

## THE REACTION OF ORGANOMERCURIC COMPOUNDS WITH NICKEL CARBONYL

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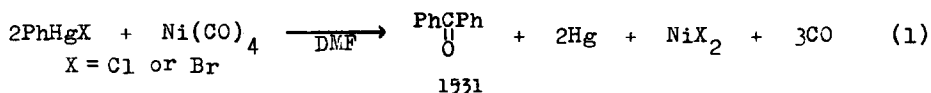
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Reactions of organometallic compounds which bear halogen on metal with metal carbonyls have recently been reported; i.e., tri-n-butyltin chloride and arylmercuric halides react with iron pentacarbonyl and dicobalt octa-carbonyl, respectively, producing symmetrical ketones.<sup>1,2</sup>

This communication deals with the synthesis of diaryl or dialkyl ketones in excellent yields by the reaction of nickel carbonyl with organomercuric halides and, furthermore, with the formation of phenyl aryl ketones by the reaction of nickel carbonyl with iodobenzene and arylmercuric chloride, which would lead to a new synthetic route to unsymmetrical ketones.

The reaction of organomercuric halide (20 mmol) with nickel carbonyl  $\text{Ni(CO)}_4$  (20 mmol) in 60 ml of N,N-dimethylformamide (DMF) was carried out under nitrogen at 60 ~ 70° for 20 hr. In the course of the reaction, the initial colorless solution turned dark green and a separation of metallic mercury was observed. The reaction mixture was decanted, poured into 300 ml of water and extracted with petroleum ether. The extract was washed with water and dried over anhydrous sodium sulfate. After removal of petroleum ether, the residue was distilled in vacuo. From phenylmercuric chloride and bromide, benzophenone was obtained in yields of 95% and 92%, respectively, along with quantitative amount of metallic mercury. The same result was obtained by using a half amount of  $\text{Ni(CO)}_4$  (10 mmol), showing the following stoichiometry (eq 1).



The reaction of  $\text{PhHgBr}$  with  $\text{Ni(CO)}_4$  in tetrahydrofuran (THF) also gave benzophenone (94%). However, in the case of  $\text{PhHgCl}$ , the formation of benzophenone was remarkably affected by the solvent used. That is, when DMF, dimethylsulfoxide (DMSO) or acetonitrile was used as a solvent, benzophenone was produced in an excellent yield (95 ~ 97%). A similar reaction in benzene, THF, ethanol, pyridine or aniline yielded diphenylmercury and only a trace amount of benzophenone. The results are summarized in Table I which covers several arylmercuric halides, phenylmercuric acetate and three examples of alkylmercuric bromides.

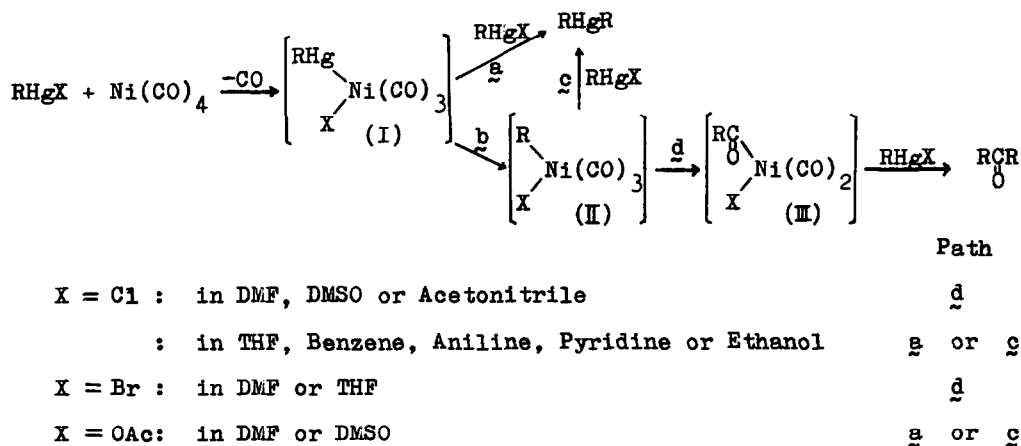
Table I The Reaction of  $\text{RHgX}$  with  $\text{Ni(CO)}_4$  (molar ratio, 1:1) at 60 ~ 70° for 20 ~ 30 hr

| $\text{RHgX}$                                  | Solvent      | Product, %        |               | $\text{RHgX}$                                  | Solvent | Product, %        |               |
|--|--------------|-------------------|---------------|--|---------|-------------------|---------------|
|  |              | $\text{RGR}$<br>0 | $\text{RHgR}$ |  |         | $\text{RGR}$<br>0 | $\text{RHgR}$ |
| $\text{C}_6\text{H}_5\text{HgCl}$              | DMF          | 95                | 0             | $\text{C}_6\text{H}_5\text{HgBr}$              | DMF     | 92                | 0             |
|  | DMSO         | 96                | 0             |  | THF     | 94                | 0             |
|  | Acetonitrile | 97                | 0             | $p\text{-CH}_3\text{C}_6\text{H}_4\text{HgBr}$ | DMF     | 100               | 0             |
|  | Benzene      | trace             | 32            |  | THF     | 99                | 0             |
|  | THF          | trace             | 85            | $n\text{-C}_4\text{H}_9\text{HgBr}$            | DMF     | 56                | 0             |
|  | Ethanol      | trace             | 44            | $i\text{-C}_5\text{H}_{11}\text{HgBr}$         | DMF     | 59                | 0             |
|  | Pyridine     | trace             | 35            | $n\text{-C}_6\text{H}_{13}\text{HgBr}$         | DMF     | 64                | 0             |
|  | Aniline      | trace             | 79            | $\text{C}_6\text{H}_5\text{HgOAc}$             | DMF     | 0                 | 91            |
| $p\text{-CH}_3\text{C}_6\text{H}_4\text{HgCl}$ | THF          | trace             | 90            |  | DMSO    | 0                 | 86            |

The results of reactions of  $\text{Ni(CO)}_4$  with alkylmercuric bromides are interesting. According to Seyferth and Spohn,<sup>2</sup> the reaction of n-butylmercuric bromide with  $\text{Co}_2(\text{CO})_8$  in THF produced 5-nonanone and a significant amount of isomerized ketone, 3-methyl-4-octanone. In the present reactions, however, all of the products were the homologous, symmetrical ketones quite free from any isomerized ketones (confirmed by nmr and glpc analyses). These results show  $\text{Ni(CO)}_4$  is a more favorable reagent than  $\text{Co}_2(\text{CO})_8$  for the synthesis of symmetrical ketones from alkylmercuric halide. Furthermore

in the case of  $\text{Ni(CO)}_4$ , mercury was separated as metallic mercury, making the work-up of the reaction mixture simple and easy in contrast to the formation of  $\text{Hg[Co(CO)}_4\text{]}_2$  from the reaction of  $\text{Co}_2(\text{CO})_8$  which requires troublesome treatments in order to remove it from organic compounds.

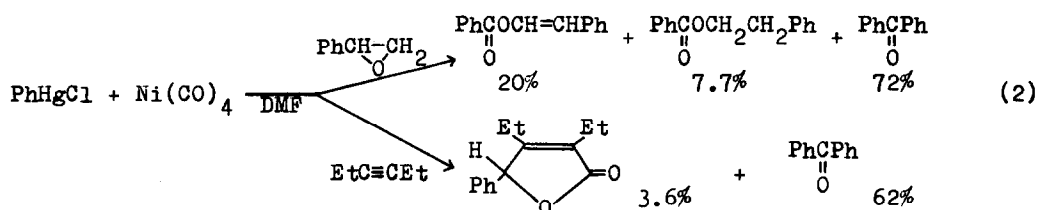
The reaction of  $\text{Ni(CO)}_4$  with  $\text{RHgX}$  seems to proceed via the paths shown in Scheme I, whose initial step would be an oxidative addition of  $\text{RHgX}$  to  $\text{Ni(CO)}_4$  to form the intermediate (I).



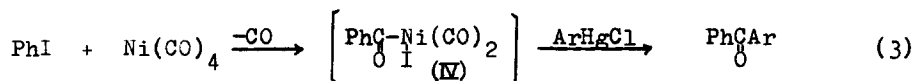
Scheme I

The remarkable solvent effect in the case of  $\text{PhHgCl}$  could be explained in terms of the decomposition behavior of the intermediate (I) or (II). For example, in THF, (I) or (II) ( $\text{R} = \text{Ph}$ ,  $\text{X} = \text{Cl}$ ) reacts with  $\text{PhHgCl}$  to give diphenylmercury (via path a or c), while in a solvent with more strong coordinating ability such as DMF or DMSO CO insertion occurred along with elimination of mercury to form benzoylnickel complex (III) (via d). It was previously reported from this laboratory<sup>3</sup> that iodobenzene reacted with  $\text{Ni(CO)}_4$  in THF to give  $\text{PhC(=O)Ni(CO)}_3$ , similar to the intermediate (III), which exhibited a high reactivity toward certain olefins, such as acrylonitrile and styrene. Therefore, if the reaction of (III) ( $\text{R} = \text{Ph}$ ,  $\text{X} = \text{Cl}$ ) with  $\text{PhHgCl}$  was slow enough, it is possible to trap the benzoyl moiety by a suitable reagent. From this point of view, the reaction of  $\text{PhHgCl}$  with  $\text{Ni(CO)}_4$  was conducted in the presence of acrylonitrile, styrene oxide or

3-hexyne. The attempt using acrylonitrile was unsuccessful, but it was found that benzoylation of styrene oxide and 3-hexyne took place although the yield was not good (eq 2). These results suggest that the reaction of (III) ( $R = Ph$ ,  $X = Cl$ ) with  $PhHgCl$  is too fast to admit the attack of acrylonitrile, producing benzophenone exclusively. Hence, organomercuric chloride was considered to be a promising reagent for capture of aroyl or acyl group in aroyl- or acylnickel complexes, yielding ketones. In accordance with this



consideration, the reaction of iodobenzene (10 mmol) with  $\text{Ni(CO)}_4$  (20 mmol) in THF in the presence of  $\text{C}_6\text{H}_5\text{HgCl}$  or  $p\text{-CH}_3\text{C}_6\text{H}_4\text{HgCl}$  (10 mmol) led to the formation of benzophenone (9.6 mmol, 96%) or  $p$ -tolyl phenyl ketone (6.8 mmol, 68%) as a result of rapid capture of the intermediate (IV) by  $\text{ArHgCl}$  (eq 3), although in the case of  $p\text{-CH}_3\text{C}_6\text{H}_4\text{HgCl}$  di- $p$ -tolyl ketone (1.5 mmol, 30%) and benzophenone (0.16 mmol, 3.3%) were also produced as byproducts. Thus, this reaction can be applicable to a new synthetic method of unsymmetrical diaryl ketones.



The study on the mechanism of these reactions and further applications to organic syntheses are now under investigation and will be reported in the near future.

#### References

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