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The Question of Electrophilic vs Nucleophilic Addition of Cyclic β-Dicarbonyl Phenyliodonium Ylides: Electrophilic Cycloaddition of Diphenylketene

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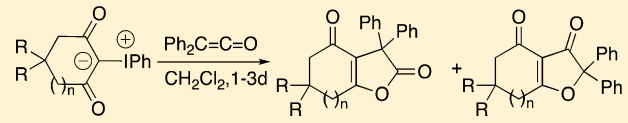
Supporting Information

ABSTRACT: The reaction of β-dicarbonyl phenyliodonium ylides with diphenylketene at room temperature affords mixtures of lactone and aurone derivatives. The initial electrophilic attack of the iodonium ylide on the C_β position of the diphenylketene, followed by cyclization of the zwitterionic species, and subsequent ejection of iodobenzene, affords the lactone and aurone cycloadducts. Treatment of β-dicarbonyl iodonium ylides with acyl chlorides yields α-chloroenones with good to excellent yields.



Iodonium ylides[1] have been used quite often as rather reactive synthetic equivalents to diazo ketones without major drawbacks such as explosive and health hazards. Iodonium ylides are easily prepared[2] from the condensation reaction of an active methylene compound with a hypervalent iodine precursor. Their fascinating chemical behavior consists of decomposition[3] in various solvents, transylidation reactions,[4] C−H insertion reactions,[5] and intra- and intermolecular cycloaddition reactions[6] under photochemical or metal-catalyzed thermal activation. This reactivity could be explained by the assumption of carbene (or carbenoid) intermediates, but such an involvement has been questioned.[7] However, in solution at room temperature without any metal catalyst or photochemical activation, a β-dicarbonyl iodonium ylide could initially behave as an enolate due to its keto-stabilized carbanionic center or as an electrophile through its positively charged iodonium center. The incentive of the present study was to distinguish between these mechanistic possibilities by examining the reaction of β-dicarbonyl iodonium ylides with diphenylketene.

Ketenes are unusual alkenes as well as carbonyl compounds that are reactive[8] toward both electrophiles and nucleophiles. Experimental and theoretical studies showed[9] that nucleophiles will approach in the plane at C_a position while electrophiles attack ketene perpendicular to the molecule plane on oxygen or C_b positions. Diphenylketene,[10] a stable ketene derivative, can be easily prepared from the action of triethylamine on diphenylacetyl chloride.

If the iodonium ylide reacts initially as a nucleophile, attack at the C_a position of the ketene would produce enolate **A**, which on subsequent intramolecular ring closure with ejection of iodobenzene should afford a mixture of lactone **3** and ketene acetal **4** (Scheme 1). In contrast, if the iodonium ylide reacts initially as an electrophile, attack at the C_b position of the ketene would produce an acylium ion **B**, which on subsequent cyclization with ejection of iodobenzene should produce a mixture of lactone **3** and aurone **5**.

We now disclose that the reaction of various cyclic β-dicarbonyl iodonium ylides with diphenylketene at room temperature yields a mixture of lactone **3** and aurone **5**.

Phenyliodonium ylide **2a**, prepared by reaction of 1,3-cyclopentanedione (**1a**) with iodobenzene diacetate in tetrahydrofuran at room temperature (Scheme 2), was collected by filtration. Ylide **2a** is highly insoluble in common organic solvents but stable, recrystallized from methanol, and can be stored in a freezer for a long time without any decomposition. An X-ray crystallographic study of a single crystal of **2a** confirms the structure. The other β-dicarbonyl phenyliodonium ylides **2b−f** were readily prepared[11] from the corresponding 1,3-cyclohexanediones **1b−f** by treatment with iodobenzene diacetate in dichloromethane at room temperature, followed by washing with 5% aqueous KOH solution (Scheme 2). All reactions of ylides **2** were run with a slight excess (2.0 equiv) of diphenylketene until complete consumption of the ylide (TLC monitoring). Lactones **3** and aurones **5** were isolated by flash chromatography on silica gel (Table 1), quantitatively.

When iodonium ylide **2a** was treated with diphenylketene at room temperature for 48 h, 3,3-diphenyl-5,6-dihydro-2*H*-cyclopenta[*b*]furan-2,4(3*H*)-dione (**3a**), 2,2-diphenyl-5,6-dihydro-2*H*-cyclopenta[*b*]furan-3,4(2*H*)-dione (**5a**), and 2-iodo-3-phenoxy-cyclopent-2-enone (**6a**) were isolated in 12%, 53%, and 33% yields, respectively (entry 1, Table 1). Iodoether **6a** is the typical[3c] decomposition product of a β-dicarbonyl iodonium ylide. When iodonium ylide **2b** was treated with diphenylketene at room temperature for 72 h, 3,3-diphenyl-6,7-dihydrobenzofuran-2,4(3*H*,5*H*)-dione (**3b**) and 2,2-diphenyl-6,7-dihydrobenzofuran-3,4(2*H*,5*H*)-dione (**5b**) were isolated in

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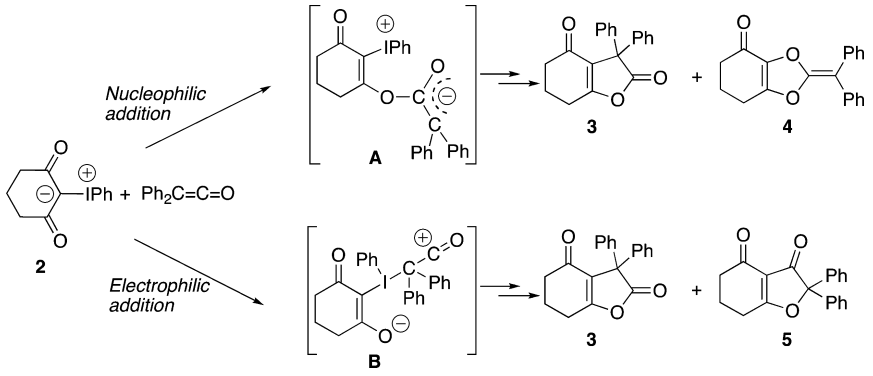
Scheme 1. Possible Mechanistic Pathways



Scheme 2. Reaction of Iodonium Ylides 2 with Diphenylketene

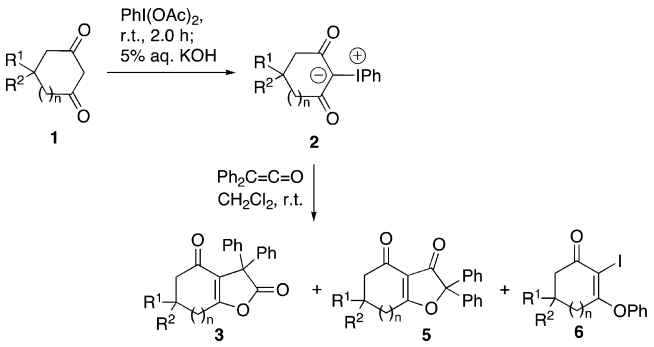


Table 1. Reaction[a] of β-Dicarbonyl Iodonium Ylides 2 with Diphenylketene

entry	*n*	R^1	R^2	Time(d)	products (% yield)[b]
1	0	H	H	2	**3a** (12), **5a** (53), **6a** (33)
2	1	H	H	3	**3b** (42), **5b** (55)
3	1	CH_3	H	1	**3c** (66), **5c** (34)
4	1	C_6H_5	H	1	**3d** (45), **5d** (54)
5	1	p-$CH_3OC_6H_4$	H	1	**3e** (39), **5e** (43)
6	1	CH_3	CH_3	3	**3f** (58), **5f** (42)

[a]All reactions were carried out on a 2.0 mmol scale with 1.0 equiv of **2** and 2.0 equiv of diphenylketene in 10 mL of CH_2Cl_2. [b]Isolated yield.

42% and 55% yields, respectively (entry 2, Table 1). Similarly, the reaction of iodonium ylides **2c–e** with diphenylketene at room temperature furnishes mixtures of lactones **3c–e** and aurones **5c–e** (entries 3–5 of Table 1), easily separable with column chromatography. Phenyliodonium ylide **2f** reacts with diphenylketene to give 6,6-dimethyl-3,3-diphenyl-6,7-dihydro-benzofuran-2,4-(3*H*,5*H*)-dione (**3f**)[11b] and 6,6-dimethyl-2,2-diphenyl-6,7-dihydro-benzofuran-3,4(2*H*,5*H*)-dione (**5f**) in 58% and 42% yields, respectively (entry 6, Table 1). The formation of iodoether **6** was only observed, when a fresh batch of iodonium ylide **2** comes in contact with diphenylketene. In such a case, an exothermic reaction occurs yielding, within minutes, mixtures of lactones **3**, aurones **5**, and iodoether **6**. The same products **3**, **5** were observed under photochemical or $Rh_2(OAc)_4$-catalyzed thermal activation but in a shorter time.

It had been reported[11b] that when phenyliodonium ylide **2f** was allowed to react with diphenylketene in dichloromethane at room temperature, lactone **3f** and ketene acetal **4f** were isolated in 32% and 44% yields, respectively. This was explained as a consequence of a formal 1,3-addition of phenyliodonium ylide **2f** on diphenylketene. On the other hand, a similar aurone derivative was isolated[12] upon catalytic carbonylation of iodonium ylide **2f** via the intermediate ketene, which was thought to be the primary unstable product of the carbonylation reaction.

The structure of lactones and aurones is in accord with HRMS, IR, ^1H, ^{13}C, and 2D NMR spectroscopy as illustrated for representative examples **3b** and **5b** (Figure 1). Lactone **3b**

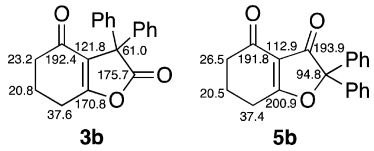


Figure 1. ^{13}C chemical shifts of lactone **3b** and aurone **5b**.

was identified by the IR carbonyl absorption of the lactone moiety at 1801 cm^{-1} and the corresponding absorption of the enone moiety at 1647 cm^{-1}. The ^{13}C resonance at δ 192.4 ppm reveals the presence of an unsaturated 6-membered carbonyl group, and the ^{13}C resonance at δ 175.7 ppm reveals the presence of a lactone carbonyl group. An X-ray crystallographic study of a single crystal of **3b** confirms the structure deduced from NMR spectroscopic studies. Aurone **5b** displays an IR absorption at 1720 cm^{-1} for its 5-membered enone and at 1655 cm^{-1} for the 6-membered unsaturated carbonyl moiety. The ^{13}C resonance at δ 191.8 ppm reveals the presence of an unsaturated 6-membered carbonyl group, and the ^{13}C resonance at δ 193.9 ppm reveals the presence of an unsaturated 5-membered carbonyl group. The structure determined from an X-ray crystallographic study of a single crystal of **5b** confirms the structure deduced from NMR spectroscopic studies.

It was anticipated that treatment of iodonium ylides **2** with an in situ generated ketene, from the appropriate acetyl chloride **7** and triethylamine, would afford mixtures of lactones and aurones. However, treatment of iodonium ylide **2b** with in situ prepared dimethylketene afforded neither the expected lactone or aurone derivative. Instead, a new compound was isolated whose spectroscopic study suggested to be α-chloroenone **8**. It is known that is difficult to complete the dehydrohalogenation of the appropriately substituted acetyl chloride with triethylamine, since the formation of ketenes from the acyl ammonium salts is reversible.[13] Presumably, the iodonium ylide reacts faster with the substituted acetyl chloride than with ketene shifting the equilibrium to the left.

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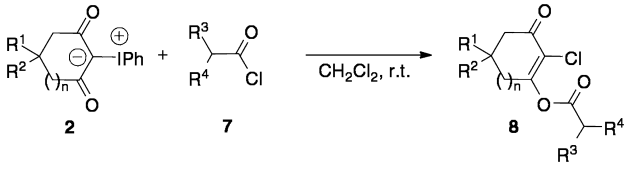
Indeed, the reaction of iodonium ylides **2** with substituted acetyl chloride **7** in dichloromethane at room temperature yields the corresponding α-chloroenones **8**[14] with good to excellent yields (Scheme 3). All reactions were run at room temperature (ca. 20 °C) until complete consumption of the ylide (TLC monitoring).

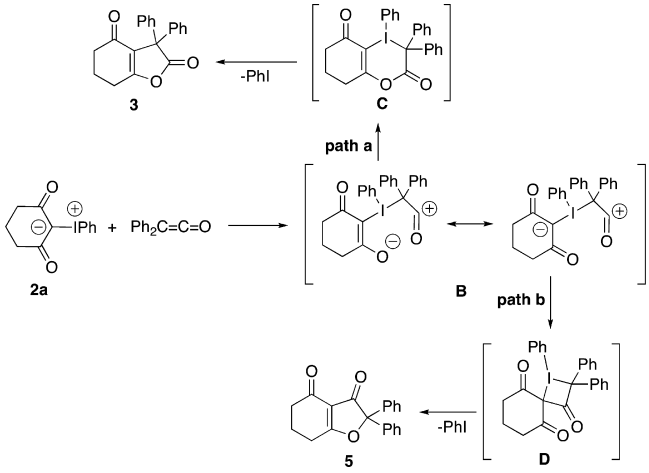
Scheme 3. Reaction of Iodonium Ylides 2 with Diphenylacetyl Chloride



The α-chloroenones **8** (Table 2) were isolated by flash chromatography on silica gel in good to excellent yields. The reaction of iodonium ylide **2a** with diphenylacetyl chloride **7a** gives 2-chloro-3-oxocyclopent-1-enyl 2,2-diphenylethanoate (**8a**) in 89% yield (entry 1, Table 2). Treatment of iodonium ylide **2b** with acyl chlorides **7b–d** yields α-chloro enones **8b–d** in excellent yields (entries 2–4, Table 1). The reaction of iodonium ylide **2b** with an equimolar amount of diphenylacetylchloride gave 2-chloro-3-oxocyclohex-1-enyl 2,2-diphenylethanoate (**8e**) in 58% yield. The yield was improved to 96% when double equivalents of $Ph_2CHCOCl$ were employed (entry 5, Table 1). Similarly, α-chloro enones **8f–g** were isolated in moderate to good yields, when iodonium ylides **2c–f** were treated with diphenylacetyl chloride **7a** at room temperature (entries 6–9, Table 2). The structure of **8e** is easily identified by the two carbonyl absorptions at 1767 and 1624 cm^{-1} associated with a vinyl ester and an enone moiety. The ^1H NMR spectrum displays the signal of the methinic proton as a singlet at δ 5.28 ppm. The ^{13}C NMR spectrum shows the signal of the enone carbon atom at δ 191.3 ppm, while the methinic carbon atom appears at δ 56.6 ppm.

For the mechanism of the formation of cycloadducts **3** and **5**, we can only offer a simple proposal (Scheme 4) that falls back on steps known from classical organic chemistry. One could assume that is unlikely that phenyliodonium ylides **2** decompose into carbenes under the mild reaction conditions without any metal-catalyzed thermal or photochemical activation. With the carbene route discounted, we could consider the enolate resonance forms I and II of iodonium ylide **2** (Figure 2) and recall that an enolate ion is an ambient anion. It is well-known that the carbon atom of an enolate is normally the site of bimolecular reactions as a nucleophile

Scheme 4. Plausible Mechanism for the Formation of Lactones 3 and Aurones 5



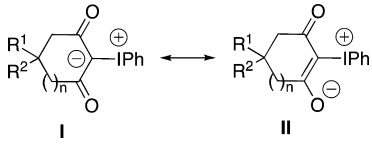


Figure 2. Resonance structures of iodonium ylide **2a**.

while, reactivity from the nucleophilic oxygen atom of an enolate is rather uncommon, the oxygen atom is typically the site of protonation. This carbanionic center of the enolate species (form I, Figure 2) is sterically hindered by three electron withdrawing groups to act as a nucleophile in bimolecular reactions and attack nucleophilically in the plane at the C_a position of diphenylketene. However, the positively charged iodonium functionality of the ylide, without steric hindrance, could attack electrophilically perpendicular to the molecular plane at the C_b position of the diphenylketene.

Either electron transfer takes place between the two reactants to afford a radical ion pair (not shown), and the latter leads on coupling to the acylium species **B**, or alternatively, the acylium intermediate **B** may be generated directly by the electrophilic attack of the iodonium functionality of the ylide to the diphenylketene, perpendicular to the plane of the ketene. In the next step, the ring closure may occur via attack of the nucleophilic oxygen atom (path a) or the nucleophilic carbon atom (path b) to the acylium carbon atom leading to 6-membered or 4-membered[15] cyclic iodine compounds **C** and **D**, respectively. Elimination of iodobenzene from **C** leads to the

Table 2. Reaction of Iodonium Ylides 2 with Acetyl Chlorides 7

entry	n	R^1	R^2	R^3	R^4	time (h)	product	yield[b] (%)
1	0	H	H	Ph	Ph	12	**8a**	89
2	1	H	H	Me	H	6	**8b**	80
3	1	H	H	Ph	H	6	**8c**	96
4	1	H	H	Me	Me	12	**8d**	88
5	1	H	H	Ph	Ph	12	**8e**	96
6	1	Me	H	Ph	Ph	12	**8f**	85
7	1	Ph	H	Ph	Ph	2	**8g**	46
8	1	$pMeOC_6H_4$	H	Ph	Ph	12	**8h**	79
9	1	Me	Me	Ph	Ph	12	**8i**	68

[a]All reactions with carried out on a 2.0 mmol scale with 1.0 equiv of **2** and 2.0 equiv of acyl chloride **7** in 10 mL of CH_2Cl_2. [b]Isolated yield.

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isolation of lactone **3**, while iodobenzene elimination from **D** results in the formation of aurone derivative **5a**.

In conclusion, we have defined that exposure of β-dicarbonyl iodonium ylides to diphenylketene yields mixtures of lactone and aurone derivatives, via the initial electrophilic attack of the iodonium ylide on the C_β position of the diphenylketene. Treatment of β-dicarbonyl iodonium ylides with acyl chlorides, precursors of the in situ ketenes, yields α-chloro enones with good to excellent yields.

EXPERIMENTAL SECTION

Preparation of Iodonium ylide 2a. A mixture of 1,3-cyclopentanedione (**1a**) (0.98 g, 10.00 mmol) and iodobenzene diacetate (3.22 g, 10.00 mmol) in tetrahydrofuran (20 mL) was stirred at room temperature for 4.0 h. The iodonium ylide **2a** was collected by filtration, washed with hexanes (100 mL), and air-dried: mp 125−126 °C (MeOH); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.84−7.78 (m, 2H), 7.59−7.52 (m, 1H), 7.43−7.35 (m, 2H), 2.72 (s, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 197.1, 133.3, 132.0, 131.9, 113.6, 83.4, 33.9; IR (KBr) ν (cm^{-1}) 3053, 2919, 1567, 1470, 1310, 1286, 989, 726.

General Procedure for the Preparation of Iodonium Ylides 2b−f. A solution of 1,3-cyclohexanedione **1b−f** (10.00−30.00 mmol) and iodobenzene diacetate (10.00−30.00 mmol) in dichloromethane (200 mL) was stirred at room temperature for 120−180 min. The yellow solution was then washed with an aqueous 5% KOH solution (2 × 100 mL) and water (2 × 50 mL) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure (water bath below 30 °C), and the solid residue triturated with hexanes (100 mL) and filtered to afford iodonium ylide **2b−f**. The spectral data were consistent with those reported in the literature.[11]

General Procedure for the Reaction of Diphenylketene with Iodonium Ylides. A solution of iodonium ylide **2** (2.00−2.55 mmol) and diphenylketene (4.12−5.15 mmol) in dichloromethane (10 mL) was stirred at room temperature (ca. 20 °C) for 1−3 d. The solvent was evaporated under reduced pressure. Purification of the residue by flash chromatography (CH_2Cl_2) afforded lactone derivative **3** and aurone derivative **5**.

*Reaction of Diphenylketene with Iodonium Ylide **2a**.* From diphenylketene (0.8 g, 4.12 mmol) and iodonium ylide **2a**(0.60 g, 2.00 mmol) in dichloromethane (10 mL), stirred at room temperature for 2.0 d. Purification by flash chromatography (CH_2Cl_2) gave the following compounds. **3,3-Diphenyl-5,6-dihydro-2*H*-cyclopenta[*b*]-furan-2,4(3*H*)-dione** (**3a**) as white crystals (0.07 g, 12% yield): mp 151−153 °C (EtOAc−hexanes); R_f 0.28 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40 (br s, 10H), 3.10−3.06 (m, 2H), 2.73−2.69 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.1, 183.2, 167.6, 136.8, 128.9, 128.6, 127.9, 87.2, 33.4, 29.9; IR (KBr) ν (cm^{-1}) 3059, 3028, 2924, 1775, 1697, 1601, 1450, 1312, 1254, 1192, 1088, 918, 748, 694; HRMS (ESI-TOF) calcd for $C_{19}H_{14}O_3Na$ 313.0835, found 313.0836. **2-Iodo-3-phenoxycyclopent-2-enone** (**6a**) as white crystals (0.20 g, 33% yield): mp 137−140 °C (EtOAc−hexanes); R_f 0.21 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ7.43−7.35 (m, 2H), 7.30−7.24 (m, 1H), 7.13−7.08 (m, 2H), 2.62−2.52 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.8, 187.8, 152.9, 129.8, 126.4, 120.9, 76.7, 32.7, 28.3; IR (KBr) ν (cm^{-1}) 3047, 2932, 1686, 1601, 1574, 1489, 1331, 1269, 1250, 1227, 1173, 1153, 918, 771, 702; HRMS (ESI-TOF) calcd for $C_{11}H_9O_2INa$ 322.9539, found 322,9543. **2,2-Diphenyl-5,6-2*H*-cyclopenta[*b*]furan-3,4-dione** (**5a**) as white needles (0.31 g, 53% yield): mp 198−199 °C (EtOAc); R_f 0.14 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.50−7.36 (m, 10H), 2.98−2.97 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 214.3, 191.7, 188.6, 136.4, 129.2, 128.7, 126.5, 119.7, 106.9, 40.0, 24.5; IR (KBr) ν (cm^{-1}) 3063, 2970, 1736, 1682, 1566, 1443, 1408, 1335, 910, 768, 748, 698; HRMS (ESI-TOF) calcd for $C_{19}H_{15}O_3$ 291.1016, found 291.1014.

*Reaction of Diphenylketene with Iodonium Ylide **2b**.* From diphenylketene (1.0 g, 5.15 mmol) and iodonium ylide **2b** (0.80 g, 2.55 mmol) in dichloromethane (10 mL), stirred at room temperature for 3.0 d. Purification by flash chromatography (CH_2Cl_2) gave the following compounds. **3,3-Diphenyl-6,7-dihydrobenzofuran-2,4-(3*H*,5*H*)-dione** (**3b**) as white crystals (0.32 g, 42% yield): mp 156−158 °C (EtOAc−hexanes); R_f 0.31 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.33 (s, 10H), 2.78−2.74 (m, 2H), 2.49−2.44 (m, 2H), 2.23−2.12 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 192.4, 175.7, 170.8, 138.4, 128.4, 128.3, 127.9, 121.8, 61.0, 37.6, 23.2, 20.8; IR (KBr) ν (cm^{-1}) 3059, 2959, 1801, 1674, 1647, 1493, 1447, 1369, 1184, 1134, 1042, 976, 899, 756, 698; HRMS (ESI-TOF) calcd for $C_{20}H_{17}O_3$ 305.1169, found 305.1172. **2,2-Diphenyl-6,7-dihydrobenzofuran-3,4(2*H*,5*H*)-dione** (**5b**) as white needles (0.42 g, 55% yield): mp 168−170 °C (EtOAc); R_f 0.07 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.46−7.42 (m, 4H), 7.33−7.22 (m, 6H), 2.93−2.88 (m, 2H), 2.46−2.41 (m, 2H), 2.18−2.08 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.1, 193.9, 191.8, 136.8, 128.8, 128.5, 126.5, 112.9, 94.8, 37.4, 26.5, 20.5; IR (KBr) ν (cm^{-1}) 3055, 2955, 2905, 1720, 1655, 1578, 1458, 1435, 1412, 1354, 1261, 1072, 960, 760, 690; HRMS (ESI-TOF) calcd for $C_{20}H_{17}O_3$ 305.1169, found 305.1165.

*Reaction of Diphenylketene with Iodonium Ylide **2c**.* From diphenylketene (0.83 g, 4.28 mmol) and iodonium ylide **2c** (0.66 g, 2.01 mmol) in dichloromethane (10 mL), stirred at room temperature for 1.0 d. Purification by flash chromatography (CH_2Cl_2) gave the following compounds. **3,3-Diphenyl-6-methyl-6,7-dihydro-benzofuran-2,4(3*H*,5*H*)-dione** (**3c**) as white crystals (0.42 g, 66% yield): mp 94−96 °C (hexanes); R_f 0.35 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.34−7.28 (m, 10H), 2.86−2.77 (m, 1H), 2.56−2.47 (m, 3H), 2.30−2.19 (m, 1H), 1.18 (d, J = 5.8 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 192.3, 175.8, 170.3, 138.4, 138.3, 128.4, 128.3, 128.2, 127.9, 127.8, 121.3, 61.0, 45.9, 31.0, 29.0, 20.8; IR (KBr) ν (cm^{-1}) 3063, 2955, 2928, 1807, 1670, 1493, 1447, 1381, 1204, 1134, 984, 937, 922, 895, 752, 694; HRMS (ESI-TOF) calcd for $C_{21}H_{19}O_3$ 319.1329, found 319.1322. **2,2-Diphenyl-6-methyl-6,7-dihydrobenzofuran-3,4-(2*H*,5*H*)-dione** (**5c**) as white needles (0.22 g, 34% yield): mp 209−211 °C (EtOAc); R_f 0.09 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.47−7.40 (m, 4H), 7.36−7.26 (m, 6H), 3.02−2.94 (m, 2H), 2.69−2.40 (m, 3H), 2.28−2.17 (m, 1H), 1.19 (d, J = 6.4 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.6, 193.6, 191.3, 136.8, 136.7, 128.9, 128.8, 128.5, 126.6, 126.4, 112.6, 95.2, 45.9, 34.3, 28.7, 20.8; IR (KBr) ν (cm^{-1}) 3063, 2939, 1724, 1663, 1574, 1439, 1323, 1231, 1072, 960, 736, 702; HRMS (ESI-TOF) calcd for $C_{21}H_{19}O_3$ 319.1329, found 319.1316.

*Reaction of Diphenylketene with Iodonium Ylide **2d**.* From diphenylketene (0.80 g, 4.12 mmol) and iodonium ylide **2d** (0.78 g, 2.00 mmol) in dichloromethane (10 mL), stirred at room temperature for 1.0 d. Purification by flash chromatography (CH_2Cl_2) gave the following compounds. **3,3,6-Triphenyl-6,7-dihydrobenzofuran-2,4-(3*H*,5*H*)-dione** (**3d**) as white crystals (0.34 g, 45% yield): mp 80−82 °C (EtOAc−hexanes); R_f 0.37 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.43−7.26 (m, 15H), 3.71−3.58 (m, 1H), 3.07−3.04 (m, 2H), 2.80−2.76 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.4, 175.7, 170.0, 141.4, 138.4, 138.2, 129.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.5, 126.6, 121.7, 61.1, 44.9, 39.4, 30.8; IR (KBr) ν (cm^{-1}) 3059, 3028, 2959, 2924, 1821, 1674, 1655, 1578, 1493, 1447, 1381, 1246, 1130, 980, 926, 764, 698; HRMS (ESI-TOF) calcd for $C_{26}H_{21}O_3$ 381.1485, found 381.1476. **2,2,6-Triphenyl-6,7-dihydrobenzofuran-3,4(2*H*,5*H*)-dione** (**5d**) as white needles (0.41 g, 54% yield): mp 130−132 °C (EtOAc−hexanes); R_f 0.14 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.58−7.26 (m, 15H), 3.65−3.53 (m, 1H), 3.19−3.16 (m, 2H), 2.82−2.78 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.2, 193.6, 190.8, 141.0, 136.69, 136.67, 129.1, 128.7, 128.6, 127.4, 126.8, 126.6, 126.5, 113.0, 95.8, 57.1, 44.9, 39.0, 34.0; IR (KBr) ν (cm^{-1}) 3063, 3024, 1728, 1701, 1578,1497, 1439, 1223, 933, 748, 698; HRMS (ESI-TOF) calcd for $C_{26}H_{21}O_3$ 381.1485, found 381.1468.

*Reaction of Diphenylketene with Iodonium Ylide **2e**.* From diphenylketene (0.81 g, 4.18 mmol) and iodonium ylide **2e** (0.84 g, 2.00 mmol) in dichloromethane (10 mL), stirred at room temperature for 1.0 d. Purification by flash chromatography (CH_2Cl_2) gave the following compounds. **3-Diphenyl-6-(*p*-methoxyphenyl)-6,7-dihydrobenzofuran-2,4(3*H*,5*H*)-dione** (**3e**) as white crystals (0.32 g, 39% yield): mp 119−121 °C (hexanes); R_f 0.31 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.51−7.47 (m, 2H), 7.40−7.35 (m, 8H), 7.21 and 6.94 (AA′BB′ system, 4H), 3.82 (s, 3H), 3.65 3.52 (m, 1H), 3.01−

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2.98 (m, 2H), 2.75−2.72 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.3, 175.6, 170.0, 158.5, 138.2, 138.1, 133.4, 128.29, 128.26, 128.2, 128.1, 127.84, 127.76, 127.5, 121.3, 114.0, 60.9, 55.0, 44.9, 38.4, 30.7; IR (KBr) ν (cm^{-1}) 3059, 2932, 1821, 1674, 1512, 1447, 1377, 1250, 1180, 1130, 1034, 980, 926, 829, 698; HRMS (ESI-TOF) calcd for $C_{27}H_{23}O_4$ 411.1590, found 411.1577. **2,2-Diphenyl-6-(*p*-methoxyphenyl)-6,7-dihydrobenzofuran-3,4(2*H*,5*H*)-dione** (**5e**) as white needles (0.35 g, 43% yield): mp 205−208 °C (EtOAc); R_f 0.09 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.50−7.33 (m, 10H), 7.18 and 6.90 (AA′BB′ system, 4H), 3.81 (s, 3H), 3.60−3.47 (m, 1H), 3.26−3.11 (m, 2H), 2.75−2.70 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.0, 193.5, 190.4, 158.8, 136.7, 136.6, 133.1, 128.93, 128.86, 128.6, 128.5, 127.6, 126.7, 126.4, 114.4, 112.9, 95.5, 55.2, 45.2, 38.3, 34.3; IR (KBr) ν (cm^{-1}) 3059, 2955, 2924, 1724, 1666, 1574, 1512, 1427, 1400, 1308, 1246, 1180, 1030, 953, 829, 764, 698; HRMS (ESI-TOF) calcd for $C_{27}H_{23}O_4$ 411.1590, found 411.1591.

Reaction of Diphenylketene with Iodonium Ylide ***2f***. From diphenylketene (1.0 g, 5.15 mmol) and iodonium ylide **2f** (0.85 g, 2.49 mmol) in dichloromethane (10 mL), stirred at room temperature for 3.0 d. Purification by flash chromatography (CH_2Cl_2) gave the following compounds. **6,6-Dimethyl-3,3-diphenyl-6,7-dihydrobenzofuran-2,4(3*H*,5*H*)-dione** (**3f**) as white crystals (0.49 g, 58% yield): mp 104−105 °C (hexanes); R_f 0.67 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.31 (s, 10H), 2.66 (s, 2H), 2.36 (s, 2H), 1.19 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 192.1, 176.0, 169.4, 138.5, 128.4, 128.3, 127.9, 120.8, 61.1, 51.8, 37.0, 33.8, 28.6; IR (KBr) ν (cm^{-1}) 3059, 2959, 1813, 1647, 1493, 1447, 1381, 1223, 1130, 987, 926, 768, 699; HRMS (ESI-TOF) calcd for $C_{22}H_{21}O_3$ 333.1491, found 333.1485. **6,6-Dimethyl-2,2-diphenyl-6,7-dihydrobenzofuran-3,4(2*H*,5*H*)-dione** (**5f**) as white needles (0.35 g, 42% yield): mp 197−200 °C (EtOAc); R_f 0.18 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.45−7.33 (m, 10H), 2.79 (s, 2H), 2.38 (s, 2H), 1.18 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 199.1, 193.6, 191.0, 136.8, 128.8, 128.5, 126.5, 111.8, 95.4, 51.8, 40.2, 33.7, 28.4; IR (KBr) ν (cm^{-1}) 3059, 2955, 1724, 1666, 1578, 1439, 1408, 1331, 1238, 1072, 953, 768, 698; HRMS (ESI-TOF) calcd for $C_{22}H_{21}O_3$ 333.1491, found 333.1494.

General Procedure for the Reaction of Diphenylacetyl Chloride with Iodonium Ylides 2. A solution of iodonium ylide **2** (1.91−2.01 mmol) and diphenylacetyl chloride (1.91−4.40 mmol) in dichloromethane (10 mL) was stirred at room temperature for 2−12 h. The solvent was evaporated under reduced pressure. The product was isolated by silica gel column chromatography with dichloromethane.

*2-Chloro-3-oxocyclopent-1-enyl 2,2-diphenylethanoate (**8a**):* white solid; 0.58 g, 89% yield; mp 110−112 °C (EtOAc−hexanes); R_f 0.35 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.43−7.31 (m, 10H), 5.33 (s, 1H), 2.92−2.88 (m, 2H), 2.53−2.50 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 197.4, 174.0, 167.4, 136.6, 128.6, 128.3, 127.6, 119.6, 56.8, 32.9, 26.6; IR (KBr) ν (cm^{-1}) 3064, 3028, 2937, 1776, 1724, 1635, 1265, 1204, 1094, 878, 737; HRMS (ESI-TOF) calcd for $C_{19}H_{15}ClNaO_3$ 349.0602, found 349.0601.

*2-Chloro-3-oxocyclohex-1-enyl 2-methylethanoate (**8b**):*[14] colorless oil; 0.33 g, 80% yield; R_f 0.42 (CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.59−2.54 (m, 2H), 2.50−2.41 (m, 4H), 2.01−1.91 (m, 2H), 1.10 (t, J = 7.5 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.1, 169.5, 164.4, 121.4, 37.0, 29.6, 27.1, 19.9, 8.5; IR (KBr) ν (cm^{-1}) 1946, 1774, 1690, 1628, 1460, 1420, 1342, 1278, 1166, 1114, 1076, 1016, 984, 840, 824.

*2-Chloro-3-oxocyclohex-1-enyl 2-phenylethanoate (**8c**):* colorless oil; 0.51 g, 96% yield; R_f 0.42 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.33 (s, 3H), 3.83 (s, 2H), 2.64−2.52 (m, 4H), 2.03−1.96 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.2, 166.8, 164.3, 132.1, 129.2, 128.6, 127.4, 121.8, 40.6, 37.0, 29.6, 19.6; IR (KBr) ν (cm^{-1}) 3030, 2961, 1763, 1684, 1576, 1340, 1327, 1109, 1014, 972, 700; HRMS (ESI-TOF) calcd for $C_{14}H_{13}ClO_3Na$ 287.0445, found 287.0430.

*2-Chloro-3-oxocyclohex-1-enyl 2,2-dimethylethanoate (**8d**):* colorless oil; 0.38 g, 88% yield; R_f 0.38 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.77−2.66 (m, 1H), 2.64−2.59 (m, 2H), 2.56−2.50 (m, 2H), 2.07−1.97 (m, 2H), 1.22 (d, J = 7.0 Hz, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.2, 172.3, 164.6, 121.7, 37.1, 34.0, 29.8, 20.0, 18.5; IR (KBr) ν (cm^{-1}) 2978, 2937, 1763, 1697, 1626, 1578, 1340, 1277, 1173, 1080, 1013, 972, 827; HRMS (ESI-TOF) calcd for $C_{10}H_{13}ClO_3Na$ 239.0445, found 239.0434.

*2-Chloro-3-oxocyclohex-1-enyl 2,2-diphenylethanoate (**8e**):* colorless oil; 0.51 g, 96% yield; R_f 0.50 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.42−7.26 (m, 10H), 5.28 (s, 1H), 2.65−2.42 (m, 4H), 2.05−1.95 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.2, 168.0, 164.2, 137.0, 128.6, 128.4, 127.6, 122.1, 56.5, 37.1, 29.4, 20.0; IR (KBr) ν (cm^{-1}) 3032, 2978, 1767, 1694, 1624, 1497, 1273, 1182, 1095, 1016, 976, 741; HRMS (ESI-TOF) calcd for $C_{20}H_{17}ClO_3Na$ 363.0758, found 363.0729.

*2-Chloro-5-methyl-3-oxocyclohex-1-enyl 2,2-diphenylethanoate (**8f**):* colorless oil; 0.60 g, 85% yield; R_f 0.55 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.39−7.30 (m, 10H), 5.31 (s, 1H), 2.66−2.39 (m, 3H), 2.31−2.18 (m, 2H), 1.04 (d, J = 6.0 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.3, 168.2, 163.7, 137.2, 128.8, 128.6, 127.8, 122.0, 56.7, 45.2, 37.3, 28.0, 20.3; IR (KBr) ν (cm^{-1}) 3026, 2966, 2891, 1747, 1691, 1635, 1265, 1188, 1113, 1088, 984, 750; HRMS (ESI-TOF) calcd for $C_{21}H_{19}ClO_3Na$ 377.0915, found 377.0889.

*2-Chloro-3-oxo-5-phenylcyclohex-1-enyl 2,2-diphenylethanoate (**8g**):* white crystals; 0.38 g, 46% yield; mp 110−111 °C; R_f 0.48 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.35−7.22 (m, 15H), 5.29 (s, 1H), 3.54−3.41 (m, 1H), 3.03 (dd, J = 17.8, 11.0 Hz, 1H), 2.96−2.73 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 190.3, 168.2, 163.1, 141.1, 137.1, 137.0, 128.9, 128.8, 128.7, 128.6, 127.7, 127.5, 126.5, 122.3, 56.7, 44.2, 38.6, 37.1; IR (KBr) ν (cm^{-1}) 3059, 3030, 1763, 1690, 1637, 1495, 1277, 1095, 974, 735, 698; HRMS (ESI-TOF) calcd for $C_{26}H_{21}ClO_3Na$ 439.1071, found 439.1041.

*2-Chloro-5-(p-methoxyphenyl)-3-oxocyclohex-1-enyl 2,2-diphenylethanoate (**8h**):* colorless oil; 0.70 g, 79% yield; R_f 0.40 (CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.47−7.34 (m, 10H), 7.15 and 6.92 (AA′BB′ system, 4H), 5.36 (s, 1H), 3.80 (s, 3H), 3.46−3.33 (m, 1H), 3.04−2.89 (m, 1H), 2.84−2.69 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 190.1, 168.0, 163.0, 158.5, 136.9, 133.0, 128.6, 128.5, 128.4, 127.5, 127.4, 122.1, 114.0, 56.4, 55.0, 44.2, 37.5, 37.1; IR (KBr) ν (cm^{-1}) 3024, 2954, 1763, 1701, 1569, 1512, 1321, 1254, 1223, 1177, 1097, 1008, 831; HRMS (ESI-TOF) calcd for $C_{27}H_{24}ClO_4$ 447.1363, found 447.1389.

*2-Chloro-5,5-dimethyl-3-oxocyclohex-1-enyl 2,2-diphenylethanoate (**8i**):* white solid; 0.51 g, 68% yield; mp 132−134 °C (EtOAc); R_f 0.62 (CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.42−7.32 (m, 10H), 5.27 (s, 1H), 2.52 (s, 2H), 2.45 (s, 2H), 1.10 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 191.1, 168.4, 162.4, 137.1, 128.8, 128.6, 127.7, 121.6, 56.6, 51.0, 43.0, 32.6, 27.8; IR (KBr) ν (cm^{-1}) 3059, 2957, 1772, 1690, 1634, 1456, 1265, 1153, 1095, 1022, 943, 760;. HRMS (ESI-TOF) calcd for $C_{22}H_{21}ClNaO_3$ 391.1071, found 391.1070.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C spectra of **2a**, **3a−f**, **5a−f**, **6a**, and **8a-I**, X-ray studies of phenyliodonium ylide **2a**; X-ray studies of lactone **3b** aurone derivative **5b**. This material is 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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