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REACTION OF PhIO·HBF$_4$/SILYL ENOL ETHER ADDUCT WITH OLEFINS AS GENERAL APPROACH TO CARBON-CARBON BOND FORMATION IN Ad$_E$ REACTIONS USING HYPERVALENT IODINE REAGENTS

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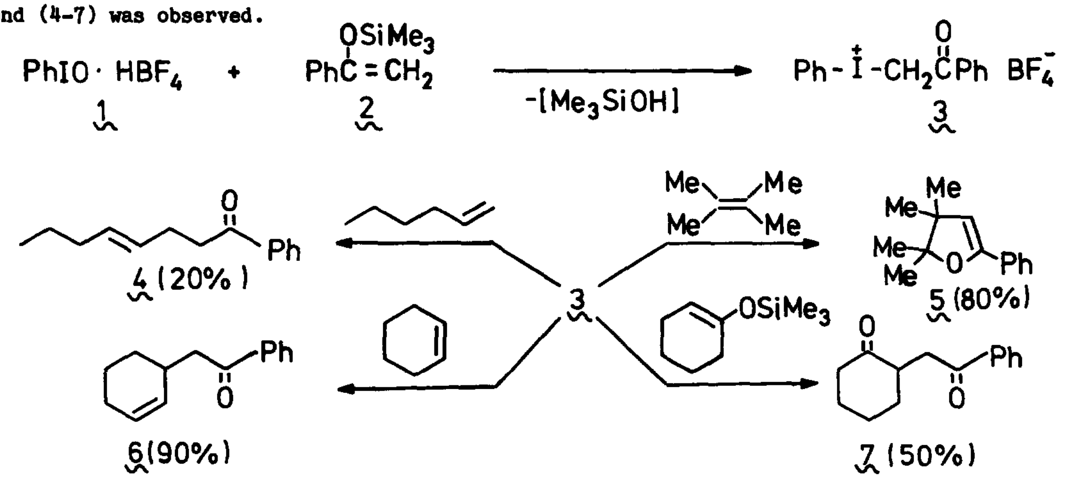
ABSTRACT: A simple method for new carbon-carbon bond formation in Ad$_E$ reactions using the PhIO·HBF$_4$ complex and silyl enol ethers has been developed.

Hypervalent iodine chemistry has attracted recently considerable attention due to the wide variety of synthetic tasks which could be solved by means of iodine(III) reagents [1-3]. One of the most remarkable achievements in recent years was the discovery of several reactions of I(III) reagents leading to the formation of new carbon-carbon bonds [2,3]. In previous papers we have reported the mild and selective reactions of iodonium ylides with a variety of alkenes under Lewis acid catalysis giving products with new C-C bonds [3]. It was demonstrated that alkyl aryl iodonium salts are reactive intermediates in these processes [3a].

In an extension of these investigations, we have developed a more convenient and common method for the generation of highly reactive iodonium salts *in situ*. This method is based on the reaction of silyl enol ethers with the electrophilic complex PhIO·HBF$_4$. We have found that iodosylbenzene reacts with HBF$_4$·Me$_2$O (1.2 equiv.) in CH$_2$Cl$_2$ at -50 - -20°C to produce a yellow solution of 1, stable up to 0°C and decomposing only at higher temperatures. When silyl enol ether 2 (1 equiv.) was added to this solution at -78°C an immediate formation of a colorless suspension was observed. The reagent formed was relatively stable, and could be stored for several hours at -50 - -20°C. Addition of this reagent to various alkenes (1 equiv.) at 0 - 20°C lead to an immediate reaction. The reaction mixtures were worked up by pouring into ice-water, extraction with CH$_2$Cl$_2$, and separation by column chromatography on silica gel. In all cases the formation of products with a new carbon-carbon bond (4-7) was observed.



$$\underset{\textbf{1}}{PhIO\cdot HBF_4} + \underset{\textbf{2}}{PhC(OSiMe_3){=}CH_2} \xrightarrow[-[Me_3SiOH]]{} \underset{\textbf{3}}{Ph\text{-}\overset{+}{I}\text{-}CH_2C(O)Ph\ BF_4^-}$$

Depending on the structure of the alkene, three different kinds of products were obtained: functionalized alkenes (4,6), dihydrofuran (5), and 1,4-diketone (7) [4]. The best yields were obtained in the reactions of cyclohexene and alkenes activated with electron-donating substituents, such as tetramethylethylene and trimethylsilyloxy cyclohexene. In all cases iodobenzene separated from the reaction mixture in a quantitative yield with acetophenone, 1,4-diphenyl-1,4-butanedione, and hydroxy acetophenone as by-products, respectively.

We propose that the iodonium salt 3 is the reactive intermediate for all of the reactions. Initial electrophilic attack of I^+ on the double bond of the alkene followed by a reductive elimination of PhI gives the final products 4-6 [5].

It is worth emphasizing that the reported reactions potentially could become a general route to new carbon-carbon bond creation. The use of the highly electrophilic complex 1 opens a pathway for the generation of various alkyl aryl iodonium salts which could be used as highly reactive reagents in electrophilic additions of different types.

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4. 4 (cis-trans, 1:1, according to GC data); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.8-0.9 (m, 7H, C_3H_7), 2.0 (m, 2H, CH_2), 3.04 (t, 2H, J = 7.7 Hz, $CH_2C{=}O$), 5.48 (m, 2H, CH=CH), 7.5 (m, 3H, Ph), 7.9 (m, 2H, Ph); MS: m/z = 202 (M^+), 159 (M^+ - C_3H_7), 133 ($PhCOCH_2CH_2$), 120 ($PhCOCH_3$), 77 (Ph). 5; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.08 (s, 6H, $2CH_3$), 1.34 (s, 6H, $2CH_3$), 7.26 (s, 1H, CH), 7.5 (m, 3H, Ph), 7.9 (m, 2H, Ph); MS: m/z = 202 (M^+), 187 (M^+ - CH_3), 172 (M^+ - $2CH_3$), 129 (M^+ - $2CH_3$ - CH_3CO), 77 (Ph). 6; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.0 - 1.1 (m, 6H, $3CH_2$), 2.95 (m, 1H, CH), 3.64 and 3.72 (2d, 2H, J = 7.4 and 6.3 Hz, CH_2CO), 5.72 (m, 2H, HC=CH), 7.5 (m, 3H), 7.9 (m, 2H); MS: m/z = 200 (M^+), 105 (PhCO), 77 (Ph). 7; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.9 - 1.4 (m, 4H, $2CH_2$), 2.18 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 3.16 (m, 1H, CHC=O), 3.60 (m, 2H, CH_2COPh), 7.5 (m, 3H), 7.9 (m, 3H); MS: m/z = 216 (M^+), 173 (M^+ - $3CH_2$), 159 (M^+ - $4CH_2$), 133 (M^+ - $4CH_2$ - CO), 120 ($PhCOCH_3$), 105 (PhCO), 77 (Ph).

5. For formation of the 1,4-diketone 7 we propose the same mechanism, as suggested by R. Moriarty in [2a].

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