α-Vinylation of 1,3-Dicarbonyl Compounds with Alkenyl(aryl)iodonium Tetrafluoroborates: Effects of Substituents on the Aromatic Ring and of Radical Inhibitors

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Direct α-vinylations of enolate anions derived from 1,3-dicarbonyl compounds with 4-*tert*-butyl-1-cyclohexenyl(aryl)iodonium **2** and 1-cyclopentenyl(aryl)iodonium tetrafluoroborates **3** are reported. Frequently, α-phenylations compete with the vinylations in the reaction of 1,3-dicarbonyl compounds with alkenyl(phenyl)iodonium salts **2a** and **3a**. Use of alkenyl(*p*-methoxyphenyl)iodonium salts **2b** and **3b**, however, leads to selective α-vinylation at the expense of the competing arylation of 1,3-dicarbonyl compounds. Use of an efficient aryl radical trap, 1,1-diphenylethylene, inhibits radical-induced decomposition of the alkenyl(aryl)iodonium salts, thereby improving the yields of α-vinylations of enolate anions derived from 1,3-dicarbonyl compounds.

Simple unactivated vinyl halides tend to be nonreactive in bimolecular displacement reactions and, consequently, fail to react with metal enolates under standard experimental conditions.[1,2] Multistep α-vinylations of metal enolates using a masked vinyl cation equivalent as an electrophile are now possible[3] because of the availability of such electrophiles as α-trimethylsilyl aldehydes,[4] α-phenylseleno aldehydes,[5] and enol ethers.[6]

Recently, Pinhey and co-workers demonstrated that alkenyllead tricarboxylates, generated *in situ* by a metal (Hg, Sn, or Zn)−lead (Pb) exchange reaction, served as useful reagents for the α-vinylation of carbonyl compounds.[7] Alkenyllead triacetates are highly labile and undergo relatively fast reductive elimination of lead(II) acetate, yielding an alkyne or an enol acetate.[8,9] Rapid generation of alkenyllead triacetates (<2 min in most cases), however, makes the α-vinylation of carbonyl compounds possible.[10] Ikegami and Hashimoto in their elegant synthesis of (+)-isocarbacyclin relied on this direct vinylation of β-keto esters as a key step.[11]

Because of an excellent nucleofugality of a phenyliodonio group, which shows a leaving group ability about 10^6 times greater than triflate,[12] alkenyl(phenyl)iodonium salts serve as the highly activated species of alkenyl halides in nucleophilic vinylic substitution reactions with a number of nucleophiles, such as organocuprates, sulfinates, thiolates, nitrites, halides, cyanides, azides, and phosphines.[13−16] Few studies of the reaction of alkenylphenyliodonium salts with enolate anions are available. Vinylation of the sodium enolate of 2-phenyl-1,3-indandione (**4a**) with (2-chloro-2-phenylethenyl)iodonium tetrafluoroborate has been reported by Beringer and Galton to give 2-(2-chloro-2-phenylethenyl)-2-phenyl-1,3-indandione in 67% yield.[17] We have already reported the reaction of 2-hexyl-1,3-indandione with (4-*tert*-butyl-1-cyclohexenyl)phenyliodonium tetrafluoroborate (**2a**) in the presence of potassium *tert*-butoxide in THF, which affords 2-(4-*tert*-butyl-1-cyclohexenyl)-2-hexyl-1,3-indandione in 64% yield.[13a] We now report in detail the scope and the limitation of this direct α-vinylation of β-dicarbonyl compounds with alkenyl(aryl)iodonium salts. Also presented here are substituent effects of alkenyl(aryl)-iodonium salts on selectivity of vinylation versus arylation as well as the effects of radical inhibitors.

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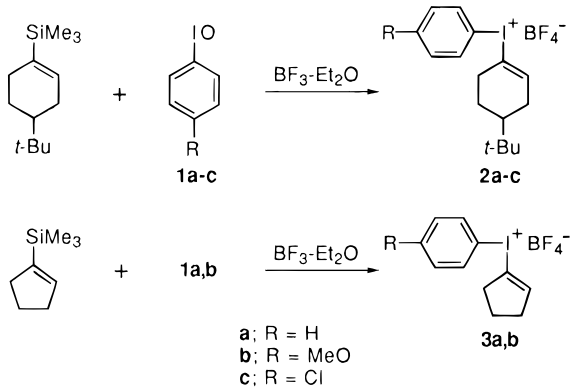
Scheme 1



Results and Discussion

Synthesis of Alkenyl(aryl)iodonium Tetrafluoroborates. 4-*tert*-Butyl-1-cyclohexenyl(aryl)iodonium tetrafluoroborates **2** were prepared by the BF_3-catalyzed silicon−iodine(III) exchange reaction of 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene[18] with iodosylbenzene (**1a**), *p*-methoxyiodosylbenzene (**1b**), or *p*-chloroiodosylbenzene (**1c**), as described previously.[12,13] In general, purification of **2** was carried out by recrystallization in dichloromethane−hexane (or diethyl ether): **2a**, 96%; **2b**, 83%; **2c**, 44%. The BF_3-catalyzed exchange reaction of 1-(trimethylsilyl)cyclopentene[18] with iodosylarenes **1a** and **1b** afforded 1-cyclopentenyliodonium salts **3a** (81%) and **3b** (73%), respectively (Scheme 1). 1-Cyclohexenyliodonium salts **2** are relatively labile and, therefore, should be kept below 0 °C. 1-Cyclopentenyliodonium salts **3**, however, remain stable for more than 1 month at ambient temperature. The very high nucleofugality of aryliodonio groups has been measured by kinetic studies of solvolysis of **2**, which generates 1-cyclohexenyl cation.[12] Thus, the reduced stability of **2** as compared with **3** would appear to reflect its tendency to dissociate to the corresponding vinyl cation, i.e., 1-cyclohexenyl cation. Generation of 1-cyclopentenyl cation has not been observed, probably because of its high energy.[19]

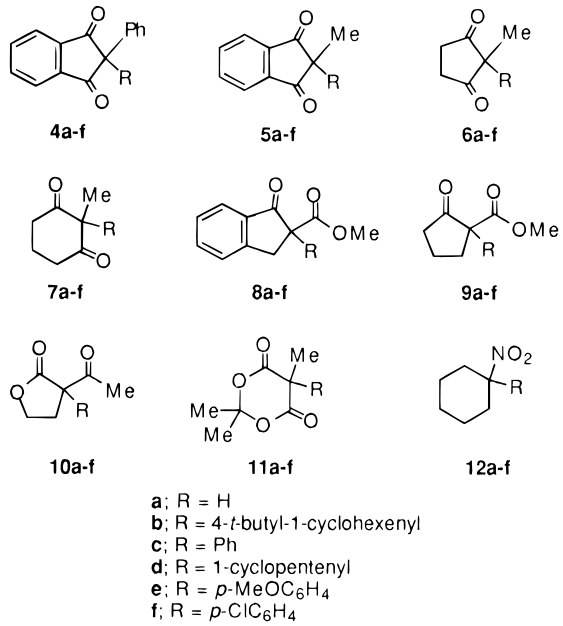
Reaction of Cyclohexenyl- (2a) and Cyclopentenylphenyliodonium Salts (3a). Exposure of the potassium enolate (1.1 equiv) of 2-phenyl-1,3-indandione (**4a**), generated by the reaction with freshly sublimed potassium *tert*-butoxide in THF for 1 h at room temperature under argon, to cyclohexenyl(phenyl)iodonium salt **2a** (1 equiv) for 4 h at room temperature resulted in nucleophilic vinylic substitutions at the *ipso* position. This direct α-vinylation of the *β*-diketone gave 2-(4-*tert*-butyl-1-cyclohexenyl)-2-phenyl-1,3-indandione (**4b**) in 86% yield. Formation of a trace amount of α-phenylation product **4c** (1%) was also detected in this reaction. The results of direct α-vinylation of 1,3-dicarbonyl compounds with cyclohexenyl-(**2a**) and cyclopentenyl(phenyl)iodonium salts (**3a**) are summarized in Table 1.

This nucleophilic vinylic substitution of **2a** with *β*-dicarbonyl compounds is very sensitive to the nature of the enolate anions. With indandiones **4a** and **5a**, the α-vinylation occurred smoothly, whereas the reaction with 1,3-cyclopentanedione **6a** was sluggish and, after prolonged treatment, gave **6b** in only 14% yield (Table 1, entry 3). It is to be noted that in the reaction with enolate anions of *β*-keto esters **8a**, **9a**, and **10a**, which afforded diastereoisomeric mixtures of α-vinylation products, the competing side reaction became serious and the undesired α-phenylation products were obtained in 7−19% yields (Table 1, entries 5−7). This situation also held true for the reaction with nitrocyclohexane (**12a**) with **2a**, in which α-phenylation was found to be a relatively major reaction process. Cyclopentenylation of *β*-diketones **4a** and **5a** with cyclopentenyl(phenyl)iodonium salt **3a** showed a similar tendency and produced a large amount of phenylation products **4c** and **5c**. Furthermore, compared to the reaction of **2a**, a longer reaction time was required for the cyclopentenylation using **3a** (Table 1, entries 1, 2, 10, and 11). The structure of **5b** was determined by spectroscopy using two-dimensional (2D) NMR techniques, i.e., ^{1}H, ^{1}H-COSY, ^{13}C, ^{1}H-COSY, and nuclear Overhauser enhancement spectroscopy (NOESY), which indicated that the nucleophilic substitution of vinyliodonium salt **2a** with **5a** takes place regioselectively at the vinylic *ipso* position.

Table 1. Reaction of 1,3-Dicarbonyl and Related Compounds with Alkenyl(phenyl)iodonium Salts 2a and 3a[a]

		iodonium	time,	product (yield,[b] %)		
entry	substrate	salt	h	vinylation	phenylation	ratio[c]
1	**4a**	**2a**	4	**4b** (86)	**4c** (1)	99:1
2	**5a**	**2a**	1	**5b** (86)	**5c** (10)	90:10
3	**6a**	**2a**	56	**6b** (14)	**6c** (0)	100:0
4	**7a**	**2a**	4	**7b** (47)	**7c** (0)	100:0
5	**8a**	**2a**	1	**8b** (19)[d]	**8c** (8)	71:29
6	**9a**	**2a**	26	**9b** (46)[e]	**9c** (19)	71:29
7	**10a**	**2a**	2.5	**10b** (53)[f]	**10c** (7)	88:12
8	**11a**	**2a**	23	**11b** (86)	**11c** (0)	100:0
9	**12a**	**2a**	2	**12b** (36)	**12c** (48)	43:57
10	**4a**	**3a**	20	**4d** (32)	**4c** (64)	33:67
11	**5a**	**3a**	44	**5d** (29)	**5c** (29)	50:50

[a] Reactions were carried out at room temperature under argon. [b] Isolated yields. [c] Ratios of vinylation versus phenylation. [d] A 2:1 mixture of diastereoisomers. [e] A 4:1 mixture of diastereoisomers. [f] A 1:1 mixture of diastereoisomers.



Not unexpectedly, *β*-diketones with an active methylene group undergo divinylation by reaction with vinyli-

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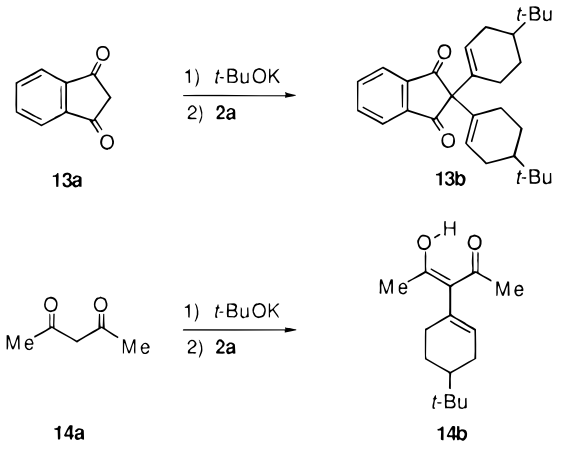
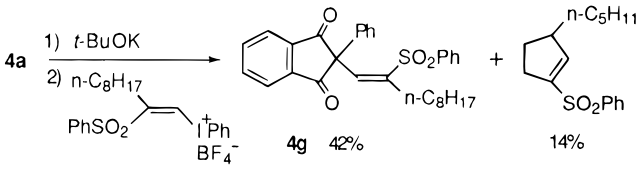
Scheme 2



Scheme 3



odonium salts. Thus, treatment of potassium enolate of **13a** with **2a** (1 equiv) afforded 2,2-bis(4-*tert*-butyl-1-cyclohexenyl)indandione (**13b**) in 9% yield (see Scheme 2). On the other hand, acetylacetone (**14a**) gave the desired olefin **14b** in 53% yield.

Alkenylphenyliodonium salts with a hydrogen atom attached to the α-vinylic carbon atom undergo a facile α-elimination by the reaction with a weak base such as Et_3N, $NaHCO_3$, and *n*-Bu_4NF to generate alkylidenecarbenes, which further undergo 1,5-carbon−hydrogen insertions, providing a useful route for the construction of substituted cyclopentenes.[20] This α-elimination pathway leading to the generation of alkylidenecarbenes appears to compete with the direct α-vinylation of 1,3-dicarbonyl compounds using alkenylphenyliodonium salts with an α-vinylic hydrogen, since enolate anions of 1,3-dicarbonyl compounds may also act as a base for α-vinylic hydrogen abstraction. Such competition between the direct α-vinylation of 1,3-dicarbonyl compounds and the α-elimination leading to the generation of alkylidenecarbenes was observed in the reaction of (*Z*)-(2-benzenesulfonyl-1-decenyl)iodonium salt with **4a**, in which a considerable amount of the alkylidenecarbene-derived 1-benzenesulfonylcyclopentene[20b] (14%) was produced along with formation of the vinyl sulfone **4g** (42%) (Scheme 3). The direct α-vinylation yielding **4g** is highly stereoselective with exclusive formation of the retained *Z*-isomer. The stereochemistry of **4g** was established by the observation of a nuclear Overhauser effect (NOE) enhancement between the vinylic and allylic protons.

Substituent Effects of Alkenyl(aryl)iodonium Salts on Selectivity of Vinylation versus Arylation. In the nucleophilic *ipso* substitution of unsymmetrical diaryliodonium salts ($ArAr'I^+X^-$), the electronic effects of substituents on the aromatic rings play an essential role in determining selectivity in that the nucleophile tends to attack the more electron-deficient aromatic ring.[16] Thus,

Scheme 4

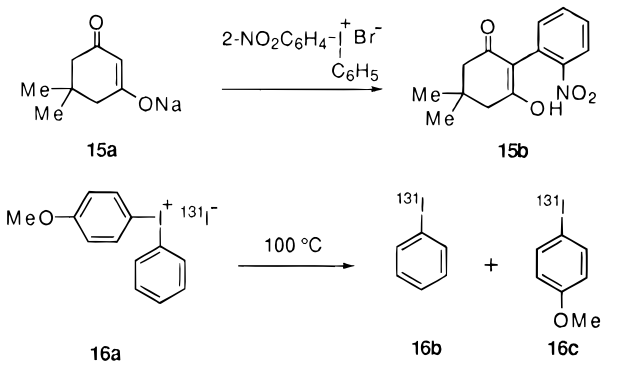


Table 2. Effects of Substituents on the Aromatic Ring of Alkenyl(aryl)iodonium Salts 2 and 3

			conditions		
entry	substrate	iodonium salt	temp, °C	time, h	product (yield,[a] %)
1	**5a**	**2b**	25	35	**5b** (72)
2	**9a**	**2b**	50	9	**9b** (61)[b]
3	**9a**	**2c**	25	1	**9b** (44)[b]
4	**10a**	**2b**	25	38	**10b** (51)[c]
5	**10a**	**2b**	50	2.5	**10b** (60)[c]
6	**10a**	**2c**	25	69	**10b** (36)[c]
7	**12a**	**2b**	50	24	**12b** (34)[d]
8	**4a**	**3b**	50	3	**4d** (51)[e]
9	**5a**	**3b**	50	14	**5d** (51)

[a] Isolated yields. [b] A 4:1 mixture of diastereoisomers. [c] A 1:1 mixture of diastereoisomers. [d] **12e** (5%) was obtained. [e] **4e** (9%) was obtained.

arylation of dimedone enolate **15a** with (*o*-nitrophenyl)-phenyliodonium salt has been shown to give 2-(*o*-nitrophenyl)dimedone (**15b**) selectively without formation of 2-phenyldimedone.[21] The presence of an electron-releasing *p*-methoxy group decelerates the nucleophilic aromatic *ipso* substitution (Scheme 4); for instance, thermolysis of **16a** affords a mixture of **16b** and **16c** in a ratio of 81:19.[22] For this reason, we sought to determine whether this substituent effect observed in the nucleophilic substitutions of diaryliodonium salts holds for those of alkenyl(aryl)iodonium salts.

Compared to the reactions of alkenyl(phenyl)iodonium salt **2a**, use of alkenyliodonium salt **2b** with a *p*-methoxyphenyl group as a ligand on the iodine(III) was found to increase the selectivity for α-vinylation at the expense of the competing α-arylation of 1,3-dicarbonyl compounds (Table 2). Thus, in marked contrast to the reaction of **2a** with enolate anions of **5a**, **9a**, and **10a** that produces 10−29% of undesired phenylation (Table 1, entries 2, 6, and 7), reactions with **2b** resulted in a highly selective α-vinylation with no sign of *p*-methoxyphenylation. α-Phenylation is a major process both for reactions of nitrocyclohexane (**12a**) with **2a** and for those of β-diketone **4a** with **3a**; however, use of (*p*-methoxyphenyl)iodonium salts **2b** and **3b** resulted in a significant selectivity for α-vinylation, although the yields were moderate (Table 2, entries 7 and 8). The presence of a *p*-methoxy group in **2b** and **3b** tends to decrease the reactivity toward the nucleophilic substitutions and,

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Table 3. Effects of Radical Inhibitors on Direct Vinylation of 1,3-Dicarbonyl and Related Compounds

				conditions		product (yield,[a] %)		
entry	substrate	iodonium salt	additive (equiv)	temp, °C	time, h	vinylation	phenylation	ratio[b]
1	**6a**	**2a**	1,1-diphenylethylene (2)	25	2	**6b** (63)	**6c** (0)	100:0
2	**7a**	**2a**	1,1-diphenylethylene (2)	25	1.5	**7b** (73)	**7c** (0)	100:0
3	**8a**	**2a**	galvinoxyl (1)	25	1.5	**8b** (23)[c]	**8c** (14)	63:37
4	**8a**	**2a**	TEMPO (1)	25	1	**8b** (70)[c]	**8c** (27)	72:28
5	**8a**	**2a**	1,1-diphenylethylene (2)	25	0.5	**8b** (74)[c]	**8c** (26)	74:26
6	**8a**	**2b**	1,1-diphenylethylene (2)	25	1.5	**8b** (79)[c]	**8e** (4)	95:5
7	**9a**	**2a**	1,1-diphenylethylene (2)	25	0.5	**9b** (72)[d]	**9c** (19)	79:21
8	**9a**	**2b**	1,1-diphenylethylene (2)	25	7	**9b** (48)[d]	**9e** (0)	100:0
9	**10a**	**2a**	1,1-diphenylethylene (2)	25	0.5	**10b** (65)[e]	**10c** (14)	82:18
10	**10a**	**2b**	1,1-diphenylethylene (2)	25	18	**10b** (66)[e]	**10e** (0)	100:0
11	**10a**	**2c**	1,1-diphenylethylene (2)	25	2	**10b** (51)[e]	**10f** (0)	100:0
12	**12a**	**2a**	1,1-diphenylethylene (2)	25	0.5	**12b** (28)	**12c** (53)	35:65
13	**12a**	**2b**	1,1-diphenylethylene (2)	50	3	**12b** (58)	**12e** (2)	96:4
14	**4a**	**3b**	1,1-diphenylethylene (2)	50	3	**4d** (66)	**4e** (24)	74:26
15	**5a**	**3a**	1,1-diphenylethylene (2)	25	24	**5d** (52)	**5c** (24)	69:31
16	**5a**	**3b**	1,1-diphenylethylene (2)	50	14	**5d** (58)	**5e** (0)	100:0

[a] Isolated yields. [b] Ratios of vinylation versus phenylation. [c] A 2:1 mixture of diastereoisomers. [d] A 4:1 mixture of diastereoisomers. [e] A 1:1 mixture of diastereoisomers.

therefore, to attain a reasonable rate; the reactions were generally carried out at 50 °C.

Interestingly, but for reasons not quite clear to us, alkenyliodonium salt **2c** with an electron-withdrawing chloro substituent at the *para* position showed selectivity similar to that of **2b**. Specifically, only α-vinylation products **9b** and **10b** were obtained in the reaction of **2c** with **9a** and **10a**, albeit in moderate yields (Table 2, entries 3 and 6).

Effects of Radical Inhibitors on Direct α-Vinylation. The extensive studies conducted by Beringer and his co-workers on arylation of enolate anions derived from 1,3-dicarbonyl compounds with diaryliodonium salts suggests that the generation of the aryl radicals by electron transfer from enolates to iodonium salts, with subsequent decomposition of the resulting 9-I-2 intermediate, are involved in this arylation reaction.[21,23,24] Barton and his co-workers,[25] however, employing spin trapping experiments using 1,1-diphenylethylene, clearly demonstrated that the reaction involves two competing mechanisms: an induced radical-chain process producing aromatic hydrocarbons and a nonradical process yielding arylation products. 1,1-Diphenylethylene is an efficient phenyl radical trap that inhibits the radical-induced decomposition of diphenyliodonium salts into benzene; accordingly, use of this trap in the reaction with enolate anions improves the yields of phenylated products.[25,26]

To investigate the occurrence of a radical process in this vinylation reaction using alkenyl(aryl)iodonium salts as well as to improve the yields of the vinylation, effects of radical inhibitors were examined. The results are summarized in Table 3. When β-keto ester **8a** was treated with cyclohexenyl(phenyl)iodonium salt **2a** in the presence of galvinoxyl (1 equiv) as an additive, the yields of vinylation and phenylation products **8b** and **8c** were only slightly increased[27] (compare Table 1, entry 5, and Table 3, entry 3). On the other hand, use of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 1 equiv) or 1,1-diphenylethylene (2 equiv) as an additive improved the yield of **8b** dramatically up to 70−74% and that of **8c** (26−27%), but did not affect the selectivity on vinylation versus phenylation. The best results, in terms of yields and selectivity, for the direct vinylation of **8a** were obtained by using cyclohexenyl(*p*-methoxyphenyl)iodonium salt (**2b**) in the presence of 1,1-diphenylethylene (Table 3, entry 6). Similarly, the addition of 1,1-diphenylethylene was found to considerably increase the yields of vinylation of β-diketones **6a** and **7a**, and β-keto ester **9a** in the reaction with **2a**. Use of this radical trap also improved the yields of cyclopentenylation of **4a** and **5a** (Table 3, entries 14−16). More than 80 mol % of 1,1-diphenylethylene is generally recovered unchanged in these reactions. Unexpectedly, conflicting results on the effects of this radical trap were obtained from the vinylation of nitrocyclohexane (**12a**); that is, the reaction of **12a** with **12b** was much improved with added 1,1-diphenylethylene, but the yield of **12b** was decreased in the reaction with **2a**. In addition, we found that the use of this trap decreased the yield of the reaction of **9a** with **2b**.

To gain a better understanding of the effects of this radical inhibitor, product analysis was carried out in detail for the vinylation of **8a** with **2a** in the presence and absence of the inhibitor. It is clear from the data presented in Scheme 5 that, in addition to the phenylation yielding **8c**, the formation of benzene (**19**) as well as 4-*tert*-butylcyclohexene (**20**) is a major competing reaction. Thus, in the absence of 1,1-diphenylethylene as an additive, benzene (**19**) and 4-*tert*-butylcyclohexene (**20**) are produced in 45% and 39% yields, respectively. In the presence of 2 equiv of 1,1-diphenylethylene, however, the yields of **19** and **20** drop to 27% and 7%, respectively.

As described above, these hydrocarbons **19** and **20** appear to be radical products. The 9-I-2 intermediate **21** (Scheme 6), probably produced by electron transfer from the enolate to iodonium salt **2a**, can decompose to

(23) (a) Beringer, F. M.; Galton, S. A.; Huang, S. J. *J. Am. Chem. Soc.* **1962**, *84*, 2819. (b) Beringer, F. M.; Forgione, P. S. *Tetrahedron* **1969**, *19*, 739. (c) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 3917.

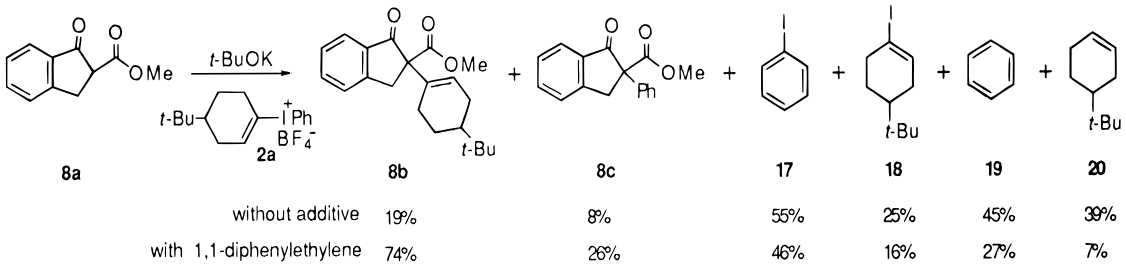
(24) (a) Chen, K.; Koser, G. F. *J. Org. Chem.* **1991**, *56*, 5764. (b) Hampton, K. G.; Harris, T. M.; Hauser, C. R. *J. Org. Chem.* **1964**, *29*, 3511.

(25) Barton, D. H. R.; Finet, J.-P.; Giannotti, C.; Halley, F. *J. Chem. Soc., Perkin Trans. 1* **1987**, 241.

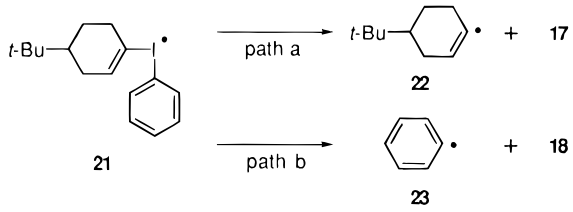
(26) (a) Lubinkowski, J. J.; Knapczyk, J. W.; Calderon, J. L.; Petit, L. R.; McEwen, W. E. *J. Org. Chem.* **1975**, *40*, 3010. (b) Lubinkowski, J. J.; Gomez, M.; Calderon, J. L.; McEwen, W. E. *J. Org. Chem.* **1978**, *43*, 2432. (c) Lubinkowski, J. J.; Arrieche, C. G.; McEwen, W. E. *J. Org. Chem.* **1980**, *45*, 2076. (d) Singh, P. R.; Khanna, R. K. *Tetrahedron Lett.* **1982**, *23*, 5355.

(27) The effects of galvinoxyl as a radical trap in the reaction are relatively small. This is probably because this radical can react with bases, in this case, enolate anions.[28]

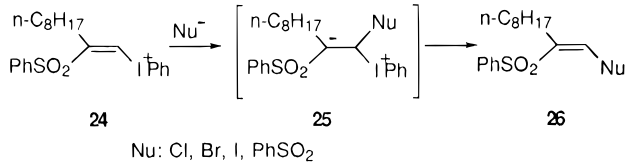
Scheme 5



Scheme 6



Scheme 7



generate 4-*tert*-butylcyclohexenyl radical **22** and iodobenzene (**17**) (path a), or to generate phenyl radical (**23**) and 4-*tert*-butyl-1-iodocyclohexene (**18**) (path b). These radicals would be responsible for the formation of **19** and **20**. Of these two pathways for the decomposition of **21**, path a would be favored over path b because of the higher stability associated with the combination of the vinyl radical **22** and **17** compared to that of the phenyl radical (**23**) and the vinyl iodide **18**.[13a,29] Clearly, 1,1-diphenylethylene is functioning as an inhibitor of a radical reaction which produces **19** and **20**, presumably by capturing the vinyl and the phenyl radicals.[25,26,28] The extent of the changes in the yield of benzene (**19**) in the presence and absence of the inhibitor suggests that some process other than a phenyl radical mechanism is responsible for the formation of **19**. It is evident from Table 3, entry 4, that the presence of TEMPO in the reaction mixture also inhibits the radical reactions.

On the basis of these findings as well as the great improvement of the yields of vinylation and phenylation products, we believe, with Barton,[25] that vinyl and phenyl radical mechanisms are not involved in either the vinylation or the phenylation reactions.

Reaction Mechanism. Many mechanisms have been recognized in nucleophilic vinylic substitutions.[30] Among them, the elimination−addition mechanism via the intermediate formation of 4-*tert*-butyl-1-cyclohexyne from **2** should be considered. Nucleophilic substitutions of 1-chlorocyclohexene in the presence of $NaNH_2$−*t*-BuONa have been shown to involve initial formation of cyclohexyne via *syn*-β-elimination, followed by nucleophilic addition.[31] Our inability to detect any 2-(5-*tert*-butyl-1-cyclohexenyl)-2-phenyl-1,3-indandione or 2-(5-*tert*-butyl-1-cyclohexenyl)-2-methyl-1,3-indandione among the products in the reactions of **4a** or **5a** with **2a**, in spite of our careful search, would seem to eliminate the possibility that cyclohexyne intermediates are involved. As mentioned above, nucleophilic substitutions of alkenyliodonium salt **2a** take place only at the vinylic *ipso* position, and furthermore, involvement of the highly labile cyclopentyne intermediate seems to be unlikely.

Solvolysis of **2** generates 1-cyclohexenyl cation even at 25 °C.[12] This vinyl cation pathway, however, cannot be applied to the direct vinylation of β-dicarbonyl compounds, because 1-cyclopentenylation with **3** also occurs smoothly even at 25−50 °C (Table 1−3). We know of no evidence verifying the generation of 1-cyclopentenyl cation.[19] Strongly bent vinyl cations, such as cyclopentenyl cations, are strained too much to be formed as an intermediate. Furthermore, the stereochemical outcome of α-vinylation of **4a** with (*Z*)-(2-benzenesulfonyl-1-decenyl)iodonium salt, leading to exclusive formation of the retained *Z*-isomer **4g** (Scheme 3), is not compatible with this vinyl cation pathway, which might expect formation of stereoisomeric mixtures.

An addition−elimination sequence at the α-vinylic carbon atoms of alkenyliodonium salts has been proposed for nucleophilic vinylic substitutions with tetrabutylammonium halides and sodium benzenesulfinate substitutions that proceed with exclusive retention of configuration (Scheme 7).[15] This mechanism nicely explains stereoselective formation of the retained *Z*-isomer **4g**. Although this pathway is the most common in nucleophilic vinylic substitutions, the presence of a highly electron-withdrawing group such as a benzene sulfonyl group promotes the formation of betaine **25**. The alkenyliodonium salts **2** and **3** do not bear substituents associated with the stabilization of betaine intermediates.

An alternative possibility, illustrated in Scheme 8, involves the intermediate formation of hypervalent organoiodane **27** and/or **28** by ligand exchange on the iodine(III). Subsequent ligand coupling on the iodine(III) of **27** or **28** would give rise to vinylation products.[22a,32] Koser and Chen have suggested the formation of similar intermediates in their elegant regiocontrolled reactions of silyl enol ethers with diphenyliodonium fluoride.[24a] Furthermore, the reported structure of crystalline diben-

(28) (a) Lai, C. C.; McEwen, W. E. *Tetrahedron Lett.* **1971**, *3271*. (b) Leardini, R.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 285.

(29) The value of $\Delta H°$ for the following reaction has been calculated to be 2.4 kcal/mol. See: Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

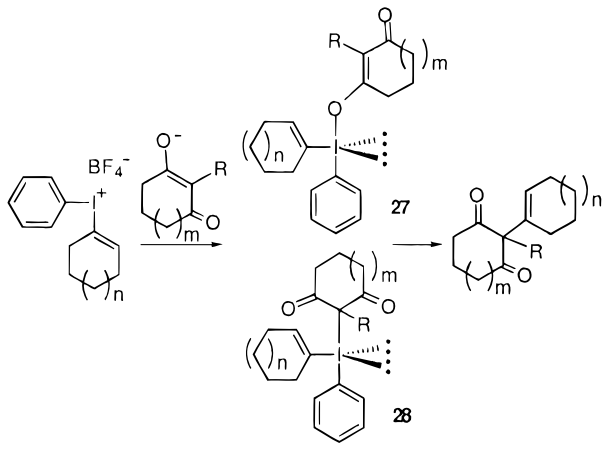
$$C_6H_5I + H_2C{=}CH^{\bullet} \rightarrow C_6H_5^{\bullet} + H_2C{=}CHI$$

(30) For reviews, see: (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (c) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211. (d) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (e) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (f) Shainyan, B. A. *Usp. Khim.* **1986**, *55*, 942. (g) Rappoport, Z. *Acc. Chem. Res.* **1992**, *25*, 474.

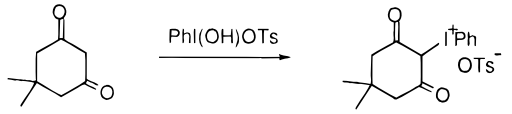
(31) Caubere, P. *Acc. Chem. Res.* **1974**, *7*, 301.

(32) (a) Oae, S. *Acc. Chem. Res.* **1991**, *24*, 202. (b) Grushin, V. V.; Shcherbina, T. M. *J. Organomet. Chem.* **1985**, *292*, 105.

Scheme 8



Scheme 9



ziodolium 1,3-diphenyl-1,3-propanedionate prepared by the reaction of dibenziodolium salt with β-diketone, in which the enolate anion serves as a chelate ligand for the iodonium cation, suggests that the oxygen-coordinated iodane **27** may serve as an intermediate.[33,34]

The conclusions of Moriarty and Koser that the α-oxysulfonylation or α-hydroxylation of ketones with [hydroxy(tosyloxy)iodo]benzene or iodosylbenzene (**1a**) under both basic and acidic conditions probably involves formation of α-aryliodonio ketones as reactive intermediates have been generally accepted.[35] In fact, 2-dimedonylphenyliodonium tosylate (**29**) has been isolated from the reaction of dimedone with [hydroxy(tosyloxy)iodo]benzene in acetonitrile at room temperature (Scheme 9).[36] Further, reaction of diphenyliodonium salts with phenyllithium has been shown to give triphenyliodine(III).[37] These results suggest that another possible structure, **28**, in which the β-diketone is coordinated as a carbon (Cα) ligand on the iodine(III), may serve as an intermediate.

In conclusion, reactions of alkenyl(aryl)iodonium tetrafluoroborates **2** and **3** with enolate anions derived from 2-substituted 1,3-dicarbonyl compounds afford 2-alkenyl-1,3-dicarbonyl compounds. Use of 1,1-diphenylethylene inhibits the radical-induced decomposition of these iodonium salts and, thereby, improves the yield of the vinylated products. Furthermore, the presence of an electron-releasing *p*-methoxy group in **2b** and **3b** improves the selectivity of the *ipso* vinylation over the arylation.

Experimental Section

General. For general experimental detail, see ref 12. Potassium *tert*-butoxide was freshly sublimed repeatedly (two times) *in vacuo* prior to use. 2-Phenyl-1,3-indandione (**4a**), 2-methyl-1,3-cyclopentanedione (**6a**), 2-methyl-1,3-cyclohexanedione (**7a**), methyl 2-oxocyclopentanecarboxylate (**9a**), 2-acetylbutyrolactone (**10a**), 2,2,5-trimethyl-1,3-dioxane-4,6-dione (**11a**), nitrocyclohexane (**12a**), and 1,3-indandione (**13a**) are commercially available. 2-Methyl-1,3-indandione (**5a**) and 2-carbomethoxyindanone (**8a**) were prepared according to literature procedure.[38,39]

(4-*tert*-Butyl-1-cyclohexenyl)phenyliodonium Tetrafluoroborate (2a) and (4-*tert*-Butyl-1-cyclohexenyl)(*p*-chlorophenyl)iodonium Tetrafluoroborate (2c). The BF_3-catalyzed silicon−iodonium exchange reaction between 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene and iodosylbenzene (**1a**) or *p*-chloroiodosylbenzene (**1c**) was carried out in the same way as described previously.[12] The yields of **2a** and **2c** were 96% and 44%, respectively.

(4-*tert*-Butyl-1-cyclohexenyl)(*p*-methoxyphenyl)iodonium Tetrafluoroborate (2b). To a stirred suspension of *p*-methoxyiodosylbenzene (1b) (38 mg, 0.15 mmol) and 4-*tert*-butyl-1-(trimethylsilyl)cyclohexene[40] (20 mg, 0.10 mmol) in dichloromethane (3 mL) was added $BF_3{\cdot}Et_2O$ (22 mg, 0.15 mmol) at 0 °C under nitrogen, and the mixture was stirred for 3 h at 0 °C and for an additional 2 h at room temperature. After the addition of a saturated aqueous sodium tetrafluoroborate solution (3 mL), the mixture was stirred for 5 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under an aspirator vacuum to give an oil, which was washed several times with hexane−diethyl ether by decantation at −78 °C. Recrystallization from hexane−diethyl ether gave the alkenyliodonium salt **2b** (36 mg, 83%) as a powder: mp 84−87 °C dec; IR (KBr) 1570, 1490, 1175, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.92 (br d, J = 8.9 Hz, 2H), 7.01 (br d, J = 8.9 Hz, 2H), 7.00−6.87 (m, 1H), 3.87 (s, 3H), 2.80−2.11 (m, 3H), 2.01−1.66 (m, 2H), 1.60−1.11 (m, 2H), 0.84 (s, 9H); FAB MS *m*/*z* 371 [$(M - BF_4)^+$]. Anal. Calcd for $C_{17}H_{24}OBF_4I$: C, 44.57; H, 5.28. Found: C, 44.40; H, 5.11.

(1-Cyclopentenyl)phenyliodonium Tetrafluoroborate (3a). To a stirred suspension of iodosylbenzene (1a) (2.1 g, 9.6 mmol) and 1-(trimethylsilyl)cyclopentene[40] (840 mg, 6.0 mmol) in dichloromethane (30 mL) was added $BF_3{\cdot}Et_2O$ (1.4 g, 9.6 mmol) at 0 °C under nitrogen, and the mixture was stirred for 1 h at 0 °C and for an additional 0.5 h at room temperature. After the addition of a saturated aqueous sodium tetrafluoroborate solution, the mixture was stirred for 15 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under an aspirator vacuum to give an oil, which was washed several times with hexane−diethyl ether by decantation at −78 °C. Recrystallization from dichloromethane−diethyl ether gave the alkenyliodonium salt **3a** (1.39 g, 81%) as colorless crystals: mp 78−79 °C; IR (KBr) 2954, 1475, 1446, 1055, 770, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (br d, J = 7.5 Hz, 2H), 7.65 (br t, J = 7.5 Hz, 1H), 7.49 (br t, J = 7.5 Hz, 2H), 6.94 (m, 1H), 2.78−2.61 (m, 4H), 2.03 (quint, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 150.7 (d), 135.6 (d), 132.7 (d), 132.4 (d), 109.5 (s), 108.8 (s), 37.9 (t), 33.8 (t), 23.1 (t); FAB MS *m*/*z* 271 [$(M - BF_4)^+$]. Anal. Calcd for $C_{11}H_{12}BF_4I$: C, 36.91; H, 3.38. Found: C, 37.12; H, 3.39.

(1-Cyclopentenyl)(*p*-methoxyphenyl)iodonium Tetrafluoroborate (3b). To a stirred suspension of *p*-methoxyiodosylbenzene (1b) (143 mg, 0.57 mmol) and 1-(trimethylsilyl)-cyclopentene[40] (50 mg, 0.36 mmol) in dichloromethane (5 mL)

(33) (a) Greidanus, J. W.; Rebel, W. J.; Sandin, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 1504. (b) Lee, P. E.; Soderberg, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 4132.

(34) For the formation of S−O sulfurane intermediates in the reaction of sulfonium salts with enolate anions, see: (a) Kobayashi, M.; Umemura, K.; Watanabe, N.; Matsuyama, H. *Chem. Lett.* **1985**, 1067. (b) Kobayashi, M.; Umemura, K.; Matsuyama, H. *Chem. Lett.* **1987**, 327. (c) Umemura, K.; Matsuyama, H.; Watanabe, N.; Kobayashi, M.; Kamigata, N. *J. Org. Chem.* **1989**, *54*, 2374. (d) Umemura, K.; Matsuyama, H.; Kobayashi, M.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3026.

(35) (a) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. (b) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. (c) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431.

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(37) (a) Wittig, G.; Rieber, M. *Ann. Chem.* **1949**, *562*, 187. (b) Claus, K. *Chem. Ber.* **1955**, *88*, 268. (c) Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1971**, *36*, 4055.

(38) Mosher, W. A.; Soeder, R. W. *J. Org. Chem.* **1971**, *36*, 1561.

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(40) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017.

was added $BF_3{\cdot}Et_2O$ (81 mg, 0.57 mmol) at 0 °C under nitrogen, and the mixture was stirred for 3 h at 0 °C and for an additional 3 h at room temperature. After the addition of a saturated aqueous sodium tetrafluoroborate solution (5 mL), the mixture was stirred for 5 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under an aspirator vacuum to give an oil, which was washed several times with hexane−diethyl ether by decantation at −78 °C. Further purification by decantation using diethyl ether gave the alkenyliodonium salt **3b** (101 mg, 73%) as an oil: IR (Nujol) 1570, 1485, 1180, 1060, 1025, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91 (br d, J = 8.9 Hz, 2H), 6.99 (br d, J = 8.9 Hz, 2H), 6.91−6.80 (m, 1H), 3.86 (s, 3H), 2.77−2.55 (m, 4H), 2.03 (quint, J = 7.6 Hz, 2H); FAB MS m/z 301 [$(M\text{-}BF_4)^+$]; HRMS (FAB) calcd for $C_{12}H_{14}OI$ [$(M - BF_4)^+$] 301.0089, found 301.0107.

General Procedure for Direct Vinylation of 1,3-Dicarbonyl Compounds with Alkenyl(aryl)iodonium Salts 2 and 3. To a stirred solution of freshly sublimed potassium *tert*-butoxide (15 mg, 0.13 mmol) in THF (2 mL) was added a 1,3-dicarbonyl compound (0.13 mmol) under argon at room temperature, and the mixture was stirred for 1 h. A solution of an alkenyl(aryl)iodonium salt **2** or **3** (0.12 mmol) in THF (3 mL) was added to this mixture at room temperature or at 50 °C, and the mixture was stirred for the periods shown in Tables 1 and 2. Water was added, the mixture was extracted with diethyl ether three times, and the combined organic phase was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated to give an oil, which was purified by preparative TLC. The yields of pure products are given in Tables 1 and 2.

2-(4-*tert*-Butyl-1-cyclohexenyl)-2-phenyl-1,3-indandione (4b): pale yellow needles; mp 102−104 °C (recrystallized from diethyl ether−hexane); IR ($CHCl_3$) 1735, 1705, 1595, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06−7.97 (m, 2H), 7.90−7.78 (m, 2H), 7.41−7.20 (m, 5H), 5.61−5.50 (m, 1H), 2.16−1.69 (m, 5H), 1.37−1.08 (m, 2H), 0.82 (s, 9H); MS m/z (relative intensity) 358 (100, M^+), 301 (15), 287 (46). Anal. Calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Found: C, 83.68; H, 7.44.

2,2-Diphenyl-1,3-indandione (4c):[23a] pale yellow prisms; mp 117−119 °C (recrystallized from ethanol); IR ($CHCl_3$) 1740, 1720, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.11−8.07 (m, 2H), 7.92−7.87 (m, 2H), 7.29 (m, 10H); MS m/z (relative intensity) 298 (100, M^+), 241 (31), 165 (32).

2-(1-Cyclopentenyl)-2-phenyl-1,3-indandione (4d): pale yellow needles; mp 134−138 °C (recrystallized from diethyl ether−hexane); IR ($CHCl_3$) 1735, 1700, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.10−7.98 (m, 2H), 7.92−7.82 (m, 2H), 7.40−7.28 (m, 5H), 5.72−5.60 (m, 1H), 2.43−2.23 (m, 4H), 1.87 (quint, J = 7.1 Hz, 2H); MS m/z (relative intensity) 288 (100, M^+), 259 (13), 231 (16), 202 (15). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.06; H, 5.81.

2-Phenyl-2-(*p*-methoxyphenyl)-1,3-indandione (4e): colorless oil; IR ($CHCl_3$) 1740, 1725, 1700, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.14−8.04 (m, 2H), 7.95−7.84 (m, 2H), 7.36−7.26 (m, 5H), 7.21 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 3.77 (s, 3H); MS m/z (relative intensity) 328 (100, M^+), 271 (13), 228 (14); HRMS calcd for $C_{22}H_{16}O_3$ (M^+) 328.1099, found 328.1095.

2-(4-*tert*-Butyl-1-cyclohexenyl)-2-methyl-1,3-indandione (5b): colorless plates; mp 102−104 °C (recrystallized from diethyl ether−hexane); IR ($CHCl_3$) 1750, 1710, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.04−7.94 (m, 2H), 7.92−7.80 (m, 2H), 5.70−5.62 (m, 1H), 2.15−1.70 (m, 5H), 1.41 (s, 3H), 1.28−1.04 (m, 2H), 0.81 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 203.6 (s), 202.8 (s), 141.4 (s), 141.3 (s), 135.8 (d), 135.8 (d), 133.9 (s), 126.7 (d), 123.7 (d), 123.5 (d), 59.6 (s), 43.3 (d), 32.1 (s), 27.2 (t), 27.2 (t), 27.1 (q), 24.1 (t), 16.9 (q); MS m/z (relative intensity) 296 (100, M^+), 239 (15), 225 (42), 161 (38); HRMS calcd for $C_{20}H_{24}O_2$ (M^+) 296.1776, found 296.1794. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.61; H, 8.25.

2-Methyl-2-phenyl-1,3-indandione (5c):[41] colorless plates; mp 159−161 °C (recrystallized from diethyl ether−hexane); IR ($CHCl_3$) 1740, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.10−8.0 (m, 2H), 7.95−7.84 (m, 2H), 7.39−7.25 (m, 5H), 1.72 (s, 3H); MS m/z (relative intensity) 236 (100, M^+), 104 (26), 77 (16); HRMS calcd for $C_{16}H_{12}O_2$ (M^+) 236.0837, found 236.0834.

2-(1-Cyclopentenyl)-2-methyl-1,3-indandione (5d): pale yellow crystals; mp 94−96 °C (recrystallized from diethyl ether−hexane); IR ($CHCl_3$) 1740, 1705, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06−7.92 (m, 2H), 7.92−7.76 (m, 2H), 5.65−5.52 (m, 1H), 2.40−2.12 (m, 4H), 1.90−1.70 (m, 2H), 1.48 (s, 3H); MS m/z (relative intensity) 226 (100, M^+), 211 (51), 197 (21), 105 (32), 77 (24). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.35; H, 6.31.

2-(4-*tert*-Butyl-1-cyclohexenyl)-2-methyl-1,3-cyclopentanedione (6b): colorless plates; mp 129−131 °C (recrystallized from diethyl ether−hexane); IR ($CHCl_3$) 1760, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.59−5.48 (m, 1H), 3.04−2.54 (m, 4H), 2.20−1.68 (m, 5H), 1.34−1.01 (m, 2H), 1.19 (s, 3H), 0.84 (s, 9H); MS m/z (relative intensity) 248 (12, M^+), 220 (100), 163 (42), 136 (39), 79 (35), 57 (38); HRMS calcd for $C_{16}H_{24}O_2$ (M^+) 248.1776, found 248.1777. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.29; H, 9.77.

2-(4-*tert*-Butyl-1-cyclohexenyl)-2-methyl-1,3-cyclohexanedione (7b): colorless plates; mp 145−147 °C (recrystallized from diethyl ether−hexane); IR ($CHCl_3$) 1720, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.45−5.34 (m, 1H), 2.94−2.67 (m, 2H), 2.58−2.35 (m, 2H), 2.23−1.64 (m, 7H), 1.30−1.00 (m, 2H), 1.25 (s, 3H), 0.85 (s, 9H); MS m/z (relative intensity) 262 (1, M^+), 206 (100), 149 (21). Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.60; H, 9.94.

2-(4-*tert*-Butyl-1-cyclohexenyl)-2-carbomethoxy-1-indanone (8b): a 2:1 mixture of diastereoisomers; colorless oil; IR ($CHCl_3$) 1710, 1655, 1605, 1230, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.79 (br d, J = 7.7 Hz, 1H), 7.61 (br t, J = 7.7 Hz, 1H), 7.44 (br d, J = 7.7 Hz, 1H), 7.38 (br t, J = 7.7 Hz, 1H), 5.69−5.59 (m, a major isomer), 5.59−5.50 (m, a minor isomer), 3.98 (d, J = 17.7 Hz, a minor isomer), 3.92 (d, J = 17.7 Hz, a major isomer), 3.76 (s, a minor isomer), 3.76 (s, a major isomer), 3.26 (d, J = 17.7 Hz, a major isomer), 3.22 (d, J = 17.7 Hz, a minor isomer), 2.50−1.64 (m, 5H), 1.40−1.10 (m, 2H), 0.83 (s, 9H); MS m/z (relative intensity) 326 (74, M^+), 267 (100), 210 (47), 182 (77), 57 (31); HRMS calcd for $C_{21}H_{26}O_3$ (M^+) 326.1882, found 326.1867.

2-Carbomethoxy-2-phenyl-1-indanone (8c): colorless oil; IR ($CHCl_3$) 1720, 1610, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (br d, J = 7.7 Hz, 1H), 7.62 (br t, J = 7.7 Hz, 1H), 7.57−7.18 (m, 7H), 4.24 (d, J = 17.3 Hz, 1H), 3.75 (s, 3H), 3.56 (d, J = 17.3 Hz, 1H); MS m/z (relative intensity) 266 (55, M^+), 238 (90), 207 (100), 178 (100); HRMS calcd for $C_{17}H_{14}O_3$ (M^+) 266.0942, found 266.0936. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.47; H, 5.34.

2-(4-*tert*-Butyl-1-cyclohexenyl)-2-carbomethoxycyclopentanone (9b): a 4:1 mixture of diastereoisomers; colorless oil; IR ($CHCl_3$) 1740, 1720, 1360, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.58−5.54 (m, a major isomer), 5.54−5.52 (m, a minor isomer), 3.74 (s, a minor isomer), 3.73 (s, a major isomer), 2.58−2.42 (m, 1H), 2.42−2.18 (m, 3H), 2.18−1.74 (m, 7H), 1.33−1.09 (m, 2H), 0.86 (s, a major isomer), 0.85 (s, a minor isomer); MS m/z (relative intensity) 278 (8, M^+), 250 (100), 222 (21), 166 (20); HRMS calcd for $C_{17}H_{26}O_3$ (M^+) 278.1882, found 278.1895.

2-Carbomethoxy-2-phenylcyclopentanone (9c): colorless oil; IR ($CHCl_3$) 1750, 1720, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40−7.28 (m, 5H), 3.71 (s, 3H), 2.89 (dt, J = 13.6, 6.4 Hz, 1H), 2.54 (dt, J = 13.6, 6.4 Hz, 1H), 2.54−2.31 (m, 2H), 2.08−1.86 (m, 2H); MS m/z (relative intensity) 218 (100, M^+), 190 (12), 175 (15), 159 (10); HRMS calcd for $C_{13}H_{14}O_3$ (M^+) 218.0943, found 218.0943.

2-Acetyl-2-(4-*tert*-butyl-1-cyclohexenyl)butyrolactone (10b): a 1:1 mixture of diastereoisomers; colorless crystals; IR ($CHCl_3$) 1760, 1710, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.99−5.90, 5.90−5.78 (each m, total 1H), 4.30−4.06 (m, 2H), 3.00, 2.93 (each t, J = 7.7 Hz, total 1H), 2.36, 2.34 (each s, total 3H), 2.21−1.57 (m, 6H), 1.35−1.00 (m, 2H), 0.87 (s, 9H); MS m/z (relative intensity) 264 (1, M^+), 222 (100), 207 (18), 138 (43). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.48; H, 9.08.

(41) Henze, H. R.; Leanza, W. J. *J. Org. Chem.* **1952**, *17*, 4.

2-Acetyl-2-phenylbutyrolactone (10c): colorless oil; IR ($CHCl_3$) 1760, 1715, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48−7.28 (m, 5H), 4.38−4.14 (m, 2H), 3.34 (ddd, J = 12.9, 7.6, 6.3 Hz, 1H), 2.37 (ddd, J = 12.9, 7.0, 6.4 Hz, 1H), 2.21 (s, 3H); MS *m/z* (relative intensity) 182 (10), 162 (100), 117 (73), 77 (34).

5-(4-*tert*-Butyl-1-cyclohexenyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (11b): white needles; mp 79−80 °C (recrystallized from diethyl ether−hexane); IR ($CDCl_3$) 1780, 1740, 1385, 1295 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91−5.80 (m, 1H), 2.36−1.79 (m, 5H), 1.76 (s, 3H), 1.73 (s, 3H), 1.66 (s, 3H), 1.33−1.03 (m, 2H), 0.86 (s, 9H); MS *m/z* (relative intensity) 294 (3, M^+), 279 (1), 208 (100), 152 (41), 124 (20); HRMS calcd for $C_{17}H_{26}O_4$ (M^+) 294.1831, found 294.1826. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.12; H, 8.83.

1-(4-*tert*-Butyl-1-cyclohexenyl)-1-nitrocyclohexane (12b): colorless plates; mp 77−79 °C (recrystallized from diethyl ether−hexane); IR ($CDCl_3$) 1530, 1445, 1365 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.98−5.91 (m, 1H), 2.56−2.40 (m, 2H), 2.20−2.04 (m, 2H), 2.00−1.73 (m, 5H), 1.73−0.98 (m, 8H), 0.85 (s, 9H); MS *m/z* (relative intensity) 219 [100, $(M - NO_2)^+$], 163 (26), 123 (53), 109 (38), 81 (44), 67 (32), 57 (78). Anal. Calcd for $C_{16}H_{27}O_2N \cdot {}^1/_4H_2O$: C, 71.20; H, 10.27; N, 5.19. Found: C, 71.28; H, 9.98; N, 4.99.

1-Nitro-1-phenylcyclohexane (12c):[42] colorless oil; IR ($CHCl_3$) 1535, 1445, 1345 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52−7.30 (m, 5H), 2.94−2.75 (m, 2H), 2.25−1.99 (m, 2H), 1.76−1.26 (m, 6H); MS *m/z* (relative intensity) 159 [93, $(M - NO_2)^+$], 91 (100).

1-Nitro-1-(*p*-methoxyphenyl)cyclohexane (12e):[43] colorless oil; IR ($CHCl_3$) 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (d, J = 9.2 Hz, 2H), 6.88 (d, J = 9.2 Hz, 2H), 3.81 (s, 3H), 2.90−1.10 (m, 10H); MS *m/z* (relative intensity) 189 [100, $(M - NO_2)^+$], 121 (100), 81 (25).

Reaction of 1,3-Indandione (13a) with 2a. To a stirred solution of freshly sublimed potassium *tert*-butoxide (8 mg, 0.07 mmol) in THF (1.5 mL) was added the diketone **13a** (11 mg, 0.07 mmol) under argon at room temperature, and the mixture was stirred for 1 h. A solution of (4-*tert*-butyl-1-cyclohexenyl)phenyliodonium salt **2a** (31 mg, 0.07 mmol) in THF (1.5 mL) was added to this mixture at room temperature, and the mixture was stirred for 2 h. Water was added, the mixture was extracted with diethyl ether three times, and the combined organic phase was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated to give an oil, which was purified by preparative TLC (8:2 hexane−diethyl ether) to give 2,2-bis(4-*tert*-butyl-1-cyclohexenyl)-1,3-indandione (**13b**) (2.8 mg, 9%) as colorless crystals: mp 144−146 °C (recrystallized from diethyl ether−hexane); IR (KBr) 1735, 1700, 1590, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.03−7.87 (m, 2H), 7.87−7.71 (m, 2H), 5.69−5.55 (m, 2H), 2.33−1.69 (m, 10H), 1.23−1.00 (m, 4H), 0.85 (s, 18H); MS *m/z* (relative intensity) 418 (100, M^+), 361 (26), 57 (26); HRMS calcd for $C_{29}H_{38}O_2$ (M^+) 418.2872, found 418.2859. Anal. Calcd for $C_{29}H_{38}O_2$: C, 83.21; H, 9.15. Found: C, 82.94; H, 9.06.

Reaction of 2,4-Pentanedione (14a) with 2a. To a stirred solution of freshly sublimed potassium *tert*-butoxide (148 mg, 1.3 mmol) in THF (25 mL) was added the diketone **14a** (130 mg, 1.3 mmol) under argon at room temperature, and the mixture was stirred for 1 h. A solution of (4-*tert*-butyl-1-cyclohexenyl)phenyliodonium salt (**2a**) (512 mg, 1.2 mmol) in THF (25 mL) was added to this mixture at room temperature, and the mixture was stirred for 8 h. Water was added, the mixture was extracted with diethyl ether three times, and the combined organic phase was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated to give an oil. Flash chromatography of the crude product using hexane−diethyl ether (9:1) yielded the olefin **14b** (149 mg, 53%) as colorless needles: mp 77−78 °C (recrystallized from methanol); IR ($CHCl_3$) 1695, 1590, 1360, 975, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 16.35 (s, 1H), 5.63−5.57 (m, 1H), 2.22−1.84 (m, 5H), 2.04 (s, 6H), 1.34−1.16 (m, 2H), 0.90 (s, 9H); MS *m/z* (relative intensity) 236 (70, M^+), 221 (14), 179 (71), 161 (33), 137 (41), 57 (40), 43 (100). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 75.85; H, 10.13.

Reaction of 4a with (*Z*)-Phenyl(2-benzenesulfonyl-1-decenyl)iodonium Tetrafluoroborate. To a stirred solution of freshly sublimed potassium *tert*-butoxide (17 mg, 0.15 mmol) in THF (1.5 mL) was added the diketone **4a** (33 mg, 0.15 mmol) under argon at room temperature, and the mixture was stirred for 1.5 h. A solution of (*Z*)-phenyl(2-benzenesulfonyl-1-decenyl)iodonium tetrafluoroborate[20b] (76 mg, 0.13 mmol) in THF (1.5 mL) was added to this mixture at room temperature, and the mixture was stirred for 24 h. Water was added, the mixture was extracted with diethyl ether three times, and the combined organic phase was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated to give an oil, which was purified by preparative TLC (dichloromethane−hexane (2:1) and ethyl acetate−hexane (2:8)) to give (*Z*)-2-phenyl-2-(2-benzenesulfonyl-1-decenyl)-1,3-indandione (**4g**) (28 mg, 42%) and 1-benzenesulfonyl-3-pentylcyclopentene[20b] (5 mg, 14%). **4g**: colorless needles; mp 114−115 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 1740, 1700, 1585, 1295, 1245, 960, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02−7.96 (m, 2H), 7.86 (br d, J = 7.3 Hz, 2H), 7.77−7.72 (m, 2H), 7.61 (br t, J = 7.3 Hz, 1H), 7.53 (br t, J = 7.3 Hz, 2H), 7.46 (br d, J = 7.3 Hz, 2H), 7.33 (br t, J = 7.3 Hz, 2H), 7.27 (br t, J = 7.3 Hz, 1H), 6.26 (t, J = 1.7 Hz, 1H), 2.16 (dt, J = 1.7, 7.3 Hz, 2H), 1.39 (quint, J = 7.3 Hz, 2H), 1.30−1.10 (m, 10H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 197.3 (s), 142.7 (s), 141.5 (s), 139.8 (s), 138.7 (s), 138.5 (d), 135.1 (d), 133.7 (d), 129.4 (d), 129.1 (d), 128.3 (d), 128.2 (d), 127.3 (d), 123.6 (d), 66.0 (s), 32.1 (t), 31.7 (t), 29.0 (t), 28.9 (t), 28.8 (t), 22.6 (t), 14.0 (q); MS *m/z* (relative intensity) 500 (15, M^+), 359 (100), 222 (43), 71 (51); HRMS calcd for $C_{31}H_{32}O_4S$ (M^+) 500.2021, found 500.2018. Anal. Calcd for $C_{31}H_{32}O_4S \cdot {}^1/_4H_2O$: C, 73.71; H, 6.48. Found: C, 73.82; H, 6.44. The stereochemistry of **4g** was established by the observation of an NOE enhancement between vinylic (δ 6.26) and allylic protons (δ 2.16).

1-Benzenesulfonyl-3-pentylcyclopentene. The title compound showed spectral properties identical with those of the compound previously synthesized.[20b]

General Procedure for Vinylation of 1,3-Dicarbonyl Compounds in the Presence of Radical Inhibitors. To a stirred solution of freshly sublimed potassium *tert*-butoxide (15 mg, 0.13 mmol) in THF (2 mL) was added a 1,3-dicarbonyl compound (0.13 mmol) under argon at room temperature, and the mixture was stirred for 1 h. A radical inhibitor (galvinoxyl (0.12 mmol), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (0.12 mmol), or 1,1-diphenylethylene (0.24 mmol)) and subsequently a solution of an alkenyl(aryl)iodonium salt **2** or **3** (0.12 mmol) in THF (3 mL) were added to this mixture at room temperature or at 50 °C, and the mixture was stirred for the periods shown in Table 3. Water was added, the mixture was extracted with diethyl ether three times, and the combined organic phase was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated to give an oil, which was purified by preparative TLC. The yields of pure products are given in Table 3.

2-Carbomethoxy-2-(*p*-methoxyphenyl)-1-indanone (8e): colorless oil; IR (neat) 1715, 1600, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (d, J = 7.7 Hz, 1H), 7.68−7.24 (6H), 6.87 (d, J = 8.7 Hz, 2H), 4.19 (d, J = 17.3 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.55 (d, J = 17.3 Hz, 1H); MS *m/z* (relative intensity) 296 (34, M^+), 268 (26), 253 (27), 237 (100), 165 (69); HRMS calcd for $C_{18}H_{16}O_4$ (M^+) 296.1049, found 296.1064.

Byproduct Analysis for Vinylation of 2-Carbomethoxyindanone (8a) with 2a. (a) Without Additive. To a stirred solution of freshly sublimed potassium *tert*-butoxide (9 mg, 0.08 mmol) in THF (0.5 mL) was added a solution of the β-keto ester **8a** (15 mg, 0.08 mmol) in THF (1 mL) under argon at room temperature, and the mixture was stirred for 1 h. A solution of the iodonium salt **2a** (31 mg, 0.07 mmol) in THF (1.5 mL) was added to this mixture at room temperature, and the mixture was stirred for 1 h. Water was added, the mixture was extracted with pentane, and the combined organic phase was washed with water and brine. The yields of byproducts were determined by analytical GC using a column of 20%

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(43) Kozyrod, R. P.; Pinhey, J. T. *Aust. J. Chem.* **1985**, *38*, 713.

silicone GE SF-96 on Chromosorb W-AWDMCS: benzene (**19**, 45%) (50 °C, heptane as the internal standard), iodobenzene (**17**, 55%), 4-*tert*-butylcyclohexene (**20**, 39%)[12] (120 °C, dodecane as the internal standard), and 4-*tert*-butyl-1-iodocyclohexane (**18**, 25%)[13a] (180 °C, pentadecane as the internal standard). For the yields of **8b** and **8c**, see entry 5 in Table 1.

(b) In the Presence of 1,1-Diphenylethylene. To a stirred solution of freshly sublimed potassium *tert*-butoxide (9 mg, 0.08 mmol) in THF (0.5 mL) was added a solution of the β-keto ester **8a** (15 mg, 0.08 mmol) in THF (1 mL) under argon at room temperature, and the mixture was stirred for 1 h. 1,1-Diphenylethylene (26 mg, 0.14 mmol)] and subsequently a solution of the iodonium salt **2a** (31 mg, 0.07 mmol) in THF (1.5 mL) was added to this mixture at room temperature, and the mixture was stirred for 0.5 h. Water was added, the mixture was extracted with pentane, and the combined organic phase was washed with water and brine. The yields of byproducts were determined by analytical GC using a column of 20% silicone GE SF-96 on Chromosorb W-AWDMCS: benzene (**19**, 27%), iodobenzene (**17**, 46%), 4-*tert*-butylcyclohexene (**20**, 7%), and 4-*tert*-butyl-1-iodocyclohexene (**18**, 16%). For the yields of **8b** and **8c**, see entry 5 in Table 3.

Supporting Information Available: ^{1}H NMR spectra for **3b**, **4e**, **4g**, **8b**, **8e**, **9b**, **9c**, and **10c** and the ^{13}C NMR spectrum for **4g** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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