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Metal-Catalyzed Thermal Reactions of Cyclic β-Dicarbonyl Phenyliodonium Ylide with Styrenes

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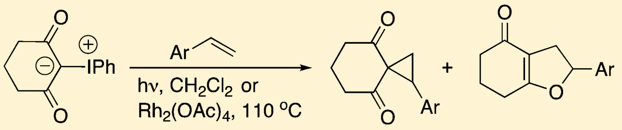
Supporting Information

ABSTRACT: A cyclic β-dicarbonyl phenyliodonium ylide reacted with various substituted styrenes under $Rh_2(OAc)_4$ catalysis to give cyclopropanes and dihydrofurans in a highly regioselective fashion. When styrenes with electron-donating substituents or disubstituted were employed, only dihydrofurans were isolated instead. A mechanism involving two competing pathways rationalizes the results.

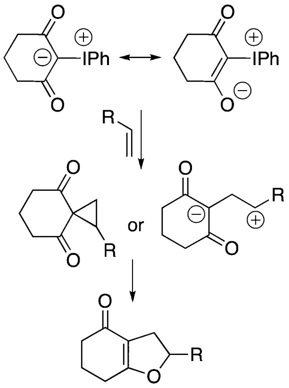


The metal-catalyzed decomposition reactions[1] of α-diazo carbonyl compounds have found broad utility as powerful approaches to generate metal carbenoids, which may subsequently lead to potentially useful transformations, such as cyclopropanation, ylide generation, and X−H bond insertion. However, when the metal carbenoids are appropriately stabilized, other reaction pathways are possible. These processes are also synthetically useful[2] and include 1,3-dipolar cycloadditions between carbenoids, derived from diazocarbonyls, and olefins, acetylenes, and nitriles as trapping agents. The actual structure of the zwitterionic intermediate in these reactions is open to debate since questions such as the role of the metal, or the relative rates on bond cleavage and formation are difficult to answer.

The employment of iodonium ylides in such chemistry has shown interesting complementary reactivity to that of diazo compounds without their major drawbacks such as health and explosive hazards. The increased reactivity of iodonium ylides compared to diazo compounds is attributed to the hyper-leaving group ability of aryl-λ^3-iodanyl groups. Under photochemical or metal-catalyzed thermal activation, an iodonium ylide manifests itself in the form of a transylidation reaction,[3] or in a C−H insertion reaction,[4] or in an intra- and intermolecular cycloaddition reaction.[5] This reactivity could be explained by the assumption of carbene (or carbenoid) intermediates, but such an involvement has been questioned.[6] However, this enhanced reactivity has allowed various cycloadditions[7] to be performed under milder conditions, with better yields, even leading to the development of more enantioselective methods.

Previous studies have shown[7a] that the photochemically activated decomposition of cyclic β-dicarbonyl phenyliodonium ylides in the presence of alkenes affords dihydrofurans in good yields. This could occur either by ring opening of an initially formed cyclopropane or by direct [3 + 2] cycloaddition of a dipolar intermediate with alkenes (Scheme 1). The dipolar intermediate pathway leading to dihydrofuran is expected[8] to be stabilized either by the second electron-withdrawing keto substituent in the cyclic β-dicarbonyl phenyliodonium ylide or with electron-donating substituents in the olefinic trapping agent. On the other hand, the thermal isomerization[9] of a cyclopropyl ketone to dihydrofuran, the heteroanalogue of vinylcyclopropanes to cyclopentene rearrangement, requires elevated temperatures to occur. Therefore, in an attempt to shift the major product away from a dihydrofuran to a cyclopropane, electron-withdrawing substituents were introduced in the alkene.

Scheme 1. Possible Mechanistic Pathways



We now disclose that the thermal $Rh_2(OAc)_4$-catalyzed reaction of phenyliodonium ylide **2** with styrene derivatives **3** yields mixtures of cyclopropanes **4** and dihydrofurans **5**, while photochemical activation gives exclusively the dihydrofuran derivatives **5**.

The β-dicarbonyl phenyliodonium ylide **2** was readily prepared[7a,10] from the corresponding 1,3-cyclohexanedione **1** by treatment with iodobenzene diacetate at room temperature (Scheme 2). All photochemical or thermal $Rh_2(OAc)_4$-catalyzed reactions of phenyliodonium ylide **2** were run with an excess of styrene. The cyclopropanes **4** and dihydrofurans **5** (Table 1) were isolated by flash chromatography on silica gel in up to 89% yield. There is a comparison of the photochemically activated

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Scheme 2. Cycloaddition of Ylide 2 with Styrenes 3

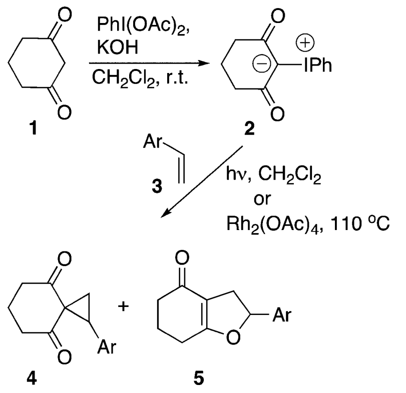


Table 1. Cycloadditions[a] of Iodonium Ylide 2 with Styrenes 3

entry	Ar	method	time (min)[b]	products (% yield)[c]
1	C_6H_5	A	60	**5a** (72)
2	C_6H_5	B	1	**4a** (26), **5a** (42)
3	*p*-$CH_3C_6H_4$	A	50	**5b** (66)
4	*p*-$CH_3C_6H_4$	B	2	**5b** (72)
5	*p*-$CH_3OC_6H_4$	A	50	**5c** (89)
6	*p*-$CH_3OC_6H_4$	B	2	**5c** (43)
7	*p*-ClC_6H_4	A	50	**5d** (59)
8	*p*-ClC_6H_4	B	2	**4d** (35), **5d** (39)
9	*m*-$NO_2C_6H_4$	A	210	**5e** (46)[d]
10	*m*-$NO_2C_6H_4$	B	2	**4e** (18), **5e** (31)
11	*o*-ClC_6H_4	A	70	**5f** (45)
12	*o*-ClC_6H_4	B	2	**4f** (35), **5f** (32)

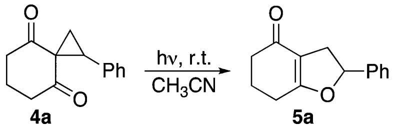
[a]**Method A**: All reactions were carried out by irradiating a solution of iodonium ylide 2 (2.01−2.10 mmol), styrene **3** (6.71−9.61 mmol) in acetonitrile (10 mL) for 50−210 min. **Method B**: All reactions were carried out by heating at 110 °C, a mixture of iodonium ylide **2** (2.01−2.10 mmol), styrene **3** (6.71−9.61 mmol), and $Rh_2(OAc)_4$ (1.0−3.0 mg) for 1−2 min. [b]Time required for the completion of the reaction. [c]Yield of isolated product after column chromatography. [d]Cyclopropane **4e** was detected in the crude reaction mixture.

cycloaddition of iodonium ylide **2** with styrenes (method A) with the results obtained from the thermal $Rh_2(OAc)_4$-catalyzed reaction of iodonium ylide **2** with styrenes (method B). Other catalysts, such as $RuCl_3$, $Pd(OAc)_2$, and $Cu(acac)_2$, have been employed in the thermal metal-catalyzed reaction of iodonium ylide **2** with styrene, yielding mixtures of 2-iodo-3-phenoxycyclohex-2-enone, the decomposition product[11] of ylide **2**, and dihydrofuran **5a**.

As for the specific styrenes examined herein, the photochemically activated cycloaddition of iodonium ylide **2** with styrene **3a** yields exclusively dihydrofuran **5a** in 72% yield (entry 1, Table 1); however, the thermal $Rh_2(OAc)_4$-catalyzed reaction of ylide **2** with styrene **3a** results in the formation of cyclopropane **4a** (26% yield) together with dihydrofuran **5a** (42% yield) (entry 2, Table 1). It is worth mentioning that the cycloaddition yielding dihydrofuran **5** exhibits high regioselectivity. One of the two carbonyl oxygens of iodonium ylide **2** added exclusively onto the more substituted carbon of the double bond; i.e., only 2-substituted dihydrofurans were isolated exclusively. The other possible regioisomer was not detected at all. A dipolar intermediate is enhanced[8] by the introduction of electron-donating substituents into the styrene. On the basis of this expectation, the cycloadditions of iodonium ylide **2** with *p*-methylstyrene **3b** and *p*-methoxystyrene **3c** were carried out under photochemical activation or thermal $Rh_2(OAc)_4$ catalysis. In both cases, only the corresponding dihydrofurans **5b,c** were isolated exclusively (entries 3−6, Table 1). The addition of electron-withdrawing groups on the styrene disfavored the dipolar intermediate. Although the photochemically activated cycloaddition of ylide **2** with *p*-chlorostyrene **3d** yields exclusively dihydrofuran **5d** in 59% yield (entry 7, Table 1), the thermal $Rh_2(OAc)_4$-catalyzed reaction of ylide **2** with styrene **3d** affords a mixture of cyclopropane **4d** and dihydrofuran **5d** in 35% and 39% yields, respectively (entry 8, Table 1). *m*-Nitrostyrene **3e** reacts similarly; cyclopropane **4e** and dihydrofuran **5e** were isolated in 18% and 31% yields, respectively, from the thermal $Rh_2(OAc)_4$-catalyzed reaction of ylide **2** with *m*-nitrostyrene **3e** (entry 10, Table 1), while dihydrofuran **5e** was isolated in 46% yield from the photochemical reaction of ylide **2** with *m*-nitrostyrene **3e** (entry 9, Table 1). Cyclopropane **4e** was detected in the crude reaction mixture of the latter process. Although the photochemically activated reaction of ylide **2** with *o*-chlorostyrene **3f** yields exclusively dihydrofuran **5f** in 45% yield (entry 11, Table 1), the thermal $Rh_2(OAc)_4$-catalyzed cycloaddition of ylide **2** with *o*-chlorostyrene **3f** results in the formation of cyclopropane **4f** and dihydrofuran **5f** in 35% and 32% yields, respectively (entry 12, Table 1).

The stability of cyclopropane **4a** under the conditions of the thermal reaction was verified [$Rh_2(OAc)_4$ at 110 °C for 1 h], and it was found that the cyclopropane **4a** does not rearrange to dihydrofuran **5a**. Thus, the thermal Rh(II)-catalyzed reaction of styrenes **3** with phenyliodonium ylide **2** proceeds via two competing pathways. The stability of cyclopropanes **4a** under the conditions of the photochemical activation was also verified (CH_3CN solution, irradiation for 1 h), and it was found that cyclopropane **4a** rearranges completely to dihydrofuran **5a** (Scheme 3). Thus, the photochemically activated reaction of styrenes **3** with ylide **2** may proceed via two competing pathways.

Scheme 3. Photochemical Isomerization of Cyclopropane 4a into Dihydrofuran 5a



At this stage, we decide to apply this strategy to disubstituted styrene derivatives **6**, which are expected to favor the dipolar intermediate pathway. Indeed, the reaction of iodonium ylide **2** with styrene derivatives **6**, either photochemically or $Rh_2(OAc)_4$-catalyzed, yields only dihydrofurans **7**[7a] in good yields (Scheme 4).

All photochemical or thermal $Rh_2(OAc)_4$-catalyzed reactions of phenyliodonium ylide **2** were run with excess disubstituted styrenes **6**. The dihydrofurans **7** were isolated by flash

Scheme 4. Cycloaddition of Ylide 2 with Disubstituted Styrenes 6

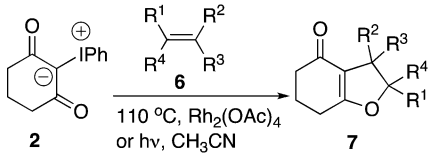


Table 2. Cycloadditions[a] of Iodonium Ylide 2 with Styrenes 6

entry	R^1	R^2	R^3	R^4	method	time (min)[b]	product	yield (%)[c]
1	CH_3	H	H	C_6H_5	A	50	**7a**	64
2	CH_3	H	H	C_6H_5	B	2	**7a**	49
3	$C_6H_4CH_2$		H	H	A	105	**7b**	50
4	$C_6H_4CH_2$		H	H	B	1	**7b**	72
5	$p$$CH_3OC_6H_4$	H	CH_3	H	A	40	**7c**	55
6	$p$$CH_3OC_6H_4$	H	CH_3	H	B	2	**7c**	23

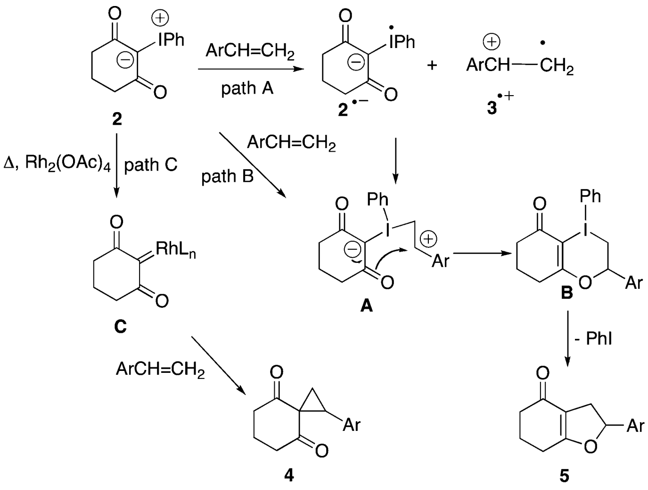
[a] **Method A**: All reactions were carried out by irradiating a solution of iodonium ylide **2** (2.01−2.10 mmol), styrene **3** (6.71−9.61 mmol) in acetonitrile (10 mL) for 50−210 min. **Method B**: All reactions were carried out by heating at 110 °C, a mixture of iodonium ylide **2** (2.01−2.10 mmol), styrene **3** (6.71−9.61 mmol), and $Rh_2(OAc)_4$ (1.0−3.0 mg) for 1−2 min. [b] Time required for the completion of the reaction. [c] Yield of isolated product after column chromatography.

chromatography on silica gel in up to 72% yield, irrespective of the method employed. There is a comparison of the photochemically activated cycloaddition of iodonium ylide **2** with disubstituted styrenes **6** (method A) with the results obtained from the thermal $Rh_2(OAc)_4$-catalyzed reaction of iodonium ylide **2** with disubstituted styrenes **6** (method B) (Table 2).

The relative photochemically activated reactivities of iodonium ylide **2** with certain olefin pairs have been determined. Irradiation of ylide **2** in mixtures of styrene **3a** (5 equiv) and *p*-methoxystyrene **3c** (5 equiv) in acetonitrile (10 mL) gave dihydrofurans **5a** and **5c** in 17% and 35% yields, respectively. The ratio of **5c** to **5a**, and thus the relative reactivity of *p*-methoxystyrene to styrene, is 2.06. In a second competitive experiment, irradiation of ylide **2** in mixtures of styrene **3a** (5 equiv) and α-methylstyrene **6a** (5 equiv) in acetonitrile (10 mL) gave dihydrofurans **5a** and **7a** in 25.3% and 39.3% yields, respectively. The relative reactivity of α-methylstyrene to styrene is 1.55. In another competitive experiment, irradiation of ylide **2** in mixtures of styrene **3a** (5 equiv) and indene **6b** (5 equiv) in acetonitrile (10 mL) gave dihydrofurans **5a** and **7b** in 23.4% and 43.8% yields, respectively. The relative reactivity of indene to styrene is 1.87. Finally, irradiation of ylide **2** in mixtures of styrene **3a** (5 equiv) and *trans*-anethole **6c** (5 equiv) in acetonitrile (10 mL) gave dihydrofurans **5a** and **7c** in 39.3% and 24.8% yields, respectively. The relative reactivity of *trans*-anethole to styrene is 0.63. The relative rate experiments thus reveal that (1) the reactivities of the olefins studied are *p*-methoxy styrene > indene > α-methylstyrene > *trans*-anethole, (2) the photochemically activated cycloadditions of iodonium ylide **2** on styrenes are electrophilic in nature, and (3) steric hindrance plays an important role on this cycloaddition.

The current results support the mechanistic scenario displayed in Scheme 5 for the reaction of iodonium ylide **2** with styrene **3**. It is reasonable to assume that the cycloaddition between the iodonium ylide **2** with styrene **3** might proceed via the zwitterionic intermediate **A**, either generated directly by nucleophilic attack of the double bond on the electrophilic iodine atom of the ylide (path B) or electron transfer takes place between the two reactants, to afford the radical ion pair and the latter leads on coupling to the zwitterionic intermediate A (path A). In such a case, the Rh(II) catalyst must promote the electron transfer reaction.[12] In the absence of the catalyst, only the known thermal isomerization[11] of iodonium ylide **2**, with 1,4-phenyl migration, into 2-iodo-3-phenoxycyclohex-2-enone was observed. Intermediate **A** is expected to have a T-shaped structure for the trivalent iodine functionality,[13] a fact that forces the carbanionic site away from the benzyl positive center. Thereby, ring closure to a four-membered ring cyclic iodinane species is prevented, which, on subsequent iodobenzene extrusion, would afford the cyclopropane product. Instead, nucleophilic attack by the enolic oxygen atom on the benzyl cationic center leads to six-membered cyclic iodinane **B**. Iodobenzene extrusion affords the observed dihydrofuran **5**. Since the dipolar cycloaddition has an electrophilic nature, the employment of electron-rich styrene, such as *p*-methylstyrene **3b**, *p*-methoxystyrene **3c**, and the disubstituted styrenes **6**, would lead exclusively to dihydrofurans **5b**,**c** and **7** via path A or B. When the employed styrene is less reactive, the rhodium(II) acetate catalyst behaves also as a trapping agent that generates the rhodium(II) carbenoid complex **C** (path C). The latter reacts with styrenes **3a**,**d**,**e**,**f**, leading to the formation of the corresponding cyclopropanes **4**.

Scheme 5. Plausible Mechanism for the Formation of Cyclopropane 4 and Dihydrofuran 5



Under photochemical activation, two competing pathways could operate also, i.e., the carbene pathway leading to cyclopropane and the dipolar cycloaddition pathway, either directly or via electron transfer, leading to dihydrofuran. The detection of cyclopropane **4e** in the photochemically activated reaction of ylide **2** with styrene **3e** is an evidence for such a mechanism. However, the complete photochemical isomerization of cyclopropane **4a** to dihydrofuran **5a** complicates the picture.

The photochemical activated or thermal $Rh_2(OAc)_4$-catalyzed reactions of a six-membered cyclic phenyliodonium ylide with various substituted styrenes have been studied. These cycloadditions provide easy access to highly substituted cyclopropanes and dihydrofurans. A mechanism involving two competing pathways, i.e., dipolar cycloaddition vs Rh(II) carbenoid complex, rationalizes these results. It may be concluded that the presence of electron-donating substituents in the styrene enhances the dipolar cycloaddition pathway, while less reactive styrenes exert the Rh(II) carbenoid complex pathway. Further transformations of these products will bring diversity to highly substituted compounds of chemical and biological interest.

■ EXPERIMENTAL SECTION

General Procedure for the Thermal $Rh_2(OAc)_4$-Catalyzed Reaction. A mixture of iodonium ylide **2** (2.01−2.10 mmol), styrene **3** (6.71−9.61 mmol), and $Rh_2(OAc)_4$ (1.0−3.0 mg) was heated at 110 °C for 1−2 min. The reaction mixture was chromatographed on silica gel [CH_2Cl_2, (8:1) CH_2Cl_2−EtOAc] to afford cyclopropane **4** and dihydrofuran **5**.

*Reaction of Iodonium Ylide **2** with Styrene **3a**.* From iodonium ylide **2** (0.66 g, 2.10 mmol), styrene **3a** (1.0 g, 9.61 mmol), and $Rh_2(OAc)_4$ (1.0 mg) heated at 110 °C for 1 min. Purification by flash chromatography gave the following compounds. 1-Phenylspiro[2.5]-octa-4,8-dione **4a** as white crystals (0.12 g, 26% yield): mp 98−100 °C ($CHCl_3$−hexanes); IR (KBr): 3031, 3010, 2945, 1704, 1677, 1326, 1024, 760 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.31−7.28 (m, 2H), 7.27−7.24 (m, 1H), 7.23−7.21 (m, 2H), 3.28 (t, J = 9.0 Hz, 1H), 2.76 (ddd, J = 17.4, 7.9, 4.8 Hz, 1H), 2.64 (ddd, J = 17.4, 7.9, 4.8 Hz, 1H), 2.54 (dd, J = 9.0, 3.9 Hz, 1H), 2.49−2.43 (m, 1H), 2.33 (dd, J = 9.0, 3.9 Hz, 1H), 2.31−2.25 (m, 1H), 2.16−2.05 (m, 2H); ^{13}C (125 MHz, $CDCl_3$): δ = 205.9, 201.9, 133.2, 129.4, 128.0, 127.9, 49.9, 48.8, 39.9, 21.1, 17.9; HRMS (ESI − TOF): Calcd for $C_{14}H_{15}O_2$ 215.1067; Found 215.1068. 2-Phenyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5a** as a colorless oil (0.19 g, 42% yield): IR (neat): 3058, 2943, 1643, 1454, 1400, 1230, 1180, 1060, 906, 702 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.40−7.26 (m, 5H), 5.72 (dd, J = 10.5, 8.0 Hz, 1H), 3.31−3.20 (m, 1H), 2.90−2.79 (m, 1H), 2.50−2.45 (m, 2H), 2.39−2.34 (m, 2H), 2.10−2.08 (m, 2H); ^{13}C (62.5 MHz, $CDCl_3$): δ = 195.3, 177.1, 140.5, 128.6, 128.3, 125.7, 112.8, 86.2, 36.3, 33.9, 23.8, 21.6; HRMS (ESI−TOF): Calcd for $C_{14}H_{15}O_2$ 215.1067; Found 215.1060.

*Reaction of Iodonium Ylide **2** with p-Methylstyrene **3b**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), *p*-methylstyrene **3b** (1.0 g, 8.47 mmol), and $Rh_2(OAc)_4$ (2.5 mg) heated at 110 °C for 2 min. Purification by flash chromatography gave 2-*p*-tolyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5b** as colorless crystals (0.32 g, 72% yield): mp 97−99 °C (hexanes); IR (KBr): 3056, 3031, 2941, 1631, 1402, 1228, 1180, 918, 813 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.24 and 7.14 (AA′BB′ system, 4H), 5.72 (dd, J = 10.5, 8.1 Hz, 1H), 3.25 (dd, J = 14.6, 10.5 Hz, 1H), 2.88 (dd, J = 14.6, 8.1 Hz, 1H), 2.49 (t, J = 6.3 Hz, 2H), 2.40−2.37 (m, 2H), 2.36 (s, 3H), 2.11−2.05 (m, 2H); ^{13}C (62.5 MHz, $CDCl_3$): δ = 195.2, 177.0, 138.2, 137.5, 129.3, 125.8, 112.9, 86.3, 36.4, 33.7, 23.8, 21.6, 21.0; HRMS (ESI−TOF): Calcd for $C_{15}H_{16}O_2Na$ 251.1043; Found 251.1030.

*Reaction of Iodonium Ylide **2** with p-Methoxystyrene **3c**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), *p*-methoxystyrene **3c** (1.0 g, 7.46 mmol), and $Rh_2(OAc)_4$ (1.6 mg) heated at 110 °C for 2 min. Purification by flash chromatography gave gave 2-*p*-methoxyphenyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5c** as colorless crystals (0.21 g, 43% yield): mp 69−71 °C ($CHCl_3$−hexanes); IR (KBr): 3051, 2958, 1622, 1514, 1402, 1228, 1176, 1033, 827 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.29 and 6.94 (AA′BB′ system, 4H), 5.72 (dd, J = 10.4, 8.1 Hz, 1H), 3.84 (s, 3H), 3.29−3.22 (m, 1H), 2.94−2.88 (m, 1H), 2.52−2.49 (m, 2H), 2.43−2.40 (m, 2H), 2.10 (quint, J = 6.4 Hz, 2H); ^{13}C (62.5 MHz, $CDCl_3$): δ = 195.5, 177.1, 159.8, 132.5, 127.6, 114.1, 113.0, 86.5, 55.3, 36.5, 33.6, 24.0, 21.7; HRMS (ESI−TOF): Calcd for $C_{15}H_{17}O_3$ 245.1172; Found 245.1169.

*Reaction of Iodonium Ylide **2** with p-Chlorostyrene **3d**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), *p*-chlorostyrene **3d** (1.0 g, 7.22 mmol), and $Rh_2(OAc)_4$ (1.5 mg) heated at 110 °C for 2 min. Purification by flash chromatography gave the following compounds. 1-(4-Chlorophenyl)spiro[2.5]octa-4,8-dione **4d** as white crystals (0.17 g, 35% yield): mp 118−120 °C ($CHCl_3$−hexanes); IR (KBr): 3058, 2950, 1708, 1678, 1492, 1330, 1095, 1026, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 and 7.13 (AA′BB′ system, 4H) 3.22 (t, J = 8.9 Hz, 1H), 2.77−2.71 (m, 1H), 2.66−2.62 (m, 1H), 2.49−2.44 (m, 2H), 2.33−2.29 (m, 2H), 2.11−2.00 (m, 2H) ; ^{13}C (62.5 MHz, $CDCl_3$): δ = 205.5, 201.8, 133.6, 131.8, 130.7, 128.1, 49.7, 47.5, 39.9, 39.2, 21.5, 17.7; HRMS (ESI−TOF): Calcd for $C_{14}ClH_{14}O_2$ 249.0677; Found 249.0682. 2-(*p*-Chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5d** as a colorless oil (0.19 g, 39% yield): IR (neat): 3056, 2952, 1636, 1402, 1230, 1182, 912, 732 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.34 and 7.25 (AA′BB′ system, 4H), 5.70 (dd, J = 10.5, 8.0 Hz, 1H), 3.30−3.23 (m, 1H), 2.83−2.77 (m, 1H), 2.51−2.48 (m, 2H), 2.39−2.36 (m, 2H), 2.07 (quint, J = 6.4 Hz, 2H); ^{13}C (62.5 MHz, $CDCl_3$): δ = 195.2, 176.8, 139.1, 134.0, 129.4, 127.7, 112.7, 85.8, 36.9, 34.5, 24.3, 22.2; HRMS (ESI−TOF): Calcd for $C_{14}ClH_{14}O_2$ 249.0677; Found 249.0676.

*Reaction of Iodonium Ylide **2** with m-Nitrostyrene **3e**.* From iodonium ylide **2** (0.66 g, 2.10 mmol), *m*-nitrostyrene **3e** (1.0 g, 6.71 mmol), and $Rh_2(OAc)_4$ (3.0 mg) heated at 110 °C for 2 min. Purification by flash chromatography gave the following compounds. 1-(3-Nitrophenyl)spiro[2.5]octa-4,8-dione **4e** as a colorless oil (0.10 g, 18% yield): IR (neat): 2950, 1748, 1634, 1532, 1348, 1230, 1182, 1062, 738 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 8.07−8.04 (m, 2H), 7.54−7.40 (m, 2H), 3.32 (t, J = 8.8 Hz, 1H), 2.76−2.66 (m, 2H), 2.56−2.43 (m, 2H), 2.37−2.27 (m, 2H), 2.11−2.06 (m, 2H); ^{13}C (62.5 MHz, $CDCl_3$): δ = 205.6, 202.4, 148.2, 136.0, 135.8, 129.2, 124.8, 123.0, 49.1, 46.3, 40.4, 39.5, 23.0, 17.9; HRMS (ESI−TOF): Calcd for $C_{14}H_{14}NO_4$ 260.0918; Found 260.0912. 2-(3-Nitrophenyl)-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5e** as a colorless oil (0.17 g, 31% yield): IR (neat): 3054, 2870, 1632, 1532, 1402, 1230, 1182, 1062, 736 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 8.17−8.15 (m, 2H), 7.64−7.52 (m, 2H), 5.86−5.79 (m, 1H), 3.39−3.28 (m, 1H), 2.84−2.75 (m, 1H), 2.57−2.50 (m, 2H), 2.40−2.36 (m, 2H), 2.14−1.89 (m, 2H); ^{13}C (62.5 MHz, $CDCl_3$): δ = 195.1, 176.6, 147.9, 142.4, 131.2, 129.4, 122.8, 120.2, 112.0, 84.0, 35.9, 33.8, 23.3, 21.1; HRMS (ESI−TOF): Calcd for $C_{14}H_{13}NO_4Na$ 282.0737; Found 282.0723.

*Reaction of Iodonium Ylide **2** with o-Chlorostyrene **3f**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), *o*-chlorostyrene **3f** (1.0 g, 7.22 mmol), and $Rh_2(OAc)_4$ (1.5 mg) heated at 110 °C for 2 min. Purification by flash chromatography gave the following compounds. 1-(2-Chlorophenyl)spiro[2.5]octa-4,8-dione **4f** as a colorless oil (0.17 g, 35% yield): IR (neat): 3062, 2958, 1681, 1573, 1323, 1184, 912, 730 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.46−7.15 (m, 4H), 3.27−3.18 (m, 1H), 2.88−2.78 (m, 1H), 2.76−2.55 (m, 1H), 2.51−2.39 (m, 2H), 2.31−2.15 (m, 2H), 2.13−1.86 (m, 2H); ^{13}C (62.5 MHz, $CDCl_3$): δ = 206.0, 202.4, 135.4, 132.0, 131.2, 129.1, 128.7, 126.3, 48.0, 46.0, 39.5, 39.2, 23.1, 18.0; HRMS (ESI−TOF): Calcd for $C_{14}ClH_{14}O_2$ 249.0677; Found 249.0662. 2-(*o*-Chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5d** as a colorless oil (0.16 g, 32% yield): IR (neat): 3062, 2950, 1634, 1404, 1232, 1184, 954, 736 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.39−7.18 (m, 4H), 6.06−5.99 (m, 1H), 3.43−3.33 (m, 1H), 2.71−2.65 (m, 1H), 2.57−2.52 (m, 2H), 2.38−2.33 (m, 2H), 2.12−2.01 (m, 2H); ^{13}C (62.5 MHz, $CDCl_3$): δ = 195.8, 177.4, 138.5, 131.4, 129.7, 129.2, 127.0, 125.9, 112.8, 83.0, 36.2, 33.6, 23.7, 21.6; HRMS (ESI−TOF): Calcd for $C_{14}ClH_{14}O_2$ 249.0677; Found 249.0668.

*Reaction of Iodonium Ylide **2** with α-Methylstyrene **6a**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), α-methylstyrene **6a** (1.0 g, 8.47 mmol), and $Rh_2(OAc)_4$ (2.5 mg) heated at 110 °C for 2 min. Purification by flash chromatography gave the 2-methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one[7a] **6a** as a colorless oil (0.22 g, 49% yield).

*Reaction of Iodonium Ylide **2** with Indene **6b**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), indene **6b** (1.0 g, 8.62 mmol), and $Rh_2(OAc)_4$ (1.9 mg) heated at 110 °C for 2 min. Purification by flash chromatography gave the 4b,6,7,8,9b,10-hexahydro-9*H*-benz[*b*]indeno-[2,1-*d*]furan-9-one[7a] **6a** as white crystals (0.15 g, 33% yield).

*Reaction of Iodonium Ylide **2** with trans-Anethole **6c**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), *trans*-anethole **6c** (1.0 g, 8.47 mmol), and $Rh_2(OAc)_4$ (2.2 mg) heated at 110 °C for 1 min. Purification by flash chromatography gave the (*E*)-2-(4-methoxyphenyl)-3-methyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one[7a] **6c** as colorless crystals (0.12 g, 23% yield).

General Procedure for the Photochemically Activated Reaction. A solution of iodonium ylide **2** (2.01−2.10 mmol) and styrene **3** (6.71−9.61 mmol) in acetonitrile (10 mL) was irradiated (400 W medium pressure Hg street lamp) at room temperature for 50−210 min. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel [CH$_2$Cl$_2$, (8:1) CH$_2$Cl$_2$−EtOAc] to afford dihydrofuran **5**.

*Photochemical Reaction of Iodonium Ylide **2** with Styrene **3a**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), styrene **3a** (1.0 g, 9.61 mmol), in acetonitrile (10 mL) irradiated at room temperature for 60 min. Purification by flash chromatography gave 2-phenyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5a** as a colorless oil (0.31 g, 72% yield).

*Photochemical Reaction of Iodonium Ylide **2** with p-Methylstyrene **3b**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), *p*-methylstyrene **3b** (1.0 g, 8.47 mmol), in acetonitrile (10 mL) irradiated at room temperature for 50 min. Purification by flash chromatography gave 2-*p*-tolyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5b** as colorless crystals (0.30 g, 66% yield).

*Photochemical Reaction of Iodonium Ylide **2** with p-Methoxystyrene **3c**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), styrene **3a** (1.0 g, 7.46 mmol), in acetonitrile (10 mL) irradiated at room temperature for 50 min. Purification by flash chromatography gave 2-(*p*-methoxyphenyl)-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5c** as colorless crystals (0.43 g, 89% yield). Photochemical reaction of iodonium ylide **2** with *p*-chlorostyrene **3d**. From iodonium ylide **2** (0.63 g, 2.01 mmol), *p*-chlorostyrene **3d** (1.0 g, 7.22 mmol), in acetonitrile (10 mL) irradiated at room temperature for 50 min. Purification by flash chromatography gave 2-(*p*-chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5d** as a colorless oil (0.29 g, 59% yield).

*Photochemical Reaction of Iodonium Ylide **2** with m-Nitrostyrene **3e**.* From iodonium ylide **2** (0.66 g, 2.10 mmol), *m*-nitrostyrene **3e** (1.0 g, 6.71 mmol), in acetonitrile (10 mL) irradiated at room temperature for 210 min. Purification by flash chromatography gave 2-(3-nitrophenyl)-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5a** as colorless oil (0.25 g, 46% yield).

*Photochemical Reaction of Iodonium Ylide **2** with o-Chlorostyrene **3f**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), *o*-chlorostyrene **3f** (1.0 g, 7.22 mmol), in acetonitrile (10 mL) irradiated at room temperature for 70 min. Purification by flash chromatography gave 2-(2-chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one **5f** as colorless oil (0.22 g, 45% yield).

*Photochemical Reaction of Iodonium Ylide **2** with α-Methylstyrene **6a**.* From iodonium ylide **2** (0.61 g, 1.94 mmol), α-methylstyrene **6a** (1.0 g, 8.47 mmol), in acetonitrile (10 mL) irradiated at room temperature for 50 min. Purification by flash chromatography gave the 2-methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one[7a] **6a** as a colorless oil (0.28 g, 64% yield).

*Photochemical Reaction of Iodonium Ylide **2** with Indene **6b**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), indene **6b** (1.0 g, 8.62 mmol), in acetonitrile (10 mL) irradiated at room temperature for 90 min. Purification by flash chromatography gave the 4b,6,7,8,9b,10-hexahydro-9*H*-benz[*b*]indeno[2,1-*d*]furan-9-one[7a] **6a** as white crystals (0.23 g, 54% yield).

*Photochemical Reaction of Iodonium Ylide **2** with trans-Anethole **6c**.* From iodonium ylide **2** (0.63 g, 2.01 mmol), *trans*-anethole **6c** (1.0 g, 8.47 mmol), in acetonitrile (10 mL) irradiated at room temperature for 40 min. Purification by flash chromatography gave the (*E*)-2-(4-methoxyphenyl)-3-methyl-2,3,6,7-tetrahydrobenzofuran-4-(5*H*)-one[7a] **6c** as colorless crystals (0.29 g, 56% yield).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C spectra of **2**, **4a**, **4d−f**, **5a−f**, and **7a−c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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