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

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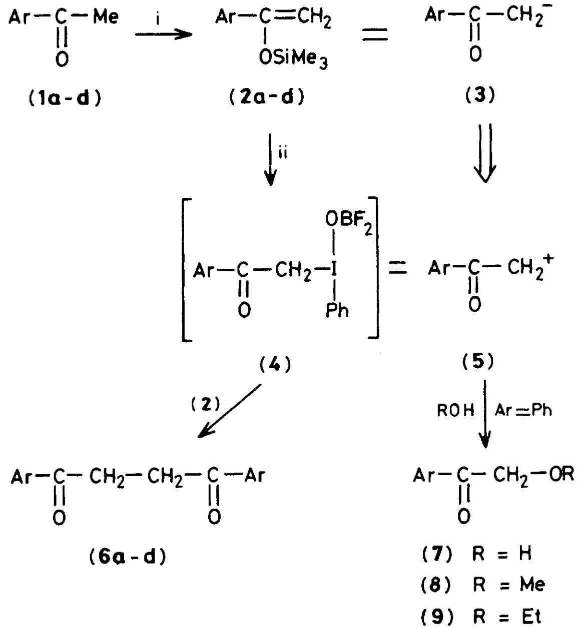
Reaction of silyl enol ethers of aryl methyl ketones with PhIO–$BF_3 \cdot Et_2O$ results in coupling to yield 1,4-diketones.

Recently we described the synthetic utility of hypervalent iodine oxidation of a wide range of compounds under basic conditions [$PhI(OAc)_2$, KOH–MeOH].[1] 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 $PhI^+–OBF_3^-$ 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**) → (**5**)] and its validity was indicated by addition of H_2O, MeOH, and EtOH to yield, respectively, the α-substituted products [(**7**)—(**9**)]† 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) 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_2O[2] and the oxidative coupling of ketone enolates with $CuCl_2$.[3]



a; Ar = Ph
b; Ar = C_6H_4OH-*o*
c; Ar = C_6H_4OMe-*p*
d; Ar = C_6H_4Cl-*p*

Scheme 1. *Reagents:* i, $ClSiMe_3$, Et_3N–dimethylformamide; ii, $BF_3 \cdot Et_2O$, PhIO.

Recently, the reaction of allylsilanes with PhIO–$BF_3 \cdot Et_2O$ 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,[4] and in another a second molecule of PhIO is considered to act as a nucleophile cleaving the $R_2CH–I^{III}$ bond to yield $R_2CH–O–I^{III}$ which subsequently decomposes to PhI aldehyde.[5] The present reaction, (**2a**—**d**) → (**6a**—**d**), represents the first example of carbon–carbon bond formation in the reaction of organosilanes with hypervalent iodine.§

We thank the USAMRDC and The Petroleum Research Fund for support of this work.

Received, 3rd December 1984; Com. 1704

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† (**7**) 57%, (**8**) 80, (**9**) 70. 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**) → (**7**)—(**9**) is the reaction of acetophenone with $PhI(OAc)_2$–$AcOH$–H_2SO_4 to yield $PhCOCH_2OAc$ (F. Mizukami, M. Ando, T. Tanaka, and J. Imamura, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 335).

‡ (**6a**) 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, 593. (**6b**) ^1H n.m.r. ($CDCl_3$) δ: 3.47 (s, 4H, $-CH_2CH_2-$), 7.00—8.10 (m, 8H, aromatic protons); i.r. (Nujol) cm^{-1}: 1655 (C=O), 3210 (OH).

§ The triethylstannyl enol ether of cyclohexanone yields the coupling product upon reaction with $PhI(OAc)_2$ [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].