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Experimental and theoretical studies of (4 + 1) annulations between α -oxoketenes and stable phosphorous, nitrogen, or sulfur ylides

David Pierrot¹ | Michel Rajzmann | Yannick Carissan¹ | Jean Rodriguez | Damien Bonne¹ | Yoann Coquerel¹

Aix Marseille Université, CNRS, Centrale Marseille, iSm2, Marseille, France

Correspondence

Damien Bonne and Yoann Coquerel, Aix Marseille Université, CNRS, Centrale Marseille, iSm2, 13397 Marseille, France. Email: damien.bonne@univ-amu.fr; yoann.coquerel@univ-amu.fr

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Abstract

α -Oxoketenes generated in situ by a microwave-assisted Wolff rearrangement at 170°C were found to react with stabilized sulfur ylides in (4 + 1) annulation processes to afford functionalized 3-hydroxyfurans. Theoretical mechanistic investigations revealed that the reaction proceeds in two steps via a short-lived betaine intermediate, a general feature of the reactions of α -oxoketenes with stable phosphorous, nitrogen, and sulfur ylides.

KEYWORDS

annulation, betaines, density functional calculations, synthetic methods, ylides

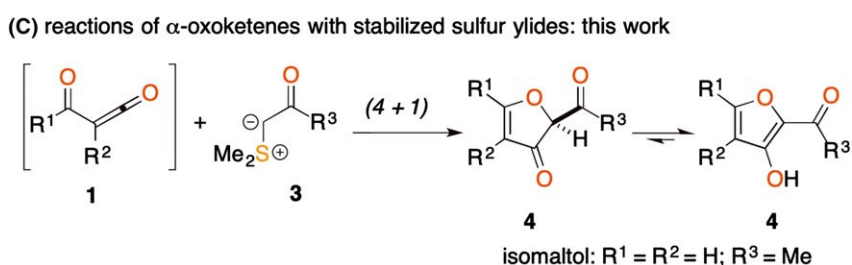
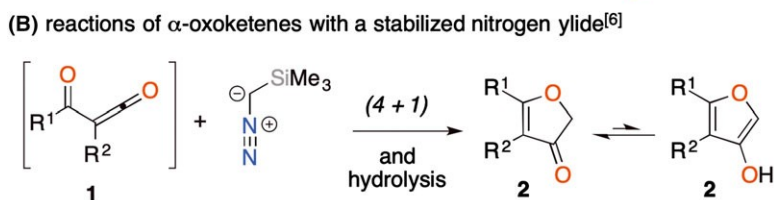
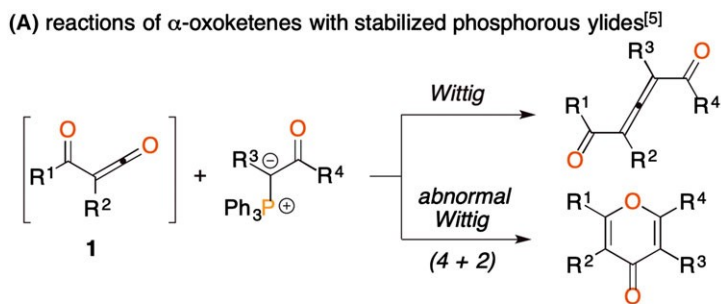
1 | INTRODUCTION

α -Oxoketenes (**1**) are very reactive short-lived synthetic intermediates that, with few exceptions, cannot be isolated and must be generated in situ with a rich chemistry.^[1] They are commonly derived from the thermal decomposition of dioxinones with concomitant extrusion of a molecule of acetone^[2] or from a thermal or photochemical Wolff rearrangement of 2-diazo-1,3-dicarbonyls extruding nitrogen gas.^[3] In the past decade, the chemistry of α -oxoketenes has been revisited and expanded, particularly taking advantage of highly efficient microwave-assisted Wolff rearrangements.^[4] Using this technique, we have recently examined their reactions with stabilized phosphorous ylides that triggered either standard or abnormal Wittig olefinations of the α -oxoketenes^[5] and with trimethylsilyldiazomethane—a nitrogen ylide—that afforded a few furan-3-ones **2** by (4 + 1) annulations followed by hydrolysis (Scheme 1).^[6] However, the synthetic value of the latter transformation was limited because it was not possible to introduce efficiently a substituent or a functional group on the one-carbon atom

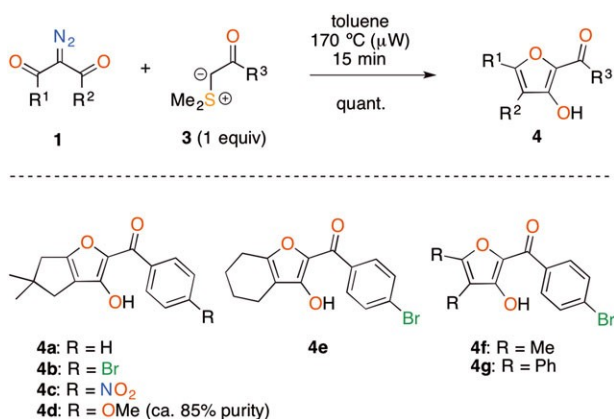
nitrogen ylide cycloaddition partner, for example using ethyl diazoacetate. This prompted us to investigate the reactivity of stable sulfur ylides **3** with α -oxoketenes in order to prepare 3-hydroxyfurans of type **4** through a related (4 + 1) annulation reaction (Scheme 1).^[7] Supportive to this idea, sulfur ylides were previously found to react with vinylketenes in (4 + 1) annulations to produce cyclopentenones.^[8] The 2-carboxy-3-hydroxyfurans **4** are analogs of isomaltol, a structurally simple 3-hydroxyfuran derivative used in the food industry as a flavor enhancer because it gives off a very pleasant smell of cooked fruit. It is also found in bread crust as the result of thermal degradation of sugars.^[9]

2 | RESULTS AND DISCUSSION

In a model experiment, a 1:1 mixture of diazodimedone as the source of α -oxoketene and the sulfur ylide **3** with $R^3 = Ph$ in toluene placed in a sealed reaction vessel was heated at 170°C for 15 minutes using microwave irradiation (Scheme 2). The only by-products of the reaction



SCHEME 1 Reactivity of α -oxoketenes with phosphorous, nitrogen, and sulfur ylides



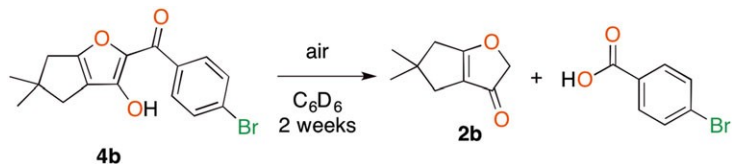
SCHEME 2 Synthesis of 3-hydroxyfurans **4**

being nitrogen gas and dimethylsulfide, a simple evaporation in vacuo enabled the clean, convenient, and quantitative isolation of the 3-hydroxyfuran **4a**. Other attempts for the same transformation with an excess of ylide (1.5-3.0 equiv) resulted in the formation of complex mixtures of products, indicating that the furan product **4a** reacts with the ylide ($R^3 = Ph$) at 170°C. We next explored the reactions of diazodimedone with other sulfur ylides having additional electron-withdrawing and electron-donating substituents. The reactions with the electron-impooverished ylides **3** having $R^3 = 4-Br-C_6H_4$ or $R^3 = 4-NO_2-C_6H_4$ afforded cleanly the corresponding 3-hydroxyfurans **4b,c** in quantitative yields. We observed a loss of efficiency in

the case of the electron-enriched ylide having $R^3 = 4-MeO-C_6H_4$, which afforded the furan product **4d** with ca. 85% purity, probably due to some overreaction with this more nucleophilic ylide.^[10] The reaction between 2-diazo-cyclohepta-1,3-dione and the ylide **3** with $R^3 = 4-Br-C_6H_4$ gave the product **4e** incorporating a fused six-membered ring still in quantitative yield. With acyclic diazo compounds, and despite the predominance of the thermodynamically preferred *s-trans* conformation of the corresponding α -oxoketenes in these cases the reaction was found equally efficient allowing for the straightforward synthesis of furans **4f,g**. As an important issue, and in contrast with isomaltol, hydroxyfurans **4a-g** were found sensitive to moisture and slowly decomposed when exposed to air for prolonged period of time, presumably due to a nucleophile-induced decarbonylation. This could be evidenced in the case of **4b**, the prolonged exposure to air of which resulted in the formation of 4-bromo-benzoic acid and furan-3-one **2b** (Scheme 3). Notably, product **2b** was previously obtained by a (4 + 1) annulation between the α -oxoketene derived from diazodimedone and trimethylsilyldiazomethane (Scheme 1b)^[6]

Using DFT calculations, we recently disclosed that the standard and abnormal Wittig olefinations of α -oxoketenes with carbonyl-stabilized phosphorous ylides are likely to proceed via stabilized betaine intermediates, a peculiarity of α -oxoketenes in Wittig olefinations.^[5] In order to get a complete picture of the reactivity of

SCHEME 3 Aerobic decomposition of 3-hydroxyfuran **4b**



α -oxoketenes with phosphorous, nitrogen, and sulfur ylides and also to gain insights on the formation and possible isolation of betaines derived from α -oxoketenes we embarked in a theoretical mechanistic study using density functional theory (DFT) methods. It was previously shown that the B3LYP-D/6-311+G(d,p) level of theory including dispersion effects^[11] coupled with the IEF-PCM continuum solvent model affords good results in the case of closely related polar reactions in solution.^[12] For the present study, we used the same level of theory supplemented with diffuse functions on hydrogen atoms [B3LYP-D/6-311++G(d,p), see Supporting Information]. The connection between the transition states and the corresponding minima was performed by intrinsic reaction coordinate (IRC) calculations. For homogeneity and reliable comparison of the relative Gibbs free energies, we started this part of the study with the re-examination of our previous results on the formation of the betaine **C** from the model phosphorous ylide **A** and the model α -oxoketene **B** (Figure 1).^[5] As expected, the betaine **C** is stabilized by an intramolecular hydrogen-bond forming a six-membered ring, and its formation was found exothermic ($-43.1 \text{ kJ mol}^{-1}$) with a low barrier ($+30.7 \text{ kJ mol}^{-1}$) from α -oxoketene **B** and ylide **A**. The existence of the stabilizing hydrogen bond was confirmed by a noncovalent interaction (NCI) region calculation.^[13] Then, the S_N2 -type cyclization of betaine **C** to give the (4 + 1) annulation product **D**, which is not observed experimentally, was examined in silico and found possible in a single step with a transition state calculated at $+100.8 \text{ kJ mol}^{-1}$. It was previously shown that the betaine **C** can evolve either to the corresponding Wittig or abnormal Wittig olefination products, with activation barriers calculated at 94.3 and $108.9 \text{ kJ mol}^{-1}$, respectively,^[5] but at a lower level of theory [B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d)] that cannot be directly compared with the present results. The energy of the transition state leading to **D** was thus recomputed at this level of theory and found at $+122.7 \text{ kJ mol}^{-1}$, indicating a kinetically disfavored (4 + 1) annulation when compared with the Wittig and abnormal Wittig olefinations that are observed experimentally. Overall, it seems that the model employed in our previous study on the Wittig-type reactions with α -oxoketenes overestimated the relative energies of most stationary points.^[5] The differences are believed to result essentially from the inclusion of stabilizing dispersion effects in the present work.^[12,14] From

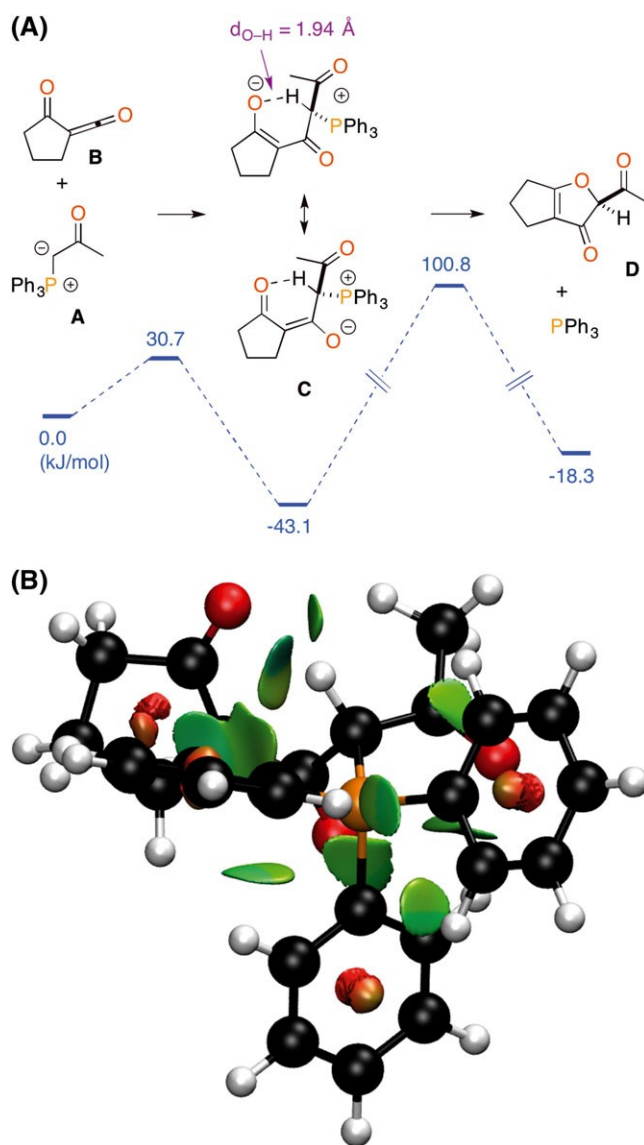


FIGURE 1 A, Calculated energy profile [DFT, B3LYP-D/6-311++G(d,p)] for the synthesis of the furan-3-one **D** from the α -oxoketene **B** and the phosphorous ylide **A**. Energies are Gibbs free energies expressed in kilojoule per mole. B, Noncovalent interaction (NCI) region calculation for betaine **C**: Blue color indicates strong attractive NCI, green color indicates weak NCI, and red color indicates strong repulsive NCI

this part of the study, we concluded that betaine **C** is a somewhat stable intermediate possibly observable and/or isolable under some specific conditions and that phosphorous ylides are not suitable to trigger (4 + 1) annulations of α -oxoketenes for kinetic reasons.

Next, we examined the formation of the model silylated furan-3-one **F**, the synthetic precursor of the corresponding desilylated furan-3-one of type **2** by hydrolysis, from the model α -oxoketene **B** and trimethylsilyldiazomethane (Figure 2). As above, it was found that the reaction is a two-step process involving first the slightly exothermic formation of the betaine intermediate **E** having an energy of -1.9 kJ mol^{-1} relative to the energy of the starting materials with a barrier calculated at $+29.6 \text{ kJ mol}^{-1}$. Then, an irreversible rate-limiting S_N^2 -type cyclization extruding nitrogen gas can occur to afford the product **F** with an overall reaction activation energy calculated at $+37.5 \text{ kJ mol}^{-1}$. Despite the existence of a stabilizing intramolecular hydrogen bond, which is confirmed by NCI analysis as above ($d_{O-H} = 1.75 \text{ \AA}$), the betaine **E** is a very short-lived intermediate.

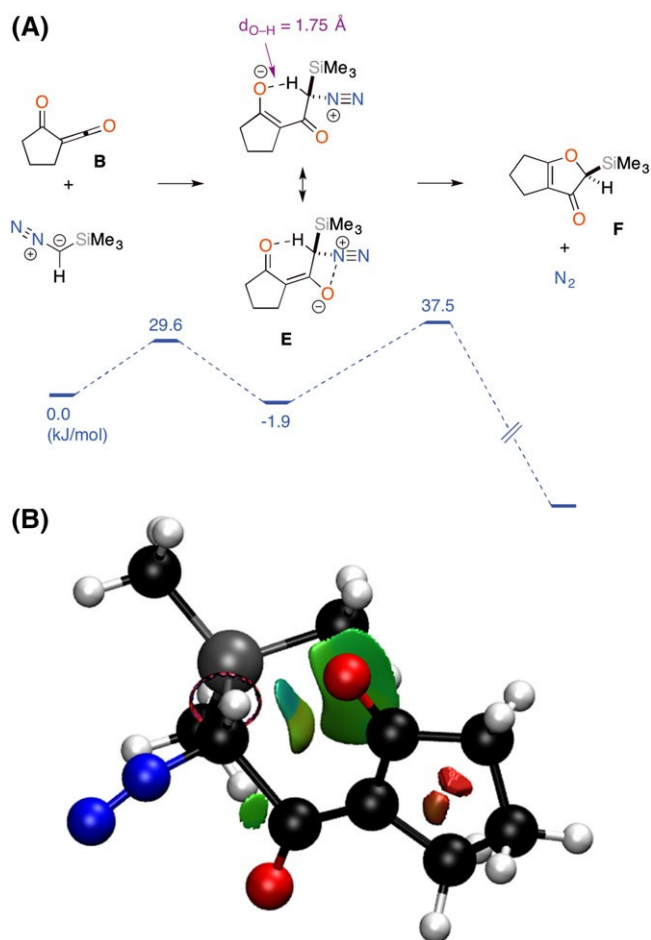


FIGURE 2 A, Calculated energy profile [DFT, B3LYP-D/6-311++G(d,p)] for the synthesis of the furan-3-one **F** from the α -oxoketene **B** and trimethylsilyldiazomethane. Energies are Gibbs free energies expressed in kilojoule per mole. B, Noncovalent interaction (NCI) region calculation for betaine **E**: Blue color indicates strong attractive NCI, green color indicates weak NCI, and red color indicates strong repulsive NCI

Finally, the reaction between the model α -oxoketene **B** and the model sulfur ylide **G** to give the bicyclic furan-3-one **I**, a precursor of the corresponding 3-hydroxyfuran of type **4** by tautomerism, was assessed (Figure 3). Expectedly, the reaction was found initiated by the exothermic formation of the corresponding betaine **H** having comparable geometrical features than the previously computed betaines **C** and **E** ($d_{O-H} = 2.04 \text{ \AA}$). An isoenergetic conformer **Hbis** could also be located, involving this time a O^-/S^+ electrostatic stabilizing interaction ($d_{O-S} = 2.64 \text{ \AA}$). From the betaine **Hbis**, a low-energy-demanding irreversible S_N^2 -type cyclization extruding dimethyl sulfide can give the furan-3-one **I**, the thermodynamically controlled tautomerism of which completes the reaction to the hydroxyfuran of type **4** (calculated at $-124.4 \text{ kJ mol}^{-1}$, not depicted). Paralleling the reactivity of betaine **E**, betaine **H** is an ephemeral intermediate.

Overall, this computational study allowed rationalizing the experimentally observed reactivity α -oxoketenes

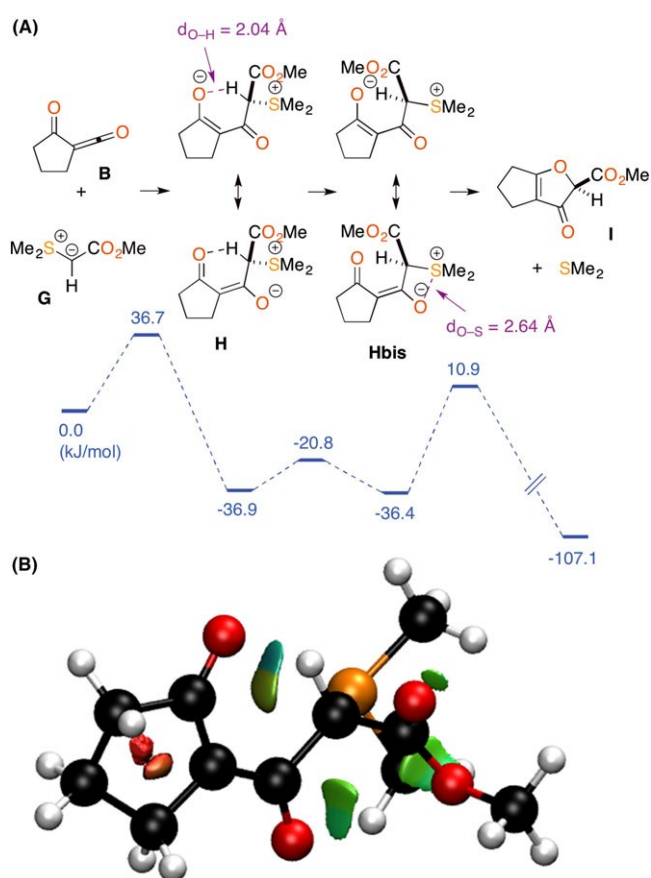


FIGURE 3 A, Calculated energy profile [DFT, B3LYP-D/6-311++G(d,p)] for the synthesis of the 3-hydroxyfuran **I** from the α -oxoketene **B** and the sulfur ylide **G**. Energies are Gibbs free energies expressed in kilojoule per mole. B, Noncovalent interaction (NCI) region calculation for betaine **H**: Blue color indicates strong attractive NCI, green color indicates weak NCI, and red color indicates strong repulsive NCI

with heteroatom-stabilized ylides: nitrogen and sulfur ylides undergo an addition/ S_{N}^2 -type cyclization sequence in (4 + 1) annulations via the intermediacy of transient betaines, while the betaines resulting from the addition of phosphorous ylides to α -oxoketenes prefer alternative decomposition paths for kinetic reasons. The relatively high energy of the transition state involved in the transformation **C** \rightarrow **D** actually reflects the much greater Lewis basicity of triphenylphosphine when compared with dimethyl sulfur and nitrogen gas.

3 | CONCLUSIONS

In summary, carbonyl-stabilized sulfur ylides were found to react with α -oxoketenes generated in situ by a Wolff rearrangement of the corresponding diazo precursors to afford functionalized 3-hydroxyfuran products through a (4 + 1) annulation. The products are generally obtained in a fast and operationally simple way with excellent purity and quantitative yields by a simple evaporation of the volatile components of the reaction mixtures. However, they were found unstable in air and slowly reacted with aerobic water in decarbonylation reactions, limiting their applications. In the second part of the manuscript, the mechanism of the reaction was investigated theoretically using DFT methods. Notably, the (4 + 1) annulation reaction between α -oxoketenes and stabilized sulfur ylides was computed as a two-step process involving the formation of a short-lived betaine intermediate. A comparable two-step mechanism was also identified for the previously reported (4 + 1) annulation reaction of α -oxoketenes with trimethylsilyldiazomethane. Finally, in silico studies for the same (4 + 1) annulation reaction with stabilized phosphorous ylides indicated a kinetically disfavored transformation when compared with Wittig-type processes, which is in perfect agreement with earlier studies.

4 | EXPERIMENTAL SECTION

4.1 | General experimental

Anhydrous toluene was obtained from a solvent purification system. All reagents were weighed and handled in air at room temperature. NMR data were recorded in *d*₆-benzene using as internal standards the residual nondeuterated solvent signal for ¹H NMR (δ = 7.16 ppm, 400 MHz) and the deuterated solvent signal for ¹³C NMR (δ = 128.06 ppm, 100 MHz). Coupling constants (*J*) are in Hertz (Hz), and the classical abbreviations are used to describe the signal multiplicities. High-resolution mass spectra were recorded in triplicate

at the Spectropole (<https://fr-chimie.univ-amu.fr/spectropole/>). The 2-diazo-1,3-dicarbonyl compounds **1** were prepared by diazo transfer reactions with tosyl azide using known procedures.^[15] The stable sulfur ylides **3** were prepared by known procedures as follows: Sulfonium salts were obtained from the corresponding α -bromoketones treated with excess dimethyl sulfur, and the salts were further reacted with aqueous sodium hydroxide to give the ylides after liquid/liquid extraction.^[16]

4.2 | General procedure

In a dry 10-mL tubular reaction vessel suitable for microwave irradiation flushed with argon gas were added the 2-diazo-1,3-dicarbonyl **1** (0.10 mmol), anhydrous toluene (2 mL, 0.05 M), and the sulfur ylide **3** (0.10 mmol), and the reaction vessel was sealed. The reaction mixture was stirred at room temperature until the ylide completely dissolved. Then, using a synthesis microwave reactor, the solution was subjected to microwave irradiation to reach 170°C as fast as possible and held at that temperature for 15 minutes, after which the reaction mixture was cooled down to 50°C with an air flow. A simple evaporation of all volatiles in vacuo afforded the pure products.

Product 4a: Following the general procedure, the reaction between diazodimedone (17 mg, 0.10 mmol) and the sulfur ylide **3** with $\text{R}^3 = \text{Ph}$ (18 mg, 0.10 mmol) afforded the furan **4a** (26 mg, quant.) as a yellow oil. ¹H NMR (400 MHz, C₆D₆) δ 8.46-8.38 (m, 2H), 7.20-7.14 (m, 3H), 2.09 (s, 2H), 2.05 (s, 2H), 0.81 (s, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 178.9 (C), 166.5 (C), 162.1 (C), 141.4 (C), 135.8 (C), 132.1 (CH), 129.3 (2CH), 128.2 (2CH), 117.5 (C), 43.84 (C), 40.69 (CH₂), 37.23 (CH₂), 29.48 (2CH₃). HRMS (ESI+): [M + Na⁺] calcd for C₁₆H₁₆NaO₃⁺ 279.0992 found 279.0994.

Product 4b: Following the general procedure, the reaction between diazodimedone (17 mg, 0.10 mmol) and the sulfur ylide **3** with $\text{R}^3 = 4\text{-Br-C}_6\text{H}_4$ (26 mg, 0.10 mmol) afforded the furan **4b** (33 mg, quant.) as a yellow oil. ¹H NMR (400 MHz, C₆D₆) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 2.09 (s, 3H), 2.04 (s, 3H), 0.82 (s, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 177.6 (C), 166.8 (C), 162.1 (C), 141.2 (C), 134.4 (C), 131.6 (2CH), 130.8 (2CH), 127.3 (C), 117.6 (C), 43.89 (C), 40.67 (CH₂), 37.18 (CH₂), 29.47 (2CH₃). HRMS (ESI+): [M + H⁺] calcd for C₁₆H₁₆BrO₃⁺ 335.0277 found 335.0273.

Product 4c: Following the general procedure, the reaction between diazodimedone (17 mg, 0.10 mmol) and the sulfur ylide **3** with $\text{R}^3 = 4\text{-NO}_2\text{-C}_6\text{H}_4$ (23 mg, 0.10 mmol) afforded the furan **4c** (30 mg, quant.) as a yellow oil. ¹H NMR (400 MHz, C₆D₆) δ 8.02 (d, *J* = 8.9 Hz,

2H), 7.81 (d, $J = 8.9$ Hz, 2H), 2.09 (s, 4H), 0.84 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 175.8 (C), 168.2 (C), 162.9 (C), 149.6 (C), 141.3 (C), 140.0 (C), 129.8 (2CH), 123.1 (2CH), 117.8 (C), 43.97 (C), 40.68 (CH_2), 37.08 (CH_2), 29.44 (2 CH_3). HRMS (ESI+): $[\text{M} + \text{H}^+]$ calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_5^+$ 302.1023, found 302.1023.

Product 4d: Following the general procedure, the reaction between diazodimedone (17 mg, 0.10 mmol) and the sulfur ylide **3** with $\text{R}^3 = 4\text{-MeO-C}_6\text{H}_4$ (21 mg, 0.10 mmol) afforded the furan **4d** (28 mg, quant.) as a yellow oil. The NMR analyses revealed the presence of an unidentified impurity in ca. 15%. ^1H NMR (400 MHz, C_6D_6) δ 8.50 (d, $J = 9.0$ Hz, 2H), 6.76 (d, $J = 9.0$ Hz, 2H), 3.20 (s, 3H), 2.14 (s, 2H), 2.11 (s, 2H), 0.85 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 178.4 (C), 165.7 (C), 163.1 (C), 161.5 (C), 141.3 (C), 131.6 (2CH), 117.4 (C), 113.7 (2CH), 54.5 (CH_3), 43.9 (C), 40.7 (CH_2), 37.3 (CH_2), 29.6 (2 CH_3). HRMS (ESI+): $[\text{M} + \text{H}^+]$ calcd for $\text{C}_{17}\text{H}_{19}\text{O}_4^+$ 287.1278, found 287.1276.

Product 4e: Following the general procedure, the reaction between 2-diazo-cycloheptan-1,3-dione (18 mg, 0.10 mmol) and the sulfur ylide **3** with $\text{R}^3 = 4\text{-Br-C}_6\text{H}_4$ (26 mg, 0.10 mmol) afforded the furan **4e** (32 mg, quant.) as a yellow oil. ^1H NMR (400 MHz, C_6D_6) δ 8.09 (d, $J = 8.6$ Hz, 2H), 7.28 (d, $J = 8.6$ Hz, 2H), 2.15 (t, $J = 5.8$ Hz, 2H), 2.03 (t, $J = 6.0$ Hz, 2H), 1.28-1.14 (m, 4H). ^{13}C NMR (101 MHz, C_6D_6) δ 178.3 (C), 162.8 (C), 158.7 (C), 135.4 (C), 134.6 (C), 131.6 (2CH), 130.8 (2CH), 111.9 (C), 23.6 (CH_2), 21.9 (CH_2), 21.6 (CH_2), 18.5 (CH_2). HRMS (ESI+): $[\text{M} + \text{H}^+]$ calcd for $\text{C}_{15}\text{H}_{14}\text{BrO}_3^+$ 321.0121, found 321.0122.

Product 4f: Following the general procedure, the reaction between α -diazoacetylacetone (13 mg, 0.10 mmol) and the sulfur ylide **3** with $\text{R}^3 = 4\text{-Br-C}_6\text{H}_4$ (26 mg, 0.10 mmol) afforded the furan **4f** (29 mg, quant.) as a yellow oil. ^1H NMR (400 MHz, C_6D_6) δ 8.05 (d, $J = 8.6$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 1.60 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 178.4 (C), 163.2 (C), 155.0 (C), 134.9 (C), 134.6 (C), 131.5 (2CH), 130.8 (2CH), 109.32 (C), 29.71 (s), 11.80 (CH_3), 5.43 (CH_3). HRMS (ESI+): $[\text{M} + \text{H}^+]$ calcd for $\text{C}_{13}\text{H}_{12}\text{BrO}_3^+$ 294.9964, found 294.9964.

Product 4g: Following the general procedure, the reaction between 2-diazo-1,3-diphenyl-propane-1,3-dione (26 mg, 0.10 mmol) and the sulfur ylide **3** with $\text{R}^3 = 4\text{-Br-C}_6\text{H}_4$ (26 mg, 0.10 mmol) afforded the furan **4g** (42 mg, quant.) as a yellow oil. ^1H NMR (400 MHz, C_6D_6) δ (d, $J = 8.6$ Hz, 2H), 7.56-7.51 (m, 2H), 7.51-7.44 (m, 2H), 7.25 (d, $J = 8.6$ Hz, 2H), 7.14-6.96 (m, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 180.1 (C), 161.0 (C), 152.9 (C), 135.5 (C), 134.5 (C), 131.7 (2CH), 130.8 (2CH), 129.8 (C), 129.6 (2CH), 129.6 (CH), 129.5 (C), 128.7 (2CH), 128.5 (2CH), 128.2 (CH), 127.3 (2CH), 125.32 (C), 115.71

(C). HRMS (ESI+): $[\text{M} + \text{H}^+]$ calcd for $\text{C}_{23}\text{H}_{16}\text{BrO}_3^+$ 419.0277, found 419.0274.

Methods and results of the theoretical studies are detailed in the Supporting Information.

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ORCID

David Pierrot  <https://orcid.org/0000-0002-3429-5711>
Yannick Carissart  <https://orcid.org/0000-0002-9876-0272>
Damien Bonne  <https://orcid.org/0000-0003-4479-4626>
Yoann Coquerel  <https://orcid.org/0000-0003-0646-006X>

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