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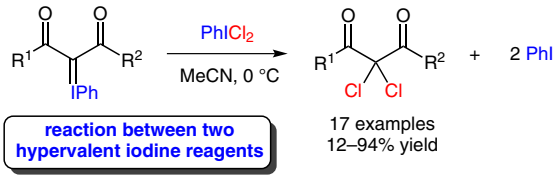
Geminal Dichlorination of Phenyliodonium Ylides of β-Dicarbonyl Compounds through Double Ligand Transfer from (Dichloroiodo)benzene

Jason Tao
Tina N. Tuck
Graham K. Murphy*

Department of Chemistry, University of Waterloo, 200 University Ave. W., Waterloo, ON, N2L 3G1, Canada
graham.murphy@uwaterloo.ca



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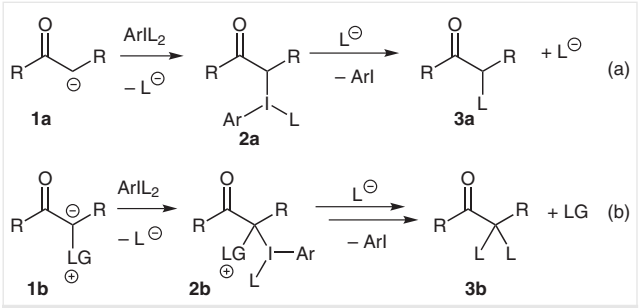
Abstract Pre-formed phenyliodonium ylides of cyclic and acyclic β-diketones, β-keto esters and β-diesters were reacted with (dichloroiodo)benzene, resulting in transfer of both chloride ligands onto the ylidic carbon. These two hypervalent iodine(III) compounds exhibit high reactivity towards each other under mild reaction conditions and typically afford the *gem*-dichloride products in good yield. Upon comparison of these chlorination reactions with those of the analogous diazocarbonyl compounds, reactions of iodonium ylides were unilaterally faster, and often gave the products in higher yield.

Key words halogenation, hypervalent iodine, iodonium ylides, diazo compounds, (dichloroiodo)benzene

Hypervalent iodine(III) (HVI) reagents represent a class of widely studied compounds in organic chemistry. The impetus for this research has been brought about by their ease of use, their low toxicity, and their wide reactivity profile. Chemical transformations affected by HVI reagents include various oxidative, carbenoid, pericyclic, and ligand transfer reactions.[1] The diversity of HVI reagents now encompasses electrophilic sources of valuable functional groups such as alkynyl,[2] aryl,[3] cyano,[4] or trifluoromethyl,[5] which can be accessed by ligand transfer reactions. (Dichloroiodo)benzene ($PhICl_2$)[6] and (difluoroiodo)toluene ($TolIF_2$),[7] are classic HVI reagents that have been used in various chlorination[8] and fluorination[9] reactions because they have similar, but much milder, reactivity compared with the respective dihalogens (Cl_2 and F_2). In analogy to the chemistry of Cl_2 and F_2, these HVI reagents can also react to deliver both halogens to differing carbon atoms of the substrate, or to deliver a single halogen with the second being discarded.

Singly functionalized products can be obtained by reacting enolates (or enolate equivalents, **1a**) with aryl-λ³-iodanes (Scheme 1, a).[1e,10] This process involves the intermediacy of alkyl(aryl)iodane **2a**, where the hypernucleofugality of its aryl-λ³-iodanyl group[11] facilitates the reductive elimination of the aryl iodide to provide the singly functionalized products (**3a**). We have been developing a process to install both halogen ligands of an iodane onto a single carbon, by pre-installing a good leaving group (LG) at the nucleophilic carbon (see **1b**; Scheme 1, b).



Scheme 1 Strategy for (a) α-carbonyl monofunctionalization and (b) α,α-carbonyl difunctionalization with aryl-λ³-iodanes

Should the nucleofugality of LG rival that of the iodanyl group of **2a**, the hypothetical intermediate **2b** would bear two excellent leaving groups, the substitution of which would furnish *gem*-dihalogenated product **3b**. Nitrogen gas (N_2) is an exceptional leaving group, and its incorporation into structures such as **1b** leads to the commonly encountered diazocarbonyl functional group. This group's nucleofugality has led to its prevalent use as a metallocarbene precursor[12] and, more relevant to our group's research goals, its use in ionic *gem*-difunctionalization reactions.[13] Therefore, we initiated our *gem*-dihalogenation studies by reacting diazocarbonyl compounds with the (dihaloiodo)arenes $PhICl_2$ and $TolIF_2$, and successfully transferred both halide ligands from the iodane onto the ylide carbon, generating geminal dihalogenation products.[14,15]

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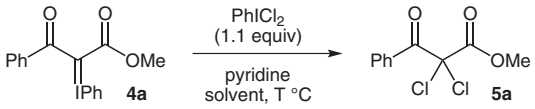
Our interest in further generalising our double ligand transfer strategy led us to explore different ylides of general structure **1b**. Given that the nucleofugality of the iodanyl group of **2a** is sufficient to undergo substitution in conventional α-carbonyl functionalisations, we anticipated that iodonium ylides (**1b**, where LG = ArI) would also be operative in the double ligand transfer reaction. This proposal is also supported by the fact that phenyliodonium ylides are the most commonly used surrogate for the diazo group in metallocarbenoid chemistry,[16] though, to our knowledge, there is no precedent for a reaction involving an iodonium ylide and a (dihaloiodo)arene.

Phenyliodonium ylides typically display low solubility and low stability in most organic solvents, often necessitating their formation in situ and immediate use.[17] In light of this, our initial dichlorination reactions were attempted as one-pot processes, in which iodonium ylides were generated in situ and immediately treated with $PhICl_2$; unfortunately, these approaches proved to be unworkable. We then elected to synthesise and isolate a variety of phenyliodonium ylides of β-dicarbonyl compounds, and investigate these in the *gem*-dichlorination reaction with $PhICl_2$.

Initial studies began with model substrate **4a** being subject to the reaction conditions that were found to be optimal for dichlorinating the analogous diazo compound **6a** (Table 1, entry 1).[14b] Analysis of the crude reaction mixture by ^1H NMR spectroscopy revealed complete consumption of the iodonium ylide **4a**, even though half of the iodane $PhICl_2$ remained intact. Though we were dismayed that the *gem*-dichloride product (**5a**) was only recovered in 52% yield, we were pleased to see that iodonium ylides are indeed operative in the *gem*-dichlorination reaction, as proposed. Though phenyliodonium ylides were often found to be unstable in solution, ylide **4a** was stable in solution at room temperature during the reaction time (5 min). We reasoned that consumption of the ylide was taking place by competing, unproductive processes, such as engaging a reactive intermediate further along the dichlorination sequence, possibly leading to iodonium ylide dimer products.[18]

To prevent such side processes from occurring, the reaction conditions were modified to reduce the relative concentration of **4a** versus $PhICl_2$ in situ. This was accomplished by exploiting the differences in solubility between these two reagents, which led to the following changes: reversing the order of addition [i.e., adding ylide **4a** to a solution of $PhICl_2$; diluting the reaction mixture; using a solvent (MeCN) in which the ylide is less soluble than $PhICl_2$; and lowering reaction temperature to 0 °C (see Table 2, entries 2–7)].[19] While varying the reaction parameters we also found pyridine activation of $PhICl_2$ to have no beneficial effect on either reaction rate or yield (entries 3 and 4). This is in stark contrast to the dichlorination of the analogous diazocarbonyl **6a** (see Table 2) for which Lewis base catalysis proved essential to obtaining **5a** chemoselectively and in good yield,[14b] speaking to the increased relative reactivity of iodonium ylides over diazo compounds towards dichlorination with $PhICl_2$. The optimised reaction conditions for the dichlorination of **4a** (Table 1, entry 5) gave product **5a** in 79% yield over 5 minutes at 0 °C, which is a drastic increase in reaction rate compared with the chlorination of the analogous diazo compound.[14b] We were pleased to observe that iodonium ylides of β-dicarbonyl compounds will undergo the ligand transfer reaction upon treatment with $PhICl_2$. Furthermore, clear differences were observed between the reactivity of ylides **4a** and **6a**, which we hoped might provide further insight into the mechanism of the dihalogenation process. Herein, we report the novel dichlorination of iodonium ylides using the iodane $PhICl_2$, and a comparison of these results with those for the dichlorination of the analogous diazonium ylides.

Table 1 Optimization of the Dichlorination of Phenyliodonium Ylide of **4a**



Entry	Solvent	*T* (°C)	Pyridine (mol%)	Time (min)	Yield (%)[a]
1	CH_2Cl_2 0.2 M	rt	5	5	52[b]
2	CH_2Cl_2 0.2 M	rt	5	5	62[c]
3	CH_2Cl_2 0.1 M	0	5	5	74[c]
4	CH_2Cl_2 0.1 M	0	0	5	79[c]
5	MeCN 0.1 M	0	0	5	79[c]
6	MeCN 0.1 M	0	0	5	66[b]
7	MeCN 0.05 M	0	0	20	70[c]

[a] Isolated yield.
[b] Reaction conditions: Ylide **4a** (1.0 equiv) was suspended in solvent, cooled to 0 °C (if necessary) and $PhICl_2$ (1.1 equiv) was added in one portion.
[c] Reverse addition: $PhICl_2$ (1.1 equiv) was dissolved in solvent, cooled to 0 °C (if necessary) and ylide **4a** (1.0 equiv) was added in one portion.

Phenyliodonium ylides of acyclic β-keto esters **4a–c** and malonate ester **4d** were subjected to the optimised reaction conditions, and the dichlorinated products were recovered in moderate to good yields (Table 2). Reaction times for iodonium ylides **4a–d** were rapid and much shorter relative to the dichlorination of the analogous diazo compounds **6a–d**. Yields for the reactions of **4a–d** were typically high, although an exception was found for β-diketone substrate **4e**, which gave a complex mixture of products, and from which **5e** could only be recovered in 28% yield. As this ylide was notably less stable in solution than ylides **4a–c**,[18] we believe it was inherently more reactive and, as a result, formed increased amounts of unwanted side products.

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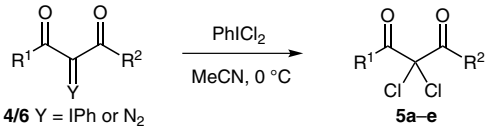
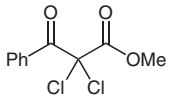
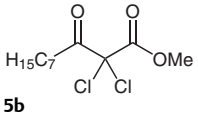
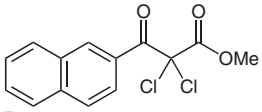
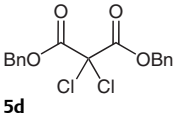
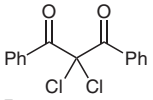
Table 2 Dichlorination of Phenyliodonium and Diazonium Ylides of Acyclic 1,3-Dicarbonyls



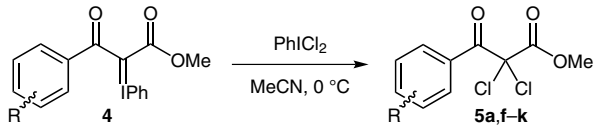
4/6 Y = IPh or N_2 **5a–e**

Entry	Substrate	Product (**5**)	Time (min)	Yield (%)[a]
1	**4a**, Y = IPh		5	79[b]
2	**6a**, Y = N_2	**5a**	1.6 h	83[c,d]
3	**4b**, Y = IPh		5	87[b]
4	**6b**, Y = N_2	**5b**	0	73[c]
5	**4c**, Y = IPh		5	55[b]
6	**6c**, Y = N_2	**5c**	20	47[c]
7	**4d**, Y = IPh		2	76[b]
8	**6d**, Y = N_2	**5d**	30	67[c]
9	**4e**, Y = IPh		5	28[b]
10	**6e**, Y = N_2	**5e**	60	60[c,d]

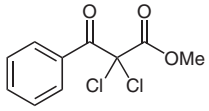
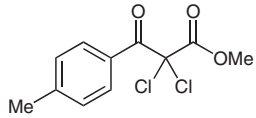
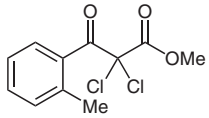
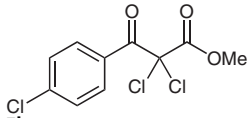
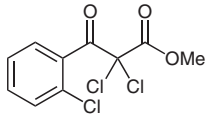
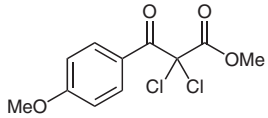
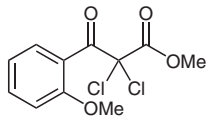
[a] Isolated yield.
[b] Reaction conditions: $PhICl_2$ (1.1 equiv) was dissolved in MeCN (0.1 M), cooled to 0 °C and ylide **4** (1.0 equiv) was added in one portion.
[c] Reaction conditions: Diazo **6** (1.0 equiv) was dissolved in CH_2Cl_2 (0.2 M), and to this was added 5 mol% pyridine, followed by $PhICl_2$ (1.1 equiv) in one portion.
[d] See Coffey and Murphy.[14b]

Aryl-substituted derivatives of ylide **4a** were synthesised to determine the effect of steric and electronic substituents on the reactivity of iodonium ylides (Table 3). Whereas no steric influence was observed in the dichlorination of **4f** versus **4g** (entries 2 and 3), a dramatic decrease in yield occurred upon moving an electron-poor chloride from the *para*- to an *ortho*-position (entries 4 and 5). Conversely, the yield of the dichlorination reaction improved as an electron-rich methoxy group was moved from the *para*- to an *ortho*-position. We therefore infer that steric hindrance has a negligible effect on the dichlorination reaction in this system, and while electronic substituents have a clear effect on the outcome of the reaction, its origins are complex and not easily elucidated. In analogy to that observed for iodonium ylide **4e** (e.g., poor solution stability resulting in poor product yield), ylides **4i** and **4j** were also relatively unstable in solution, gave complex product mixtures, and low isolated product yields.

Table 3 Substitution Effects on Dichlorination of **4a** Derivatives[a]



4 **5a,f–k**

Entry	Substrate	Product	Time (min)	Yield (%)[b]
1	**4a**, R = H	 **5a**	5	79
2	**4f**, R = 4-Me	 **5f**	5	70
3	**4g**, R = 2-Me	 **5g**	5	72
4	**4h**, R = 4-Cl	 **5h**	10	70
5	**4i**, R = 2-Cl	 **5i**	10	30
6	**4j**, R = 4-OMe	 **5j**	5	12[c]
7	**4k**, R = 2-OMe	 **5k**	5	51

[a] Reaction conditions: $PhICl_2$ (1.1 equiv) was dissolved in MeCN (0.1 M), cooled to 0 °C and ylide **4** (1.0 equiv) was added in one portion.
[b] Isolated yield.
[c] Reaction performed at –78 °C due to the instability of **4j**.

The iodonium ylides of cyclic β-dicarbonyl compounds were subsequently investigated, from which products **5l**–**p** were recovered in varying yield (Table 4). β-Diketone **4l** was

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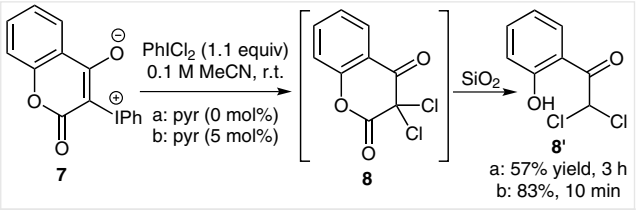
converted into **5l** in excellent yield (94%), but the structurally similar ylide **4m** gave product **5m** in 32% yield. Low yields were also observed for the *gem*-dialkylated β-keto ester (**4n**) and β-diester (**4o**) substrates (34 and 44% yield, respectively). Given the similarity between these substrates, especially **4l** and **4m**, we believe the *gem*-disubstitution is imparting a negative steric influence on the reaction. This proposal is further supported by the dichlorination of the less sterically hindered iodonium ylide **4p**, from which **5p** was recovered in 85% yield. Rates of these dichlorination reactions were very fast, especially relative to the rates for the pyridine-catalysed dichlorinations of the analogous diazo compounds **6o** and **6p**. While these diazo substrates either failed to react (**6o**), or did so very sluggishly (**6p**, 3 days),[14b] the corresponding iodonium ylides of Meldrum's acid (**4o**) and *N*,*N*′-dimethylbarbituric acid (**4p**) reacted[21] in 30 or 100 minutes, respectively.

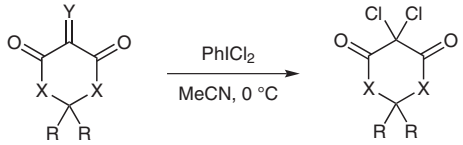
In contrast to the high reactivity of the solution-unstable ylides **4e**, **4i** and **4j**, the iodonium ylide of 4-hydroxycoumarin (**7**) has exceptional thermal and solution stability,[20] and, as a result, also has decreased relative reactivity. These properties were observed during its dichlorination, as the reaction at 0 °C was poor, and its room temperature reaction required three hours for consumption of the ylide, after which dichloride product **8′** was recovered in 57% yield, presumably via intermediate **8** (Scheme 2, a). Its decreased reactivity could be overcome by the addition of pyridine, as previously used in the dichlorination of diazo compounds, which presumably facilitated the initial association of **7** and the pyridine-activated iodane complex.[14a–c] A significant rate acceleration was achieved upon addition of 5 mol% pyridine, and the consumption of **7** was complete in 10 minutes, giving **8′** in 83% yield (Scheme 2, b).



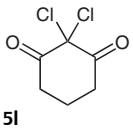
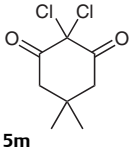
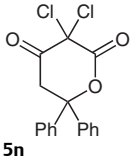
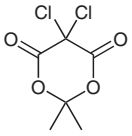
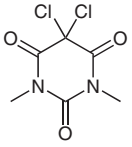
Scheme 2 Dichlorination of iodonium ylide **7** (a) without and (b) with the addition of pyridine as an iodane activator

Elucidation of the mechanistic pathway for the transformation of iodonium ylides into α,α-dichloro products has proven challenging due to the typically high reactivity, low solution stability and low solubility (in the reaction solvent) of the ylides. Nonetheless, our ability to dichlorinate analogous diazonium (**6**) and phenyliodonium (**4**) ylides using $PhICl_2$ supports our conceptual view of the double ligand transfer process proposed in Scheme 1 (b). We attempted to better understand the dichlorination mechanism for ylides **4** and **6** by analysing the side products

Table 4 Dichlorination of Phenyliodonium and Diazonium Ylides of Cyclic 1,3-Dicarbonyls



4/6 Y = IPh or N_2 **5l–p**

Entry	Substrate	Product	Time (min)	Yield (%)[a]
1	**4l**, Y = IPh		5	94[b]
2	**6l**, Y = N_2	**5l**	60	39[c,d]
3	**4m**, Y = IPh		5	32
4	**6m**, Y = N_2	**5m**	16 h	73[c,d]
5	**4n**, Y = IPh	 **5n**	5	32[e]
6	**4o**, Y = IPh		30	44[f]
7	**6o**, Y = N_2	**5o**	no reaction[c,d]	–
8	**4p**, Y = IPh		100	85
9	**6p**, Y = N_2	**5p**	3 d	60[c,d]

[a] Isolated yield.
[b] Reaction conditions: $PhICl_2$ (1.1 equiv) was dissolved in MeCN (0.1 M), cooled to 0 °C and ylide **4** (1.0 equiv) was added in one portion.
[c] Reaction conditions: Diazo **6** (1.0 equiv) was dissolved in CH_2Cl_2 (0.2 M), and to this was added 5 mol% pyridine, followed by $PhICl_2$ (1.1 equiv) in one portion.
[d] See Coffey and Murphy.[14b]
[e] Product isolated as $Ph_2C{=}CHC(O)CHCl_2$ (**5n′**) after column chromatography.
[f] Reaction mixture contained 5 mol% pyridine and was allowed to warm from 0 °C.

recovered from their respective reaction mixtures. For example, in the dichlorination of α-diazo-β-dicarbonyl compounds **6**,[14b] α-chloro-β-dicarbonyl (monochloride) side products such as **9** (Figure 1) were routinely observed, but none were detected in the reactions of iodonium ylides. However, GC-MS analysis of products recovered during the dichlorination of **4i** revealed a compound containing a sig-

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nal at *m*/*z* 420.0 with an isotope pattern indicative of a dichlorinated compound (*m*/*z* [M], [M+2], [M+4]; 9:6:1 ratio). We attribute this signal's origin to ylide 'dimerisation' side product **10** (Figure 1). These dimerisation products were not observed during the dichlorination reactions of diazo compounds. The mutually exclusive side products observed in the dichlorination of phenyliodonium and diazonium ylides suggests at minimum that the competing side reactions in each are different.

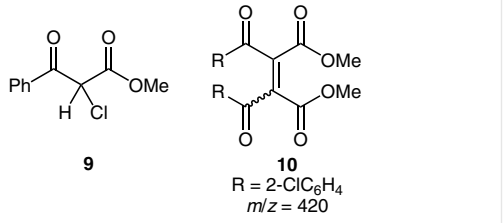
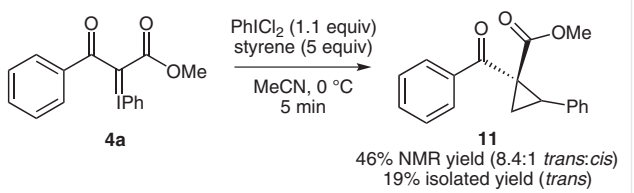


Figure 1 Side products identified after dichlorination of diazonium ylides (**9**) and dichlorination of iodonium ylides (**10**) using $PhICl_2$

Dimerisation products are usually a clear indicator of carbenoid chemistry, and their observation in the dichlorination reactions of iodonium ylides led us to test whether carbenoid-type processes were operative. This hypothesis is supported by the fact that iodonium ylides are commonly used as metallocarbene precursors. Furthermore, metallocarbenes derived from iodonium and diazonium ylides display differing reactivity, which is in accord with the reactivity pattern observed herein.

In an attempt to trap any carbenoid intermediates that might be generated during the dichlorination reaction, a fivefold excess of styrene was added to the reaction of **5a** and $PhICl_2$. In the event, cyclopropanation product **11** was observed in 46% NMR yield as an 8.4:1 mixture of diastereomers (Scheme 3). Given that iodonium ylides of β-dicarbonyl systems such as **4** are known precursors to free carbenes at elevated temperatures,[22] it is therefore possible that this cyclopropanation side-product is derived from free carbene intermediates, but is highly improbable at such a low temperature. Furthermore, metal-free intermolecular cyclopropanation reactions of iodonium ylides are known to proceed very poorly (<2% yield), if at all.[22] Therefore, we propose that the dimerisation and cyclopropanation products generated during the dichlorination reactions are products of reaction pathways that do not involve free carbene intermediates. However, it is an interesting discovery that products typical of metallocarbenoid processes can be generated from the metal-free reaction between two organic HVI [iodonium ylide and (dihaloiodo)arene] reagents.



Scheme 3 Iodonium ylide dichlorination with styrene added as a 'carbenoid' trap

In summary, we have shown that phenyliodonium ylides of β-dicarbonyl compounds are viable substrates in the *gem*-dichlorination reaction mediated by $PhICl_2$. A series of cyclic and acyclic iodonium ylides were synthesised, isolated, and treated with $PhICl_2$, which rapidly generated the α,α-dichloro-β-dicarbonyl products in moderate to excellent yield. In comparison to the reactions of the analogous diazo compounds, reactions of iodonium ylides were unilaterally faster, and often gave the products in higher yield. In contrast to the reactions of the diazo substrates, iodonium ylides display high reactivity in the dichlorination reaction without requiring Lewis base activation of $PhICl_2$.[23] Lastly, we discovered a new type of reactivity for HVI reagents, where products typical of metallocarbene chemistry are generated under metal-free conditions. The addition of iodonium ylides as possible substrates for our HVI double ligand transfer reaction opens a new avenue for future investigations into ligand-transfer strategies. Advancements in this area, such as difluorination using $TolIF_2$ (preliminary attempts at which suggest an incompatibility with ylide **4a**), as well as our work on the novel metal-free 'carbenoid' chemistry will be disclosed in due course.

All reactions (except the formation of phenyliodonium ylides) were performed with oven-dried or flame-dried glassware under a positive pressure of nitrogen. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes. Anhydrous CH_2Cl_2 was obtained by using a JC Meyer solvent purification system, and anhydrous MeCN was obtained by allowing the solvent to sit over activated 3Å molecular sieves overnight and were used without further purification. Thin-layer chromatography was performed on glass plates pre-coated with 0.25 mm Kieselgel 60 F_{254} (Aldrich). Unless otherwise stated, flash chromatography columns were packed with 230–400 mesh silica gel (Aldrich). ^{1}H NMR spectra were recorded at 300 or 500 MHz, relative to the residual chloroform peak (δ = 7.26 ppm), coupling constants (*J*) are reported in hertz (Hz). ^{13}C NMR were recorded at 125 MHz and are reported (ppm) relative to the centre line of the triplet from $CDCl_3$ (δ = 77.16 ppm). Positive ion electrospray (ESI) was performed with a ThermoFisher Scientific Q-Exactive hybrid mass spectrometer. Accurate mass determinations were performed at a mass resolution of 70,000. For ESI, samples were infused at 5 µL/min in 1:1 MeOH–(H_2O+0.1% formic acid) or 1:1 MeOH–(H_2O+0.2% NH_4OH).

Compounds (**4a**, **4e**, **4l**, **4m**),[24] **4o**,[25] **6d**,[26] and **7**,[27] were synthesised according reported procedures and their spectra matched those described.

Note: Due to instability of iodonium ylides, the identity of ylides **4** were confirmed by ^{1}H and ^{13}C NMR analysis and the material was immediately used in the following reactions without further purification. NMR data acquisition was performed as soon as possible after

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the ylides were dissolved. Iodonium ylides can be unpredictably difficult to isolate for reasons such as instability (e.g., **4j**) or difficulties in purification by precipitation (e.g., **4c**, **4d**).

Iodobenzene Dichloride ($PhICl_2$)

Iodobenzene (2.0 g) was suspended in No Name bleach (5.25%) and was stirred vigorously at r.t. Conc. HCl (20 mL) was then added dropwise from a graduated cylinder over 2 min. The flask was sealed with a cap and the mixture was stirred for 5 min. The solid was collected by filtration and washed with H_2O (2 × 200 mL) and then hexanes (50 mL). The solid was then transferred into a 50 mL beaker and stored in a dessicator in the dark overnight to give the title compound (2.5 g, 93%) as a pale-yellow solid; mp 110–112 °C.

Synthesis of the Phenyliodonium Ylides of β-Keto Esters; General Procedure A

In a dry, two-neck flask equipped with a reflux condenser and rubber septum and a stir bar, NaH (60% wt in mineral oil, 4.0 g, 100 mmol) was suspended in toluene (8 mL) and dimethylcarbonate (9.1 g, 100 mmol, 2.5 equiv) was added. The mixture was heated to reflux and acetophenone (4.8 g, 40 mmol, 1.0 equiv) in toluene (20 mL) was added dropwise. The reaction mixture was stirred for 30 min when hydrogen evolution had ceased. The suspension was cooled to 0 °C, diluted with EtOAc (150 mL) and the reaction was carefully quenched with MeOH (10 mL), followed by H_2O, and then acidified to pH < 5 using 1 N HCl. The organic layer was separated and then washed with H_2O (200 mL) then brine (100 mL), and dried over $MgSO_4$, and concentrated in vacuo. The resulting biphasic liquid was partitioned between MeCN (20 mL) and hexanes (10 mL) and then washed with hexanes (2 × 25 mL) and concentrated in vacuo to give the β-keto ester. Dicarbonyl compound (6 mmol) was dissolved in MeOH (6 mL) and then cooled in a brine-ice bath. Then, 30% KOH in MeOH (6 mL) solution was added dropwise and the mixture was stirred for 2 min, after which a solution of iodobenzene diacetate (6 mmol) in MeOH (8 mL) was added dropwise and the resulting mixture was stirred for 1 h and then poured onto ice-water (100 mL). The suspension was then extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were dried over $MgSO_4$, filtered through a Büchner funnel, then concentrated in vacuo to approximately one third of the original volume. The ylide was slowly precipitated using Et_2O and/or hexanes, and cooled to 0 °C and isolated by filtration.

Phenyliodonium of Methyl Octanoylacetate (4b)

Methyl octanoylacetate was synthesised according to a reported procedure.[28] Ylide formation protocol described in General Procedure A was followed using methyl octanoylacetate (1.20 g, 6 mmol). The crude material was precipitated from CH_2Cl_2 and Et_2O using hexanes, and cooled to 0 °C to afford a white amorphous solid (1.41 g, 58%). This material decomposed slightly upon NMR acquisition.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 8.3, 0.9 Hz, 2 H), 7.52 (t, *J* = 7.4 Hz, 1 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 3.66 (s, 3 H), 2.99 (t, *J* = 7.7 Hz, 2 H), 1.68–1.62 (m, 2 H), 1.37–1.22 (m, 9 H), 0.89–0.84 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.3, 165.3, 132.9, 131.5, 131.3, 112.7, 51.8, 38.1, 31.9, 29.8, 29.3, 26.8, 22.8, 14.2.

Phenyliodonium Ylide of Methyl (2-Naphthoyl)acetate (4c)

General Procedure A was followed using 2-acetylnaphthalene (6.81 g, 40 mmol) to afford methyl (2-naphthoyl)acetate (8.12 g, 89%) as an orange-red liquid that became a yellow solid upon standing.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.45 (s, 1 H), 8.01 (d, *J* = 8.7 Hz, 1 H), 7.98 (s, 1 H), 7.91 (d, *J* = 8.7 Hz, 1 H), 7.88 (d, *J* = 8.2 Hz, 1 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 4.14 (s, 2 H), 3.77 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.4, 168.2, 136.0, 133.5, 132.5, 130.8, 129.8, 129.06, 128.88, 127.9, 127.1, 123.9, 52.7, 45.9.

This spectral data is consistent with previously reported data.[29]

Subsequent ylide formation was achieved using methyl (2-naphthoyl)acetate (1.37 g, 6 mmol) and the crude material was precipitated from CH_2Cl_2 and Et_2O using hexanes to afford a yellow amorphous solid (0.76 g, 29%). This material decomposed slightly upon NMR acquisition.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.91 (d, *J* = 8.0 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.65 (dd, *J* = 8.4, 1.4 Hz, 1 H), 7.55 (app. t, *J* = 7.0 Hz, 1 H), 7.49–7.45 (m, 2 H), 7.41 (t, *J* = 7.8 Hz, 2 H), 3.46 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 186.0, 165.2, 137.1, 134.2, 133.6, 132.8, 131.65, 131.55, 128.9, 128.1, 127.8, 126.77, 126.64, 126.3, 126.0, 113.0, 83.8, 51.9.

Phenyliodonium Ylide of Dibenzylmalonate (4d)

This compound was synthesised according to a reported procedure.[16e] KOH (3.02 g, 169 mmol, 16.9 equiv) was stirred in MeCN (30 mL) and cooled to 0 °C. Dibenzyl malonate (2.843 g, 10 mmol, 16.9 equiv) was added dropwise, followed by $PhI(OAc)_2$ (3.22 g, 10 mmol, 16.9 equiv) in one portion and the mixture was stirred for 2 h. The mixture was poured onto ice-water and filtered. The solid was washed with cold Et_2O, collected, and dried in vacuo to yield the title compound (3.82 g, 87%) as a white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.82 Hz, 2 H), 7.49 (t, *J* = 7.25 Hz, 1 H), 7.37–7.25 (m, 12 H), 5.20 (s, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6, 137.4, 132.1, 131.4, 128.5, 127.9, 127.7, 114.6, 66.7 (C=I not observed).

Note: When using the authors' new general procedure for the synthesis of iodonium ylides, we obtained ylide **4d** as a brown liquid, as reported by the authors. This compound was instead synthesised by using the alternate literature procedure reported therein for bis(methoxy-carbonyl)(phenyliodinio)methanide, which gave ylide **4d** as a white solid.

Phenyliodonium of Methyl (4-Toluoyl)acetate (4f)

General Procedure A was followed by using of 4′-methylacetophenone (6.81 g, 20 mmol) to afford methyl (4-toluoyl)acetate (3.49 g, 89%) as a yellow liquid in a 4:1 keto/enol ratio.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.49 (s, 0.2), 7.84 (d, *J* = 7.9 Hz, 1.6 H), 7.67 (d, *J* = 8.4 Hz, 0.4 H), 7.27 (d, *J* = 8.2 Hz, 1.6 H), 7.22 (d, *J* = 8.3 Hz, 0.4 H), 5.64 (s, 0.2 H), 3.98 (s, 1.6 H), 3.79 (s, 0.5), 3.75 (s, 1 H, 2.3 H). The spectral data for this compound matched previously reported data.[29]

Ylide formation was achieved using methyl (4-toluoyl)acetate (1.15 g, 6 mmol), and precipitation from CH_2Cl_2 and Et_2O gave the title compound (0.73 g, 31%) as a white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.6 Hz, 2 H), 7.52 (t, *J* = 7.4 Hz, 1 H), 7.46 (d, *J* = 7.5 Hz, 2 H), 7.39 (t, *J* = 7.4 Hz, 2 H), 7.14 (d, *J* = 7.5 Hz, 2 H), 3.49 (s, 3 H), 2.36 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 186.1, 165.1, 139.8, 136.5, 133.3, 131.6, 131.4, 128.6, 128.1, 113.1, 51.8, 21.6 (C=I not observed).

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Phenyliodonium of Methyl (2-Toluoyl)acetate (4g)

General Procedure A was followed using 2′-acetophenone (5.36 g, 40 mmol) to afford methyl (2-toluoyl)acetate as a yellow liquid (6.60 g, 86%) as a 4:1 mixture of keto/enol tautomers. R_f 0.42 (EtOAc–hexanes, 20%).

IR (ATR): 2953, 1743, 1698, 1626, 1434, 1245, 1201, 1037 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.46 (s, 0.2 H, enol form), 7.73 (d, *J* = 7.7 Hz, 0.8 H, keto form), 7.49–7.46 (m, 1 H), 7.40–7.32 (m, 2 H), 7.29 (d, *J* = 8.4 Hz, 0.4 H, enol form), 5.36 (s, 0.2 H, enol form), 4.04 (s, 1.6 H, keto form), 3.87 (s, 0.6 H, enol form), 3.81 (s, 2.4 H, keto form), 2.62 (s, 2.3 H, keto form), 2.53 (s, 0.6 H, enol form).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.2, 174.8, 172.9, 167.9, 139.2, 136.3, 135.8, 134.2, 132.07, 132.01, 130.8, 129.9, 129.1, 128.2, 125.66, 125.57, 91.1, 52.0, 51.1, 47.6, 21.4, 20.3.

HMRS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{13}O_3$: 193.0859; found: 193.0860.

Ylide formation using methyl (2-toluoyl)acetate (1.15 g, 6 mmol) gave the title compound (1.58 g, 67%) as an amorphous white solid.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.8 Hz, 2 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.35 (t, *J* = 7.7 Hz, 2 H), 7.19–7.12 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 186.3, 164.7, 140.8, 134.0, 133.0, 131.4, 131.2, 129.7, 127.9, 126.3, 125.1, 113.2, 51.8, 19.2. (C=I carbon not observed).

Phenyliodonium of Methyl (4-Chlorobenzoyl)acetate (4h)

General Procedure A was followed using 4′-chloroacetophenone (6.19 g, 40 mmol) to afford methyl (4-chlorobenzoyl)acetate as a red liquid (7.03 g, 82.7%) in a 5:1 ratio of keto/enol tautomers.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.49 (s, 0.3 H, enol form), 7.89 (d, *J* = 8.6 Hz, 1.5 H, keto form), 7.71 (d, *J* = 8.6 Hz, 0.5 H, enol form), 7.46 (d, *J* = 8.5 Hz, 1.5 H, keto form), 7.39 (d, *J* = 8.4 Hz, 0.5 H, enol form), 5.64 (s, 0.3 H, enol form), 3.98 (s, 1.5 H, keto form), 3.80 (s, 0.8 H, enol form), 3.75 (s, 2.2 H, keto form). This data is consistent with previously reported data.[30]

Ylide formation using methyl (4-chlorobenzoyl)acetate (2.56 g, 12 mmol) gave the title compound (2.39 g, 48%) as a white amorphous solid. This compound decomposed slightly during NMR analysis.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.9 Hz, 2 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.45 (s, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 3.49 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 184.8, 165.0, 137.9, 135.5, 133.4, 131.6, 131.5, 129.8, 127.6, 113.0, 100.1, 83.0, 51.9.

Phenyliodonium of Methyl (2-Chlorobenzoyl)acetate (4i)

General Procedure A was followed using 2′-chloroacetophenone (3.09 g, 20 mmol) to afford methyl (2-chlorobenzoyl)acetate (2.02 g, 48%) as a red liquid in a 2:1 ratio of keto/enol tautomers. R_f 0.45 (EtOAc–hexanes, 20%).

IR (ATR): 2953, 1743, 1698, 1626, 1589, 1471, 1434, 1245, 1201, 1038 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.41 (s, 0.3 H, enol form), 7.64 (d, *J* = 7.7 Hz, 0.7 H, keto form), 7.60 (dd, *J* = 7.4, 1.7 Hz, 0.3 H, enol form), 7.48–7.46 (m, 1.7 H), 7.41–7.33 (m, 1.4 H), 5.60 (s, 0.3 H enol form), 4.09 (s, 1.4 H, keto form), 3.84 (s, 1.0 H, enol form), 3.77 (s, 2.1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.5, 173.0, 170.5, 167.4, 137.6, 133.5, 132.7, 132.1, 131.6, 131.2, 130.79, 130.63, 130.15, 130.05, 127.1, 126.9, 93.0, 77.4, 77.2, 76.9, 52.4, 51.6, 48.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{10}O_3Cl$: 213.0313; found: 213.0313.

Ylide formation using (2-chlorobenzoyl)acetate (1.28 g, 6 mmol) gave the title compound (1.81 g, 73%) as an eggshell-white amorphous solid after precipitation from CH_2Cl_2 and Et_2O. The product decomposed slightly during NMR analysis.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.7 Hz, 2 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.8 Hz, 2 H), 7.35–7.31 (m, 1 H), 7.25–7.21 (m, 3 H), 3.46 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.9, 164.7, 140.2, 137.6, 133.0, 131.7, 131.5, 130.4, 129.14, 129.08, 127.9, 126.5, 112.9, 52.1 (C=I not observed).

Phenyliodonium of Methyl (4-Anisoyl)acetate (4j)

General Procedure A was followed using 4′-methoxyacetophenone (6.01 g, 60 mmol), to afford methyl (4-anisoyl)acetate (8.14 g, 98%) as a white solid.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 9.0 Hz, 2 H), 6.95 (d, *J* = 8.9 Hz, 2 H), 3.96 (s, 2 H), 3.88 (s, 3 H), 3.75 (s, 3 H). This data is consistent with previously reported data.[30]

Ylide formation using methyl (4-anisoyl)acetate (1.25 g, 6 mmol). Precipitation from a mixture of CH_2Cl_2 and Et_2O using hexanes and cooling to –78 °C afforded the title compound (2.15 g, 87%) as yellow solid. NOTE: All manipulations with this compound after its precipitation were performed using labware cooled by dry-ice. The product decomposed slightly during NMR analysis.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J* = 8.6 Hz, 2 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 6.81 (d, *J* = 8.6 Hz, 2 H), 3.76 (s, 3 H), 3.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 185.2, 165.1, 160.9, 137.3, 132.9, 131.2, 131.0, 130.6, 113.2, 112.5, 82.8, 55.2, 51.6.

Phenyliodonium Ylide of Methyl (2-Anisoyl)acetate (4k)

General Procedure A was followed using 2′-methoxyacetophenone (6.01 g, 40 mmol) to afford methyl (2-anisoyl)acetate (8.16 g, 98%) as a red liquid. R_f 0.18 (EtOAc–hexanes, 20%; UV active).

IR (ATR): 2950, 2842, 1738, 1669, 1597, 1485, 1463, 1485, 1242, 1161, 1019 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.8 Hz, 1 H), 7.51 (app. t, *J* = 7.5 Hz, 1 H), 7.03 (app. t, *J* = 7.3 Hz, 1 H), 6.97 (d, *J* = 8.4 Hz, 1 H), 3.98 (s, 2 H), 3.90 (s, 3 H), 3.72 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.9, 168.6, 152.9, 134.8, 131.0, 130.9, 126.1, 120.8, 111.7, 111.4, 55.4, 52.0, 50.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{13}O_4$: 209.0808; found: 209.0808.

Ylide formation from methyl (2-anisoyl)acetate (2.50 g, 12 mmol). The title compound (1.39 g, 28%) was isolated as a light-orange solid. The product decomposed slightly during NMR analysis.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 7.7 Hz, 2 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.33 (t, *J* = 7.7 Hz, 2 H), 7.26 (t, *J* = 7.8 Hz, 1 H), 7.17 (dd, *J* = 7.4, 1.4 Hz, 1 H), 6.93 (t, *J* = 7.4 Hz, 1 H), 6.87 (d, *J* = 8.3 Hz, 1 H), 3.77 (s, 3 H), 3.41 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 183.8, 165.0, 156.0, 137.6, 132.2, 131.6, 131.1, 129.5, 127.9, 120.4, 113.0, 110.8, 55.8, 51.9.

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Phenyliodonium Ylide of 6,6-Diphenyldihydro-2*H*-pyran-2,4(3*H*)-dione (4n)

A solution of *i*-Pr_2NH (4.68 g, 46.25 mmol, 2.5 equiv) in THF (46.25 mL) was cooled to –20 °C, *n*-BuLi (2.5 M, 18.5 mL, 46.25 mmol, 2.5 equiv) was added dropwise and the mixture was stirred for 15 min then cooled to –78 °C. Methyl acetoacetate (2.15 g, 18.5 mmol, 1.0 equiv) was added dropwise and allowed to react for 40 min. Benzophenone (4.05 g, 22.2 mmol, 1.2 equiv) in THF (5 mL) was then added dropwise and the mixture was stirred for 1 h then acidified to pH 1 with 1 N HCl and allowed to warm to r.t. The mixture was then extracted with Et_2O (100 mL) and concentrated in vacuo. The crude mixture was treated with 1 M KOH (200 mL) and stirred for 16 h. The resulting suspension was filtered and the filtrate was cooled to 0 °C, acidified with conc. HCl to pH 1, extracted with CH_2Cl_2 (100 mL), then concentrated in vacuo. The resulting solid was triturated with Et_2O to yield the title compound (2.83 g, 57%) as a white solid; mp 171–173 °C; R_f 0.50 (EtOAc).

IR (ATR): 3028 (br), 1674, 1614, 1470, 1449, 1321, 1236, 1007 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.31 (m, 10 H), 3.39 (s, 2 H), 3.18 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.8, 167.5, 141.8, 129.2, 128.8, 125.9, 84.8, 50.4, 46.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{15}O_3$: 267.1016; found: 267.1015.

Ylide formation was achieved by dissolving 6,6-diphenyldihydro-2*H*-pyran-2,4(3*H*)-dione (2.64 g, 10 mmol) in EtOH (10 mL) at r.t. and treatment with 10% aq. $NaCO_3$ (30 mL), followed by addition of $PhI(OAc)_2$ (3.22 g, 10 mmol) and stirring at r.t. for 2 h. The mixture was poured onto ice and extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were dried over $MgSO_4$ and concentrated in vacuo to approximately a third of its original volume. Et_2O was added and the mixture was cooled in an ice water bath. The solid was isolated by filtration and dried in vacuo to yield the compound (1.81 g, 39%) as a white amorphous solid.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.47–7.14 (m, 15 H), 3.46 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 183.8, 165.5, 143.3, 132.9, 131.2, 131.1, 128.6, 127.8, 126.0, 112.7, 84.5, 74.9, 46.7.

Dichlorination of Phenyliodonium Ylides; General Procedure B

$PhICl_2$ (0.66 mmol, 1.1 equiv) was dissolved in MeCN (6 mL) with sonication. The yellow solution was cooled to 0 °C and ylide (0.6 mmol, 1.0 equiv) was added in one portion. The reaction mixture was stirred at 0 °C until the insoluble ylide could not be observed (typically 5–10 min). The reaction mixture was concentrated in vacuo and purified by flash chromatography (silica gel; column 1 cm × 12 cm).

Methyl Benzoyldichloroacetate (5a)

General Procedure B was followed using ylide **4a** (124 mg, 0.5 mmol) to afford the title compound (98 mg, 79%) as a clear, colourless liquid. R_f 0.50 (EtOAc–hexanes, 20%; UV active).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.7 Hz, 2 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.46 (t, *J* = 7.9 Hz, 2 H), 3.84 (s, 3 H). This data is consistent with reported data.[14b]

Methyl Octanoyldichloroacetate (5b)

General Procedure B was followed using ylide **4b** (121 mg, 0.6 mmol). Column chromatography (EtOAc–hexanes, 5%) gave the title compound (70 mg, 87%) as a clear, colourless liquid. R_f 0.56.

IR (ATR): 2956, 2927, 2857, 1770, 1747, 1244, 1006 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 2.80 (t, *J* = 7.3 Hz, 2 H), 1.66 (app. quint, *J* = 7.2 Hz, 2 H), 1.30–1.26 (m, 8 H), 0.86 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.4, 164.1, 81.8, 55.0, 35.8, 31.7, 29.0, 28.8, 24.3, 22.7, 14.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{19}O_3Cl_2$: 269.0705; found: 269.0706.

Methyl (2-Naphthoyl)dichloroacetate (5c)

General Procedure B was followed using ylide **4c** (129 mg, 0.3 mmol) to provide the title compound (49 mg, 55%) as a yellow liquid after column chromatography (EtOAc–hexanes, 5 then 10%); R_f 0.41 (EtOAc–hexanes, 10%).

IR (ATR): 3060, 2956, 1765, 1705, 1435, 1240, 1009 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.03 (dd, *J* = 8.7, 1.7 Hz, 1 H), 7.97 (d, *J* = 8.2 Hz, 1 H), 7.89 (app. t, *J* = 9.0 Hz, 2 H), 7.65 (app. t, *J* = 7.3 Hz, 1 H), 7.58 (app. t, *J* = 7.5 Hz, 1 H), 3.87 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 183.4, 164.9, 135.9, 132.7, 132.2, 130.1, 129.6, 128.7, 128.03, 127.89, 127.3, 125.1, 82.0, 55.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}O_3Cl_2$: 297.0080; found: 297.0080.

Dibenzyl Dichloromalonate (5d)

General Procedure B was followed using ylide **4d** (97 mg, 0.2 mmol) to afford the title compound (54 mg, 76%) as a clear, colourless liquid after column chromatography (EtOAc–hexanes 5 then 10%); R_f 0.52 (EtOAc–hexanes, 20%; visualised by CAM stain).

IR (ATR): 3035, 1762, 1456, 1233, 1000, 694 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.33 (m, 6 H), 7.31–7.27 (m, 4 H), 5.26 (s, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.7, 134.0, 129.0, 128.8, 128.4, 77.5, 70.0.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{17}H_{18}O_4NCl_2$: 370.0607; found: 370.0612.

Dibenzoyldichloromethane (5e)

General Procedure B was followed using ylide **4e** (85 mg, 0.2 mmol) to afford the title compound (16 mg, 28%) as a faintly yellow film; R_f 0.43 (EtOAc–hexanes, 20%; UV active).

^1H NMR (500 MHz, $CDCl_3$): δ = 7.97 (dd, *J* = 8.3, 0.9 Hz, 4 H), 7.54 (t, *J* = 7.4 Hz, 2 H), 7.40 (t, *J* = 7.8 Hz, 4 H). This data is consistent with previously reported data.[14b]

Methyl (4-Toluoyl)dichloroacetate (5f)

General Procedure B was followed using ylide **4f** (118 mg, 0.6 mmol) to afford the title compound (55 mg, 70%) as a faintly yellow liquid; R_f 0.44 (EtOAc–hexanes, 10%).

IR (ATR): 2956, 1766, 1684, 1707, 1683, 1244, 1185, 1011, 860 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 7.7 Hz, 2 H), 3.85 (s, 3 H), 2.42 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 183.0, 164.9, 145.7, 130.4, 129.5, 128.1, 81.9, 55.1, 21.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{11}O_3Cl_2$: 261.0080; found: 261.0080.

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Methyl (2-Toluoyl)dichloroacetate (5g)

General Procedure B was followed using ylide **4g** (236 mg) to afford the title compound (113 mg, 72%) after column chromatography (silica gel; EtOAc–hexanes, 5 then 10%) as a yellow liquid. R_f 0.62 (EtOAc–hexanes, 10%).

IR (ATR): 2957, 1768, 1712, 1435, 1236, 1000 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.8 Hz, 1 H), 7.41 (app. t, *J* = 7.5 Hz, 1 H), 7.30 (d, *J* = 7.6 Hz, 1 H), 7.23 (app. t, *J* = 7.6 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.1, 164.6, 139.8, 132.34, 132.26, 132.10, 128.1, 125.3, 81.9, 55.0, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{11}O_3Cl_2$: 261.0080; found: 261.0079.

Methyl (4-Chlorobenzoyl)dichloroacetate (5h)

General Procedure B was followed using ylide **4h** (249 mg, 0.6 mmol) to afford the title compound (118 mg, 70%) as a clear colourless liquid after column chromatography (EtOAc–hexanes, 5 then 10%); R_f 0.52 (EtOAc–hexanes, 10%; UV active).

IR (ATR): 2957, 1766, 1587, 1247, 1092, 1008 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.7 Hz, 2 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 3.87 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.4, 164.4, 141.1, 131.7, 129.2, 81.5, 55.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_8O_3Cl_2$: 280.9534; found: 280.9522.

Methyl (2-Chlorobenzoyl)dichloroacetate (5i)

General Procedure B was followed using ylide **4i** (249 mg, 0.6 mmol) to afford the title compound (51 mg, 30%) as a clear colourless liquid after silica gel chromatography (hexanes then EtOAc–hexanes); R_f 0.26 (EtOAc–hexanes, 10%).

IR (ATR): 2958, 1769, 1769, 1744, 1589, 1434, 1235, 1000, 756 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.49 (dd, *J* = 8.1, 0.9 Hz, 1 H), 7.45 (app. td, *J* = 7.7, 1.5 Hz, 1 H), 7.34 (app. td, *J* = 7.5, 1.0 Hz, 1 H), 3.93 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 187.9, 164.0, 134.0, 132.5 (2C), 130.8, 128.6, 126.5, 81.3, 55.2.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_7O_3Cl_3Na$: 302.9353; found: 302.9353.

Methyl (4-Anisoyl)dichloroacetate (5j)

General Procedure B was followed using ylide **4j** (123 mg, 0.3 mmol) to afford the title compound (9 mg, 12% yield) as a clear, colourless film after column chromatography (hexanes, then EtOAc–hexanes, 10 then 20%).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 9.0 Hz, 2 H), 6.93 (d, *J* = 9.1 Hz, 2 H), 3.89 (s, 3 H), 3.87 (s, 3 H). This data is consistent with previously reported data.[31]

Methyl (2-Anisoyl)dichloroacetate (5k)

General Procedure B was followed using ylide **4k** (124 mg, 0.3 mmol) to afford the title compound (42 mg, 51%) as a clear colourless liquid after column chromatography (hexanes, then EtOAc–hexanes, 5 then 10%); R_f 0.30 (EtOAc–hexanes, 20%).

IR (ATR): 2953, 1768, 1693, 1596, 1487, 1252, 1017 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.94 (dd, *J* = 7.8, 1.7 Hz, 1 H), 7.61–7.58 (m, 1 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 6.99 (d, *J* = 8.4 Hz, 1 H), 3.87 (s, 3 H), 3.85 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 184.2, 168.3, 164.3, 163.9, 157.6, 135.5, 133.0, 122.4, 121.6, 111.8, 85.3, 55.0, 54.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{11}O_4Cl_2$: 277.0029; found: 277.0030.

2,2-Dichlorocyclohexane-1,3-dione (5l)

The iodonium ylide of dimedone **4l** (125 mg, 0.4 mmol, 1.0 equiv) was suspended in MeCN (4 mL) at 0 °C. To this suspension, $PhICl_2$ (121 mg, 0.44 mmol, 1.1 equiv) was added and the mixture was stirred for 5 min. The solvent was removed by rotary evaporation, and remaining volatiles were removed by heating the crude mixture to 30 °C under high vacuum (0.2 torr) to the give title compound (68 mg, 94%) as a yellow solid.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.04 (t, *J* = 6.9 Hz, 4 H), 1.99 (quint, *J* = 7.0 Hz, 2 H). This data is consistent with reported data.[14b]

2,2-Dichloro-5,5-dimethylcyclohexane-1,3-dione (5m)

General Procedure B was followed using ylide **4m** (205 mg, 0.6 mmol) to afford the title compound (40 mg, 32%) as a white solid after column chromatography (EtOAc–hexanes, 10 then 20%).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.95 (s, 4 H), 1.04 (s, 6 H). This data is consistent with reported data.[14b]

1,1-Dichloro-4,4-diphenylbut-3-en-2-one (5n′)

General Procedure B was followed using ylide **4n** (280 mg, 0.6 mmol) to afford the title compound (59 mg, 34%) as a yellow liquid after column chromatography (hexanes then EtOAc–hexanes, 5 then 10%); R_f 0.56.

IR (ATR): 3060, 1698, 1567, 1445, 1132, 906 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.41 (m, 4 H), 7.39–7.36 (m, 4 H), 7.25–7.23 (m, 2 H), 7.02 (s, 1 H), 5.78 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 185.6, 161.2, 140.6, 138.2, 130.6, 129.30, 129.24, 129.0, 128.7, 128.4, 117.4, 70.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{13}OCl_2$: 291.0338; found: 291.0337.

5,5-Dichloro-Meldrum's Acid (5o)

$PhICl_2$ (182 mg, 0.66 mmol, 1.1 equiv) was dissolved in anhydrous MeCN (6 mL) assisted by sonication. The mixture was placed in a 0 °C water bath and pyridine (10% solution CH_2Cl_2, 24 µL, 5 mol%) was added. Ylide **4o** (208 mg, 0.6 mmol, 1.0 equiv) was added in one portion and the mixture was stirred for 20 min as the bath warmed to ambient temperature. Following the reaction time in which the colloidal suspension became a pale-yellow solution, the mixture was concentrated in vacuo and purified by column chromatography (hexanes followed by EtOAc–hexanes, 5 then 10%) to give the title compound (56 mg, 44%) as a white solid. R_f 0.0 (decomposed, EtOAc–hexanes, 10%; visualised by bromophenol blue stain); mp 44–46 °C.

IR (ATR): 1788, 1754, 1395, 1383, 1293, 1195, 1099 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.89 (s).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.0, 159.4, 108.0, 67.5, 28.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_6H_7O_4Cl_2$: 212.9727; found: 212.9718.

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***N,N*-Dimethyl-5,5-dichlorobarbituric Acid (5p)**

$PhICl_2$ (91 mg, 0.33 mmol, 1.1 equiv) was dissolved in anhydrous MeCN (3 mL) assisted by sonication. The mixture was placed in a 0 °C water bath and pyridine (10% solution in CH_2Cl_2, 12 µL, 5 mol%) was added. Ylide **4p** (107 mg, 0.3 mmol, 1.0 equiv) was added in one portion and the mixture was stirred for 100 min as the bath warmed to ambient temperature. Following the reaction time, in which the colloidal suspension became a pale-yellow solution, the mixture was concentrated in vacuo and purified by column chromatography (hexanes followed by EtOAc–hexanes, 10 then 20%) to give the title compound (57 mg, 85%) as a colourless film; R_f 0.40 (EtOAc–hexanes, 20%; UV active).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.42 (s).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.4, 148.9, 71.9, 30.6. NMR data is consistent with reported data.[14b]

Methyl 2-Diazo-3-oxodecanoate (6b)

Methyl octanoylacetate (1.0 g, 5 mmol, 1.0 equiv) was dissolved in MeCN (30 mL), and (*p*-acetamidobenzene)sulfonylazide (1.2 g, 5 mmol, 1.0 equiv) was added in one portion followed by dropwise addition of Et_3N (0.66 g, 0.65 mmol, 1.3 equiv). The mixture was stirred overnight, diluted with EtOAc (30 mL), and washed with sat. NH_4Cl (3 × 30 mL), brine (30 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. Silica gel chromatography (EtOAc–hexanes, 5 then 10%) afforded the title compound (1.05 g, 93%) as a yellow liquid. R_f 0.47 (EtOAc–hexanes, 20%; UV active).

IR (ATR): 2927, 2856, 2131, 1720, 1656, 1436, 1306, 1218, 1138 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 2.83 (t, *J* = 7.5 Hz, 2 H), 1.62 (t, *J* = 7.3 Hz, 2 H), 1.32–1.27 (m, 8 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.1, 162.0, 52.3, 40.4, 31.8, 29.3, 29.2, 24.5, 22.8, 14.2. (C=N_2 not observed).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{19}O_3N_2$: 227.1390; found: 227.1390.

2′-Hydroxy-2,2-dichloroacetophenone (8′)

Ylide **7** (109 mg, 0.3 mmol, 1 equiv) was suspended in anhydrous MeCN (3 mL) at r.t. Pyridine (1.2 µL, 0.015 mmol, 5 mol%) was then added, followed by $PhICl_2$ (91 mg, 0.33 mmol, 1.1 equiv) in one portion and the mixture was stirred for 10 min at ambient temperature, during which the mixture became a clear, light-brown solution. The mixture was concentrated in vacuo and purified by column chromatography (EtOAc–hexanes, 5 then 10%) to yield the title compound (51 mg, 83%) as a yellow liquid. R_f 0.49 (EtOAc–hexanes, 10%; UV active).

IR (ATR): 3119, 2924, 1648, 1615, 1486, 1452, 1255, 1157 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.4 (s, 1 H), 7.87 (dd, *J* = 8.2, 1.5 Hz, 1 H), 7.57 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1 H), 7.07 (dd, *J* = 8.5, 0.7 Hz, 1 H), 6.97 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H), 6.75 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.9, 164.3, 138.3, 130.2, 119.5, 119.4, 114.6, 67.2.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_8H_6O_2Cl_2$: 202.9672; found: 202.9660.

***trans*-Methyl 1-Benzoyl-2-phenylcyclopropanecarboxylate (11)**

$PhICl_2$ (60 mg, 0.22 mmol, 1.1 equiv) was dissolved in MeCN (2 mL) with the aid of sonication. The solution was then cooled to 0 °C in an ice-water bath, then, in rapid succession, styrene (86 mg, 5.0 equiv) and ylide **5a** (76 mg, 0.2 mmol) were each added in one portion. The mixture was stirred for 5 min and then the volatiles were removed in vacuo. Hexamethyldisiloxane (16 µL, 0.075 mmol) was added to the crude mixture (as an internal standard) before dissolving the mixture in $CDCl_3$. The NMR yield was obtained by comparison of the peak integrals for signals found at δ = 1.9 ppm (*trans*-isomer) and δ = 1.78 ppm (*cis*-isomer) relative to the internal standard. The NMR sample was concentrated in vacuo and subjected to column chromatography (EtOAc–hexanes, 5 then 10%). Secondary silica gel column chromatography (1 cm by 15 cm; 60Å 40–63 µm mesh purchased from Sorbtech) allowed partial separation of the title compound (10 mg, 19%) as a white solid; R_f 0.28 (EtOAc–hexanes, 10%).

IR (ATR): 2952, 1716, 1667, 1432, 1331, 1278, 1143, 1013 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 8.2, 1.0 Hz, 2 H), 7.40 (tt, *J* = 7.4, 1.4 Hz, 1 H), 7.28 (t, *J* = 7.7 Hz, 2 H), 7.12–7.01 (m, 5 H), 3.60 (s, 3 H), 3.52 (app. t, *J* = 8.6 Hz, 1 H), 2.45 (dd, *J* = 8.0, 5.1 Hz, 1 H), 1.81 (dd, *J* = 9.2, 5.1 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.5, 171.8, 137.1, 134.0, 132.8, 128.6, 128.28, 128.26, 128.0, 127.3, 52.7, 41.8, 34.0, 18.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}O_3$: 281.1172; found: 281.1172.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561283.

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