

Supporting Information

An Efficient Direct α -Alkylation of Ketones with Primary Alcohols Catalyzed by [Ir(cod)Cl]₂/PPh₃/KOH System without Solvent

Kazuhiko Taguchi, Hideto Nakagawa, Tomotaka Hirabayashi,
Satoshi Sakaguchi and Yasutaka Ishii*

General Procedures. All starting materials were commercially available and used without any purification. GLC analysis was performed with a flame ionization detector using a 0.2 mm x 25 m capillary column (OV-1). ¹H- and ¹³C-NMR were measured at 270 MHz and 67.5 MHz, respectively, in CDCl₃ with Me₄Si as the internal standard. Infrared (IR) spectra were measured using NaCl plates.

A typical reaction procedure is as follows: To a mixture of [IrCl(cod)]₂ (0.02 mmol), KOH (0.2 mmol), and PPh₃ (0.08 mmol) were added ketone (2 mmol) and alcohol (4 mmol) under Ar. The reaction mixture was stirred at 100 °C for 4 h. The product was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane : ethyl acetate = 20:1). The conversions and yields of products were estimated from the peak areas based on the internal standard technique using GC. The isolated yields of **3fa** and **3gb** were given in Table 3. The products **3aa**,¹ **3ca**,² **3ea**,³ **3fa**,⁴ **3ab**,⁵ **3ac**,⁶ **3ad**,⁷ **3ae**,⁸ and **3gb**⁹ were reported previously. **3ba** (Aldrich), **3da** (Lancaster Synthesis), and **3bb** (Lancaster Synthesis) were commercially available.

The reaction of 1a with 2a. As shown in Table 1 Run 15, the reaction under equimolar amounts of starting substrates, **1a** and **2a**, for 4 h produced **3aa** (68%), **4aa** (1%) and **5a** (5%). For a longer time (8 h), almost the same yield (70%) of **3aa** was obtained at 85% conversion of **1a**. In these reactions, several side-products having high-boiling temperature were detected in 1~3% yields, respectively, by GC-MS analysis. These by-products were identified as 5-butyl-dodecan-6-one, (*E*)- and (*Z*)-5-butyl-4-dodecen-6-one *etc.* derived from **3aa** and butyl aldehyde. In the case of the reaction of **1a** with two equimolar amount of **2a** (Table 1 Run 1), almost the same side-products were produced in 1~3% yields, respectively, and most of **2a** was recovered unchanged.

References

(1) Choppin, S.; Gros, P.; Fort, Y. *Tetrahedron* **1999**, *55*, 9261-9268.

- (2) Hayes, J. F.; Shipman, M.; Twin, H. *J. Org. Chem.* **2002**, *67*, 935-942.
- (3) Bartoli, G.; Bosco, M.; Sambri, L.; Marcantoni, E. *Tetrahedron Lett.* **1994**, *35*, 8651-8654.
- (4) Cho, C. S.; Kim, B. T.; Kim, T.-J.; Shim, S. C. *J. Org. Chem.* **2001**, *66*, 9020-9022.
- (5) Lee, D.-Y.; Moon, C. W.; Jun, C.-H. *J. Org. Chem.* **2002**, *67*, 3945-3948.
- (6) Zafiriadis, Z. *Compt. Rend.* **1950**, *230*, 452-453..
- (7) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1988**, *53*, 45-49.
- (8) Rabilloud, G. *Bull. Soc. Chim. Fr.* **1966**, 634-639.
- (9) Hayes, J. F.; Shipman, M.; Twin, H. *J. Org. Chem.* **2002**, *67*, 935-942.