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Dimerization of Indanedioneketene to Spiro-oxetanone: A Theoretical Study

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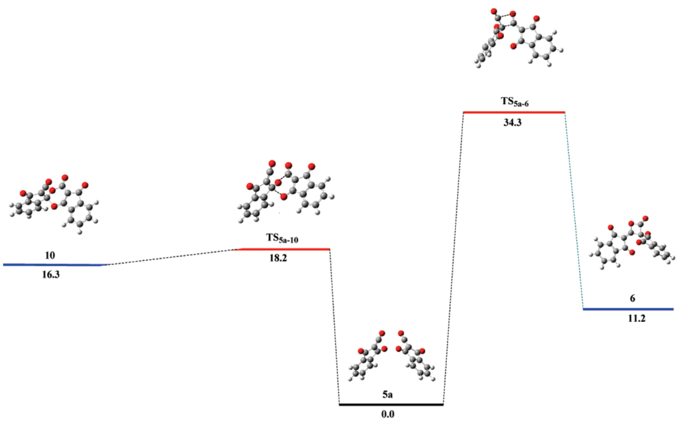
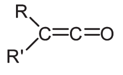


Indanedioneketene, a compound resulting from the thermal degradation of the phenyliodonium ylide of lawsone, dimerizes quantitatively to a spiro-oxetanone derivative, a key compound for further transformations. A theoretical electronic structure study of this unusual for α-oxoketenes [2 + 2] cyclization reaction both in the gas phase (DFT, MP2) and in dichloromethane solution (DFT), provides support for (a) a single-step, transition-state (involving a four-membered cyclic ring) charge-controlled, concerted mechanism and (b) a [4 + 2] cyclization reaction, not observed but studied theoretically in this study. A parallel study of an open-chain α,α′-dioxoketene dimerization explains the difference in the stability and reactivity observed experimentally between the cyclic and open-chain products.

Introduction

Ketenes **1** constitute a most interesting class of compounds with a chemistry extending to a period more than a century.[1] The familiar to many chemists group C=C=O exhibits a versatility of reactivity depending greatly on the nature of the substituents R and R′. Among the various types of ketenes, α-oxoketenes **2** play an important role in organic synthesis, and their chemistry has been previously reviewed.[2] Although a great number of α-oxoketenes have been reported in the literature, there are only a few examples of α,α′-dioxoketenes **3**, especially those bearing at least one keto group.[3]



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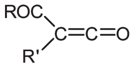

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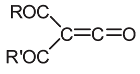

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In the course of our studies on the chemistry of zwitterionic iodonium compounds,[4] we have encountered such an α,α′-dioxoketene, namely indanedioneketene **5**. This compound is

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(1) Tidwell, T. T. *Ketenes*; John Wiley & Sons: Hoboken, NJ, 2006.

(2) (a) Wentrup, C.; Heilmayer, W.; Kollenz, G. *Synthesis* **1994**, 1219. (b) Kollenz, G.; Heilmayer, W.; Kappe, C. O.; Wallfisch, B.; Wentrup, C. *Croat. Chem. Acta* **2001**, *74*, 815.

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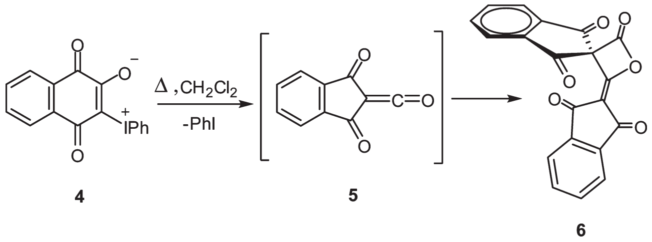
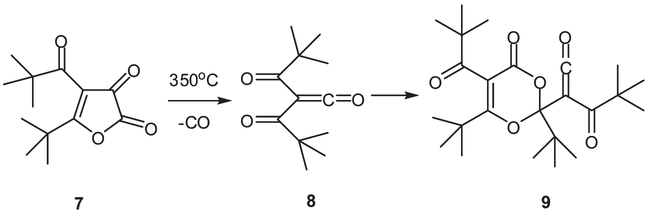
SCHEME 1. Thermal Degradation of Phenyliodonium Ylide of Lawsone (4) to Indanedioneketene (5) and Dimerization of the Latter to Spiro-oxetanone (6)



SCHEME 2. Thermal Degradation of 2,3-Dihydrofuran-2,3-dione (7) to Open-Chain Dipivaloylketene (8) and Dimerization of the Latter to Six-Membered Dioxinone Derivative (9)



the result of the thermal degradation of the phenyliodonium ylide of lawsone **4** (Scheme 1).

Indanedioneketene **5** cannot be isolated, but it can be trapped with a variety of nucleophiles to yield interesting structures. For example, with amines it gives enolamides,[5] and compounds with enolamide structure are also obtained from the reaction with amino esters, amino acids, amino alcohols, and urea.[6] The intermediate ketene **5** also acylates indole derivatives and other C-nucleophiles, such as pyrrole, furan, and enamines.[7] With water present in the solvent (especially in acetonitrile), ketene **5** forms the corresponding unstable carboxylic acid, which is spontaneously decarboxylated to indanedione,[8] a reaction that has found application for the preparation of substituted 3-cyclopentene-2,5-dione derivatives[9] and analogous compounds,[10] using phenyliodonium ylides of other hydroxyquinones.

In the absence of nucleophiles, ketene **5** dimerizes to spirooxetanone **6**, which can be isolated by careful crystallization in quantitative yields.[7,11] This is a labile compound and reacts further with amines producing interesting enolic structures of imino esters and iminoamides,[11] which can be further oxidized to fused indenodiazepinones and indenopyrazolinones,[12] and with aminopyridines and aminopyrimidines to indeno[1,2-*d*]pyrido[1,2-*a*]pyrimidines and indeno[1,2-*d*]pyrimido[1,2-*a*]pyrimidines, respectively, compounds acting as potential receptor tyrosine kinase inhibitors.[13] Finally, upon careful hydrolysis of the imino esters obtained from the reaction of **6** with amines, enamino derivatives of the unstable 1,3-dioxoindane-2-carboxylic acid[14] were isolated.

From the previous discussion, it is obvious that both indanedioneketene **5** and its dimerization product, spirooxetanone **6**, are potential building blocks for the construction of more complicated organic structures. This possibility, combined with the easy access to both compounds, prompted us to theoretically investigate the course of their formation reactions.

The first step of the sequence depicted in Scheme 1, namely the ring contraction of ylide **4** to ketene **5**, is an unusual one: In all other cases of aryliodonium ylides of cyclic β-diketones, an aryl migration from iodine to oxygen is observed upon heating, and the same is true for the ylides of the corresponding nitrogen counterparts of 2-hydroxyquinones, 2-aminoquinones.[15] A previous density functional theory (DFT) study of this thermal aryl migration mechanism provided support for a concerted mechanism in full agreement with experimental results.[16] The different thermal behavior of ylides of hydroxyquinones and, in particular, the formation of α,α'-dioxoketenes,[17] was investigated using electronic structure calculations at the DFT level with the B3LYP functional. It was shown that the ketene formation pathway is both kinetically and thermodynamically more favorable than the phenyl migration, in excellent agreement with the predominant ketene formation found experimentally for these ylides and the fact that the reaction follows a single-step concerted mechanism via a four-membered [1.1.0] bicyclic ring transition state. The formation of carbenes as intermediates is also unfavorable.

The second step of the sequence is also unusual, since α-oxoketenes and α,α'-dioxoketenes dimerize in a [4 + 2] manner yielding the analogous six-membered cyclization products[2,3] (Scheme 2). Especially noteworthy is the dimerization of dipivaloylketene **8** to dioxinone derivative **9**, a stable and persistent ketene the structure of which was verified by X-ray crystallography.[3a]

In order to explain this difference in reactivity and the formation of the spiro-oxetanone **6**, being a potential building block for further transformations, we studied the dimerization profile of **5** to **6** by performing electronic structure calculations in both the gas phase (DFT, MP2) and in dichloromethane solution (DFT).

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(3) (a) Kappe, C. O.; Evans, R. A.; Kennard, C. H. L.; Wentrup, C. *J. Am. Chem. Soc.* **1991**, *113*, 4234. (b) Kappe, C. O.; Färber, G.; Wentrup, C.; Kollenz, G *J. Org. Chem.* **1992**, *57*, 7078. (c) Kappe, C. O.; Kollenz, G.; Fabian, W. M. F.; Wentrup, C.; Färber, G. *J. Org. Chem.* **1993**, *58*, 3361. (d) Stadler, A.; Zangger, K.; Belaj, F.; Kollenz, G. *Tetrahedron* **2001**, 6757. (e) Wallfisch, B. C.; Belaj, F.; Wentrup, C.; Kappe, C. O.; Kollenz, G. *J. Chem. Soc., Perkin Trans. 1* **2002**, 599.

(4) Malamidou-Xenikaki, E.; Spyroudis, S. *Synlett* **2008**, 2725.

(5) Malamidou-Xenikaki, E.; Spyroudis, S.; Tsanakopoulou, M. *J. Org. Chem.* **2003**, *68*, 5627.

(6) Spagou, K.; Malamidou-Xenikaki, E.; Spyroudis, S. *Molecules* **2005**, *10*, 226.

(7) Koulouri, S.; Malamidou-Xenikaki, E.; Spyroudis, S.; Tsanakopoulou, M. *J. Org. Chem.* **2005**, *70*, 5627.

(8) Hatzigrigoriou, E.; Spyroudis, S.; Varvoglis, A. *Liebigs Ann. Chem.* **1989**, 167.

(9) Papoutsis, I.; Spyroudis, S.; Varvoglis, A. *Tetrahedron Lett.* **1994**, *35*, 8449.

(10) (a) Spyroudis, S.; Xanthopoulou, N. *J. Org. Chem.* **2002**, *67*, 4612. (b) Spyroudis, S.; Xanthopoulou, N. *ARKIVOC.* **2003**, *vi*, 95. (c) Mehta, G.; Singh, S. R. *Tetrahedron Lett.* **2005**, *46*, 2079. (d) Mehta, G.; Singh, S. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2079. (e) Yang, R.-Y.; Kizer, D.; Wu, H.; Volckova, E.; Miao, X.-S.; Ali, S. M.; Tandon, M.; Savage, R. E.; Chan, T. C. K.; Ashwell, M. A. *Bioorg. Med. Chem.* **2008**, *16*, 5635.

(11) Malamidou-Xenikaki, E.; Spyroudis, S.; Tsanakopoulou, M.; Krautscheid, H. *J. Org. Chem.* **2007**, *72*, 502.

(12) Malamidou-Xenikaki, E.; Spyroudis, S.; Tsanakopoulou, M.; Hadjipavlou-Litina, D. *J. Org. Chem.* **2009**, *74*, 7315.

(13) Tsanakopoulou, M.; Cottin, T.; Büttner, A.; Sarli, V.; Malamidou-Xenikaki, E.; Spyroudis, S.; Giannis, A. *ChemMedChem* **2008**, *3*, 429.

(14) Malamidou-Xenikaki, E.; Spyroudis, S.; Tsanakopoulou, M.; Krautscheid, H. *J. Org. Chem.* **2008**, *73*, 8392.

(15) Papoutsis, I.; Spyroudis, S.; Varvoglis, A.; Raptopoulou, C. *Tetrahedron* **1997**, *53*, 6097.

(16) Bakalbassis, E. G.; Spyroudis, S.; Tsiotra, E. *J. Org. Chem.* **2006**, *71*, 7060.

(17) Bakalbassis, E. G.; Spyroudis, S.; Tsipis, C. A. *Eur. J. Org. Chem.* **2008**, 1783.

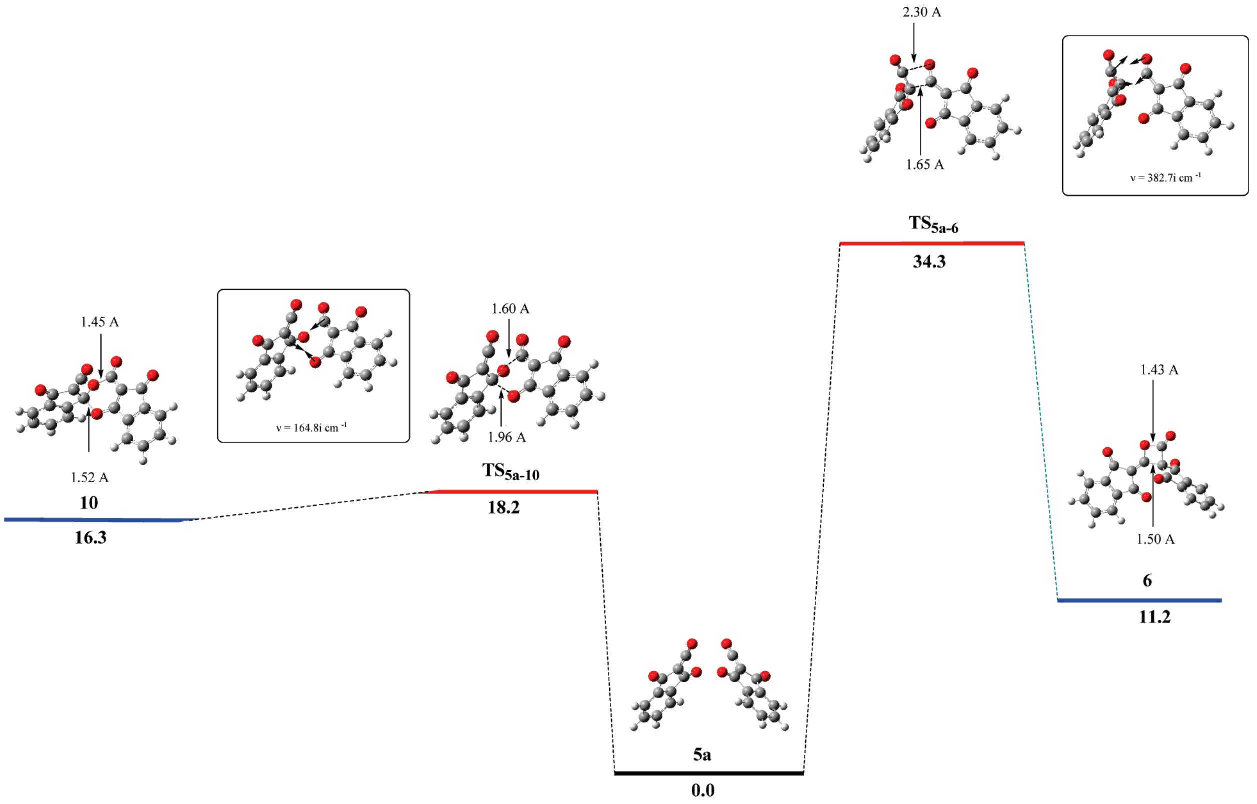


FIGURE 1. MPW1K/6-311+G(d,p) gas-phase reaction profiles (Gibbs free energies) of the dimerization of indanedioneketene **5** to oxetanone **6** (isolated) and dioxinone **10** (not observed) along with selected structural data.

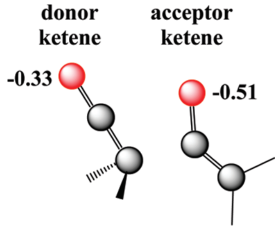
Results and Discussion

The MPW1K/6-311+G(d,p) gas-phase reaction profile (at 40 °C) for the thermal dimerization of indanedioneketene to spiro-oxetanone **6** (Figure 1) was examined first. The dimerization proceeds via the transition state $\mathbf{TS_{5a-6}}$ with an activation barrier of 34.3 kcal·mol^{-1}. The normal coordinate vectors (arrows) of the vibrational modes, corresponding to the imaginary frequency of 382.7*i* cm^{-1} for $\mathbf{TS_{5a-6}}$, indicate that the dominant motions involve the formation of one four-membered ring containing weak C−C and C−O linkages. The thermal dimerization in **5** is a low endothermic process [$\Delta_R G$ = 11.2 kcal·mol^{-1}]. This suggests that the dimerization of **5** requires heating in solution, in excellent agreement with the experimental findings requiring heating of ylide **4** in refluxing (40 °C) dichloromethane.[7,11] Moreover, the relative instability of the final product **6**, compared to the initial indanedioneketene **5a** being a ground-state complex of two molecules of **5**, could also account for the relative instability of the former, as was observed experimentally. Since the α,α′-dioxoketenes also dimerize in a [4 + 2] manner producing the analogous six-membered cyclization products,[2,3] the gas-phase reaction profile for the thermal dimerization of indanedioneketene **5** to a dioxinone derivative **10** (Figure 1), analogous to the corresponding **9**, was examined next in an attempt to explain this difference in reactivity. This dimerization proceeds via the transition state $\mathbf{TS_{5a-10}}$ with an activation barrier of 18.2 kcal·mol^{-1}, which is much less than that of **6**.

The normal coordinate vectors (arrows) of the vibrational modes corresponding to the imaginary frequency of 164.8*i* for $\mathbf{TS_{5a-10}}$ show that the dominant motions involve the formation of one six-membered ring containing only weak C−O linkages. The thermal dimerization to six-membered cyclization in **5** is also an endothermic process [$\Delta_R G$ = 16.3 kcal·mol^{-1}]. This suggests that, while the dimerization of **5** to spiro-oxetanone **6** requires heating in a dichloromethane solution (40 °C), the corresponding six-membered cyclization requires only slight or no heating. Hence, the six-membered cyclization product **10** is not "favored" under the experimental conditions applied for **6**; still, its facile reaction (being the reverse one) exhibits a much lower barrier (1.9 kcal·mol^{-1}) than **6** (23 kcal·mol^{-1}), accounting for its instability. Consequently, it would be worth trying to isolate **10** experimentally by applying another approach for the formation of ketene **6** at lower temperature. Moreover, the above kinetic and thermodynamic data are still in line with (a) a heating demanding dimerization to **6**, (b) a slight or no heating demanding dimerization to **10**, and (c) unstable **6** and **10** final products.

Contrary to the gas-phase calculations that suggest a stable **5a**, the dichloromethane solution calculations failed to support this at both PCM and SCIPCM models used to simulate the liquid phase (vide infra). The inability of the former model to afford a stable **5a** could be attributed to its cavity consisting of overlapping atomic spheres. Hence, despite the almost identical atomic charges obtained in both the gas-phase and the dichloromethane solution calculations, in the latter case the two indanedioneketene molecules could be hindered in approaching each other enough for the dipole−dipole interactions to take effect.

SCHEME 3. **Acceptor and Donor Ketenes Forming the TS of 6**



Consequently, the double sum of the dichloromethane solution ketene energy was considered as the zero-energy level (Figure S1, Supporting Information) compared to that of **5a** in the gas phase. This is because in the former case the possible existence of an analogous dichloromethane solution **5a** would further lower the zero-level energy only. Therefore, the main conclusions derived from the gas-phase reaction profiles of the dimerization would remain unaffected.

The gas-phase calculated natural atomic charges[18] on the two α and α′-carbonyl O atoms as well as on the O and the two C atoms of the ketene group of **5** amount to −0.52, −0.33, and 0.76 (*ipso* to O carbon atom) and −0.39 |e|, respectively. The existence of the above dipoles in each ketene could account for the dipole−dipole interactions (observed at a distance of 2.98 Å between the negatively charged carbonyl O of the α-CO group on one ketene and the positively charged ipso C to O atom of the ketene group on the other) forming **5a**.

It seems that the specific structure of α,α′-dioxoketene **5** involving the two α and α′-carbonyl O atoms is the main reason for both (i) the above dipole−dipole interactions, leading to the stable **5a**, and (ii) the absence of analogous interactions in the literature. Yamabe and Minato[19] studied theoretically the formation mechanism of the simple (parent) ketene dimerization. The profound difference of the latter structure, as compared to **5**, leads to the lack of the above interactions. However, not unlikely for a simple ketene, in the TS of **6**, (a) the "acceptor" ketene becomes more bend (ketenic O charge = −0.51 |e|), compared to the almost linear structure of the "donor" one (ketenic O charge = −0.33 |e|) and (b) the C···C bond length, formed between the two ketenic groups, is closely to that of the parent ketene (1.65 compared to 1.70 Å, respectively). Contrary to the assumption made by the same authors, namely that substituted ketenes would suffer the steric repulsion in the donor−acceptor orientation, thus accounting for their low reactivity for the formation of diketene, **5** forms diketene easily (Scheme 3). Moreover, the vicinity of the unsaturated cyclopentenedione ring to the ketene group in **5** could also account well for the differences observed in the nature of the frontier molecular orbitals (FMOs)[20] of **5** (see Figure 2), compared to those of the parent ketene. For instance, the LUMO of **5** is mostly localized on the two C−C bonds of the cyclopentenedione ring, while both its LUMO+1 and HOMO-1 resemble closely those of the LUMO and HOMO of the parent ketene, respectively. Consequently, contrary to the parent ketene's (homo → LUMO) charge-transfer configuration, giving rise to the C−C bond formation, between the two ketenes, that of **5** is the HOMO-1 → LUMO+1 one (Scheme 4).

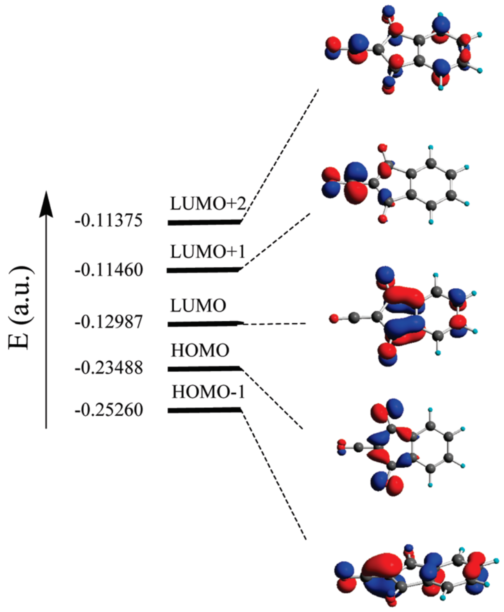
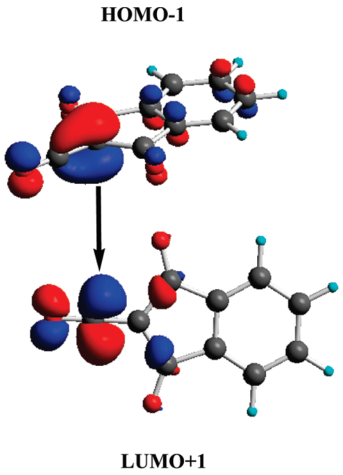


FIGURE 2. Gas-phase MPW1K/6-311+G(d,p) FMOs of indanedioneketene.

SCHEME 4. **HOMO-1 → LUMO+1 CT Configuration Forming the C−C Bond of 6**



Finally, the formation of **10** involves a different interaction between the two ketenes, as one of the two initial dipole interactions seen in **5a** is retained and the other one being the dipole−dipole interactions between two α-CO groups belonging to different indanedioneketene molecules.

The gas-phase reaction profile of the analogous dimerization of an open-chain ketene, namely dipivaloylketene **8**, was also studied since the latter, contrary to the indanedioneketene dimerization, produced stable single crystals of **9**, which have been observed during a previous X-ray crystallographic

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[18] (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Weinhold, F. Natural Bond Orbital Methods. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; John Wiley & Sons: Chichester, 1998; p 1792. (c) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, 2001.

[19] Yamabe, S.; Minato, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3233.

[20] Starikov, E.; Lewis, J.; Tanaka, S. *Modern Methods for Theoretical Physical Chemistry of Biopolymers*: Elsevier: New York, 2006.

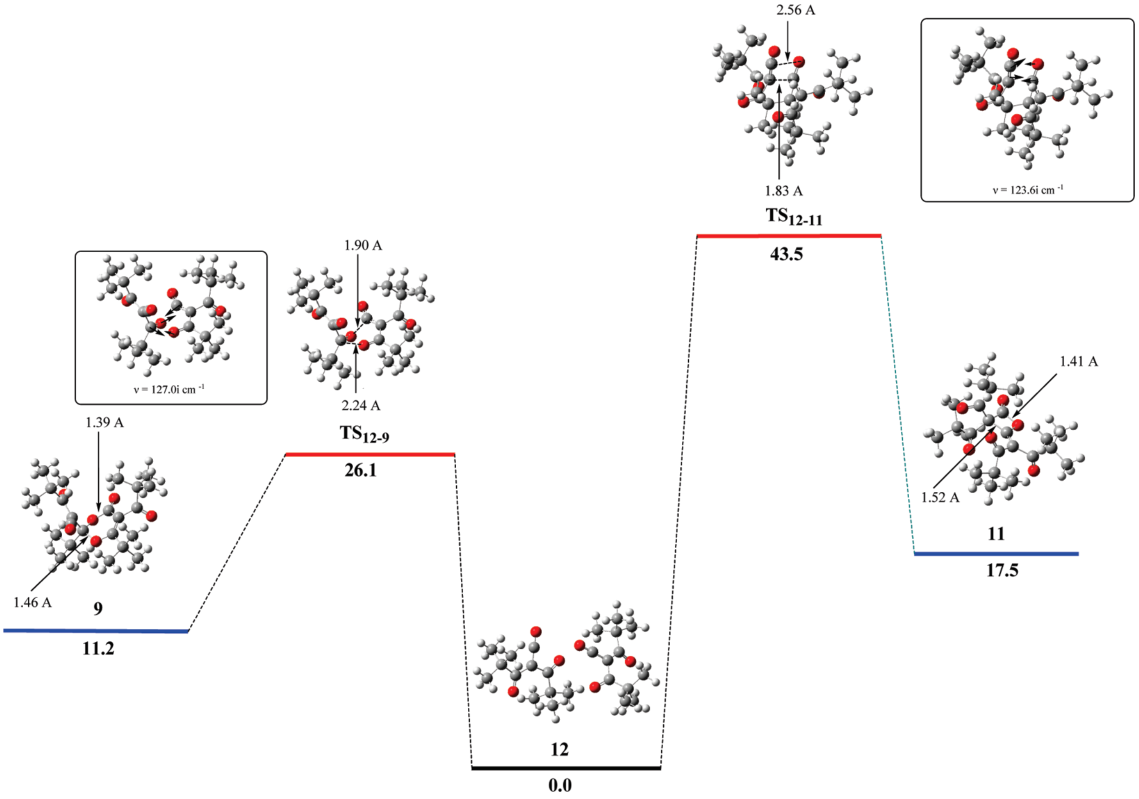

FIGURE 3. Gas-phase MPW1K/6-311+G(d,p) reaction profiles (Gibbs free energies) of the dimerization of dipivaloylketene **8** to **9** (isolated) and **11** (not observed), along with selected structural data.

study.[3a] It should be noted here that **9** is a permanently and surprisingly stable oxoketene, as it remains unchanged for months in open air under high humidity. The oxetanone derivative **11**, analogous to **6**, was not observed during this dimerization.

The MPW1K/6-311+G(d,p) gas-phase reaction profile (at 40 °C) for the thermal dimerization of dipivaloyketene **8** to **9** (isolated) and **11** (not observed) is shown in Figure 3. The former dimerization proceeds via the transition state TS$_{12-9}$ with an activation barrier of 26.1 kcal·mol^{-1}. This suggests that dimerization of **8** requires only slight or no heating, in excellent agreement with experimental findings.[3a] The normal coordinate vectors (arrows) of the vibrational modes corresponding to the imaginary frequency of 127.0*i* for **TS$_{12-9}$** suggest that the dominant motions involve the formation of one six-membered ring containing weak C−O linkages. The thermal dimerization in **8** is a low endothermic process [$\Delta_R G$ = 11.2 kcal·mol^{-1}], followed by a concomitant barrier of 14.9 kcal·mol^{-1} for the reverse reaction, accounting well for the very low relative instability of the final product **9**, as observed experimentally,[3a] when compared to the dipivaloylketene **12**. Moreover, since α,α′-dioxoketenes can also dimerize in a [2 + 2] manner yielding the analogous four-membered cyclization products, the gas-phase reaction profile for the thermal dimerization of dipivaloylketene **8** to **11** (not observed)[3a] was examined next in an attempt to explain this difference in reactivity. This dimerization proceeds via the transition state **TS$_{12-11}$** with an activation barrier of 43.5 kcal·mol^{-1} that is much higher than that of **9**. The normal coordinate vectors (arrows) of the vibrational modes corresponding to the imaginary frequencies of 123.6*i* for **TS$_{12-11}$** indicate that the dominant motions involve the formation of one four-membered ring containing weak C−C and C−O linkages. The thermal dimerization to four-membered cyclization in **8** is also an endothermic process ($\Delta_R G$ = 17.5 kcal·mol^{-1}). This suggests that while the dimerization of **8** to oxetanone **11** requires heating, the corresponding six-membered cyclization requires only slight or no heating. Therefore, in this case, the four-membered cyclization product **11** is not "favored" under the experimental conditions applied for **9**. In addition, the reverse reactions exhibit a higher barrier (26.0 kcal·mol^{-1}) for the former, compared to 14.9 kcal·mol^{-1} for the latter. Consequently, since **11** cannot be isolated under the experimental conditions applied (reaction at room temperature), it would be worth trying to isolate it experimentally by applying another route for the formation of ketene **9** at a higher temperature.

Structural data of the dimeric products, **6**, **9**, **10**, and **11** are given in the Supporting Information.

Conclusions

In summary, theoretical DFT and MP2 calculations in both the gas and liquid phases of the dimerization of cyclic and open-chain α,α′-dioxoketenes reveal two different unstable dimeric products. In the case of indanedioneketene, spiro-oxetanone **6** is more stable than dioxinone **10** (the latter not observed but studied theoretically by us, for the first time), and the dimerization follows a concerted mechanism. This charge-controlled mechanism is a single-step one with a four- or six-membered cyclic ring transition state without intermediates. The better experimental stability of the open-chain products, when compared to that of the cyclic ones, could be attributed to their reverse reactions exhibiting higher barriers than those of the former ones.

Computational Details

The DFT methodology with the modified Perdew–Wang one-parameter model for kinetics (MPW1K)[21] functional (suitable to predict energy profiles) was used, in conjunction with the 6-311+G(d,p) basis set, as implemented in the Gaussian 03 programs suite.[22] The complexity of the calculations necessitated the use of the faster and more economical DFT as opposed to an ab initio treatment, despite the scepticism raised by Schleyer et al.[23] for the former methodology. In order to assess the accuracy of the MPW1K results, we have performed additional single-point MP2/6-311++G** calculations along the two energy profiles (five stationary points per energy profile) shown in Figures 1 and 3 at the corresponding MPW1K/6-311+G(d,p) gas-phase geometries. These calculations amounted to 628 and 912 basis functions for each point on the potential energy of the two systems, respectively. For the reaction profile of Figure 1, the two barriers are 18.1 and 28.6 $\text{kcal}\cdot\text{mol}^{-1}$ at the MP2/6-311++G** level, in agreement with the 18.2 and 34.3 $\text{kcal}\cdot\text{mol}^{-1}$ obtained at the MPW1K/6-311+G(d,p) level of theory (see Table S7 in the Supporting Information). However, the relative energetics of stable intermediates **6** and **10** with respect to **5a** are found to be much smaller at the MP2 when compared with the MPW1K results. For the reaction profile of Figure 3 (see Table S8 in the Supporting Information) the MP2 barriers are 20.1 and 32.6 $\text{kcal}\cdot\text{mol}^{-1}$, about 25% smaller than the DFT results. The same holds for the relative energetics of **9** and **11**, which are now both stabilized with respect to **12**. These results suggest that the MPW1K functional in general overestimates the barriers when compared to MP2.

It should be emphasized that the use of the above larger basis set for the heavy atoms and H, when compared to the smaller 6-31+G(d,p) set suggested in ref 21, was necessary in the present study for direct comparisons with previous results.[17] Moreover, with the exception of the reaction profile of the larger open chain ketene molecules, the polarized continuum model (PCM),[24,25] was also used for the treatment of the solvent effects. Attempts to also use SCIPCM[26] continuum model have been unsuccessful for the compounds examined in the present study. Full geometry optimizations with tight convergence criteria and no symmetry constraints were performed for each species. All stationary points (reactants, transition states and products) located on the potential energy surfaces (PES) were fully optimized in the gas-phase at the MPW1K/6-311+G(d,p) level of theory. These fully optimized gas-phase geometries of all stationary points were subsequently used as the starting geometries for the calculations in the liquid phase. Harmonic frequencies were computed at the same level of theory, at 40 °C, and the nature of the stationary points was determined in each case according to the number of the negative eigenvalues of the Hessian matrix (zero and one imaginary frequencies for the minima and transition states, respectively). Gibbs free energies, ΔG_R, at $T = 273 + 40$ and $P = 1$ atm were used for the discussion of the relative stabilities of the chemical structures involved. The quasi-Newton transit-guided (QSTN) method[27] was employed for the determination of the transition-state structures. Moreover, the determination of the appropriate transition states connecting reactants and products has been confirmed by intrinsic reaction coordinate (IRC) calculations, during which intrinsic reaction paths (IRPs) were traced from the various transition structures to ensure that no further intermediates exist.[28] Finally, it is worth mentioning that for ketene the singlet state is well below the triplet by ca. 57.6 $\text{kcal}\cdot\text{mol}^{-1}$ at the MPW1K level.

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Supporting Information Available: Complete ref 22. Structural data of the dimeric products (3 pages). The liquid-phase MPW1K/6-311+G(d,p) reaction profiles (Figure S2) of the dimerization of indanedioneketene **5** to oxetanone **6** and dioxinone **10**, along with selected structural data. The Cartesian coordinates and energies of all stationary points are compiled in Tables S3–S8, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.

[22] Frisch, M. J. T.; et al. *Gaussian 03*, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.

[23] Wodrich, M. D.; Corminboeuf, C.; Schreiner, P. R.; Fokin, A. A.; Schleyer, P. v. R. *Org. Lett.* **2007**, *9*, 1851.

[24] Miertus, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117.

[25] Cammi, R.; Tomasi, J. *J. Chem. Phys.* **1994**, *100*, 7495.

[26] Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098.

[27] Head-Gordon, M. P.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503.

[28] (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.