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# THE REACTION OF α-IODOMERCURIC KETONES WITH NICKEL CARBONYL IN THE PRESENCE OF CARBONYL COMPOUNDS

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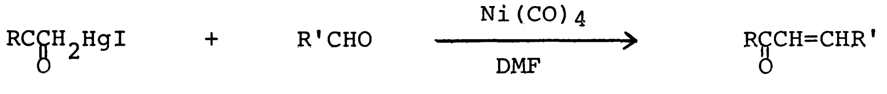
The reaction of a variety of α-iodomercuric ketones with nickel carbonyl was carried out in the presence of aldehydes or ketones to afford α,β-unsaturated ketones in good yields.

The use of organomercurials in organic synthesis via transmetalation is of current interest.[1)] We have reported that the reaction of arylmercuric halides with nickel carbonyl, $Ni(CO)_4$, in N,N-dimethylformamide (DMF) produced the corresponding symmetrical diaryl ketones, whereas the reaction of arylmercuric halides and aryl iodides with $Ni(CO)_4$ in benzene gave unsymmetrical aryl ketones.[2)] In the former reaction, it is suggested that oxidative addition of aryl mercuric halide to $Ni(CO)_4$ forms an intermediate, aroyl nickel complex, via arylnickel complex. Our attention was then payed to the use of alkylmercuric halides in the similar transmetalation systems.

This paper describes the reaction of α-iodomercuric ketones, which are readily accesible by treatment of enol silyl ethers,[3)] with $Ni(CO)_4$ in the presence of aldehydes or ketones. It was expected that oxidative addition of an α-halomercuric ketone to $Ni(CO)_4$ might form an intermediate which is essentially a nickel enolate, capable of nucleophilic attack to carbonyl carbon. The typical procedure is as follows. The reaction of α-iodomercuric acetophenone (5 mmol) with $Ni(CO)_4$ (10 mmol) in the presence of benzaldehyde (20 mmol) was carried out at 50-55°C for 6 h in DMF (30 ml). The color of the reaction mixture turned green from colorless and metallic Mercury deposited. The reaction mixture was then poured into 50 ml of aqueous 2M-HCl and extracted with hexane followed by drying with magnesium sulfate. The product obtained was identified to be benzalacetophenone (80%).

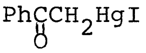
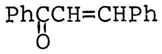
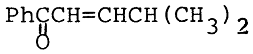
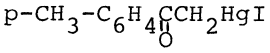
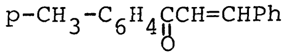
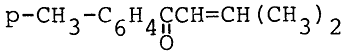
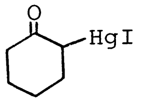
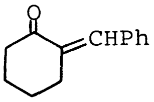
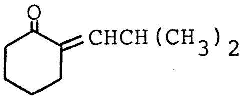
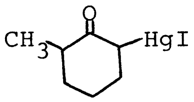
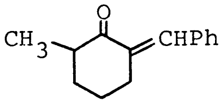
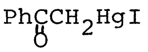
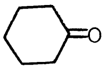
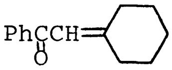
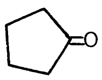
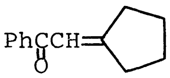
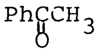
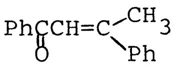


$$R\underset{\underset{O}{\|}}{C}CH_2HgI \quad + \quad R'CHO \quad \xrightarrow[DMF]{Ni(CO)_4} \quad R\underset{\underset{O}{\|}}{C}CH{=}CHR'$$

The results of the reaction of α-iodomercuric ketones with aldehydes or ketones are summarized in Table 1. Ketones were less reactive than aldehydes in the present reaction. The reaction of α-iodomercuric acetophenone with cyclohexanone (run 9 in Table 1) gave the corresponding α,β-unsaturated ketone in 20% yield at 55°C, while at higher temperature (75°C) the yield was satisfactorily improved.

Interestingly, the nickel enolate from α-mercuric ketone in the present study underwent cross-condensation, while that from α-haloketone reacted with α-haloketone itself.[4]

Table 1. The reaction of α-iodomercuric ketones with $Ni(CO)_4$ in the presence of aldehydes or ketones

| run | RHgI | Aldehyde or Ketone | Product | Yield (%)* |
|---|---|---|---|---|
| 1 |  $\mathrm{Ph\underset{\underset{O}{\|}}{C}CH_2HgI}$ | PhCHO |  $\mathrm{Ph\underset{\underset{O}{\|}}{C}CH{=}CHPh}$ | 80 |
| 2 | | $(CH_3)_2CHCHO$ |  $\mathrm{Ph\underset{\underset{O}{\|}}{C}CH{=}CHCH(CH_3)_2}$ | 92 |
| 3 |  $\mathrm{p\text{-}CH_3\text{-}C_6H_4\underset{\underset{O}{\|}}{C}CH_2HgI}$ | PhCHO |  $\mathrm{p\text{-}CH_3\text{-}C_6H_4\underset{\underset{O}{\|}}{C}CH{=}CHPh}$ | 73 |
| 4 | | $(CH_3)_2CHCHO$ |  $\mathrm{p\text{-}CH_3\text{-}C_6H_4\underset{\underset{O}{\|}}{C}CH{=}CH(CH_3)_2}$ | 80 |
| 5 |  | PhCHO |  | 80 |
| 6 | | $(CH_3)_2CHCHO$ |  | 85 |
| 7 |  | PhCHO |  | 75 |
| 8 |  $\mathrm{Ph\underset{\underset{O}{\|}}{C}CH_2HgI}$ | $CH_3CH{=}CHCHO$ |  $\mathrm{Ph\underset{\underset{O}{\|}}{C}CH{=}CHCH{=}CHCH_3}$ | 50 |
| 9 | |  |  | 20 (90)** |
| 10 | |  |  | 30** |
| 11 | |  $\mathrm{Ph\underset{\underset{O}{\|}}{C}CH_3}$ |  | 40** |

*Based on organomercuric halide used. **Conducted at 75°.

## REFERENCES

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4) E. Yoshisato and S. Tsutsumi, J. Am. Chem. Soc., 90, 4488 (1968); Chem. Comm., 33 (1968).

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