

mass spectrum,  $m/z$  (relative intensity) 290 ( $M^+$ , 25), 275 (7), 205 (28), 119 (100), 91 (82); exact mass calcd for  $C_{19}H_{30}O_2$  290.2247, found 290.2244.

**Ring-Cleavage Product 21.** A ring-cleavage reaction was performed, starting from 157.8 mg (0.543 mmol) of 19, by a procedure similar to the one described above. Flash chromatography (20–25%) gave 191.2 mg (86%) of 21: oil;  $^1H$  NMR  $\delta$  0.84 (3 H, d,  $J = 6.4$  Hz,  $CH_3$ ), 0.89 (3 H, d,  $J = 6.0$  Hz,  $CH_3$ ), 1.10–1.95 [13 H, m, including d (3 H,  $J = 6.4$  Hz,  $CH_3$ ) at 1.15], 2.05–2.56 (4 H, m), 2.80 (1 H, br s), 2.93 (1 H, d,  $J = 15.6$  Hz,  $CH_2COPh$ ), 2.93 (1 H, br s), 3.04 (1 H, m,  $CH_2O$ ), 3.36 (3 H, m,  $CH_2O$ ), 3.57 (1 H, d,  $J = 15.6$  Hz,  $CH_2COPh$ ), 6.09 (2 H, m, 2  $CH=$ ), 7.13 (3 H, m, Ar), 7.99 (2 H, m, Ar); IR (liquid film) 3560 (br) 1680 (s), 1020 (s), 1000 (s), 750 (s), 685  $cm^{-1}$  (s); mass spectrum, 410 ( $M^+$ , <1), 257 (48), 137 (60), 105 (100); exact mass calcd for  $C_{27}H_{38}O_3$  410.2822, found 410.2821.

**Mono-THP Derivative 22.** This material was prepared, starting from 21, in 87% overall yield by a procedure similar to the one described in the preparation of 11. 22:  $^1H$  NMR  $\delta$  1.15–1.80 (9 H, m), 2.54 (2 H, m), 2.82 (2 H, m), 3.08–3.85 (6 H, m), 4.56 (1 H, br s), 6.03 (2 H, br s); IR (liquid film) 3410 (br), 3060 (m), 1030 (s), 730  $cm^{-1}$  (s). The optical purity of 22 was also determined after the conversion of 22 into the corresponding (*R*)-(+)-MTPA ester followed by the removal of the THP group. (*R*)-MTPA ester: oil;  $^1H$  NMR  $\delta$  1.30 (1 H, br d,  $J = 8.4$  Hz), 1.48 (1 H, t, d,  $J = 1.7$  and 8.4 Hz), 2.32–2.63 (2 H, m), 2.80 (1 H, br s), 2.91 (1 H, br s), 3.35 (2 H, d,  $J = 7.3$  Hz), 3.53 (3 H, q,  $J = 1.2$  Hz), 4.04 (1 H, dd,  $J = 6.4$  and 10.6 Hz), 4.18 (1 H, dd,  $J = 9.4$  and 10.6 Hz), 6.08 (1 H, dd,  $J = 3.2$  and 5.6 Hz), 6.16 (1 H, dd,  $J = 3.2$  and 5.6 Hz), 7.42 (3 H, m), 7.50 (3 H, m). **Mono (*R*)-MTPA ester derived from diol 16:** oil;  $^1H$  NMR  $\delta$  1.30 (1 H, m), 1.48 (1 H, m), 2.3–2.6 (2 H, m), 2.84 (1 H, br), 2.91 (1 H, br s), 3.33 and 3.35 [2 H, br d ( $J = 7.4$  Hz) and d, respectively], 3.53 and 3.55 (3 H, q,  $J = 1.2$  Hz), 4.0–4.25 (2 H, m), 6.12 (2 H, m), 7.42 (3 H, m), 7.50 (3 H, m).

**(2*S*,3*R*)-Lactone 23.** To a solution of oxalyl chloride (98  $\mu$ L, 1.12 mmol) in  $CH_2Cl_2$  (1 mL) were added a  $CH_2Cl_2$  solution (0.27 mL) of dimethyl sulfoxide (196 mg, 78.1 mmol) and a  $CH_2Cl_2$  solution (0.27 mL) of 22 (110.2 mg, 0.426 mmol) at  $-75^\circ C$ , and the mixture was stirred for 20 min. To this was added 330  $\mu$ L (2.37 mmol) of triethylamine, and then the mixture was stirred at room temperature for 1 h. After aqueous workup (brine/

$CH_2Cl_2$ ), the crude material was dissolved in aqueous 30% EtOH (10 mL) containing 23 mg of PTS and the mixture was heated at  $50^\circ C$  for 40 min. After aqueous workup (brine/ethyl acetate) followed by concentration in vacuo, the crude mixture was treated with pyridinium chlorochromate (150 mg, 0.70 mmol) in  $CH_2Cl_2$  (3 mL) at room temperature for 3 h. After the usual workup, purification by flash chromatography (50%) gave 11.5 mg (18% overall yield) of 23: oil;  $[\alpha]_D^{25} +136^\circ$  (c 1.00,  $CHCl_3$ ) [lit.<sup>2b</sup>  $[\alpha]_D^{25} +143.2$  (c 5.2,  $CHCl_3$ )];  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.45 (1 H, br d,  $J = 8.4$  Hz), 1.64 (1 H, br d,  $J = 8.4$  Hz), 3.00–3.37 (4 H, m), 3.78 (1 H, dd,  $J = 3.1$  and 9.5 Hz), 4.29 (1 H, dd,  $J = 8.2$  and 9.5 Hz), 6.30 (2 H, br s); IR (liquid film) 1750 (s), 1175 (s), 1045 (s), 1000  $cm^{-1}$  (s).

**Registry No.** 6a, 41235-26-1; 6b, 39789-20-3; 6c, 119972-72-4; 6d, 119972-73-5; 7a, 119972-74-6; 7b, 119972-75-7; 7c, 119972-76-8; 7d, 119972-77-9; 8a, 120053-10-3; 8b, 120053-11-4; 8c, 120053-12-5; 8d, 120053-13-6; 9a, 119972-78-0; 9b, 119972-79-1; 9c, 119972-80-4; 9d, 119972-81-5; 10a, 120053-14-7; 10b, 120053-15-8; 10c, 119972-82-6; 10d, 119972-83-7; 11, 120053-19-2; 11 acetate, 119972-90-6; 12, 119972-88-2; 13, 120053-18-1; 14, 58502-00-4; (*R*)-15, 64363-90-2; 16, 699-97-8; 16 (mono (*R*)-MTPA ester), 119972-97-3; 17, 119972-91-7; 18, 43187-61-7; 19, 119972-92-8; 20, 120142-40-7; 21, 119972-94-0; 22, 119972-95-1; 22 ((*R*)-MTPA ester), 119972-96-2; 23, 95340-88-8; *l*-menthone, 14073-97-3; acetophenone enol, 13735-81-4; (1*S*,2*R*)-2-(methoxymethoxy)cyclopentyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 119972-84-8; (1*R*,2*S*)-2-(methoxymethoxy)cyclopentyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 120053-16-9; (1*S*,2*R*)-2-(methoxymethoxy)cyclohexyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 119972-85-9; (1*R*,2*S*)-2-(methoxymethoxy)cyclohexyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 120053-17-0; (1*R*,2*S*)-2-(methoxymethoxy)cyclooctyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 119972-86-0; (1*S*,2*R*)-2-(methoxymethoxy)cyclooct-5-enyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 119972-87-1; (1*R*,2*S*)-2-(methoxymethoxy)cyclooct-5-enyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 120142-38-3; (1*R*,2*S*)-2-hydroxycyclohexyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 119972-89-3; (1*S*,2*R*)-2-hydroxycyclohexyl (*R*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetate, 120142-39-4; *l*-menthone dimethyl acetal, 119972-93-9.

## Carbon-Carbon Bond Formation in Reactions of $PhIO \cdot HBF_4$ /Silyl Enol Ether Adduct with Alkenes or Silyl Enol Ethers

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A new method for generation of reactive  $\alpha$ -ketomethyl arylidonium intermediates from silyl enol ethers and  $PhIO \cdot HBF_4$  has been developed. Reactions of  $PhIO \cdot HBF_4$ /silyl enol ether adduct with alkenes (1-hexene, cyclohexene,  $\alpha$ -methylstyrene, allyltrimethylsilane, 2,3-dimethyl-2-butene) yielded products of allylic alkylation or (in case of 2,3-dimethyl-2-butene) a substituted dihydrofuran. Reactions of adducts from  $PhIO/HBF_4$  and silyl enol ethers of acetophenone, *p*-chloroacetophenone, *p*-methylacetophenone, and *p*-nitroacetophenone with various silyl enol ethers led to unsymmetrical 1,4-butanediones as major products.

There is a considerable current interest in polyvalent iodine chemistry.<sup>1</sup> Although I(III) reagents have been

used for solution of a wide variety of synthetic tasks, the main application is usually connected with different oxidations.<sup>1</sup> But in recent years it has been shown that polyvalent iodine chemistry can be applied for more complicated purposes such as transformation of alkenes<sup>2,3</sup> or

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Table I. Reactions of PhIO•HBF<sub>4</sub>/Silyl Enol Ether Adducts (3) with Silyl Enol Ethers or Alkenes

reagent	substrate	product (yield, %) <sup>a</sup>	mass spectra, m/e	<sup>1</sup> H NMR, <sup>b</sup> δ	
3a	2b	4a (42)	272, 274 (M <sup>+</sup> ), 139, 141 (C <sub>10</sub> H <sub>8</sub> CO), 111, 113 (C <sub>10</sub> H <sub>8</sub> ), 105 (PhCO), 77 (Ph)	8.1–7.4 (9 H, m), 3.45 (4 H, s)	
	2c	4d (27)	282 (M <sup>+</sup> ), 150 (NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO), 105 (PhCO), 77 (Ph)	8.3–7.5 (9 H, m), 3.5 (4 H, s)	
	2d	4c (34)	268 (M <sup>+</sup> ), 163 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COCH <sub>2</sub> CH <sub>2</sub> ), 135 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CO), 107 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ), 105 (PhCO), 77 (Ph)	8.0–7.0 (9 H, m), 3.8 (3 H, s), 3.45 (4 H, s)	
	2e	4b (40)	252 (M <sup>+</sup> ), 119 (CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CO), 105 (PhCO), 77 (Ph)	7.9–7.2 (9 H, m), 3.45 (4 H, s), 3.65 (3 H, s)	
	5	6a (50) <sup>c</sup>	216 (M <sup>+</sup> ), 173, 159, 133, 120, 105 (PhCO), 77 (Ph)	7.9–7.5 (5 H, m), 3.6 (2 H, m), 3.16 (1 H, m), 2.4 (2 H, m), 2.1–1.4 (6 H, m)	
	7	8a (40)	202 (M <sup>+</sup> ), 160, 105 (PhCO), 77 (Ph)	7.9–7.5 (5 H, m), 3.5 (2 H, m), 2.6 (1 H, m), 2.5–1.6 (6 H, m)	
	9	10 (20) <sup>c,d</sup>	202 (M <sup>+</sup> ), 159 (M – C <sub>3</sub> H <sub>7</sub> ), 133 (PhCOCH <sub>2</sub> CH <sub>2</sub> ), 105 (PhCO), 77 (Ph)	7.9–7.5 (5 H, m), 5.48 (2 H, m), 3.04 (2 H, t, J = 7.7 Hz), 2.0 (2 H, m), 1.8–0.9 (7 H, m)	
	11	12 (90) <sup>c</sup>	200 (M <sup>+</sup> ), 105 (PhCO), 77 (Ph)	7.9–7.5 (5 H, m), 5.72 (2 H, m), 3.64 and 3.72 (2 H, 2 d, J = 7.4, and 6.3), 2.95 (1 H, m), 2.0–1.1 (6 H, m)	
	13	14 (63) <sup>c</sup>	160 (M <sup>+</sup> ), 105 (PhCO), 77 (Ph), 55 (CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> )	7.9–7.5 (5 H, m), 5.92 (1 H, m), 5.05 (2 H, m), 3.08 (2 H, t, J = 7.5 Hz), 2.5 (2 H, m)	
	15	16 (59) <sup>c</sup>	236 (M <sup>+</sup> ), 132, 105 (PhCO), 77 (Ph)	8.0–7.2 (10 H, m), 4.8 (2 H, m), 2.9 (2 H, m), 2.3 (2 H, m)	
	17	18 (80) <sup>c</sup>	202 (M <sup>+</sup> ), 187 (M – Me), 172 (M – 2Me), 129 (M – 2Me – CO), 77 (Ph)	7.0–7.5 (5 H, m), 7.2 (1 H, s), 1.3 (6 H, s), 1.1 (6 H, s)	
	3b	2a	4a (46)		
		2d	4f (51)	302, 304 (M <sup>+</sup> ), 139, 141 (C <sub>10</sub> H <sub>8</sub> CO), 135 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CO), 111, 113 (C <sub>10</sub> H <sub>8</sub> ), 107 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )	8.0–6.9 (8 H, m), 3.8 (3 H, s), 3.45 (4 H, s)
2e		4e (43)	286, 288 (M <sup>+</sup> ), 139, 141 (C <sub>10</sub> H <sub>8</sub> CO), 119 (CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CO), 111, 113 (C <sub>10</sub> H <sub>8</sub> ), 91 (CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )	8.0–7.2 (8 H, m), 3.5 (4 H, s), 2.65 (3 H, s)	
7		8b (44)	236, 238 (M <sup>+</sup> ), 194, 196 (M – COCH <sub>2</sub> ), 139, 141 (C <sub>10</sub> H <sub>8</sub> CO), 111, 113 (C <sub>10</sub> H <sub>8</sub> ), 97	7.9–7.4 (4 H, m), 3.46 (2 H, m), 2.6 (1 H, m), 2.4–1.6 (6 H, m)	
3c	2b	4g (38)	317 (M <sup>+</sup> ), 150 (NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO), 139, 141 (C <sub>10</sub> H <sub>8</sub> CO), 111, 113 (C <sub>10</sub> H <sub>8</sub> )	8.4–7.4 (8 H, m), 3.5 (4 H, s)	
	2d	4h (61) <sup>e</sup>	313 (M <sup>+</sup> ), 150 (NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO), 135 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CO), 107 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )	8.2–6.9 (8 H, m), 3.8 (3 H, s), 3.45 (4 H, s)	
	7	8c (75)	247 (M <sup>+</sup> ), 205 (M – COCH <sub>2</sub> ), 150 (O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CO)	8.3–8.0 (4 H, m), 3.5 (2 H, m), 2.6 (1 H, m), 2.4–1.6 (6 H, m)	
3d	2a	4c (31)			
	7	8d (30)	232 (M <sup>+</sup> ), 190 (M – COCH <sub>2</sub> ), 149 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COCH <sub>2</sub> ), 135 (CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )	7.9 (2 H, m), 6.9 (2 H, m), 3.8 (3 H, s), 3.45 (2 H, m), 2.6 (1 H, m), 2.4–1.6 (6 H, m)	
3e	5	6b (50)	230 (M <sup>+</sup> ), 187 (M – 3CH <sub>2</sub> ), 173 (M – 4CH <sub>2</sub> ), 145 (M – 4CH <sub>2</sub> – CO), 133 (CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COCH <sub>2</sub> ), 119 (CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )	7.8 (2 H, m), 7.25 (2 H, m), 3.5 (2 H, m), 3.15 (1 H, m), 2.33 (3 H, s), 2.5–1.4 (8 H, m)	
	7	8e (55)	216 (M <sup>+</sup> ), 174 (M – COCH <sub>2</sub> ), 133 (CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COCH <sub>2</sub> ), 119 (CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )	7.8 (2 H, m), 7.3 (2 H, m), 3.45 (2 H, m), 2.6 (1 H, m), 2.4 (3 H, s), 2.4–1.6 (6 H, m)	

<sup>a</sup>Yields were determined by GC analyses. <sup>b</sup>All spectra were measured in CDCl<sub>3</sub> (TMS) as internal standard at 200 MHz. <sup>c</sup>Yield of isolated product. <sup>d</sup>1:1 mixture of cis and trans isomers according to GC data. <sup>e</sup>4h, mp 145–146 °C, is in agreement with that reported first in ref 8.

alkyl iodides<sup>4</sup> into tosylates,<sup>2–4</sup> triflates,<sup>3,4</sup> perchlorates;<sup>3,4</sup> α-functionalization of ketones<sup>5</sup> and β-dicarbonyl compounds;<sup>6</sup> synthesis of allyl azides from allylsilanes;<sup>7</sup> and even creation of new carbon–carbon bonds.<sup>8–11,13–15</sup> The

last kind of reaction is one of the most important for organic synthesis and has attracted substantial attention of different groups of researchers. Formation of new car-

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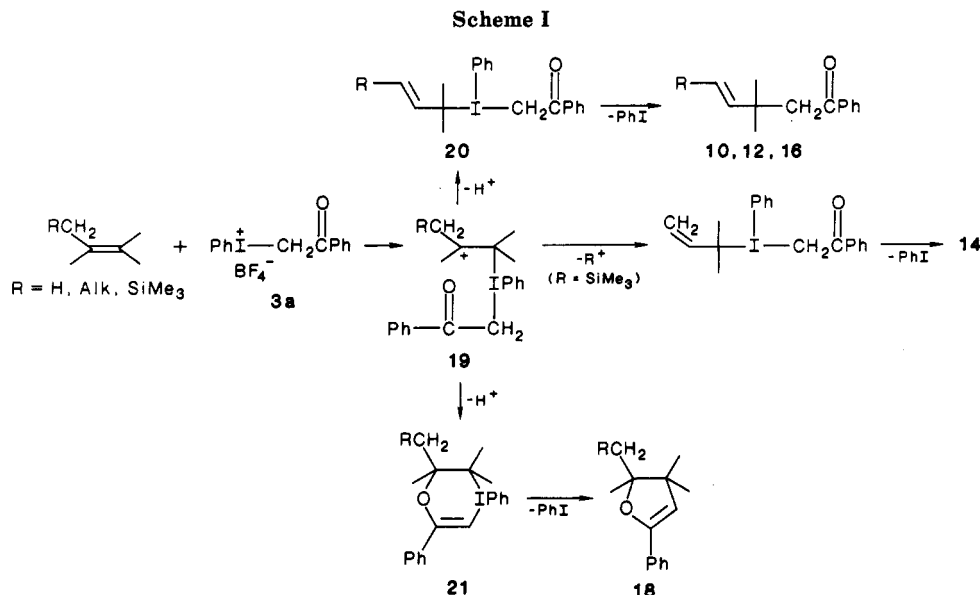
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bon-carbon bonds is possible in the reactions of organic substrates with iodonium precursors which can be either stable iodonium salts or reaction intermediates with general formula  $\text{ArI}^+\text{R X}^-$ . At present four main types of stable iodonium salts are known, in which R = aryl, alkynyl, vinyl, and perfluoroalkyl. All these reagents can react with organic substrates with formation of a new C-C bond.<sup>8-11</sup> Diaryliodonium salts are relatively unreactive, but it was shown that they can arylate  $\beta$ -dicarbonyl compounds.<sup>8</sup> Alkynyliodonium<sup>9</sup> and vinyliodonium<sup>10</sup> salts can give coupling products with organocopper reagents. Perfluoroalkyliodonium salts react under mild conditions with aromatic compounds,<sup>11a</sup> alkynes,<sup>11a</sup> alkenes,<sup>11c</sup> and silyl enol ethers<sup>11d</sup> introducing the perfluoroalkyl group into an organic substrate.

In contrast to fluorinated derivatives, alkylidonium salts are frequently unstable at room temperature, although a few stable examples have been synthesized by G. Olah.<sup>12</sup> It has been shown, for example, that  $\text{PhI}^+\text{CH}_3 \text{SbF}_6^-$  can exist only several hours at 20 °C, and then decomposition readily occurs.<sup>12a</sup> But there is strong evidence that alkylidonium salts participate as unstable intermediates in many reactions of polyvalent iodine reagents including transformations leading to new C-C bond formation. There are several ways of generation of alkylidonium salts in situ as reactive intermediates in the latter type of reaction. Recently we have shown that iodonium ylides can react with Lewis acids yielding reactive iodonium intermediates which can transform alkenes or silyl enol ethers into products with new C-C bond.<sup>13</sup> We even could separate and identify a relatively stable product of the addition of  $\text{SO}_3$  to an iodonium ylide and study its reactions with alkenes.<sup>13a</sup> A second way of generation of iodonium salts in situ was developed by R. Moriarty.<sup>14</sup> In this case silyl enol ethers and  $\text{PhIO}/\text{BF}_3$  were used as precursors for generation of  $\alpha$ -ketomethyl aryliodonium intermediates which immediately reacted with the excess of the silyl enol ether to give a product of symmetric coupling.<sup>14</sup> In the present paper we describe a method for the generation of iodonium intermediates from silyl enol ethers and  $\text{PhIO}/\text{HBF}_4$  and their reactions with alkenes or silyl enol ethers (preliminary communication, see ref 15).

### Results and Discussion

We have found that iodosobenzene reacts with  $\text{HBF}_4$ .

$\text{Me}_2\text{O}$  in methylene chloride at -50 to 0 °C with formation of a yellow solution of the highly electrophilic complex 1. This complex is unstable at room temperature and decomposes within a few minutes to give a black tar. But at low temperatures it is stable and very reactive toward unsaturated substrates. Addition of 1 equiv of a silyl enol ether 2 to this solution at -78 °C caused immediate decolorization with formation of a white suspension. No stable product could be isolated from this mixture, but results of its reactions with unsaturated compounds suggest the structure of the  $\alpha$ -ketomethyl phenyliodonium salt 3 for this reagent. We have studied reactions of this reagent with various silyl enol ethers and alkenes. Reactions were carried out by a rapid addition of reagent 3d at -78 °C to a stirred solution of a substrate (silyl enol ether or alkene) in methylene chloride. Products were separated by column chromatography on silica gel and identified with NMR and mass spectra. Yields of products and their spectral characteristics are summarized in Table I.

Initially the coupling reactions of iodonium salts 3 with silyl enol ethers were examined. Attempts to generate reagent 3 from silyl enol ethers of aliphatic ketones (pinacolone, cyclohexanone, cyclopentanone) and  $\text{PhIO}\cdot\text{HBF}_4$  were unsuccessful: we did not obtain any product of coupling after addition of this mixture to a substrate. But reactions of iodonium salts 3 generated with silyl enol ethers of acetophenones 2a-e gave more positive results, yielding products of coupling with the second silyl enol ether (1 equiv).

Average yield of coupling products 4, 6, 8 was about 50%, and the usual byproducts were corresponding acetophenones and products of symmetric couplings (less than 10%). Yields of products sharply depended upon reaction conditions (ratio of starting reagents, temperature, etc.). We could not find any correlation between yields and nature of the substituent in the aromatic ring of the silyl enol ether. It is worth emphasizing that this method works well for coupling of acetophenones with cyclohexanone and cyclopentanone. The recently reported coupling with  $\text{PhIO}\cdot\text{BF}_3$  did not work in this case.<sup>14</sup> For the formation of 1,4-diketones 4, 6, 8 we propose the same mechanism as suggested by Moriarty.<sup>14</sup>

Subsequently the reactions of reagent 3a (generated from silyl enol ether of acetophenone) with alkenes were studied. Reactions were performed by addition of a cold solution of reagent 3a to a solution of alkene (2-3 equiv)

