

PRELIMINARY COMMUNICATION

SYNTHESIS OF UNSYMMETRIC KETONES FROM ORGANOMERCURY COMPOUNDS

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At present the reaction of acyl halides with organocadmium compounds, first discovered by Gilman¹⁻³, is a common procedure for the synthesis of unsymmetric ketones. But when Gilman extended this reaction to organomercury compounds⁴; the yields of ketones were only 30% although the reaction was been carried out under severe conditions (temperature 120–160°).

Smooth reactions of acyl halides with α -mercurated carbonyl compounds do not give ketones, but proceed via a transfer of the reaction centre to the oxygen atom with the result that the enol-acetates are the reaction products⁵. No reaction was observed in the case of alkyl organomercury derivatives⁶. Acyl halides react with chloromercurated heterocyclic derivatives of thiophene^{7,8}, selenophene⁹, furan¹⁰ and diphenyl ether¹¹ giving more or less satisfactory yields. Skoldinov and Kocheshkov prepared benzophenone by benzoylation of diphenylmercury (47%) and phenylmercury chloride (59%) in the presence of aluminium chloride in carbon disulfide¹².

We have shown that symmetric aromatic, alkylaromatic and primary aliphatic mercury compounds are smoothly acylated by aliphatic and aromatic acyl halides in the presence of aluminium bromide. The catalytic effects of the Lewis acids were studied for the reaction of diphenylmercury with acetyl chloride in methylene chloride at 20° for 3 hours (Table 1).

TABLE 1

| Lewis acids | Yield of acetophenone |
|-------------------|-----------------------|
| SnCl ₄ | — |
| SbCl ₅ | — |
| SbF ₅ | 28 |
| BF ₃ | 33 ^a |
| AlBr ₃ | 100 |

^a In the reaction:



TABLE 2

| RCOCl | R ₂ Hg | Ketone | Yield(%) |
|--|--|--|----------|
| CH ₃ COCl | (C ₂ H ₅) ₂ Hg | CH ₃ COC ₂ H ₅ | 100 |
| CH ₃ COCl | (n-C ₄ H ₉) ₂ Hg | CH ₃ CO-n-C ₄ H ₉ | 85 |
| CH ₃ COCl | (n-C ₆ H ₁₁) ₂ Hg | CH ₃ CO-n-C ₆ H ₁₁ | 79 |
| CH ₃ COCl | (p-ClC ₆ H ₄) ₂ Hg | p-ClC ₆ H ₄ COCH ₃ | 95 |
| CH ₃ COCl | (p-CH ₃ C ₆ H ₄) ₂ Hg | p-CH ₃ C ₆ H ₄ COCH ₃ | 100 |
| n-C ₃ H ₇ COCl | (C ₂ H ₅) ₂ Hg | n-C ₃ H ₇ COC ₂ H ₅ | 83 |
| n-C ₃ H ₇ COCl | (n-C ₄ H ₉) ₂ Hg | n-C ₃ H ₇ CO-n-C ₄ H ₉ | 75 |
| n-C ₄ H ₉ COCl | (n-C ₄ H ₉) ₂ Hg | n-C ₄ H ₉ CO-n-C ₄ H ₉ | 80 |
| C ₆ H ₅ COCl | (n-C ₄ H ₉) ₂ Hg | C ₆ H ₅ CO-n-C ₄ H ₉ | 73 |
| p-NO ₂ C ₆ H ₄ COCl | (n-C ₄ H ₉) ₂ Hg | n-C ₄ H ₉ COC ₆ H ₄ -p-NO ₂ | 70 |
| n-C ₄ H ₉ COCl | (C ₆ H ₅) ₂ Hg | n-C ₄ H ₉ COC ₆ H ₅ | 92 |
| p-NO ₂ C ₆ H ₄ COCl | (C ₆ H ₅) ₂ Hg | p-NO ₂ C ₆ H ₄ COC ₆ H ₅ | 88 |

For the preparation of ketones aluminium bromide was found to be most effective under these conditions, the reaction being completed after several minutes.

Primary aliphatic organomercury compounds are readily acylated in the presence of aluminium bromide (equimolar amounts) in methylene chloride solution. The reaction is carried out at -20° and the reaction mixture is then kept at 20–35° for 20 hours. The yields of the corresponding ketones are listed in Table 2.

Most of these ketones were isolated in the form of their 2,4-DNPH* derivatives. This method may be also helpful in the case of organomercury salts. However, the preparation of ketones from the alkylmercury salts proceeds more slowly and the yields are much lower than in the case of the totally substituted compounds.

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*DNPH = dinitrophenylhydrazine.