Preliminary communication

Interaction of acetonylmercuric bromide and bis(acetonyl)mercury with aldehydes

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Organomercury compounds containing effective electron-withdrawing groups are poorly reactive under S_E2 reaction conditions. However, under conditions of anionic catalysis the compounds will react even with rather weak electrophiles $[S_E1(N)]^1$. In view of this we wish to report the carrying out of a "Grignard-like" reaction of carbonyl compounds with organomercurials in the presence of an anionic catalyst. We found that acetonylmercuric bromide and bis(acetonyl)mercury react with pentafluorobenzaldehyde (PFBA) with bromide ions as catalyst:the ketoalcohols are formed after hydrolysis.

$$C_6F_5CHO + (CH_3COCH_2)_2Hg \xrightarrow{Br^-} C_6F_5CH(OH)CH_2COCH_3$$

The reaction was carried out in dimethoxyethane (DME) at room temperature during one day (no reaction was observed under these conditions in the absence of bromide ions).

After the reaction mixture had been acidified, C_6F_5 CH(OH)CH₂ COCH₃ was isolated as its 2,4-dinitrophenylhydrazone (DNPH) (yield 65%). Found: C, 44.10; H, 2.42; F, 22.45. $C_6H_{11}F_5N_4O_5$ calcd.: C, 44.25; H, 2.55; F, 21.87%). Under bromide ion catalysis, other organomercury compounds, R_2 Hg and RHgX, (R = effective electronegative group will also react with PFBA.

The reaction of chloral with acetonylmercuric bromide occurs even without the presence of bromide ions. After the reaction mixture consisting of equimolar amounts of the reagents was heated in DME at 60–70° during about 30 h, the yield of CCl₃CH(OH)CH₂COCH₃, isolated as its DNPH, was about 60%. (Found: C, 34.06; H, 29.8; Cl, 27.67. C₁₁H₁₁Cl₃N₄O₅ calcd.: C, 34.26; H, 2.87; Cl, 27.58%).

REFERENCE

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