyl esters are achieved by the carbonylation of organomercurials in methanol catalyzed by triphenylphosphine complexes of palladium. Ester yields are decreased by hydrogenolysis of the organomercurial to hydrocarbon, a side reaction sensitive to steric and electronic factors. Selectivity to ester is a function of solvent system and catalyst selection; carbonylation to free carboxylic acid is favored by rhodium (and possibly platinum) catalysts and by sterically hindered alcohols. In carboxylic acid and aqueous solvents, carboxylic acids are the exclusive carbonylation products.

Experimental Section

All reagents were purchased from commercial sources and used as received. Organomercury compounds were prepared by published procedures.[3–10] Group 9 and 10 metal complexes were either purchased from commercial suppliers or synthesized by published procedures.[26–28] Reaction products were identified by comparison with authentic compounds. Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. NMR spectra were measured on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Vapor-phase chromatography was performed on a Perkin-Elmer Model 226 capillary gas chromatograph equipped with 300 ft × 0.01 in. DC-550 silicone columns.

Representative experimental procedures are given below. For additional examples of these reactions see ref 25 and 29.

Carbonylation of Ethylmercuric Acetate. Into a 45-mL Parr stainless steel reactor[30] were charged 0.29 g (1 mmol) of ethylmercuric acetate, 0.02 g (0.02 mmol) of tris(triphenylphosphine)chlororhodium(I), 10 mL of methanol, and a small magnetic stirrer. The bomb was closed, purged with carbon monoxide, and pressurized to 500 psig. The bomb was suspended in an oil bath at 100 °C and stirred overnight. The bomb was cooled, and its contents were analyzed. A 66% yield of methyl propionate based on ethylmercuric acetate was recovered along with a 75% yield of metallic mercury. Thiocyanate titration of the reaction mixture accounted for 25% of unreacted ethylmercuric acetate.

Carbonylation of Phenylmercuric Trifluoroacetate. To a 1000-mL Parr Series 4500 pressure reactor[30] were charged 29.2 g (74 mmol) of phenylmercuric trifluoroacetate, 250 mL of methanol, and 0.007 g (0.01 mmol) of bis(triphenylphosphine)dichloropalladium(II). The reactor was pressured to 90 psig with carbon monoxide and stirred at 85–90 °C for 1.5 h. The reaction yielded 68% methyl benzoate and gave a 75% yield of mercury.

Synthesis of Mercury(II) Trifluoroacetate. A 50-mL glass pressure tube was charged with 1.02 g (5 mmol) of mercury, 5 mL of trifluoroacetic acid, and 0.04 g (0.45 mmol) of concentrated nitric acid. The tube was pressurized with oxygen to 60 psig and was then shaken at room temperature for 1 h, during which the pressure decreased to 38 psig. Thiocyanate titration of the solution showed 100% conversion to mercury(II). Removal of the solvent gave a 98% yield of crystalline mercury(II) trifluoroacetate.

Anal. Calcd for $C_4F_6O_4Hg$: C, 11.25; Hg, 47.01. Found: C, 11.87; Hg, 45.90.

The mercury(II) trifluoroacetate was stirred overnight at room temperature with benzene to give a quantitative yield of phenylmercuric trifluoroacetate, which was shown to be identical with an authentic sample.

Synthesis of Mercury(II) Acetate. Into a 50-mL glass pressure tube were charged 20 mL of acetic acid, 1 g (4.8 mmol) of mercury, 0.02 g (0.23 mmol) of concentrated nitric acid, and 0.04 g (0.05 mmol) of bis(triphenylphosphine)dichloropalladium(II). The reaction was pressurized with oxygen to 60 psig and agitated at 65 °C for 24 h. Thiocyanate titration gave a 96% yield of mercury(II) acetate, which was recovered by evaporation of the solvent.

Anal. Calcd for $C_4H_6O_4Hg$: C, 15.07; H, 1.90; Hg, 62.95. Found: C, 15.42; H, 1.82; Hg, 62.73.

The mercury salt was reacted with benzene in acetic acid to give authentic phenylmercuric acetate.

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(30) Parr Instrument Co., Moline, IL.

(31) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Reaction of Nucleophiles with Bridgehead Carbocations Derived from 1-Bromobicyclo[2.2.2]octanes and 1-Bromobicyclo[3.3.1]nonanes

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Both intramolecular and intermolecular reactions of bridgehead carbocations are described. The carbocations are best generated from the corresponding halide with silver triflate. The carbocations reacted effectively with allyltrimethylsilane, ethyl acetoacetate, benzene, and enol silyl ethers. Bridgehead radicals were also examined.

While many synthetic chemists have studied the applications of aliphatic and alicyclic carbocations, the area of bridgehead carbocations has been studied primarily by physical organic chemists.[1]