Reaction of Alkynyl(phenyl)(*p*-phenylene)bisiodonium Ditriflates with Nucleophiles. High Reactivity of the Alkynyl Component

Tsugio Kitamura,* Takahiro Fukuoka, Lei Zheng, Takeshi Fujimoto, Hiroshi Taniguchi, and Yuzo Fujiwara

Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University 36, Hakozaki, Fukuoka 812-81

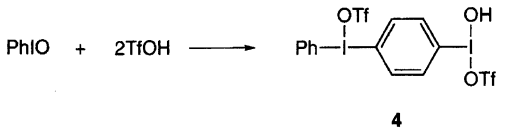
(Received May 8, 1996)

Reaction of alkynyl (*p*-phenylene) bisiodonium ditriflates with potassium thiocyanate in DMF gave alkynyl thiocyanates and *p*-iodophenyl (phenyl) iodonium triflate. The latter was readily removed by washing with water. The exclusive sulfur attack of thiocyanate ion suggests that the alkynyl group behaves as a soft acceptor of nucleophiles. The reactions with the enolate anion of 2-phenyl-1,3-indandione in DMF afforded 2-(1-cyclopentenyl)-2-phenyl-1,3-indandiones in the cases of 1-hexynyl- and 1-octynyl-(*p*-phenylene)bisiodonium ditriflates. In the reactions of 3,3-dimethyl-1-butynyl-, phenylethynyl-, and trimethylsilylethynyl-(*p*-phenylene) bisiodonium ditriflates, 2-alkynyl-2-phenyl-1,3-indandiones were obtained. The same reactions with the enolate anion of 2-phenyl-1,3-indandione in a mixed solvent of 2-methyl-2-propanol and THF improved the yields of the 1-cyclopentenyl- and alkynyl-substituted indandiones. A large difference in the reaction pathways between the (*p*-phenylene) bisiodonio and phenyliodonio moieties was observed in the sterically hindered 3,3-dimethyl-1-butynyl systems.

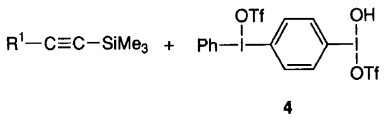
Recently much attention has been paid to functionalized iodonium salts because of their unique properties and synthetic utility.[1] Especially, alkynyl(phenyl)iodonium salts are valuable in organic synthesis.[2] They act as Michael acceptors, as synthon for "alkynyl cations", and as 1,3-dipolarophiles. Equally, the reaction of alkynyliodonium salts with nucleophiles is mechanistically important because the reaction provides "unsaturated carbenes", e.g., alkylidenecarbenes, as the reactive intermediates.

Alkynyliodonium salts prepared so far are alkynyl(phenyl)iodonium salts (**1**).[2] Various substituents (R) have been introduced by using terminal alkynes and alkynylsilanes and -stannanes. However, there are few investigations with respect to the nature of the phenyl part. Ochiai et al.[3] reported the preparation of alkynyl-substituted cyclic iodinanes (1,2-benziodoxol-3(1*H*)-ones) (**2**) without any chemical reactions. Recently we[4] and Zhdankin et al.[5] have independently reported alkynyl(*o*-carboxyphenyl)iodonium salts (**3**). These functionalized alkynyliodonium salts **2** and **3** are specially interesting because the functionality of the phenyl group is expected to affect the reactivity of alkynyliodonium salts (Chart 1).

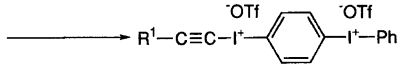
In the course of the studies on the activation of PhIO by TfOH,[6] we have noticed that PhIO dimerizes with an excess of TfOH to form 1-[(hydroxy)(trifluoromethylsulfonato)iodo]-4-[(phenyl)(trifluoromethylsulfonato)iodo]-benzene (**4**).[7] This reagent has two iodine(III) atoms at the para position in the aromatic ring and is useful as a transfer reagent of (*p*-phenylene)bisiodine(III) group. In fact, the reaction of (*p*-phenylene) bisiodine(III) reagent **4** with 1-trimethylsilyl-1-alkynes gave alkynyl (*p*-phenylene) bisiodonium ditriflates (**5**) in good to high yields (Eqs. 1 and 2).[8] The alkynyl (*p*-phenylene) bisiodonium salts have different substituents at two iodine(III) atoms and are good substrates to investigate the reactivity and selectivity toward nucleophiles. Thus, we examined the reaction of alkyny (*p*-phenylene) bisiodonium ditriflates **5** with nucleophiles. In this paper we wish to report a high reactivity of the alkynyl component in the reaction of **5** with nucleophiles and the comparison with alkynyl(phenyl)iodonium salts **1**.



4 (1)



4



5 (2)

Results and Discussion

Reaction of Alkynyl(*p*-phenylene)bisiodonium Ditri-

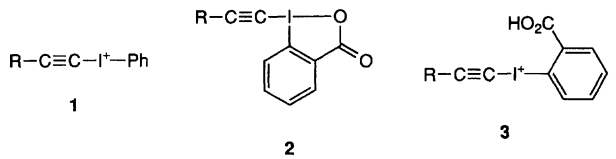
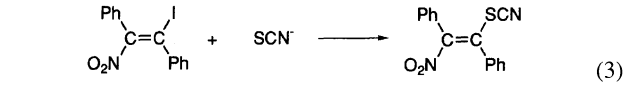
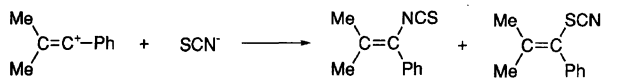


Chart 1.

flates (5) with Thiocyanate Ion. Thiocyanate ion is classified as a soft nucleophile and is one of the ambident nucleophiles.[9] The reaction of thiocyanate ion indicates the relative softness of the reaction center. Nucleophilic substitution on vinylic carbons occurs at the softer sulfur atom in the case of vinyl derivatives (Eq. 3)[10] in which the reaction proceeds with addition–elimination mechanism. In the case of vinyl cations where the reaction center is harder, however, the reaction of thiocyanate ion takes place at both sides of thiocyanate ion (S and N-atoms) (Eq. 4).[11] Accordingly, the softness of the acetylenic carbons of alkynyliodonium salts can be qualitatively decided by the reaction with thiocyanate ion. Previous works by Stang[12] and us[13] indicated that the reaction with alkynyl(phenyl)iodonium salts selectively provides alkynyl thiocyanates (**6**).

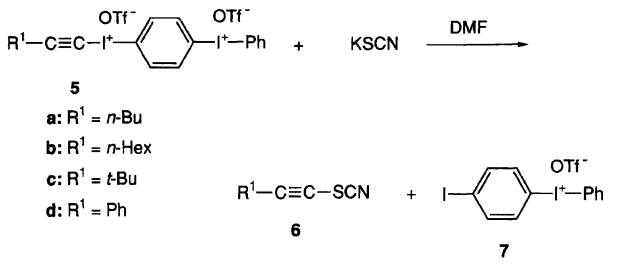


(3)



(4)

When alkyny (*p*-phenylene) bisiodonium ditriflates **5** were allowed to react with potassium thiocyanates in DMF at room temperature, alkynyl thiocyanates **6** were obtained as the sole product in 87—97 yields (Eq. 5). This result indicates that the reaction of thiocyanate ion occurs at the sulfur atom and the alkynyl group of **5** behaves as a soft acceptor of nucleophiles. Although there are several possible reaction sites in the alkynyl(*p*-phenylene)bisiodonium substrate, the alkynyl moiety is apparently superior to the other *p*-phenylene part. In addition to **6**, the reaction of thiocyanate ion yielded *p*-iodophenyl(phenyl)iodonium triflate (**7**) as the by-product, which could easily be removed by washing with water during the workup. Alkynyl thiocyanates **6** could be obtained as the pure form ($\gg$ 95%) by extraction with ether. Accordingly, the merits using **5** are a simple preparation and an easy isolation of the product.



(5)

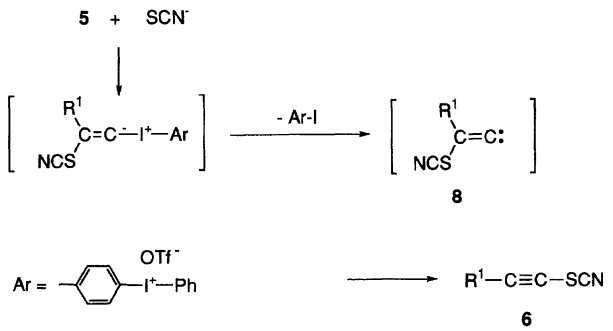
The reaction of **5** with thiocyanate ion proceeds with a nucleophilic attack of sulfur atom on the β carbon of the alkynyl group, followed by elimination of *p*-iodophenyl-(phenyl)iodonium ion (Scheme 1). Thus, the resulting alkylidenecarbene (**8**) undergoes 1,2-migration to give **6**. The 1, 2-migration efficiently occurs owing to the high migratory aptitude of sulfur group.[14]

Reaction of 5 with the Enolate Anion of 2-Phenyl-1,3-indandione. The enolate anions of 1,3-dicarbonyl compounds are typical carbon nucleophiles to react with alkynyl(phenyl)iodonium salts **1** and have been widely investigated.[15] Here we examined the reaction of alkynyl(*p*-phenylene)bisiodonium ditriflates **5** with the enolate anion of 2-phenyl-1,3-indandione and considered the influence of the (*p*-phenylene)bisiodonium moiety on the reaction behavior.

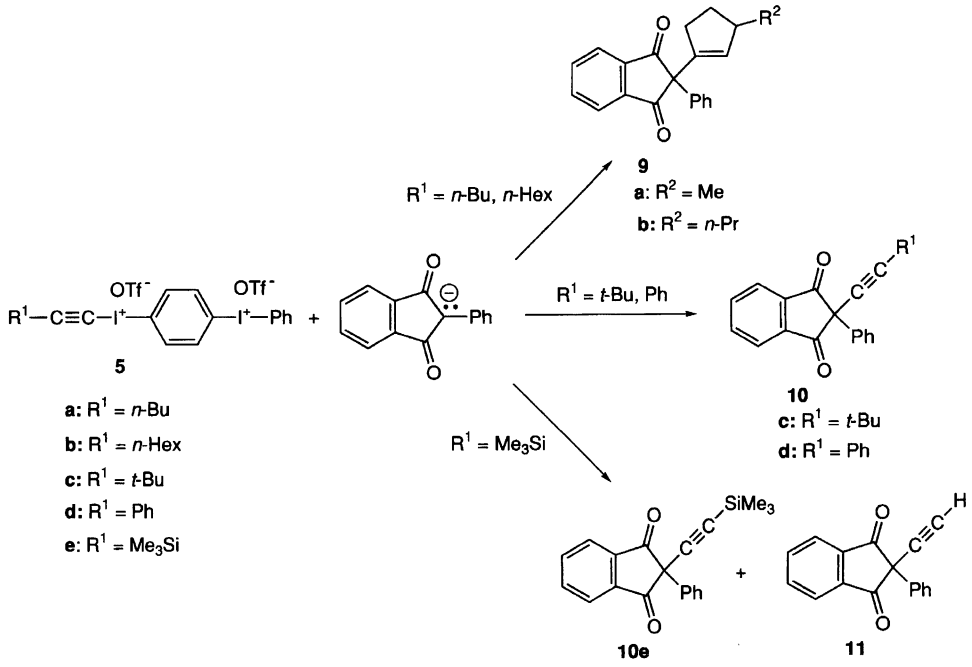
The phenylindandione enolate ion was prepared by reaction of 2-phenyl-1,3-indandione with potassium 2-methyl-2-propoxide in DMF and was reacted with **5**. The products were strongly dependent upon the substituent of the alkynyl group. In the cases of **5** with linear alkyl groups, butyl and hexyl (R^1=*n*-Bu and *n*-Hex), the reactions with the phenylindandione enolate gave 2-(1-cyclopentenyl)-1,3-indandiones (**9**) (Scheme 2). The formation of **9** is explained by a mechanism involving Michael addition of the phenylindandione enolate, followed by generation and 1,5-C–H insertion of alkylidenecarbenes.[15]

On the other hand, in the cases of **5** with *t*-butyl and phenyl groups (R^1=*t*-Bu and Ph), 2-alkynyl-2-phenyl-1,3-indandiones (**10**) were obtained. The reaction of trimethylsilylethynyl(*p*-phenylene)bisiodonium ditriflate (**5e**) gave desilylated ethynyl derivative **11** as the major product. The formation of the alkynyl-substituted indandiones **10** can be explained by 1,2-migration of the β substituent in the alkylidenecarbenes generated by Michael addition and the successive elimination of the iodoarene (Scheme 3). This 1, 2-migration is similar to the reaction with thiocyanate ion, which has a high migratory aptitude and undergoes exclusive migration. The results are summarized in Table 1.

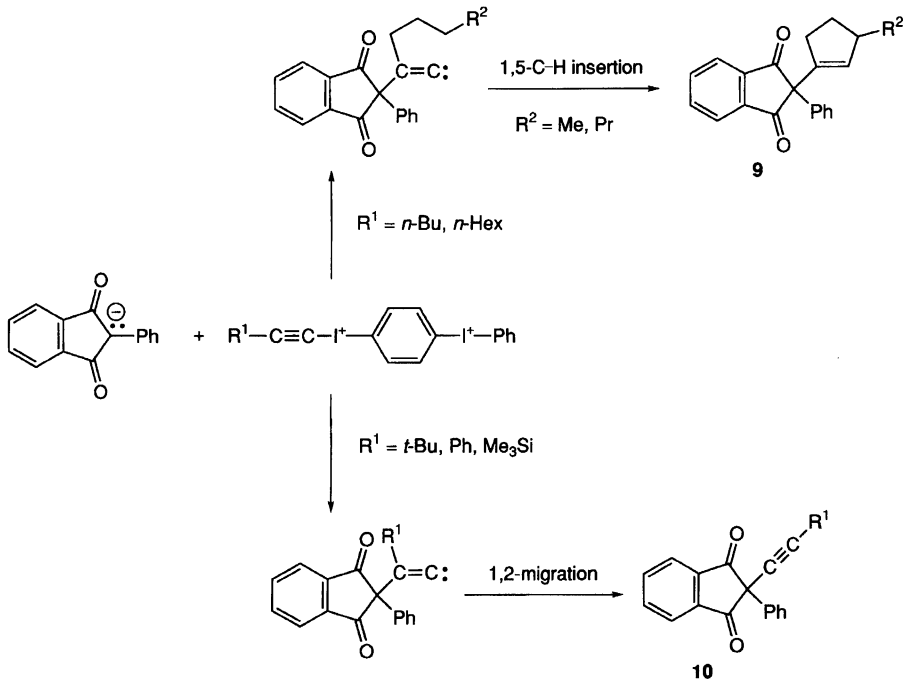
A large improvement of the product formation was observed when a mixed solvent of 2-methyl-2-propanol and THF was used instead of DMF. The results are given in Table 1. In contrast to the reaction in DMF, the yields of **9** or **10** are remarkably increased. The relatively low yield of **10** from the *t*-butyl derivative **5c** (R^1=^{t}Bu) can be attributed to a steric reason of the bulky *t*-butyl group.



Scheme 1.

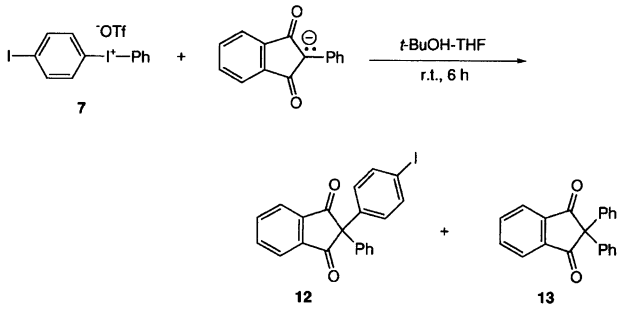


Scheme 2.



Scheme 3.

In the reactions with phenylindandione enolate, 2-(4-iodophenyl)-2-phenyl-1,3-indandione (**12**) and 2,2-diphenyl-1,3-indandione (**13**) were formed as by-products. In order to confirm the formation path of the by-products **12** and **13**, we examined the fate of the resulting (4-iodophenyl)(phenyl)iodonium triflate **7** during the reaction of **5**. When the reaction of **7** with the phenylindandione enolate was conducted in *t*-BuOH–THF at room temperature, **12** and **13** were obtained in 43 and 33% yields, respectively (Eq. 6). This result suggests that the by-products **12** and **13** may be formed via **7** during the reaction of **5**.



(6)

Table 1. Reaction of Alkynyl(*p*-phenylene)bisiodonium Ditriflates **5** with Phenylindandione Enolate[a)]

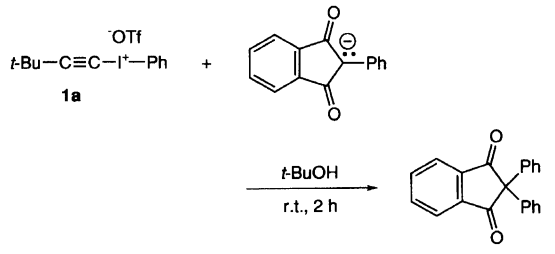
Alkynyliodonium salt **5**		Solvent	Products/%[b)]		
	R[1]		**9**	**10**	**11**
a	*n*-Bu	DMF	18	0	—
b	*n*-Hex	DMF	43	0	—
c	*t*-Bu	DMF	0	11	—
d	Ph	DMF	0	57	—
e	Me_3Si	DMF	0	2	42
a	*n*-Bu	*t*-BuOH–THF	70	0	—
b	*n*-Hex	*t*-BuOH–THF	75	0	—
c	*t*-Bu	*t*-BuOH–THF	0	39	—
d	Ph	*t*-BuOH–THF	0	82	—
e	Me_3Si	*t*-BuOH–THF	0	86	0

a) Substrate **5** (1 mmol) and phenylindandione enolate (2 mmol) in DMF (20 ml) or in *t*-BuOH (15 ml)–THF (10 ml). b) Isolated yields by column chromatography on silica gel. Indandiones **12** and **13** were also formed as the by-products in 18—49% yields.

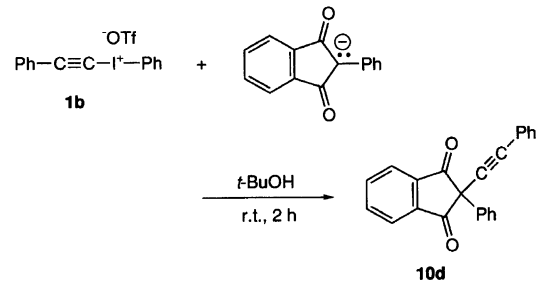
The high yields of the products are achieved by using 2-methyl-2-propanol as the co-solvent. This is explained by the solvation of the phenylindandione enolate with *t*-BuOH. The solvation by hydrogen bonding decreases the reactivity of the phenylindandione enolate and the selective reaction of the alkynyl moiety takes place. Also, in the case of **1e**, the desilylation was completely restrained by using 2-methyl-2-propanol as the co-solvent.

Reaction of Alkynyl(phenyl)iodonium Triflates (1) with the Enolate Anion of 2-Phenyl-1,3-indandione. To clarify the effect of the (*p*-phenylene) bisiodonium moiety, we conducted the reaction of alkynyl (phenyl) iodonium salts **1** with the phenylindandione enolate ion. In the reaction with thiocyanate ion, the same products **6** are formed in the reactions of both **1**[12,13)] and **5**. Interestingly, the reaction of 3,3-dimethyl-1-butynyl(phenyl)iodonium triflate (**1a**) with the phenylindandione enolate ion in 2-methyl-2-propanol did not give alkynyl-substituted indandione **10c**, but 2,2-diphenylindandione (**13**) (Eq. 7). The formation of **13** suggests that the phenylindandione enolate ion attacks the phenyl group rather than the bulky alkynyl group, in contrast to the reaction of **5c**. The difference of the reaction paths may be attributed to the higher activation of alkynyl group by the (*p*-phenylene)bisiodonium moiety, which has more electron-withdrawing nature than phenyl group and increases the contribution of **14b** in **5** (Chart 2). Therefore, a large effect of the (*p*-phenylene)bisiodonium moiety was observed in the sterically hindered 3,3-dimethylbutynyl-substituted iodonium systems **1a** and **5c**.

However, the reaction with phenylethynyl(phenyl)iodonium triflate (**1b**) indicated a similar result that 2-phenyl-2-(phenylethynyl)indandione **10d** is predominantly formed (Eq. 8). This type of reaction was also observed in the reaction of phenylethynyl(phenyl)iodonium chloride.[16)] Similarly, in the reactions of the substrates bearing long alkyl side chains at the alkynyl group, cyclopentene formation is the major process.[15)]



(7)



(8)

In summary, we have investigated the reactions of alkynyl(*p*-phenylene)bisiodonium ditriflates **5** with thiocyanate and 2-phenyl-1,3-indandione enolate ions. The reactions indicated a high reactivity of the alkynyl part to give alkynyl thiocyanates **6** and cyclopentenyl- or alkynyl-substituted indandiones **9** and **10**. In the sterically hindered alkynyl systems, interesting difference of the chemical behavior between alkynyliodonium salts **1** and **5** was observed.

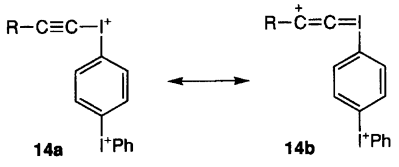


Chart 2.

Experimental

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AC-250P (250 MHz) spectrometer, and ^{13}C NMR spectra with a Bruker AC-250P (62.9 MHz) spectrometer. Chemical shifts

are given in ppm units. IR spectra were obtained with a Horiba FT-200 spectrometer. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. Iodosylbenzene (PhIO) was prepared from (diacetoxy)iodobenzene (Aldrich Chemical Co.) according to the reported procedure.[17] Alkynyl(*p*-phenylene)bis-iodonium ditriflates (**5**) were prepared according to our procedure.[8]

Reaction with Thiocyanate Ion. To a solution of KSCN (0.29 g, 3.0 mmol) in DMF (10 ml) was added crystalline **5** (1.0 mmol) at room temperature under N_2 atmosphere and the mixture was stirred for 20 min. The reaction mixture was poured into water and the product was extracted with ether. The ethereal solution was washed with water, saturated NaCl, and dried over anhydrous Na_2SO_4. The evaporation of the ether gave oily **6**. Further purification was carried out by column chromatography on silica gel.

1-Hexynyl Thiocyanate (6a):[12] Yield, 90%; ^{1}H NMR (250 MHz, $CDCl_3$) δ=0.92 (3H, t, J=7 Hz, Me), 1.34—1.60 (4H, m, CH_2), and 2.36 (2H, t, J=7 Hz, CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=13.49, 19.79, 21.94, 29.82, 52.40, 102.46, and 107.31; IR (neat) 2204 (C≡C) and 2168 cm^{-1} (SCN).

1-Octynyl Thiocyanate (6b):[8a] Yield, 97%; ^{1}H NMR (250 MHz, $CDCl_3$) δ=0.90 (3H, t, J=7 Hz, Me), 1.26—1.43 (6H, m, CH_2), 1.49—1.61 (2H, m, CH2), and 2.36 (2H, t, J=7 Hz, CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=14.04, 20.11, 22.52, 27.76, 28.50, 31.23, 52.36, 102.52, and 107.33; IR (neat) 2204 (C≡C) and 2166 cm^{-1} (SCN).

3,3-Dimethyl-1-butynyl Thiocyanate (6c):[12] Yield, 94%; ^{1}H NMR (250 MHz, $CDCl_3$) δ=1.26 (9H, s, Me); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=29.04, 30.03, 51.42, 107.49, and 109.43; IR (neat) 2208, 2177 (C≡C), and 2168 cm^{-1} (SCN).

Phenylethynyl Thiocyanate (6d):[12] Yield, 87%; ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.28—7.47 (5H, m, Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=62.09, 99.45, 106.49, 120.53, 128.61, 130.38, and 132.38; IR (neat) 2183 (C≡C) and 2166 cm^{-1} (SCN).

Reaction with 2-Phenyl-1,3-indandione Enolate. In DMF: To a solution of potassium 2-methyl-2-propoxide (224 mg, 2.0 mmol) in DMF (10 ml) was added 2-phenyl-1,3-indandione (445 mg, 2.0 mmol) at room temperature under N_2 atmosphere and the mixture was stirred for 1 h. To the resulting 2-phenyl-1,3-indandione enolate solution was added dropwise a solution of **5** (1.0 mmol) in DMF (10 ml) at 0 °C and the reaction mixture was stirred for 30 min at room temperature. The reaction mixture was poured into water and the products were extracted with CH_2Cl_2. The organic layer was washed with water and saturated NaCl, and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by column chromatography on silica gel (hexane–CH_2Cl_2) gave cyclopentene **9** or acetylene **10** or **11**. The yields of the products are given in Table 1. As the by-products, **12** and **13** were obtained in 19-49% yields.

2-(3-Methyl-1-cyclopentenyl)-2-phenyl-1,3-indandione (9a): Mp 99.5—100.5 °C (EtOH); ^{1}H NMR (250 MHz, $CDCl_3$) δ=1.00 (3H, d, J=7 Hz, Me), 1.30—1.44 (1H, m, CH), 2.02—2.15 (1H, m, CH), 2.21—2.41 (2H, m, CH_2), 2.71—2.81 (1H, m, CH), 5.57—5.59 (1H, m, =CH), 7.28—7.34 (5H, m, Ph), 7.86 (2H, dd, J=3 and 6 Hz, ArH), and 8.04 (2H, dd, J=3 and 6 Hz, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=20.66, 32.30, 32.32, 39.99, 65.55, 123.89, 123.92, 127.68, 128.01, 128.62, 135.59, 135.97, 138.04, 138.93, 141.07, 141.10, and 199.26; IR (KBr) 1709 and 1743 cm^{-1} (C=O). Found: C, 83.24; H, 5.99%. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00%.

2-Phenyl-2-(3-propyl-1-cyclopentenyl)-1,3-indandione (9b): Mp 115—116 °C (MeOH); ^{1}H NMR (250 MHz, $CDCl_3$) δ=0.86 (3H, t, J=7 Hz, Me), 1.15—1.50 (5H, m, CH), 2.00—2.11 (1H, m, CH), 2.20—2.40 (2H, m, CH_2), 2.60—2.65 (1H, m, CH), 5.64 (1H, d, J=2 Hz, =CH), 7.26—7.34 (5H, m, Ph), 7.85 (2H, dd, J=3 and 6 Hz, ArH), and 8.03 (2H, dd,J=3 and 6 Hz, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=14.23, 20.88, 30.24, 32.15, 37.93, 45.38, 65.63, 123.84, 123.87, 127.65, 128.02, 128.59, 135.66, 135.96, 136.51, 139.23, 141.06, 141.08, and 199.17; IR (KBr) 1705 and 1741 cm^{-1} (C=O). Found: C, 83.58; H, 6.69%. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71%.

2-(3,3-Dimethybutynyl)-2-phenyl-1,3-indandione (10c): Mp 105.0—107.5 °C (MeOH); ^{1}H NMR (250 MHz, $CDCl_3$) δ=1.25 (9H, s, Me), 7.29—7.35 (5H, m, Ph), 7.94 (2H, dd, J=3 and 6 Hz, ArH), and 8.12 (2H, dd,J=3 and 6 Hz, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=27.71, 30.83, 58.23, 72.73, 96.32, 124.79, 127.21, 128.09, 128.80, 135.75, 136.34, 141.49, and 196.11; IR (KBr) 1728 and 1759 cm^{-1} (C=O). Found: C, 83.23; H, 6.01%. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00%.

2-Phenyl-2-phenylethynyl-1,3-indandione (10d):[16] Mp 114—115 °C (MeOH); ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.25—7.50 (10H, m, Ph), 7.95 (2H, dd, J=3 and 6 Hz, ArH), and 8.15 (2H, dd, J=3 and 6 Hz, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=58.91, 83.38, 86.86, 122.03, 124.88, 127.30, 128.33, 128.79, 128.97, 132.11, 135.23, 136.57, 141.44, and 195.25; IR (KBr) 1716 and 1755 cm^{-1} (C=O).

2-Phenyl-2-trimethysilylethynyl-1,3-indandione (10e): Mp 125—127 °C (hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ=0.19 (9H, s, Me), 7.33 (5H, s, Ph), 7.95 (2H, dd, J=3 and 6 Hz, ArH), and 8.13 (2H, dd, J=3 and 6 Hz, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=59.57, 77.41, 92.74, 98.68, 125.07, 127.37, 128.45, 129.09, 135.28, 136.68, 141.66, and 195.30; IR (KBr) 1268 (C≡C), 1713 and 1759 cm^{-1} (C=O). Found: C, 75.42; H, 5.78%. Calcd for $C_{20}H_{18}O_2Si$: C, 75.43; H, 5.70%.

2-Ethynyl-2-phenyl-1,3-indandione (11): Mp 153—154 °C (hexane–CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ=2.61 (1H, s, ≡CH), 7.31—7.38 (5H, m, Ph), 7.95 (2H, dd, J=3 and 6 Hz, ArH), and 8.13 (2H, dd, J=3 and 6 Hz, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=58.18, 75.15, 78.16, 124.88, 127.07, 128.42, 128.99, 134.61, 136.68, 141.34, and 194.73; IR (KBr) 3282 (≡C–H) and 1713 cm^{-1} (C=O). Found: C, 82.78; H, 4.09%. Calcd for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09%.

2-(4-Iodophenyl)-2-phenyl-1,3-indandione (12): Mp 153—156 °C (hexane–CH_2Cl_2); ^{1}H–NMR (250 MHz, $CDCl_3$) δ=7.03 (2H, d, J=8.5 Hz, ArH), 7.23—7.31 (5H, m, Ph), 7.64 (2H, d, J=8.5 Hz, ArH), 7.91 (2H, dd, J=3 and 6 Hz, ArH), and 8.09 (2H, dd, J=3 and 6 Hz, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=67.03, 76.05, 93.96, 124.20, 127.97, 128.65, 128.76, 130.79, 136.39, 137.68, 137.75, 141.47, and 199.18; IR (KBr) 1701 and 1740 cm^{-1} (C=O). Found: C, 59.48; H, 3.16%. Calcd for $C_{21}H_{13}IO_2$: C, 59.46; H, 3.09%.

2,2-Diphenyl-1,3-indandione (13): Mp 123—124 °C (lit,[19] mp 123—124 °C); ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.26 (10H, s, Ph×2), 7.78—7.81 (2H, m, ArH), and 8.01—8.05 (2H, m, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=67.47, 123.96, 127.64, 128.50, 128.69, 136.15, 137.95, 141.44, and 199.56.

In 2-Methyl-2-propanol–THF. To a solution of potassium 2-methyl-2-propoxide (224 mg, 2.0 mmol) in *t*-BuOH (15 ml) and THF (10 ml) was added 2-phenyl-1,3-indandione (445 mg, 2.0 mmol) at room temperature under N_2 atmosphere and the mixture was stirred for 1 h. To the resulting 2-phenyl-1,3-indandione enolate solution was then added **5** (1.0 mmol) at room temperature, the reaction mixture was stirred for 3 h. The solvent was evaporated in vacuo and ether was added to the residue. The resulting undis-

solved salts were filtered off and the mother ethereal solution was concentrated to yellow oil, which was submitted to column chromatography on silica gel (hexane–CH_2Cl_2) to yield cyclopentene **9** or acetylene **10**. The yields of the products are given in Table 1. As the by-products, **12** and **13** were obtained in 18—31% yields.

Reaction of (4-Iodophenyl)(phenyl)iodonium Triflate (7) with 2-Phenyl-1,3-indandine Enolate. To a solution of potassium 2-methyl-2-propoxide (224 mg, 2.0 mmol) in *t*-BuOH (15 ml) and THF (10 ml) was added 2-phenyl-1,3-indandione (445 mg, 2.0 mmol) at room temperature and the mixture was stirred for 1 h. To the resulting 2-phenyl-1,3-indandine enolate solution was added **7** (556 mg, 1.0 mml) and the mixture was then stirred for 6 h at room temperature. The work-up similar to that for the reaction of **5**, followed by column chromatography on silica gel gave **12** and **13** in 43 and 33% yields, respectively.

Reaction of 3,3-Dimethyl-1-butynyl(phenyl)iodonium Triflate (1a) with 2-Phenyl-1,3-indandione Enolate. To a solution of 2-phenyl-1,3-indandione (222 mg, 1.0 mmol) in *t*-BuOH (20 ml) was added potassium 2-methyl-2-propoxide (112 mg, 1.0 mmol) at 30 °C under N_2 atmosphere and the mixture was stirred for 1 h at room temperature. 3,3-Dimethyl-1-butynyl(phenyl)iodonium triflate (**1a**)[18] (1.0 mmol) was added to the solution and stirred for 2 h. After evaporation of the solvent the residue was submitted to column chromatography on silica gel to give 2,2-diphenyl-1,3-indandione (**13**) in 28% yield.

Reaction of Phenyl(phenylethynyl)iodonium Triflate (1b) with 2-Phenyl-1,3-indandione Enolate. To a solution of 2-phenyl-1,3-indandione (222 mg, 1.0 mmol) in *t*-BuOH (20 ml) was added potassium 2-methyl-2-propoxide (112 mg, 1.0 mmol) at 30 °C under N_2 atmosphere and the mixture was stirred for 1 h at room temperature. Phenyl(phenylethynyl)iodonium triflate (**1b**)[18] (1.0 mmol) was added to the solution and this mixture was stirred for 2 h. After evaporation of the solvent, the residue was submitted to column chromatography on silica gel to give 2-phenyl-2-phenylethynyl-1,3-indandione (**10d**) in 89% yield.

The authors gratefully acknowledge support for this work from a Grant-in-Aid for Scientific Research (C) and Grand-in-Aid for Scientific Research on Priority Area of Reactive Organometallics from the Ministry of Education, Science, Sports and Culture.

References

1) A. Varvoglis, *Chem. Soc. Rev.*, **10**, 377 (1981); T. Umemoto, *Yuki Gosei Kagaku Kyokai Shi*, **41**, 251 (1983); G. F. Koser, "The Chemistry of Functional Groups, Supplement D," ed by S. Patai and Z. Rappoport, John Wiley & Sons, New York (1983), Chaps. 18 and 25; A. Varvoglis, *Synthesis*, **1984**, 709; R. M. Moriarty and O. Prakash, *Acc. Chem. Res.*, **19**, 244 (1986); M. Ochiai and Y. Nagao, *Yuki Gosei Kagaku Kyokai Shi*, **44**, 660 (1986); E. B. Merkushev, *Russ. Chem. Rev. (Eng. Transl.)*, **56**, 826 (1987); R. M. Moriarty and R. K. Vaid, *Synthesis*, **1990**, 431; R. M. Moriarty, R. K. Vaid, and G. F. Koser, *Synlett*, **1990**, 365; A. Varvoglis, "The Organic Chemistry of Polycoordinated Iodine," VCH Publishers, Inc., New York (1992); Y. Kita, H. Tohma, and T. Yakura, *Trends Org. Chem.*, **3**, 113 (1992); O. Prakash and P. S. Singh, *Aldrichimica Acta*, **27**, 15 (1994); T. Kitamura, *Yuki Gosei Kagaku Kyokai Shi*, **53**, 893 (1995).

2) M. Ochiai, *Rev. Heteroatom Chem.*, **2**, 92 (1989); P. J. Stang, *Angew. Chem., Int. Ed. Engl.*, **31**, 274 (1992); G. F. Koser, in "Supplement D2: The Chemistry of Halides, Pseudo-Halides and Azides," ed by S. Patai and Z. Rappoport, John Wiley & Sons, Chichester (1995), Chap. 21.

3) M. Ochiai, Y. Masaki, and M. Shiro, *J. Org. Chem.*, **56**, 5511 (1991).

4) T. Kitamura, K. Nagata, and H. Taniguchi, *Tetrahedron Lett.*, **36**, 1081 (1995).

5) V. V. Zhdankin, C. J. Kuehl, J. T. Bolz, M. S. Formaneck, and A. J. Simonsen, *Tetrahedron Lett.*, **35**, 7323 (1994).

6) T. Kitamura, R. Furuki, H. Taniguchi, and P. J. Stang, *Tetrahedron Lett.*, **31**, 703 (1990); T. Kitamura, R. Furuki, H. Taniguchi, and P. J. Stang, *Tetrahedron*, **48**, 7149 (1992); T. Kitamura, J. Matsuyuki, K. Nagata, R. Furuki, and H. Taniguchi, *Synthesis*, **1992**, 945; T. Kitamura, J. Matsuyuki, and H. Taniguchi, *Synthesis*, **1994**, 147.

7) T. Kitamura, R. Furuki, H. Taniguchi, and P. J. Stang, *Mendeleev Commun.*, **1991**, 148; T. Kitamura, R. Furuki, K. Nagata, H. Taniguchi, and P. J. Stang, *J. Org. Chem.*, **57**, 6810 (1992); T. Kitamura, R. Furuki, K. Nagata, L. Zheng, and H. Taniguchi, *Synlett*, **1993**, 193.

8) a) T. Kitamura, R. Furuki, L. Zheng, T. Fujimoto, and H. Taniguchi, *Chem. Lett.*, **1992**, 2241; b) T. Kitamura, R. Furuki, L. Zheng, K. Nagata, T. Fukuoka, Y. Fujiwara, and H. Taniguchi, *Bull. Chem. Soc. Jpn.*, **68**, 3637 (1995).

9) G. W. Klumpp, "Reactivity in Organic Chemistry," Wiley-Interscience, New York (1982).

10) Z. Rappoport and A. Topol, *J. Am. Chem. Soc.*, **102**, 406 (1980).

11) T. Kitamura, S. Kobayashi, and H. Taniguchi, *Chem. Lett.*, **1984**, 1523; T. Kitamura, S. Kobayashi, and H. Taniguchi, *J. Org. Chem.*, **55**, 1801 (1990).

12) D. R. Fischer, B. L. Williamson, and P. J. Stang, *Synlett*, **1992**, 535.

13) M. Sakurai, R. Tanaka, T. Kitamura, H. Taniguchi, and P. J. Stang, "57th National Meeting of the Chemical Society of Japan," Sendai, September1988, Abstr. Vol. I, p. 141, 2C110.

14) M. Ochiai, M. Kunishima, S. Tani, and Y. Nagao, *J. Am. Chem. Soc.*, **113**, 3135 (1991).

15) M. Ochiai, M. Kunishima, Y. Nagao, K. Fuji, M. Shiro, and E. Fujita, *J. Am. Chem. Soc.*, **108**, 8281 (1986); R. R. Tykwinski, P. J. Stang, and N. E. Persky, *Tetrahedron Lett.*, **35**, 23 (1994); M. Ochiai, T. Ito, Y. Takaoka, Y. Masaki, M. Kunishima, S. Tani, and Y. Nagao, *J. Chem. Soc., Chem. Commun.*, **1990**, 118.

16) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **30**, 1930 (1965).

17) H. Saltzman and J. G. Sharefkin, *Org. Synth.*, Coll. Vol. 5, 658 (1973).

18) M. D. Bachi, N. Bar-Ner, C. M. Crittell, P. J. Stang, and B. Williamson, *J. Org. Chem.*, **56**, 3912 (1991).

19) F. M. Beringer, W. J. Daniel, S. A. Galton, and G. Rubin, *J. Org. Chem.*, **31**, 4315 (1966).