

tate, 4.87 g (11 mmol) of lead tetraacetate, 0.022 g (0.1 mmol) of palladium acetate, and 10 ml of acetonitrile under 40 psi of propylene at 50° for 2 hr. Analyses of glpc showed that the solution was now 0.141 M in 1-phenyl-2-propyl acetate and 0.09 M in *trans*-1-phenyl-1-propene.

Acknowledgments. The nmr spectra were measured by Mr. C. R. Boss and Dr. M. M. Anderson. The experimental work was carried out with the assistance of Mr. Joseph Keelins.

A Synthesis of Diaryl Ketones from Arylmercuric Salts

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Abstract: Arylmercuric chlorides react with carbon monoxide and palladium or rhodium halide catalysts to form diaryl ketones in fair yields.

Chlorobis(triethylphosphine)methylpalladium reacts readily with carbon monoxide to form the corresponding acylpalladium compound.¹ Carbon monoxide insertions also appear to occur in numerous palladium-catalyzed carbonylation reactions. For example, in the formation of esters from olefins² or dienes,³ in the formation of 3-chloroacyl chlorides from olefins,⁴ in the formation of muconic acid esters from acetylene,⁵ in the carbonylation of allylic halides,⁶ or π -allylpalladium halides,⁷ and in the synthesis of isocyanates from amines and carbon monoxide.^{8,9} Recently Henry⁹ has found that arylpalladium salts, prepared *in situ* from arylmercuric salts and various palladium compounds, react with carbon monoxide in hydroxylic solvents to form arylcarboxylic acids or their derivatives depending upon the solvent. While investigating this reaction independently, it was found that under some conditions diaryl ketones could also be formed in moderate yields from arylmercuric salts and carbon monoxide with a palladium salt catalyst. Rhodium trichloride and its trialkylphosphine derivatives proved to be better catalysts than palladium salts; they produced diaryl ketones in better yields, generally without the concurrent formation of appreciable amounts of carboxylic acid derivatives.

Results and Discussion

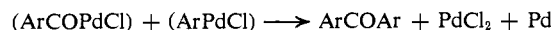
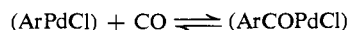
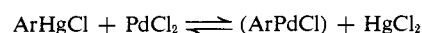
The diaryl ketones were generally prepared by combining an arylmercuric salt or other arylating agent and the catalyst in a solvent, such as acetonitrile under about 50 psig of carbon monoxide with stirring for 1–24 hr at 25–100° depending upon the reactants. The experiments are summarized in Table I.

Arylmercuric chlorides react with palladium salts in the absence of carbon monoxide to form biaryls in good

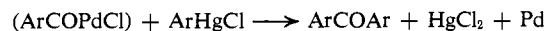
yields.¹⁰ The addition of carbon monoxide to the reaction mixture results in the formation of benzoyl chlorides or benzoate esters and diaryl ketones at the expense of the biaryls. At 50 psig of carbon monoxide generally little biaryl is formed. Diaryl ketones appear to be formed in preference to benzoyl chlorides or benzoate esters at higher pressures of CO. The use of rhodium catalysts for the diaryl ketone syntheses is preferred because generally much less of the biaryl and benzoic acid derivatives are formed relative to the diaryl ketone, and because mercuric chloride is apparently able to reoxidize Rh(I) to the catalytically active Rh(III). To achieve a catalytic reaction with palladium, stoichiometric amounts of cupric chloride are required.

Diaryl ketones are produced by this reaction in a variety of solvents, but hydroxylic solvents are generally to be avoided because larger amounts of benzoic acid derivatives are usually formed in these solvents. Acetonitrile has proved to be the most useful solvent. Acetone may also be used. Even hydrocarbons such as toluene can be used if toluene soluble catalysts of the type RhCl(CO)(PR₃)₂ are employed.

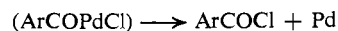
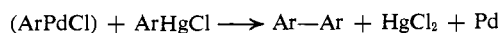
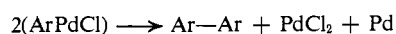
The mechanism of formation of diaryl ketones from arylmercuric chlorides is not clear, but probably it involves a reaction of an acylpalladium (or rhodium) compound with an arylpalladium (or rhodium) or



or



arylmercuric compound. Aroyl chlorides and biaryls are probably formed by the side reactions



We have not observed the formation of benzil-type products by coupling of two acylpalladium (rhodium) compounds even at very high carbon monoxide pres-

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(10) R. R. Josephson, unpublished work.

Table I. Diaryl Ketone Syntheses

Arylating agent	CO pressure, psig	Catalyst	Solvent	Temp, ^d °C	Reaction time, hr	Products
C ₆ H ₅ HgCl	50	Li ₂ PdCl ₄ -CuCl ₂	CH ₃ OH	RT	1	16% benzophenone ^a 30% methyl benzoate ^a
C ₆ H ₅ HgCl	Atmospheric	LiPdCl ₃ -CuCl ₂	CH ₃ CN	30	1.5	11% benzophenone ^a 18% biphenyl ^a ~40% benzoyl chloride ^{a, b}
C ₆ H ₅ HgCl	50	LiPdCl ₃ -CuCl ₂	CH ₃ CN	RT	1	11% chlorobenzene ^a 29% benzophenone ^a 2% biphenyl ^a ~22% benzoyl chloride ^{a, b}
3-NO ₂ C ₆ H ₄ HgCl	Atmospheric	LiPdCl ₃	CH ₃ CN	RT	3.5	12% chlorobenzene ^a 25% 3,3'-dinitrobenzophenone ^c
C ₆ H ₅ HgCl	35	RhCl ₃ ·3H ₂ O	CH ₃ CN	100	5	48% benzophenone ^a
(C ₆ H ₅) ₄ Pb	50	RhCl ₃ ·3H ₂ O	CH ₃ CN	100	20	9% benzophenone ^a
(C ₆ H ₅) ₄ Sn	50	RhCl ₃ ·3H ₂ O	CH ₃ CN	100	20	7% benzophenone ^a
4-CH ₃ OC ₆ H ₄ HgCl	50	RhCl ₃ ·3H ₂ O	CH ₃ CN	100	20	31% bis- <i>p</i> -anisyl ketone ^a
3-CH ₃ OCOC ₆ H ₄ HgCl	50	RhCl ₃ ·3H ₂ O	CH ₃ CN	100	20	8% 3,3'-bis(carbomethoxy)benzophenone ^c
3,4-(NO ₂) ₂ (Cl)C ₆ H ₃ HgCl	50	RhCl ₃ ·3H ₂ O	CH ₃ CN	100	72	7% 4,4'-dichloro-3,3'-dinitrobenzophenone ^c
C ₆ H ₅ HgCl	Atmospheric	RhCl(CO)(PEt ₃) ₂	Toluene	50	20	50% benzophenone ^a
C ₆ H ₅ HgCl	50	RhCl(CO)[P(<i>n</i> -Bu ₃) ₂] ₂	Toluene	100	2.5	44% benzophenone ^a
4-CH ₃ OC ₆ H ₄ HgCl	50	RhCl(CO)[P(<i>n</i> -Bu ₃) ₂] ₂	Toluene	100	24	30% bis- <i>p</i> -anisyl ketone ^a 10% bis- <i>p</i> -anisyl ^a

^a Yield determined by glpc. ^b Analyzed as methyl benzoate by adding methanol to the reaction mixture. ^c Yield of isolated product. ^d RT = room temperature.

tures. This reaction would have been expected on the basis of the report by Booth and Chatt¹ that (CH₃CO)₂-Pt[P(C₂H₅)₃]₂, formed from (CH₃)₂Pt[P(C₂H₅)₃]₂ and CO, decomposes very readily to biacetyl.

Experimental Section

Reagents. The arylmercuric salts and palladium compounds used in this work were obtained as described previously.¹¹

Benzophenone Prepared from Phenylmercuric Chloride and a Palladium Catalyst. A. To a heavy-walled Pyrex bottle containing a magnetic stirring bar, 10 mmol of phenylmercuric chloride and 10 mmol of cupric chloride were added. The bottle was capped with a butyl rubber lined metal cap and air was replaced by carbon monoxide at 50 psig by alternately pressuring and evacuating the bottle through a hypodermic needle inserted through the rubber lined cap. Then 10 ml of 0.1 *M* Li₂PdCl₄ in methanol was injected by means of a hypodermic syringe. The carbon monoxide pressure was kept at 50 psig while the solution was stirred at room temperature for 1 hr. Analyses by glpc on a 60-ft Carbowax 20M column showed that the solution was 0.080 *M* in benzophenone and 0.30 *M* in methyl benzoate.

B. In a gasometric apparatus thermostated at 30° was placed 10 mmol of phenylmercuric chloride and 10 mmol of cupric chloride. The apparatus was flushed with carbon monoxide at atmospheric pressure and 10 ml of 0.1 *M* Li₂PdCl₃ in acetonitrile was added. In 1.3 hr, 116 ml of gas had been absorbed and analyses by glpc showed the solution to be 0.094 *M* in biphenyl, 0.11 *M* in chlorobenzene, 0.058 *M* benzophenone, and, after adding 10 ml of 1.0 *M* NaOCH₃ in methanol, 0.20 *M* in methyl benzoate.

C. A reaction was carried as in A above but with 10 ml of 0.1 *M* Li₂PdCl₃ in acetonitrile instead of in methanol. After reacting for 1 hr at room temperature, analyses by glpc showed that the solution was 0.010 *M* in biphenyl, 0.145 *M* in benzophenone, 0.12 *M* in chlorobenzene, and, after adding 10 ml of 1.0 *M* NaOCH₃ in methanol, 0.11 *M* in methyl benzoate.

3,3'-Dinitrobenzophenone. In a 500-ml, three-necked flask equipped with a mechanical stirrer, a condenser, a gas inlet tube, a gas exit tube with mercury bubbler attached at the top of the condenser, and a rubber stopple for injection of solutions from hypodermic syringes, was placed 7.16 g (20 mmol) of 3-chloromercurinitrobenzene.¹² The flask was flushed with carbon monoxide at atmospheric pressure and 200 ml of 0.1 *M* Li₂PdCl₃ in acetonitrile was added. The mixture was stirred vigorously for 3.5 hr while a slow stream of carbon monoxide was passed through. The reaction mixture was filtered and the residue of palladium metal was rinsed several times with hot chloroform. The filtrate was evaporated under vacuum and the residue was recrystallized twice from aqueous acetic acid to give 0.68 g of off-white crystals of 3,3'-dinitrobenzophenone, mp 155.0–155.5° (lit.¹³ mp 155°). The product had a carbonyl absorption band in the infrared region at 1675 cm⁻¹ in chloroform solution.

Anal. Calcd for C₁₃H₆O₃N₂: C, 57.36; H, 2.96; N, 10.29. Found: C, 57.40; H, 3.44; N, 10.21.

Benzophenone from Phenylmercuric Chloride with a Rhodium Chloride Catalyst. In a heavy-walled Pyrex bottle containing a magnetic stirring bar was placed 10 mmol of phenylmercuric chloride and 0.1 mmol of rhodium trichloride trihydrate. The bottle was capped and flushed with carbon monoxide to 50 psig. After injecting 10 ml of acetonitrile, the solution was stirred at 100° in a steam bath for 5 hr. Analyses by glpc showed the solution to be 0.25 *M* in benzophenone. Longer heating did not improve the yield. There was no significant amount of benzoyl chloride formed.

Benzophenone from Tetraphenyllead and a Rhodium Chloride Catalyst. A reaction was carried out as in the preceding example employing 10 mmol of tetraphenyllead in place of phenylmercuric chloride. After reacting at 100° overnight, the solution was found to be 0.045 *M* in benzophenone.

Benzophenone from Tetraphenyltin and a Rhodium Chloride Catalyst. A reaction was carried out as in the preceding example employing tetraphenyltin in place of tetraphenyllead. The reaction mixture was found to be 0.033 *M* in benzophenone. The low

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yields obtained in this and the preceding experiments are probably the result of not including a reagent to reoxidize Rh(I).

Bis(*p*-anisyl) Ketone from *p*-Anisylmercuric Chloride and a Rhodium Chloride Catalyst. In a heavy-walled Pyrex bottle with a magnetic stirring bar was placed 10 mmol of *p*-anisylmercuric chloride and 0.1 mmol of rhodium trichloride trihydrate. The bottle was capped and flushed with carbon monoxide and 10 ml of acetonitrile was injected. The reaction mixture was stirred under 50 psig of carbon monoxide at 100° overnight. Analyses by glpc showed the solution to be 0.32 *M* in bis(*p*-anisyl) ketone. No *p*-anisyl chloride was detected.

3,3'-Bis(carbomethoxy)benzophenone from 3-Carbomethoxyphenylmercuric Chloride. A reaction was carried out as in the preceding example using 10 mmol of 3-carbomethoxyphenylmercuric chloride in place of *p*-anisylmercuric chloride. Evaporation of the reaction mixture and recrystallization of the product from a mixture of benzene and hexane gave 0.23 g of 3,3'-bis(carbomethoxy)benzophenone, mp 129–130° (lit.¹⁴ mp 130°).

4,4'-Dichloro-3,3'-dinitrobenzophenone from 4-Chloro-3-nitrophenylmercuric Chloride. A reaction was carried out as in the above experiment using 10 mmol of 4-chloro-3-nitrophenylmercuric chloride instead of 3-carbomethoxyphenylmercuric chloride. Isolation of the product in the same manner and two recrystallizations from aqueous acetic acid gave 0.22 g of product, mp 129.5–130.5° (lit.¹⁵ mp 133–134°).

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Benzophenone from Phenylmercuric Chloride and Rh(CO)Cl(PR₃)₂ Catalysts. A. In a gasometric apparatus were placed 1.0 mol of RhCl(CO)[P(C₂H₅)₃]₂¹⁶ and 10 mmol of phenylmercuric chloride. The air in the apparatus was replaced by carbon monoxide at atmospheric pressure and 10 ml of toluene was added. In 4 hr at 50°, 46 ml of gas was absorbed and a slow absorption continued. After reacting overnight, analyses by glpc showed the solution to be 0.25 *M* in benzophenone with only a trace of biphenyl.

B. In a heavy-walled Pyrex bottle containing a magnetic stirring bar was placed 10 mmol of phenylmercuric chloride and 0.1 mmol of RhCl(CO)[P(*n*-Bu)₃]₂.¹⁶ The bottle was capped and flushed with carbon monoxide. After the injection of 10 ml of toluene, the reaction mixture was pressured to 50 psig with carbon monoxide and stirred for 2.5 hr at 100°. After cooling, analyses by glpc showed the solution to be 0.24 *M* in benzophenone.

Di-*p*-anisyl Ketone from *p*-Anisylmercuric Chloride and RhCl(CO)[P(*n*-Bu)₃]₂ as Catalyst. A reaction was carried out as in B using 10 mmol of *p*-anisylmercuric chloride in place of phenylmercuric chloride. Analysis showed the solution to be 0.15 *M* in di-*p*-anisyl ketone. Evaporation of solvent and recrystallization of the product from aqueous ethanol gave 0.23 g of di-*p*-anisyl ketone, mp 140.5–141.5° (lit.¹⁷ mp 143–144°).

Acknowledgment. Most of the experimental work was carried out with the assistance of Mr. Joseph Keelins.

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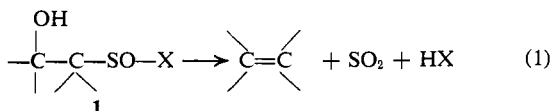
The Synthesis of Olefins and Ketones from Carbonyl Compounds and Sulfinamides

E. J. Corey and T. Durst

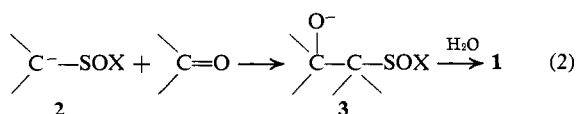
Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received April 18, 1968

Abstract: The reaction of α -lithio sulfinamide derivatives with aldehydes and ketones affords β -hydroxy sulfinamides by carbonyl addition. These adducts undergo smooth thermolysis in the range 80–110° to form olefins along with sulfur dioxide and the appropriate amine. These reactions constitute a new synthetic route to olefins. A new and useful one-step synthesis of ketones from esters and α -lithio sulfinamide derivatives is also described.

The investigations reported herein originated from the hypothesis that olefins might be produced from β -hydroxy sulfinyl derivatives by the elimination process outlined in eq 1, and additionally from the possibility that the required intermediate **1** might be accessible



by the reaction of an α -sulfinylcarbanion of type $>\text{C}^--\text{SOX}$ (**2**) with an aldehyde or ketone (eq 2).



Transformations 2 and 1 in sequence would constitute an interesting and possibly useful alternative to the Wittig reaction, one based on a key role for sulfur rather than phosphorus in the carbon-bond-forming

and elimination steps. It was clear from previous work that β -alkoxy sulfoxide derivatives, represented by **3** with, e.g., X = alkyl or aryl are not particularly susceptible to olefin-forming elimination under mild conditions.^{1,2} However, little was known about the possibility of effecting elimination from *hydroxy* sulfinyl compounds of type **1** either with sulfoxides or other sulfinyl derivatives such as X = NR₁R₂ or X = OR. Most of our studies to date have been concerned with β -hydroxy sulfinamides and, more specifically, with β -hydroxy sulfinanilides and β -hydroxy sulfin-*p*-toluidides of general formula **4** and **5**, respectively, these being the most readily available sulfinamide-carbonyl adducts. As described in a preliminary publication³ these adducts which are accessible from the

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(2) For a special case of olefin formation from an intermediate of type **3** under forcing conditions see, E. J. Corey and M. Chaykovsky, *J. Org. Chem.*, **28**, 254 (1963), and also C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963).

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