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Phosphine-Promoted Cyclization of Dicyclopropenones

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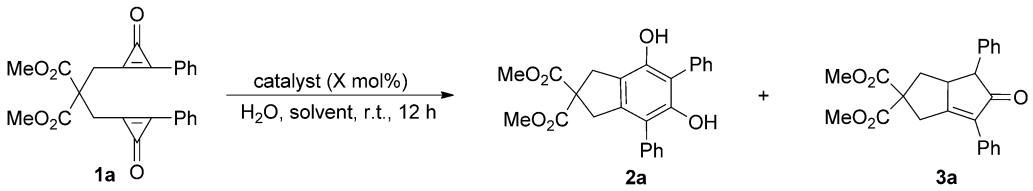
Abstract: A novel phosphine-promoted intramolecular cyclization of dicyclopropenones **1** has been described in this contribution. A variety of 2,3-dihydro-1*H*-indene-4,6-diol derivatives **2** and hexahydropentalen-2-one derivatives **3** were obtained selectively in moderate to good yields under mild conditions through different phosphine-promoted reactions.

Keywords: cyclization; cyclopropenones; phosphines; selectivity

Cyclopropenones, first prepared by Breslow et al.[1] and Volpin and co-workers[2] more than 50 years ago, have often been developed as useful building blocks for the construction of natural products and bioactive compounds.[3] Cyclopropenones possessing amphiphilic properties can act both as good electrophiles for 1,2- or 1,4-addition and as precursors for the stable 2π-aromatic hydroxycyclopropenium cation generated readily by protonation of the carbonyl group.[3a,4–6] The chemical reactivity of the cyclopropenone ring is dominated by two processes:[4,7] (i) nucleophilic attack on the carbonyl carbon with the formation of acrylic acid derivatives[8] and (ii) decarbonylation to alkynes under high temperature pyrolysis or in the presence of various catalysts.[9] Acetylenes were also observed as intermediates[10,11] or were even isolated[1e,8,12] in the photolysis of some cyclopropenones. This remarkable three-membered small ring has gained much attention in the past decades.[13] Boger and Nakamura have reported that cyclopropenone ketals, either thermally (*via* dipolar cycloaddition)[13a] or with a $Pd(OAc)_2$ catalyst,[13b] undergo cycloaddition with various π-systems to provide cyclopentadienones after ketal hydrolysis. In 2006, Wender[13c] reported rhodium(I)-catalyzed [3+2] cycloaddition reactions of cyclopropenones and alkynes to afford cyclopentadienones. And López-Leonardo et al.[13e] focused on the reaction of diphenylcyclopropenone with a series of *N*-alkyl- and *N*-arylamino-*P*,*P*-diphenylphosphanes to produce the ketene intermediates and in turn to afford β-phosphinoyl carboxamides under the standard conditions.[14] More recently, Lambert and co-workers disclosed a catalytic strategy for the promotion of dehydrative reactions[15e] using simple cyclopropenones as catalysts. This strategy, which relies on the facile formation of cyclopropenium cations for substrate activation,[15] was first demonstrated in the context of alcohol chlorodehydration using oxalyl chloride as the activating agent and source of nucleophile. Inspired by the chemistry of cyclopropenones and as a part of our continuing interest on nucleophilic phosphine-mediated reactions, we systematically investigated the reactions of dicyclopropenones in the presence of phosphines. Herein, we wish to report a novel phosphine-promoted cyclization of dicyclopropenones.

Initially, we started our investigation by using dicyclopropenone **1a**, 20 mol% triphenylphosphine and 1.0 equiv. of water in dry tetrahydrofuran (THF) at room temperature, the desired product dimethyl 4,6-dihydroxy-5,7-diphenyl-1*H*-indene-2,2(3*H*)-dicarboxylate **2a** was obtained in 16% yield with 47% of the starting materials being recovered after 12 h (Table 1, entry 1). The structure of **2a** has been unequivocally confirmed by X-ray diffraction studies.[16] Based on our previous work,[17] we increased the phosphine loading to 100 mol% (Table 1, entry 2), and compound **2a** was obtained in 48% yield. Decreasing the phosphine loading to 50 mol% (Table 1, entry 3) gave a similar result. Other phosphines, such as tris(*para*-tolyl)phosphine, tris(3,5-dimethylphenyl)phosphine, tris(4-methoxyphenyl)phosphine gave no better results than PPh_3 (Table 1, entries 4–6). To our delight, use of 50 mol% of bis(diphenylphosphino)methane (dppm) significantly increased the yield of the desired product **2a** to 79% (Table 1, entry 7). Instead of THF,

Table 1. Optimization of the reaction conditions.[a]



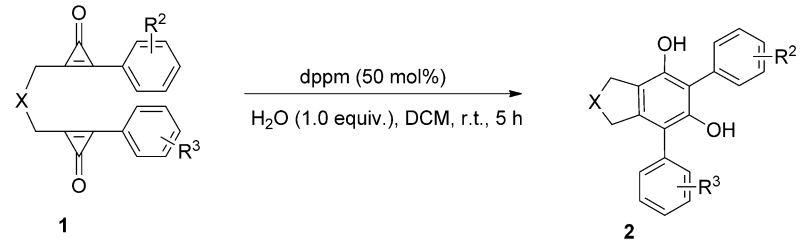
Entry[a]	Catalyst (X mol%)	H_2O (Y equiv.)	Solvent	Yield [%][b]	
				2a	**3a**
1[c]	Ph_3P (20)	1.0	THF	16	-
2	Ph_3P (100)	1.0	THF	48	-
3	Ph_3P (50)	1.0	THF	48	-
4	$(4\text{-MePh})_3P$ (50)	1.0	THF	37	-
5	tris(3,5-xylyl)phosphine (50)	1.0	THF	40	-
6	$(4\text{-MeOPh})_3P$ (50)	1.0	THF	43	-
7	dppm (50)	1.0	THF	79	-
8	dppm (50)	1.0	DCM	82	-
9[d]	**dppm (50)**	**1.0**	**DCM**	**82**	**-**
10[d]	dppm (50)	2.0	DCM	46	-
11[d]	dppm (50)	3.0	DCM	46	-
12	Me_3P (50)	1.0	THF	48	44
13	$(n\text{-Bu})_3P$ (50)	1.0	THF	45	41
14	$MePh_2P$ (50)	1.0	THF	48	trace
15	Me_2PhP (50)	1.0	THF	26	34
16	Me_3P (100)	1.0	THF	41	29
17	$(n\text{-Bu})_3P$ (100)	1.0	THF	53	24
18	$MePh_2P$ (100)	1.0	THF	58	trace
19	**Me_2PhP (100)**	**1.0**	**THF**	**20**	**64**

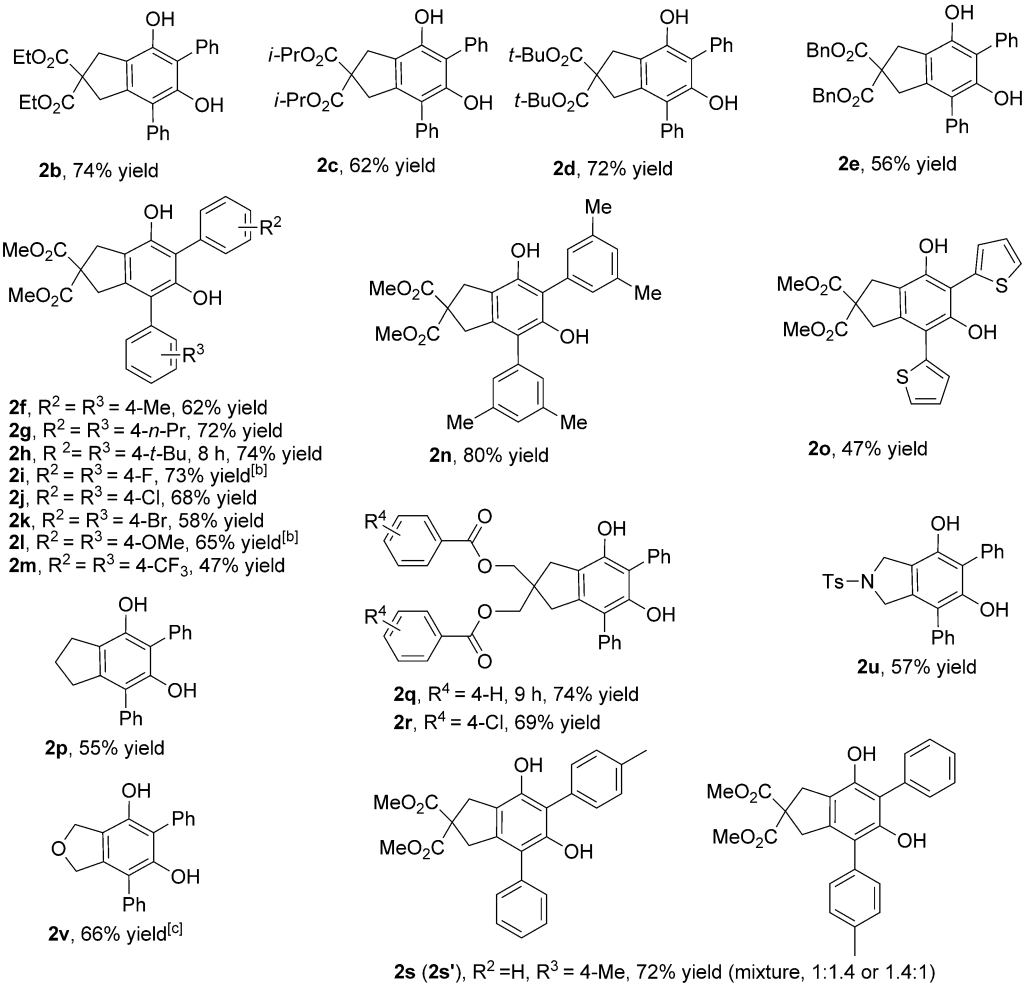
[a] *Reaction conditions:* 0.1 mmol **1a**, X mol% catalyst, Y equiv. H_2O, 1.0 mL dry solvent.
[b] Isolated yields.
[c] 47% of **1a** were recovered.
[d] The reaction was run at room temperature for 5 h.

use of dichloromethane (DCM) as the solvent slightly increased the yield of **2a** (Table 1, entry 8). Shortening the reaction time to 5 h did not influence the yield (Table 1, entry 9) and increasing the amount of water decreased the yield (Table 1, entries 10 and 11). Variation of the phosphines or solvents (see the Supporting Information) led to a decrease in chemical yield. Interestingly, when alkylphosphines were employed, the desired product **2a** and another new product **3a** were obtained (Table 1, entries 12–18). The structure of **3a** has been unequivocally confirmed by X-ray diffraction studies.[18] When the reaction was carried out in THF with 1.0 equiv. dimethylphenylphosphine, compounds **2a** and **3a** were obtained in 20% and 64% yields after 12 h, respectively (Table 1, entry 19). Thus, finally, we established the optimal reaction conditions: 50 mol% of dppm in DCM at room temperature for the synthesis of compound **2a** or 100 mol% of dimethylphenylphosphine in THF at room temperature for the synthesis of compound **3a**.

With these optimized reaction conditions in hand, we turned our attention to determine the scope and limitations of the reaction in the presence of dppm (50 mol%). As summarized in Table 2, diethyl, diisopropyl, di-*tert*-butyl and dibenzyl malonates were appropriate substrates, and the cyclization of dicyclopropenones proceeded smoothly to give the corresponding products **2b**–**2e** in moderate yields. Next, the influence of the terminal aryl moieties was investigated. Dicyclopropenones **1f**–**1l**, having electron-donating alkyl and methoxy substituents or electron-withdrawing halogen substituents, underwent the reactions smoothly to give **2f**–**2l** in 58–73% yields. Moreover, increasing the electron density of the aryl functionalities in dicyclopropenone **1n** by introducing two electron-donating methyl groups led to the formation of the corresponding product **2n** in 80% yield. Furthermore, a range of substrate types including those containing protected alcohols (**1q** and **1r**) and those tethered by a nitrogen or an oxygen atom (**1u** and **1v**) were also suitable for this cyclization reaction, giving the corresponding cyclized products in moderate yields. The simple carbon tether analogue **1p** without the *gem*-disubstituent effect also provided the indene derivative **2p** in 55% yield. When the substituents on the aryl moieties were different (**1s**), the corresponding products **2s** and **2s′** could also be obtained as a mixture in 72% yield, with a 1:1.4 ratio. When the substituent on the aryl moieties was trifluoromethyl (**1m**) and the dicyclopropenone **1o** with thiophene ter-

Table 2. Scope of the cyclization in the presence of dppm.[a]





[a] *Reaction conditions:* 0.1 mmol **1**, 50 mol% dppm, 1.0 equiv. H_2O, 1.0 mL DCM, yields are of isolated products.

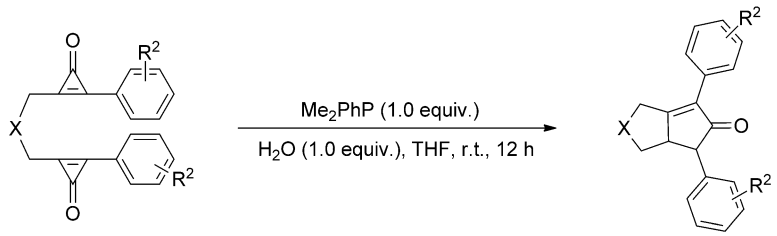
[b] The solvent was THF.

[c] The reaction was run in THF at room temperature with 1.0 equiv. Me_2PhP and 1.0 equiv. H_2O for 48 h.

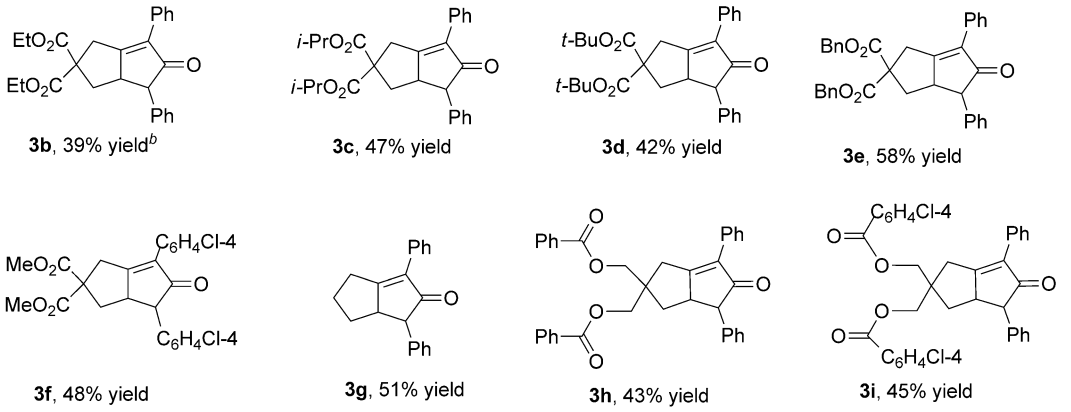
minal groups could also undergo the cyclization, however, affording the corresponding products in 47% yields. Only when the terminal group is an aliphatic group such as substrates **1t** (see the Supporting Information), the reaction did not provide the desired product under the standard conditions.

Further experiments were performed to extend the scope of this cyclization to afford compounds **3** under the optimized conditions (Table 1, entry 19); the results are presented in Table 3. As can be seen from Table 3, all of the reactions proceeded smoothly to give the corresponding products **3b**–**3e** in 39–58% yields at room temperature when the substituents of the malonates were diethyl, diisopropyl, di-*tert*-butyl and dibenzyl. Dicyclopropenone **1j**, having an electron-withdrawing chlorine substituent on the benzene

Table 3. Scope of the cyclization in the presence of Me_2PhP.



1 3



3b, 39% yield[b] **3c**, 47% yield **3d**, 42% yield **3e**, 58% yield

3f, 48% yield **3g**, 51% yield **3h**, 43% yield **3i**, 45% yield

[a] *Reaction conditions:* 0.1 mmol **1**, 1.0 equiv. Me_2PhP, 1.0 equiv. H_2O, 1.0 mL THF, yields are of isolated products.
[b] A 20% yield of **2b** was obtained.

ring, was smoothly converted to **3f** in 48% yield. The simple carbon tether analogue **1p** without the *gem*-disubstituent effect also provided the desired product **3g** in 51% yield. Moreover, substrates containing protected alcohols such as **1q** and **1r** were also suitable for this cyclization, providing products **3h** and **3i** in 43% and 45% yields, respectively.

The unique phosphine-promoted cyclization of dicyclopropenones encouraged us to investigate the reaction mechanism. First, we have done ^{31}P NMR tracing experiments, which indicate that triphenylphosphine plays the role as a reagent, not as a catalyst (Figure 1, for details, see the Supporting Information).

Furthermore, the isotopic labeling experiments were performed. As shown in Scheme 1, the control experiments were carried out by adding two equiv. of D_2O (D content = 99.96%) or $H_2{}^{18}O$ (^{18}O content = 98%) into the Ph_3P/THF system, and the product was analyzed by ^1H NMR spectroscopy and GC-MS (see the Supporting Information). We found that in the presence of $H_2{}^{18}O$, **2a** was formed with no ^{18}O-label in 48% isolated yield along with a 29% yield of $^{18}O{=}PPh_3$, in which the ^{18}O content is *ca.* 60%. The result indicated that the oxygen atom of the triphenylphosphine oxide was transferred from $H_2{}^{18}O$. In the presence of D_2O (2.0 equiv.), **3c**-*d* was formed in 41% yield with D contents of 75% and 84%, respectively. This result suggested that the D of **3c**-*d* was transferred from D_2O.

Plausible mechanisms for this reaction are outlined in Scheme 2 on the basis of the above isotopic labeling and control experiments. The transformation is believed to proceed *via* conjugate addition of phosphine to one of the cyclopropenones, affording zwitterionic species **A**, followed by [2+2] addition to form intermediate **C** stepwise *via* intermediate **B**. From intermediate **C**, there are two possible reaction pathways. In path a, ring expansion occurs to generate intermediate **E** *via* transition state **D**. Intermediate **E** is tautomerized to **E′**, which abstracts a proton from water to produce intermediate **F**, followed by attack of hydroxide at the phosphonium ion before **F** collapses to $Ph_3P{=}O$ and intermediate **G**.[19] Finally, **G** undergoes aromatization, leading to **2a**. The nucleophilicities of phosphines with alkyl groups are generally superior to those of phosphines with aryl groups,[20] meanwhile, the phosphines with alkyl groups are more basic than those phosphines with aryl groups.[21] The nucleofugicities of phosphines with alkyl groups are presumably also superior to those of phosphines with aryl groups.[22] Thus, in path b, from intermediate **C** involving a phosphine with alkyl groups it is probably easier to release phosphine, generating α,β-unsaturated ketone **I** *via* transition state **H**, followed by attack of water at the carbonyl group to produce in-

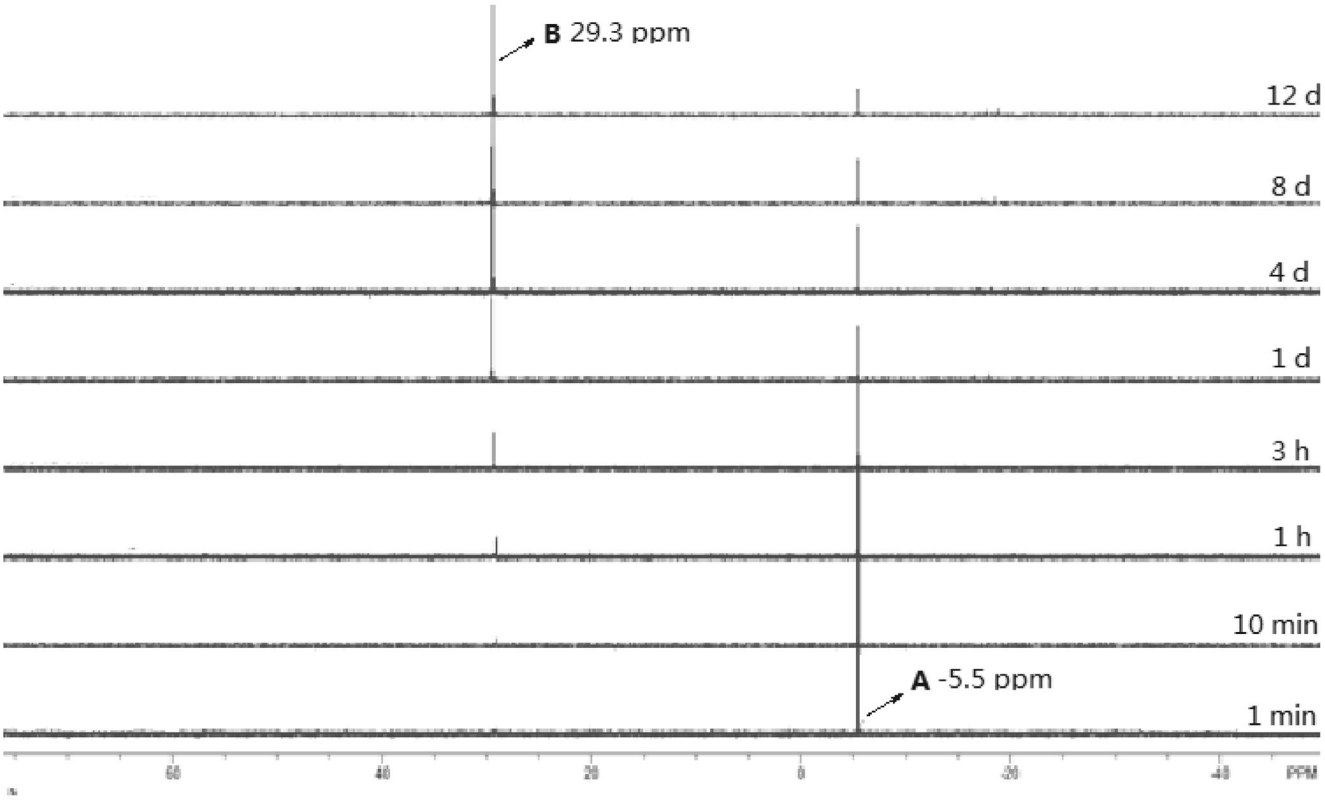
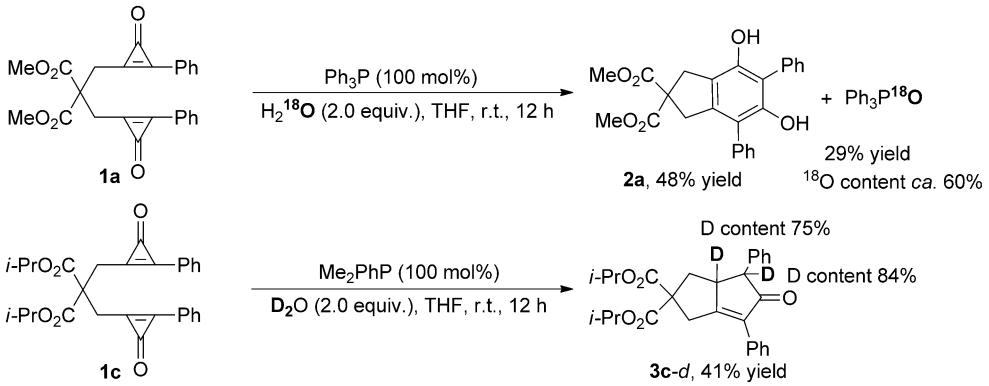


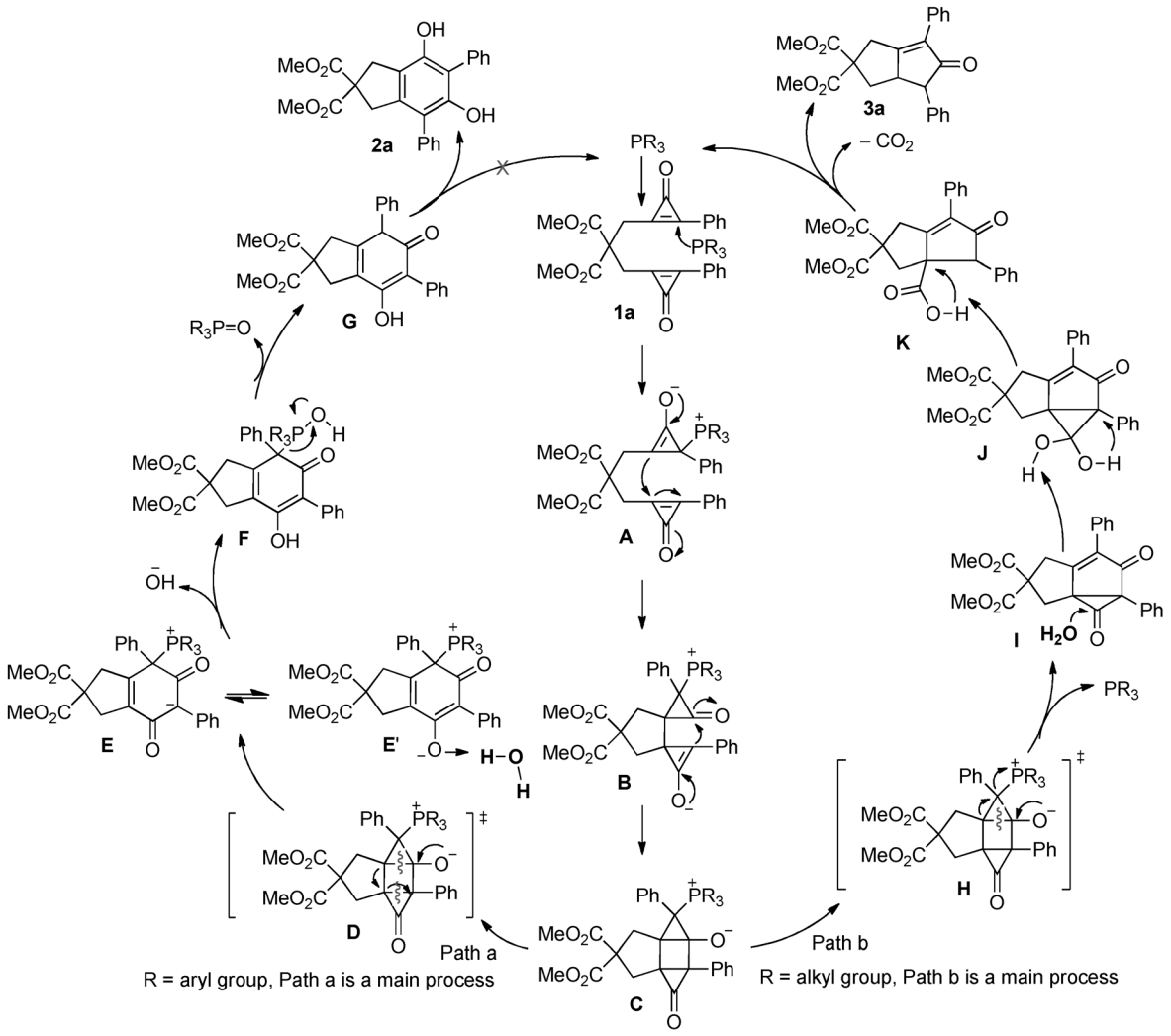
Figure 1. Reaction of **1a** with PPh_3 monitored by ^{31}P NMR spectroscopy (400 MHz, $CDCl_3$). **A** = PPh_3, **B** = Ph_3PO.



Scheme 1. Isotopic labeling experiments.

termediate **J**, which undergoes two-fold proton transfer and releases carbon dioxide *via* intermediate **K** to give **3a** as the major product.

To understand clearly the mechanism of phosphine-promoted intramolecular cyclization of dicyclopropenones, we have theoretically investigated the reaction pathways. All calculations have been performed at the mPW1K/6-31G(d) level with the Gaussian 09 program.[23] The DFT calculations support our proposed PPh_3-promoted intramolecular cyclization of dicyclopropenones shown in Scheme 3 and the calculated full reaction pathway for this process is shown in Scheme SI-1 (for details, see the Supporting Information). In the case of PMe_3, two possible reaction pathways were investigated theoretically, and the calculated full reaction pathways are shown in Scheme SI-2 (for details, see the Supporting Information). As shown in Scheme 3, the reaction starts from conjugate addition of PMe_3 to cyclopropenone **1**, affording zwitterionic intermediate **4**. The zwitterionic intermediate **4** undergoes the carbon-carbon bond formation to afford intermediate **6** *via* transition state **5** with an energy barrier of 19.8 kcal mol^{-1}. Subsequently, **6** undergoes another carbon-carbon bond formation to afford inter-



Scheme 2. A plausible reaction mechanism.

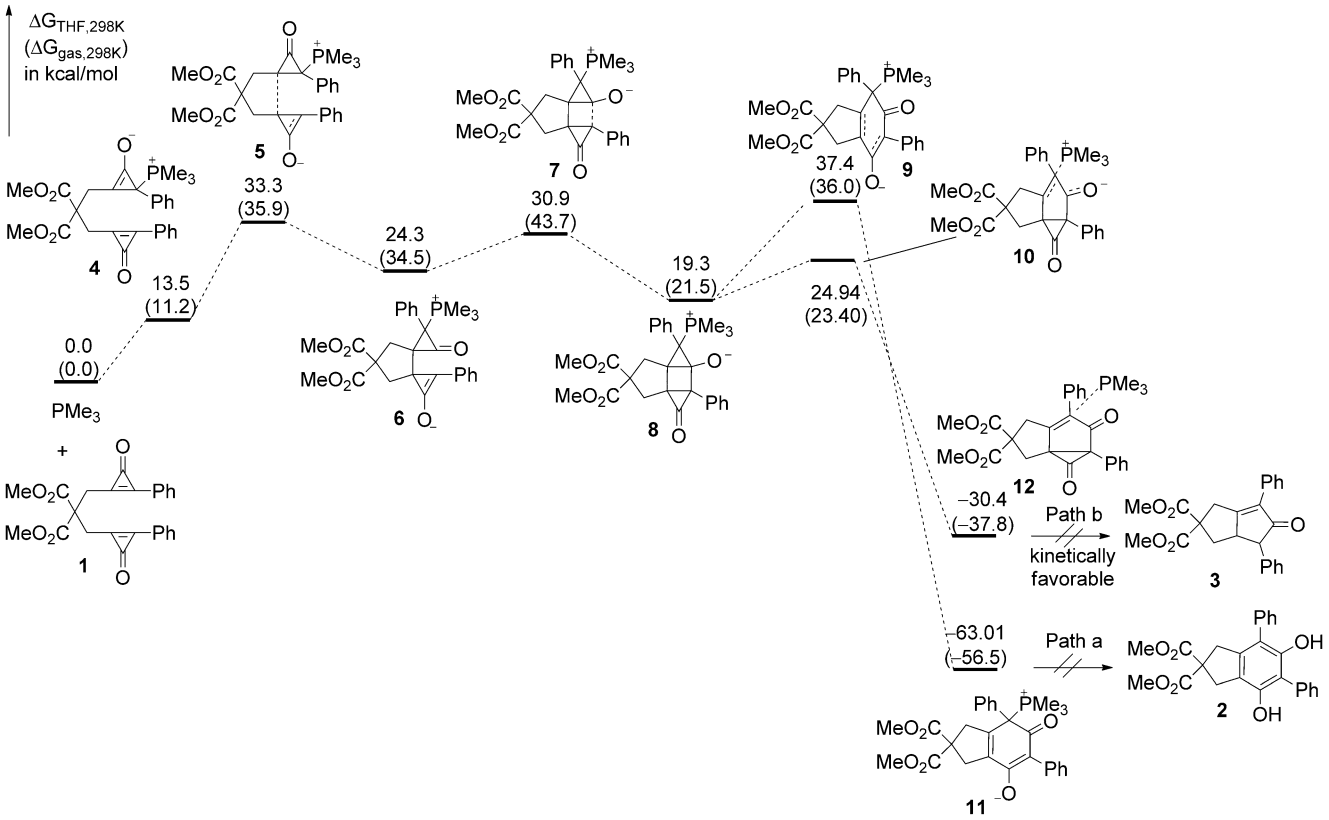
mediate **8** *via* transition state **7** with an energy barrier of 6.6 kcal mol^{-1}. At this stage, the reaction may diverge, and two distinct pathways lead to products **2** or **3**, respectively. In path a, passing through transition state **9** with an energy barrier of 18.1 kcal mol^{-1}, a ring expansion occurs to give intermediate **11**, which continues to react with H_2O, leading to product **2**. In path b, passing through transition state **10** with a lower energy barrier of 5.6 kcal mol^{-1}, the PMe_3 is released to afford intermediate **12**, which continues to react with H_2O, leading to product **3**. In this case, the path b is kinetically favorable, and this calculation result may account for the fact that the product **3** is experimentally obtained as the main product (for the details, see the Supporting Information).

In summary, we have developed a novel phosphine-promoted cyclization of dicyclopropenones system. ^{18}O-labeling experiments strongly supported the cleavage of the C–P bond. The reaction mechanism has been proposed on the basis of isotopic labeling and control experiments, and is also supported by DFT calculations. Further applications of this novel phosphine-promoted cyclization and more detailed mechanistic investigations are underway in our laboratory.

Experimental Section

General Procedure

Under an argon atmosphere, dry DCM (1.0 mL) containing 1.0 equiv. of H_2O was added to a mixture of **1** (0.10 mmol) and dppm (19.2 mg, 0.05 mmol). The reaction system was stirred for 5 h at room temperature until **1** was completely consumed as shown by TLC monitoring. Then the solvent was removed under reduced pressure. The residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 5/1) to give the product **2** as a colorless solid.



Scheme 3. Theoretical investigations for the formation of **2a** and **3a**.

Supporting Information

Spectroscopic data of the compounds shown in this article, the detailed descriptions of experimental procedures and the crystal structures of **2a** and **3a** are available in the Supporting Information. CCDC 884906 (**2a**) and CCDC 902788 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] a) R. Breslow, R. R. Haynie, J. Mirra, *J. Am. Chem. Soc.* **1959**, *81*, 247–248; b) R. Breslow, R. Peterson, *J. Am. Chem. Soc.* **1960**, *82*, 4426–4427; c) R. Breslow, J. Posner, A. Krebs, *J. Am. Chem. Soc.* **1963**, *85*, 234–234; d) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, J. Posner, *J. Am. Chem. Soc.* **1965**, *87*, 1320–1325; e) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, J. Posner, *J. Am. Chem. Soc.* **1965**, *87*, 1326–1331.

[2] D. N. Kursanov, M. E. Volpin, Y. D. Koreshkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1959**, 560.

[3] a) T. Eicher, J. L. Weber, *Top. Curr. Chem.* **1975**, *57*, 1–109; b) K. Komatsu, T. Kitagawa, *Chem. Rev.* **2003**, *103*, 1371–1428.

[4] K. T. Potts, J. S. Baum, *Chem. Rev.* **1974**, *74*, 189–213.

[5] Z. Yoshida, H. Konishi, in: *Houben-Weyl – Methods oif Organic Chemistry*, 4th ed., Vol. El7d, (Ed.: A. de Meijere), Thieme, Stuttgart, **1997**, Chapter 5.

[6] R. Gleiter, M. Merger, *Angew. Chem.* **1997**, *109*, 2532–2546; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2426–2439.

[7] B. Halton, M. G. Banwell, in: *The Chemistry of the Cyclopropyl Group*, (Ed.: Z. Rappoport), Wiley, New York, **1987**, p 1300.

[8] a) J. Ciabattoni, E. C. Nathan, *J. Am. Chem. Soc.* **1969**, *91*, 4766–4771; b) E. V. Dehmlow, R. Neuhaus, H. G. Schell, *Chem. Ber.* **1988**, *121*, 569–571; c) S. S. Dehmlow, E. V. Dehmlow, *Z. Naturforsch. B.* **1975**, *30*, 404–408; d) E. V. Dehmlow, *Leibigs Ann.* **1969**, *729*, 64–68.

[9] D. H. Wadsworth, B. A. Donatelli, *Synthesis* **1981**, 285–286.

[10] a) Y. Chiang, A. J. Kresge, V. V. Popik, *J. Am. Chem. Soc.* **1995**, *117*, 9165–9171; b) Y. Chiang, A. J. Kresge, S. W. Paine, V. V. Popik, *J. Phys. Org. Chem.* **1996**, *9*, 361–370; c) Y. Chiang, A. J. Kresge, V. V. Popik, *J. Am. Chem. Soc.* **1999**, *121*, 5930–5932; d) A. Poloukhtine,

V. V. Popik, *J. Org. Chem.* **2003**, *68*, 7833–7840; e) A. V. Kuzmin, V. V. Popik, *Chem. Commun.* **2009**, 5707–5709.
[11] a) B. D. Wagner, M. Z. Zgierski, J. Lusztyk, *J. Am. Chem. Soc.* **1994**, *116*, 6433–6434; b) G. Quinkert, K. Opitz, W. W. Wiersdorff, J. Weinlich, *Tetrahedron Lett.* **1963**, *4*, 1863–1868; c) O. L. Chapman, J. Gano, R. P. West, M. Regitz, G. Maas, *J. Am. Chem. Soc.* **1981**, *103*, 7033–7036; d) A. Krebs, W. Cholcha, M. Mueller, T. Eicher, H. Pielartzik, H. Schnoeckel, *Tetrahedron Lett.* **1984**, *25*, 5027–5030; e) S. Murata, T. Yamamoto, H. Tomioka, *J. Am. Chem. Soc.* **1993**, *115*, 4013–4023; f) K. Sung, D.-C. Fang, D. Glenn, T. T. Tidwell, *J. Chem. Soc. Perkin Trans. 2* **1998**, 2073–2080.
[12] a) I. Agranat, A. Barak, M. R. Pick, *J. Org. Chem.* **1973**, *38*, 3064–3065; b) T. Eicher, V. Schmieder, *Synthesis* **1989**, 372–378; c) C. H. Weidner, D. H. Wadsworth, C. S. Knop, A. I. Oyefesso, B. L. Hafer, R. J. Hartman, R. C. Mehlenbacher, S. C. Hogan, *J. Org. Chem.* **1994**, *59*, 4319–4322.
[13] a) D. L. Boger, C. E. Brotherton, *J. Am. Chem. Soc.* **1986**, *108*, 6695–6713; b) H. Isobe, S. Sato, T. Tanaka, T. H. Okuyama, E. Nakamura, *Org. Lett.* **2004**, *6*, 3569–3571; c) P. A. Wender, T. J. Paxton, T. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 14814–14815; d) P. A. O'Gorman, T. Chen, H. E. Cross, S. Naeem, A. Pitard, M. I. Qamar, K. Hemming, *Tetrahedron Lett.* **2008**, *49*, 6316–6319; e) M. Alajarín, C. López-Leonardo, Á. Álvarez-García, P. Llamas-Lorente, P. Sánchez-Andrada, J. Berná, A. Pastor, D. Bautista, P. G. Jones, *Chem. Eur. J.* **2010**, *16*, 3728–3735.
[14] a) A. Hamada, T. Takizawa, *Tetrahedron Lett.* **1972**, *13*, 1849–1850; b) A. Kascheres, A. C. Joussef, H. C. Duarte, *Tetrahedron Lett.* **1983**, *24*, 1837–1840.
[15] a) B. D. Kelly, T. H. Lambert, *J. Am. Chem. Soc.* **2009**, *131*, 13930–13931; b) D. J. Hardee, L. Kovalchuke, T. H. Lambert, *J. Am. Chem. Soc.* **2010**, *132*, 5002–5003; c) C. M. Vanos, T. H. Lambert, *Chemical Science* **2010**, *1*, 705–708; d) B. D. Kelly, T. H. Lambert, *Org. Lett.* **2011**, *13*, 740–743; e) C. M. Vanos, T. H. Lambert, *Angew. Chem.* **2011**, *123*, 12430–12434; *Angew. Chem. Int. Ed.* **2011**, *50*, 12222–12226; f) E. D. Nacsa, T. H. Lambert, *Org. Lett.* **2013**, *15*, 38–41.
[16] See the Supporting Information for details.
[17] a) W. Zhang, M. Shi, *Chem. Commun.* **2006**, 1218–1220; b) M. Shi, X.-G. Liu, Y.-W. Guo, W. Zhang, *Tetrahedron* **2007**, *63*, 12731–12734; c) S.-H. Cao, X.-C. Zhang, Y. Wei, M. Shi, *Eur. J. Org. Chem.* **2011**, 2668–2672; d) Y. Wei, X.-G. Liu, M. Shi, *Eur. J. Org. Chem.* **2012**, 2386–2393.
[18] See the Supporting Information for details.
[19] I. Erden, C. Gärtner, M. S. Azimi, *Org. Lett.* **2009**, *11*, 3986–3989.
[20] B. Kempf, H. Mayr, *Chem. Eur. J.* **2005**, *11*, 917–927.
[21] K. Haav, J. Samme, A. Kütt, I. Leito, *Eur. J. Org. Chem.* **2012**, 2167–2172.
[22] For Mayr's findings on nitrogen-containing organocatalysts, see: M. Baidya, S. Kobayashi, F. Brotzel, U. Schmidhammer, E. Riedle, H. Mayr, *Angew. Chem.* **2007**, *119*, 6288–6292; *Angew. Chem. Int. Ed.* **2007**, *46*, 6176–6179.
[23] M. J. Frisch, et al. *Gaussian 09*, revision A.01, Gaussian, Inc., Wallingford, CT, **2009**.

