

Supporting Information

Reduction of Benzophenone by SmI₂: The Role of Proton Donors in Determining Product Distribution.

Gregory Kleiner, Alexander Tarnopolsky and Shmaryahu Hoz*

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel
shoz@mail.biu.ac.il

Experimental

THF was purified by distillation from benzophenone radical anion solution under nitrogen. Methanol was distilled from Mg/I₂ under nitrogen. Benzophenone and SmI₂ solutions (0.1M in THF) were purchased from Sigma-Aldrich Fine Chemicals.

Reactions with SmI₂ were performed in a glove box under dry inert (N₂) atmosphere.

Spectra were obtained using a Stopped Flow Spectrophotometer SF61-DX2 (Hi-Tech Ltd). ¹H-NMR spectra were obtained on a Bruker AM300 instrument. HPLC analysis was performed on a system consisting of a Waters 501 pump, a Waters 490 MWL detector, a 20μl Rheodyne 7125 loop injector and an Alltech Econosil (Si) 10μ 4.6×250mm column.

General procedure for the determination of product distribution in reactions of SmI₂ with benzophenone: Desired amount of ROH solution in THF was added to the flask containing a solution of benzophenone in THF. A solution of SmI₂ in THF was then added to this mixture under vigorous stirring. Aliquots were withdrawn from the reaction mixture at desired time intervals and quenched in a vial containing iodine solution (0.02M). Excess of iodine in quenched samples was removed by addition of concentrated Na₂S₂O₃ solution. 10 ml of 1% HCl was then added to each sample and organic products were extracted by CH₂Cl₂ (3×30 ml). Organic products were analyzed by ¹H-NMR { for the spectra of the benzophenone, benzhydrol and benzpinacol see Pouchert, C.J.; Behnke, J. The Aldrich Library of ¹³C and ¹H FT-NMR spectra, 1st Ed, Aldrich, USA, 1993 } or by HPLC.

HPLC conditions: 1ml/min isocratic CH₂Cl₂, detection on 250nm and 255nm.

Retention times and response factors are summarized in the following table:

Compound	RT(min)	255 nm		250 nm	
		RF(M ⁻¹)	Correlation	RF(M ⁻¹)	Correlation
Benzophenone	8.33	2.00E+11	0.990	2.08E+11	0.988
Benzpinacol	4.62	1.05E+10	0.984	9.51E+10	0.993

Benzhydrol	15.45	4.29E+10	0.999	3.59E+10	0.999
------------	-------	----------	-------	----------	-------

Absorbance spectrum of the reaction mixture in the range 350-700nm was recorded by a Diode Array detector immediately (~ 1 ms) after the mixing of SmI_2 solution (5mM) with benzophenone solution (5mM) in the SF61-DX2 spectrophotometer. The subsequent spectral changes were monitored by the Diode Array detector recording spectra with 0.2msec interval. Absorbance decay at 570nm fits well to second order kinetics. The second order rate constant (referred as k_1 in the manuscript) was calculated using KinetAsystTM 2.2 software (Hi- Tech Ltd, Salisbury, UK).

