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Nucleophilic Migratory Cyclopropenation of Activated Alkynes: A Nonmetal Approach to Unbiased Cyclopropenes

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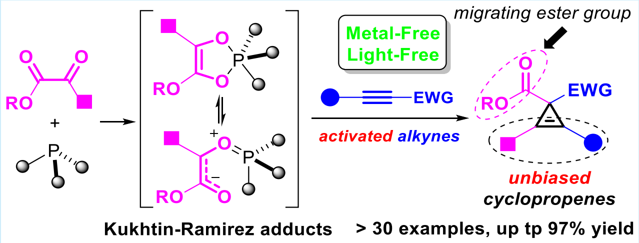
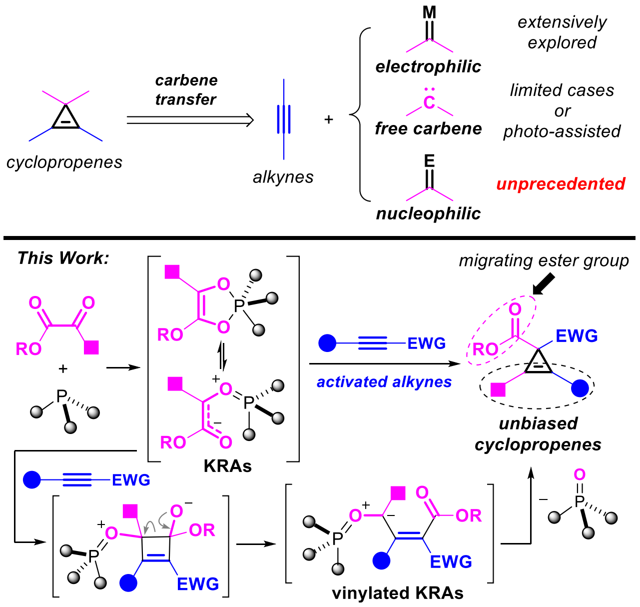
ABSTRACT: An unprecedented reductive [2 + 1] annulation of α-keto esters with alkynones mediated by $P(NMe_2)_3$ is described. Although this nonmetal cyclopropenation is a nucleophilic process, attributed to the ester migration via a formal [2 + 2] cycloaddition reaction of Kukhtin−Ramirez adducts and alkynones followed by a fragmentation, cyclopropenes with an unbiased alkene scaffold are formed in good to excellent yields, thus providing a promising complementarity to electrophilic metal-catalyzed cyclopropenation.



As the smallest unsaturated carbocyclic compounds with an *endo*-cyclic double bond, cyclopropenes are highly strained and reactive and serve as important synthons in organic synthesis.[1] Therefore, considerable effort has been devoted toward the synthesis of this class of molecules. Besides the classical cyclopropene generation from 1,2-elimination of halocyclopropanes[2] and the rearrangement of the vinylcarbene intermediates,[3,4] carbene transfer to alkynes is one of the most straightforward constructions of such carbocycles (Scheme 1).[1] Nevertheless, most of such carbene transfer processes are generally promoted by electrophilic transition metal catalysts.[1,5] Despite difluorocarbene is known to add direct to alkynes for a long time,[6,7] until recently transfer of nonfluorinated carbenes to alkynes has been realized by the use of the isolable *N*,*N*′-diamidocarbene[8] or blue-light irradiation.[9] Remarkably differing from the viability of alkene cyclopropanation with both electrophilic transition metal carbenoids and nucleophilic ylides,[10] we intriguingly found that, to the best of our acknowledge, cyclopropenation of activated alkynes with the nucleophilic carbenoids like ylides is yet unprecedented (Scheme 1),[11] though alkenylation of ylides with activated alkynes has been reported.[12,13]

Scheme 1. Cyclopropenes *via* Carbene Transfer to Alkynes



The adducts of trivalent phosphorus agents with 1,2-dicarbonyl compounds, known as the Kukhtin−Ramirez adducts (KRAs), have been widely used as convenient nucleophilic carbenoids in organic synthesis,[14,15] especially for rapid access to the highly substituted cyclopropanes from electron-deficient alkenes.[16] However, there is no report on the reaction of KRAs with activated alkynes. In continuation of our interest in the vinylated KRAs,[17] we recently tried to prepare the vinylated KRAs from simple KRAs with activated alkynes via a formal [2 + 2] cycloaddition/fragmentation sequence like insertion of alkynes/arynes into β-dicarbonyl compounds.[18] To our surprise, we found that KRAs reacted smoothly with activated alkynes to give cyclopropenes with the unbiased alkene scaffold, featuring migration of the unreacted ester group in 1,2-dicarbonyl substrates (Scheme 1). The stronger leaving ability of P(V) oxides and the lack of the stabilizing α-substituents in the in situ formed vinylated KRAs may account

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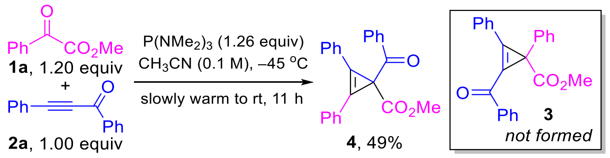
for the outcome of cyclopropenes. Due to the inherent low reactivity of the related diazo compounds in transition-metal-catalyzed cyclopropenation,[5f] preparation of the 3,3-acceptor/acceptor cyclopropenes is often restricted to terminal alkynes.[19,20] Moreover, such transition-metal-catalyzed approaches for these cyclopropenes also suffer from the cycloisomerization to the furan derivatives promoted by the same electrophilic transition-metal catalysts.[21] In this context, we herein report a metal-free P(III) reagent mediated cyclopropenation reaction for such unbiased cyclopropenes as a promising alternative.

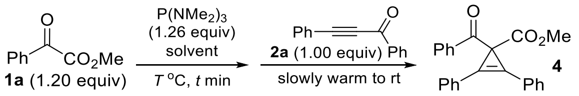
Initially, the KRA derived from methyl benzoylformate (**1a**) and $P(NMe_2)_3$ was subjected to react with alkynone **2a** in frozen CH_3CN, which, after slowly warmed to rt and stirred at rt for 11 h, afforded cyclopropene **4** in 49% yield with no formation of **3** (Scheme 2). Compound **3** was independently synthesized by blue-light induced cyclopropenation of the propargylic alcohol with diazo compound followed by the Dess–Martin oxidation.[9b] Furthermore, **3** was not an intermediate product of the reaction, since no conversion of **3** to **4** under the reaction condition was observed. The structure of **4** was unambiguously confirmed by single-crystal X-ray crystallography of its analogues **10** and **37**.

Scheme 2. Cyclopropenation of Alkynone 2a with KRA



The unexpected formation of **4**, featuring the shift of an ester group and an olefinic bond, prompts us to investigate the reaction further. Among the examined solvents, DCM is the most effective (Table 1, entries 1–3). While reactions in DCE and DCM at −35 °C gave comparable reaction efficiency (Table 1, entries 4 and 5), an improved yield of **4** was obtained from the reaction in DCM at −53 °C (Table 1, entry 6), at which temperature DCE is frozen. The addition of $P(NMe_2)_3$ to the mixture of **1a** and **2a** slightly affect the reaction (Table 1, entry 7); on the other hand, the warming rate of the reaction is critical, since the immediate removal of the cooling bath after the addition of **2a** resulted in an evident jump of the yield (Table 1, entry 8). Pleasingly, the reaction performed in a higher concentration remarkably improved the product yield of **4** to 89% (Table 1, entry 9). The yield of **4** was slightly improved by the use of 1.50 equiv of the KRAs (Table 1, entry 10). By contrast, trimethyl phosphite is not an effective promoter (Table 1, entry 11).

Table 1. Optimization of Reaction Conditions

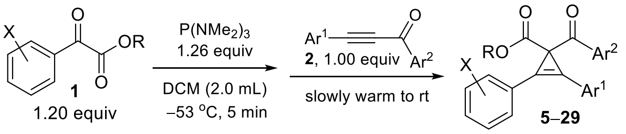


entry	**2a** (*c*) (M)	*T* (°C)	time (min)	solvent	**4**[a] (yield, %)
1	0.1	−78	10	THF	32
2	0.1	−78	10	$PhCH_3$	18
3	0.1	−78	10	DCM	44
4[b]	0.1	−35		DCE	57
5[b]	0.1	−35		DCM	58
6	0.1	−53	5	DCM	65
7[b]	0.1	−53		DCM	63
8[c]	0.1	−53	5	DCM	47
9[d]	0.2	−53	5	DCM	89
10[d,e]	0.2	−53	5	DCM	93
11[d,f]	0.2 M	−53	5	DCM	<5

[a] Performed on a 0.20 mmol scale of **2a**. Isolated yield. [b] **1a** and **2a** were first dissolved in solvent before cooling. [c] The cooling bath was removed after stirring for 10 min with the addition of **2a**. [d] **2a** (0.40 mmol). [e] **1a** (1.50 equiv) and $P(NMe_2)_3$ (1.58 equiv). [f] $P(OMe_3)$ (1.26 equiv) was used as the promoter.

As depicted in Table 2, this nonmetal cyclopropenation reaction tolerates a wide range of various functionalities. Ethyl (**1b**) and benzyl (**1c**) benzoylformates are as reactive as **1a**; however, the hindered alkyl benzoylformates are much less efficient (Table 2, entries 3 and 4). Reactions with α-keto esters **1** bearing the electron-withdrawing groups at the *para*-position of the aromatic ring gave the desired products in good

Table 2. Nonmetal Cyclopropenation of Alkynones (2) with Various Aryl α-Ketoesters (1)



entry	**1** (X, R)	**2** (Ar^1, Ar^2)	yield[a] (%)
1	**1b** (H, Et)	**2a** (Ph, Ph)	**5**, 79
2	**1c** (H, Bn)	**2a** (Ph, Ph)	**6**, 85
3	**1d** (H, ^iPr)	**2a** (Ph, Ph)	**7**, 43
4	**1e** (H, ^tBu)	**2a** (Ph, Ph)	**8**, 13
5	**1f** (4-Cl, Me)	**2a** (Ph, Ph)	**9**, 94
6	**1g** (4-Br, Me)	**2a** (Ph, Ph)	**10**, 94
7	**1h** (4-F, Me)	**2a** (Ph, Ph)	**11**, 66
8	**1i** (4-Me, Me)	**2a** (Ph, Ph)	**12**, 54
9	**1j** (4-OMe, Me)	**2a** (Ph, Ph)	**13**, 16
10	**1k** (4-CN, Me)	**2a** (Ph, Ph)	**14**, 90
11	**1l** (4-I, Et)	**2a** (Ph, Ph)	**15**, 88
12	**1m** (3-F, Me)	**2a** (Ph, Ph)	**16**, 97
13	**1n** (3-Cl, Me)	**2a** (Ph, Ph)	**17**, 81
14	**1o** (3-Br, Me)	**2a** (Ph, Ph)	**18**, 90
15	**1p** (3-Me, Me)	**2a** (Ph, Ph)	**19**, 76
16	**1q** (3-OMe, Me)	**2a** (Ph, Ph)	**20**, 87
17	**1r** (3-Br,4-F, Me)	**2a** (Ph, Ph)	**21**, 88
18	**1a (H, Me)**	**2b (4-ClC$_6$H$_4$, Ph)**	**9, 71**
19	**1a (H, Me)**	**2c (4-BrC$_6$H$_4$, Ph)**	**10, 72**
20	**1a (H, Me)**	**2d (4-FC$_6$H$_4$, Ph)**	**11, 90**
21	**1a (H, Me)**	**2e (4-MeC$_6$H$_4$, Ph)**	**12, 77**[b]
22	**1a (H, Me)**	**2f (4-MeOC$_6$H$_4$, Ph)**	**13, 83**[b]
23	**1a (H, Me)**	**2g (4-NCC$_6$H$_4$, Ph)**	**14, 70**[b]
24	**1a (H, Me)**	**2h (3-MeC$_6$H$_4$, Ph)**	**19, 71**
25	**1a (H, Me)**	**2i (2-ClC$_6$H$_4$, Ph)**	**22, 43**
26	**1a** (H, Me)	**2j** (Ph, 4-FC_6H_4)	**23**, 84
27	**1a** (H, Me)	**2k** (Ph, 4-ClC_6H_4)	**24**, 75
28	**1a** (H, Me)	**2l** (Ph, 4-BrC_6H_4)	**25**, 72
29	**1a** (H, Me)	**2m** (Ph, 4-MeC_6H_4)	**26**, 80[b]
30	**1a** (H, Me)	**2n** (Ph, 4-MeOC_6H_4)	**27**, 77[c]
31	**1a** (H, Me)	**2o** (Ph, 3-MeC_6H_4)	**28**, 68[b]
32	**1a** (H, Me)	**2p** (Ph, 2-MeC_6H_4)	**29**, 89[b]

[a] Performed on a 0.40 mmol scale of **2**. Isolated yield. [b] **1a** (1.50 equiv) and $P(NMe_2)_3$ (1.58 equiv). [c] **1a** (1.58 equiv) and $P(NMe_2)_3$ (1.65 equiv).

to excellent yields, whereas reactions with those substituted by the electron-donating groups at the *para*-position produced the desired products in much lower yields (Table 2, entries 5−11). A small electronic effect of the *meta*-substituents in aryl α-keto esters was observed (Table 2, entries 12−17).

Benefiting from the shift of the ester group and the olefinic bond, the aryl groups in α-keto esters and alkynones converted to the unbiased cyclopropenes are equivalent to each other, thus providing two alternatives for these strained carbocycles. For example, **9**−**14** and **19** were also successfully prepared from the cyclopropenation of alkynones **2b**−**h** with **2a** and $P(NMe_2)_3$ in good yields (Table 2, entries 18−24), although alkynones with electron-donating or strongly electron-withdrawing aryl groups are not as reactive as **2a**. Notably, for the challenging electron-rich α-keto esters **1j** (Table 2, entry 9), the other method was proved to be promising, which gave the target product **13** in 83% yield with the use of 1.50 equiv of **1a** (Table 2, entry 22). Even though *ortho*-substituted aryl α-keto esters were unreactive, *o*-chlorophenyl cyclopropene **22** could be obtained in 43% yield from *ortho*-substituted aryl alkynone **2i** with **1a** (Table 2, entry 25).

With respect to the aroyl groups of alkynones, those substituted by the electron-withdrawing halo groups (**2j**−**l**) are generally more reactive than those functionalized with electron-donating methyl or methoxy groups (**2m**−**p**), regardless of the substituted position on the aromatic ring. Gratifyingly, for the latter cases, good isolated yields of the products remained accessible by using more equivalents of α-keto esters and $P(NMe_2)_3$ (Table 2, entries 29−32).

Heteroaryl-substituted cyclopropenes are also accessible by this $P(NMe_2)_3$-mediated nucleophilic cyclopropenation reaction. As shown in Figure 1, thienyl-derived cyclopropenes were generally obtained in better yields than either pyridinyl- or furyl-substituted ones, presumably due to the weak electronic effect of the thienyl ring. Like the aryl substrates, two synthetic routes for the heteroaryl cyclopropenes like **30** are effective as well and improved product yields could be obtained by using more equivalents of KRAs, for example, the synthesis of **34**.

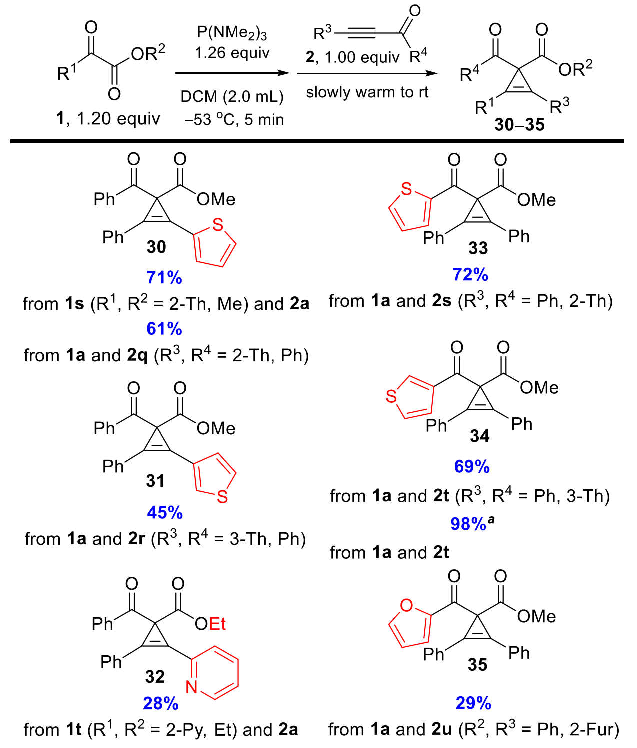


Figure 1. Access to heteroaryl-substituted cyclopropenes: **1** (0.48 mmol), **2** (0.40 mmol, 0.2 M), and $P(NMe_2)_3$ (0.50 mmol) in DCM. Isolated yield. (a) **1a** (1.50 equiv) and $P(NMe_2)_3$ (1.58 equiv).

Unfortunately, alkyl substituents in both reagents, such as phenylethyl-, methyl-, and *tert*-butyl-substituted α-keto esters or methyl- and *tert*-butyl-substituted alkynones, are problematic for this reaction at this stage.

To show the synthetic complementarity of this reaction to the transition-metal carbenoid method, cyclopropenes **36** and **37** were selectively prepared from α-keto esters **1u** and **1v** bearing an alkenyl or an alkynyl group with suitable alkynones in good yields, respectively, which otherwise would be quite cumbersome to prepare by transition-metal-catalyzed carbene transfer to alkynes (Figure 2). For the synthesis of **36**, the metal carbenoid intermediate bearing the allyl group prefers intramolecular cyclopropanation.[14c,22] On the other hand, the discrimination of the metal carbenoid toward the two alkynyl units with small electronic and steric differences in the diyne **38** is apparently challenging.[23]

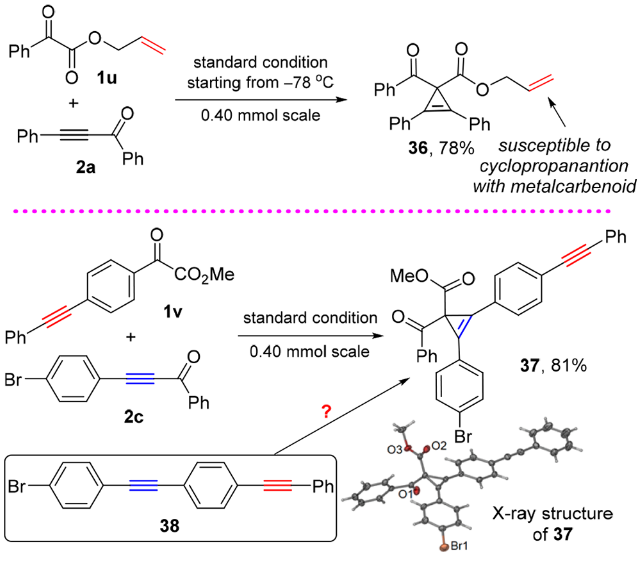
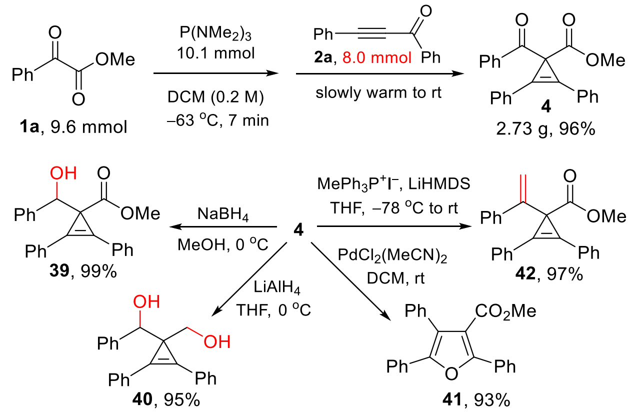


Figure 2. Selective synthesis of **36** and **37**. Thermal ellipsoid is set at 50% probability.

As shown in Scheme 3, gram-scale cyclopropene **4** was readily obtained by this nonmetal cyclopropenation without any loss of the product yield. Besides the potential decoration of cyclopropenes such as **10**, **15**, and **25** via cross-coupling reactions, **4** was converted to compounds **39**−**42** by selective reduction, cycloisomerization,[21c] and Wittig-olefination as well (Scheme 3).

In summary, we have developed a nucleophilic cyclopropenation reaction of alkynones with the Kukhtin−Ramirez adducts derived from α-keto esters and $P(NMe_2)_3$, which involves an unexpected migration of the ester group, thereby giving cyclopropenes with the unbiased *endo*-cyclic double bond. The mild and efficient nonmetal access to unbiased cyclopropenes in a nucleophilic manner would provide a promising complementarity to the well-explored electrophilic metal-catalyzed cyclopropenation in both reactivity and selectivity issues.

Scheme 3. Gram-Scale Cyclopropenation and Conversions



■ ASSOCIATED CONTENT

Supporting Information

TThe Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00498.

Mass spectra list reports (PDF)
Experimental procedures, characterization data, and spectra (PDF)

Accession Codes

CCDC 2059829−2059830 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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