## Carbon–Carbon Bond Formation using Hypervalent lodine under Lewis Acid Conditions: 1,4-Diarylbutane-1,4-diones

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Reaction of silyl enol ethers of aryl methyl ketones with PhIO-BF3 Et2O results in coupling to yield 1,4-diketones.

Recently we described the synthetic utility of hypervalent iodine oxidation of a wide range of compounds under basic conditions [PhI(OAc)<sub>2</sub>, KOH-MeOH].<sup>1</sup> We now report on the hypervalent iodine oxidation of silyl enol ethers (2a-d) under Lewis acid conditions. In this system we propose that electrophilic attack of PhI<sup>+</sup>-OBF<sub>3</sub><sup>-</sup> occurs upon (2) to yield intermediate (4) which is the synthetic equivalent of carbonium ion (5). This sequence may be viewed as an umpolung of the enol system [(3)  $\rightarrow$  (5)] and its validity was indicated by addition of H<sub>2</sub>O, MeOH, and EtOH to yield, respectively, the  $\alpha$ -substituted products [(7)-(9)]<sup>†</sup> in excellent yield.

Because of the primacy of carbon-carbon bond formation in organic synthesis we sought to capture intermediate (4) with a carbanion equivalent. We find now that silyl enol ethers such as (2a-d) [formally equivalent to (3)] fulfil this role providing a useful synthetic route to 1,4-diketones (Scheme 1).

In a typical experiment  $BF_3 \cdot Et_2O$  (0.0075 mol) was added to PhIO (0.0025 mol) in dry  $CH_2Cl_2$  or diethyl ether (50 ml)



Scheme 1. Reagents: i, ClSiMe<sub>3</sub>, Et<sub>3</sub>N-dimethylformamide; ii,  $BF_3 \cdot Et_2O$ , PhIO.

under argon. The mixture was cooled to -40 °C, then (2a–d) (0.006 mol) was added with stirring and the reaction system was kept at -40 °C for 2 h, then at room temperature for 2 h. Water was added and the product was isolated by concentrating the organic solvent to yield (6a), 45%; (6b), 43; (6c), 58; (6d), 62.‡ This procedure may be compared with the synthesis of 1,4-diketones by the reaction of silyl enol ethers with Ag<sub>2</sub>O<sup>2</sup> and the oxidative coupling of ketone enolates with CuCl<sub>2</sub>.<sup>3</sup>

Recently, the reaction of allylsilanes with PhIO-BF<sub>3</sub>·Et<sub>2</sub>O has been reported. In one case a product resulting from intramolecular attack of a neighbouring hydroxy group upon  $-CH_2=CH-CH_2-IOR(Ph)$  to yield a cyclic ether was observed,<sup>4</sup> and in another a second molecule of PhIO is considered to act as a nucleophile cleaving the R<sub>2</sub>CH-I<sup>III</sup> bond to yield R<sub>2</sub>CH-O-I<sup>III</sup> which subsequently decomposes to PhI aldehyde.<sup>5</sup> The present reaction, (**2a**-**d**)  $\rightarrow$  (**6a**-**d**), represents the first example of carbon-carbon bond formation in the reaction of organosilanes with hypervalent iodine.§

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<sup>† (7) 57%, (8) 80, (9) 70.</sup> In the case of (7) the product was isolated by direct crystallization; m.p. 86—87 °C (lit. 85—86 °C: P. Hunaeus and T. Zincke, *Ber.*, 1877, 10, 1486). The yields of (8) and (9) were determined by n.m.r. spectroscopy. A reaction which is both formally and mechanistically related to  $(1a) \rightarrow (7)$ —(9) is the reaction of acetophenone with PhI(OAc)<sub>2</sub>-AcOH-H<sub>2</sub>SO<sub>4</sub> to yield PhCO-CH<sub>2</sub>OAc (F. Mizukami, M. Ando, T. Tanaka, and J. Imamura, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 335).

<sup>‡ (6</sup>a) m.p. 143—144 °C (lit. 144 °C: P. S.Bailey and R. E. Lutz, J. Am. Chem. Soc., 1948, 70, 2412); (6b) m.p. 184—185 °C [lit. 186 °C: F. Eiden and L. Prielipp, Arch. Pharm. (Weinheim, Ger.), 1977, 310, 109]; (6c) m.p. 150—151 °C (lit. 151 °C: E. E. Campagine and W. O. Faye, J. Org. Chem., 1952, 17, 1405); (6d) m.p. 150—151 °C (lit. 150 °C: E. Lutz, J. Am. Chem. Soc., 1923, 13, 1306). The n.m.r. and i.r. spectra of (6a—d) were in agreement with recently published data, (6a) H. Stetter and F. Jonas, Chem. Br., 1980, 114, 564; (6c) V. Singh, T. C. Sharma, and M. M. Bokadia, Indian J. Chem., Sect. B, 1979, 17, 644; (6d) F. Barba, M. D. Velasco, and A. Guirado, Synthesis, 1984, 1984, 393. (6b) 'H n.m.r. (CDCl<sub>3</sub>) &: 3.47 (s, 4H,  $-CH_2CH_2-$ ), 7.00—8.10 (m, 8H, aromatic protons); i.r. (Nujol) cm<sup>-1</sup>: 1655 (C=O), 3210 (OH).

<sup>§</sup> The triethylstannyl enol ether of cyclohexanone yields the coupling product upon reaction with PhI(OAc)<sub>2</sub> [A. N. Kashin, M. L. Tulichinskit, N. A. Bumagin, I. P. Beletskaya, and O. A. Reutov, J. Org. Chem. USSR (Engl. Transl.), 1982, **18**, 1390].