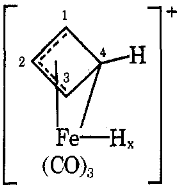
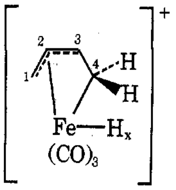
present NMR spectroscopic data are inconsistent with the originally suggested C-protonated cyclobutenyliron tricarbonyl cation (**2**, R = H),[6] although this ion still could be formed under kinetically controlled conditions, but is not the thermodynamically favored species.



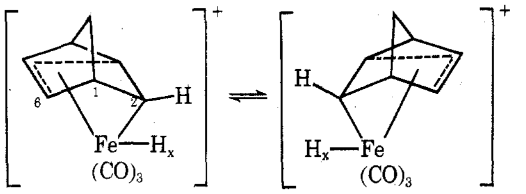
5

$J_{H_4\text{-}Fe\text{-}H_x} = 29.0$ Hz
$J_{^{13}C_4\text{-}Fe\text{-}H_x} = 81.2$ Hz



7

$J_{H_4\text{-}Fe\text{-}H_x} = 22$ Hz
$J_{^{13}C_4\text{-}Fe\text{-}H_x} = 73.7$ Hz



8

$J_{H_{2(6)}\text{-}Fe\text{-}H_x} = 13$ Hz (av)
$J_{^{13}C_{2(6)}\text{-}Fe\text{-}H_x} = 37.8$ Hz (av)

Both experimental data and theoretical calculations have shown the homoaromatic nature of the parent cyclobutenyl cation 4 and its puckered structure.[7] Nonplanar structures are also indicated in a number of cyclobutenylmetal complexes,[9] such as the σ complex of tetramethylcyclobutadiene with aluminum trichloride.[10] Although the present NMR spectra obtained for the protonated (deuterated) cyclobutadieneiron tricarbonyl **5** (**6**) indicate that **5** should possess a plane of symmetry, they do not allow clear differentiation as to whether the ion is planar or puckered. They indicate, however, clearly, the formation of a new carbon–iron σ bond, and the transformation of the original nonconjugated cyclobutadiene system into an allylic cyclobutenyl system.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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George A. Olah,* Gao Liang
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Received March 26, 1976

Organomercury Compounds as Synthetic Intermediates. Coupling of Arylmercuric Salts

Summary: Arylmercuric salts are converted to biaryls in high yield upon treatment with copper and a catalytic amount of palladium chloride in pyridine.

Sir: The preparation of biaryls is ordinarily accomplished by the metal promoted decomposition of aryl halides, which includes the Ullmann reaction[1] and the use of zerovalent nickel complexes.[2] In addition, the reaction of an arylmagnesium halide[3] or aryllithium reagent[3e–g,4] with a salt such as a thallium, uranium, or first group transition metal salt has also been found to be preparatively useful for the generation of biaryls. The Ullmann reaction, however, is often unsatisfactory since (1) temperatures in excess of 200 °C are frequently required; (2) the reaction fails when the aromatic nucleus carries functional groups such as $-NH_2$, $-NHCOCH_3$, and $-NHCH_3$; and (3) a satisfactory result may require the use of relatively inaccessible aryl iodides when an activating substituent is not present. The alternative coupling of aryl halides with a zerovalent nickel complex suffers from one or more operational disadvantages which include air[2] and thermal sensitivity[2a] of the complex and the generation of difficulty separable by-products.[2b,c] Finally, the generation of biaryls from arylmagnesium halides or aryllithium reagents is suitable only in the absence of reactive functional groups.

We wish to report that arylmercuric salts are converted to biaryls in high yield (Table I) and under mild reaction conditions by treatment with copper metal and a catalytic amount of palladium chloride in the presence of pyridine according to eq 1. The reaction is compatible with most functional groups, and the arylmercuric salts required as starting materials are readily available[5] and are easily purified by crystallization. Ordinarily, the reaction is complete within 1 or 2 h at reflux temperature, but longer reaction times are not ordinarily harmful and serve to ensure completion of the reaction.

$$2ArHgX + Cu \xrightarrow[PdCl_2,\ 115\ ^\circ C]{\text{pyridine}} Ar\text{-}Ar + Hg + CuX_2 \qquad (1)$$

The experimental procedure is illustrated by the conversion of 4-chlorophenylmercuric acetate to 4,4′-dichlorobiphenyl.

A mixture of 4-chlorophenylmercuric acetate (2.001 g, 5.48 mmol), copper powder (1.501 g, 23.62 g-atoms), and palladium chloride (0.101 g, 0.57 mmol) in 20 ml of pyridine was heated under reflux in a nitrogen atmosphere with stirring for 5 h. The resulting mixture was filtered while hot through Celite, and the inorganic residues were washed with 75 ml of benzene. The combined filtrates were washed three times with 50-ml portions of 15% ammonium hydroxide, three times with 50-ml portions of 3 M HCl, and once with 50 ml of saturated brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give 0.515 g of tan needles. Recrystallization from ethanol afforded pure 4,4′-dichlorobiphenyl (0.377 g, 62%), mp 145–148 °C (lit.[6] mp 147–148 °C).

It is known that exposure of diarylmercury compounds to temperatures of 200–400 °C either in the absence[7] or presence[8]

Table I. Coupling of Arylmercuric Salts with Palladium Chloride and Copper in Pyridine [a]

Arylmercuric salt	Coupling product	Yield, %[b]
Phenylmercuric acetate	Biphenyl	86
2-Methoxyphenylmercuric acetate	2,2′-Dimethoxybiphenyl	84
4-Methoxyphenylmercuric acetate	4,4′-Dimethoxybiphenyl	90
4-Aminophenylmercuric acetate	Benzidine	76
4-Acetamidophenylmercuric acetate	4,4′-Diacetamidobiphenyl	69
4-Chlorophenylmercuric acetate	4,4′-Dichlorobiphenyl	62[c]
2-Chloromercurifuran	2,2′-Bifuran	86
2-Chloromercurithiophene	2,2′-Bithophene	95
1-Chloromercurinaphthalene	1,1′-Binaphthalene	47
4-Chloromercuribenzoic acid	None	0
4-Chloromercuriphenol	None	0
Mesitylmercuric acetate	None	0

[a] The reactions were carried out at reflux under a nitrogen atmosphere for a period of 22 h unless otherwise specified. [b] Isolated yield. [c] A reaction period of 5 h was used.

of metals such as Pd, Pt, Ag, Au, Co, Cu, Fe, and Ni results in the extrusion of elemental mercury and the formation of biaryls in modest to very low yields. In addition, several literature reports describe the conversion of diarylmercury compounds[9] and arylmercuric salts[9,10] to biaryls in low yield by treatment with palladium salts. As a result of one or more deficiencies which include low yields, by-product formation, and vigorous reaction conditions, these previous reports do not, however, describe a synthetically useful route to biaryls.

The use of pyridine as the solvent is an important factor in the success of the reaction. The use of nonbasic solvents such as dibutyl ether and toluene results in low yields of coupling product and the formation of by-products. In addition, both copper metal and catalytic amounts of palladium chloride are necessary. The omission of either copper[11] or palladium chloride results in a failure of the coupling reaction. The precise physical form of the copper is unimportant, however, and both wire and powder are equally suitable.

The reaction set forth in eq 1 has two modest limitations which are illustrated by the entries in Table I. The presence of acidic functional groups such as hydroxyl and carboxyl serve to inhibit the coupling reaction. The Ullmann reaction, however, also fails in the presence of these groups as well as in the presence of $-NH_2$ and $-NHCOCH_3$ groups.[1] In contrast, the present reaction affords high yields of biaryls in the presence of $-NH_2$ and $-NHCOCH_3$ groups (Table I).

The presence of bulky ortho substituents has an undesirable effect on the reaction. The preparation of 1,1′-binaphthalene proceeds in a somewhat modest yield of 47%. The presence of two ortho substituents, in the case of mesitylmercuric acetate, results in a complete failure of the coupling reaction.

Preparation of the unsymmetrical compound, 4-methoxybiphenyl, by crossed coupling of equimolar amounts of phenylmercuric acetate and 4-methoxyphenylmercuric acetate resulted in the formation of 33% biphenyl, 48% 4-methoxybiphenyl, and 19% 4,4′-dimethoxybiphenyl.[12] Consequently, very little selectivity is observed as the product distribution is close to a statistical 1:2:1 ratio.

The mechanism of the coupling reaction is unclear. It may be noted, however, that a highly satisfactory method for symmetrization of organomercuric salts consists of their reaction with copper in the presence of pyridine (eq 2).[13] If this symmetrization reaction occurs as an initial step, the resulting diarylmercury compound would be expected to undergo rapid reaction with catalytic amounts of either palladium metal or a palladium salt to form an unstable arylpalladium derivative which would decompose to yield the observed biaryl.[9,14]

$$ArHgX + Cu \rightarrow Ar_2Hg + 2CuX + Hg \qquad (2)$$

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Richard A. Kretchmer,* R. Glowinski

Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Received May 17, 1976