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Alkyne and Reversible Nitrile Activation: *N*,*N*′-Diamidocarbene-Facilitated Synthesis of Cyclopropenes, Cyclopropenones, and Azirines

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Supporting Information

ABSTRACT: We report the synthesis of a variety of diamidocyclopropenes by combining an isolable and readily accessible *N*,*N*′-diamidocarbene (DAC) with a range of alkynes (nine examples, 68−97% yield). Subsequent hydrolysis of selected cyclopropenes afforded the corresponding cyclopropenones or *α*,*β*-unsaturated acids, depending on the reaction conditions. In addition, the combination of a DAC with alkyl or aryl nitriles was found to form 2*H*-azirines in a reversible manner (four examples, K_{eq} = 4−72 M^{-1} at 30 °C in toluene).

As the smallest unsaturated carbo- and heterocycles, cyclopropenes and azirines have attracted considerable interest for their unique structural characteristics.[1] Indeed, the high degree of ring strain possessed by these species has enabled them to serve many roles in the synthesis of substituted alkynes, allenes, heterocycles, and other important substrates.[2,3] Cyclopropenes are typically prepared via the metal-mediated addition of electrophilic carbenes to alkynes or the 1,2-elimination of halocyclopropanes.[1,2b,c,3] In contrast, azirines are often synthesized in situ using the Neber rearrangement of activated oximes or via the pyrolysis/photolysis of vinyl azides.[2a,4] A practical and atom-economical alternative to the aforementioned methods is the [2 + 1] cycloaddition of isolable carbenes with alkynes or nitriles. Unfortunately, such synthetic approaches are relatively unexplored, largely because of a lack of suitable carbenes. For example, Arduengo has shown that exposure of *N*,*N*′-dimesityl-4,5-dihydroimidazol-2-ylidene (SIMes), a well-known, stable, and basic[5] N-heterocyclic carbene (NHC),[6] to acetylene (Figure 1 top) or acetonitrile results in formal C−H insertion rather than cycloaddition.[7] Indeed, Bertrand's phosphinosilyl carbene[8] is the only stable carbene known to undergo chelotropic reactions with compounds possessing triple bonds and may be limited to phosphaalkynes (R−C≡P) and aryl nitriles (Ar−C≡N).[9]

Herein we disclose that the *N*,*N*′-diamidocarbene (DAC)[10] **1** is the first isolable carbene to undergo formal [2 + 1] cycloadditions with alkynes as well as alkyl and aryl nitriles. DACs are an emerging class of stable carbenes that display many reactivities often expected from in situ-generated electrophilic carbenes, such as methylene.[10] Simply exposing **1**, which can be isolated in one step from the condensation product of *N*,*N*′-dimesitylformamidine and dimethylmalonyl dichloride,[10d] to various alkynes was found to afford the corresponding diamidocyclopropenes in high yields. These products were successfully hydrolyzed to afford cyclopropenones or *α*,*β*-unsaturated acids.[11] Additionally, treatment of **1** with aryl or alkyl nitriles resulted in the first examples of the formation of 2*H*-azirines in a reversible fashion.[12] In all cases, the cycloaddition reactions were found to proceed rapidly to high conversions under mild conditions.

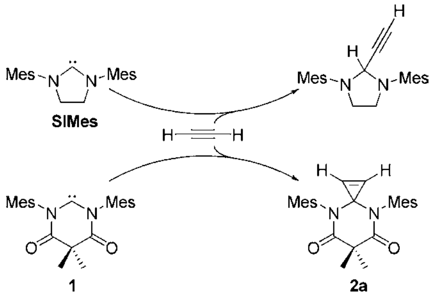

Figure 1. (top) Exposure of SIMes to acetylene affords the formal C−H insertion product shown. Conditions: 1.1 equiv of acetylene, THF, −196 to 23 °C, 16 h (93% yield).[7] (bottom) Exposure of DAC **1** to acetylene affords cyclopropene **2a**. Conditions: 1 atm acetylene, C_6H_6, 23 °C, 8 h (81% yield). Mes = 2,4,6-trimethylphenyl.

Our initial experiments explored the reaction of **1** with acetylene. Stirring a solution of **1** in C_6H_6 ($[\mathbf{1}]_0$ = 0.13 M) under acetylene (1 atm) for 8 h at ambient temperature resulted in the formation of a cloudy solution that, upon concentration and washing with diethyl ether, afforded a white solid in 81% yield.[13] The isolated product was identified as cyclopropene **2a** (Figure 1 bottom), in part on the basis of the appearance of signals associated with a strained olefin observed at 7.23 (2H) and 117.9 ppm ($CDCl_3$) in the compound's ^1H and ^{13}C NMR spectra, respectively. The structure of **2a**, which constitutes a rare[14] example of a diamidocyclopropene, was unambiguously elucidated by single-crystal X-ray diffraction (XRD) analysis (Figure 2).

DAC **1** was found to undergo [2 + 1] cycloadditions with a variety of terminal, internal, aryl, alkyl, and silyl-protected alkynes to give the corresponding cyclopropenes in good to excellent isolated yields (68−97%; Table 1). In general, the terminal alkynes were reacted at equimolar concentration with **1** ($[\mathbf{1}]_0$ = 0.20 M) in C_6H_6 for 16 h at 23 °C, whereas the internal alkynes were stirred at 60 °C using 2 equiv of alkyne under otherwise identical conditions. With the exception of **2h**,

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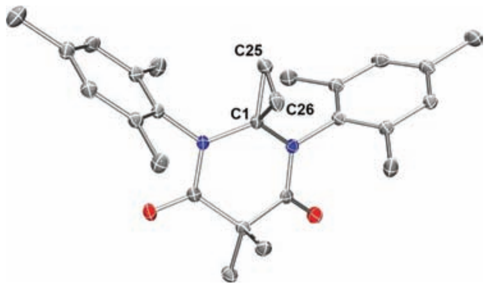
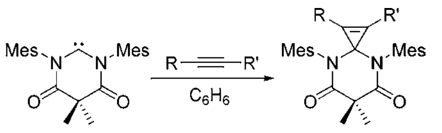
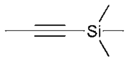


Figure 2. ORTEP diagram of **2a**, with thermal ellipsoids drawn at 50% probability and H atoms omitted for clarity. Selected distances (Å) and angles (deg): C1–C25, 1.464(2); C1–C26, 1.471(2); C25–C26, 1.285(2); C25–C1–C26, 51.90(10); C26–C25–C1, 64.32(11); C25–C26–C1, 63.78(11).

Table 1. Summary of the [2 + 1] Cycloadditions of DAC 1 with Various Alkynes^{a}

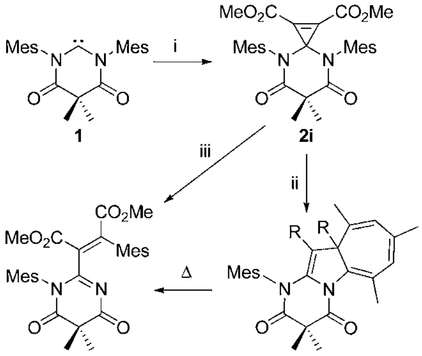


1 **2a-h**

Product	Alkyne	Isolated Yield^{b}
2a	H—≡—H	81%^{c}
2b	H—≡—4-^{t}BuPh	74%
2c	H—≡—Cy	68%^{d}
2d	H—≡—Bu	93%^{d}
2e	—≡—Pr	89%^{e}
2f	Ph—≡—Et	97%
2g	Ph—≡—Ph	92%^{c}
2h		93%^{e}

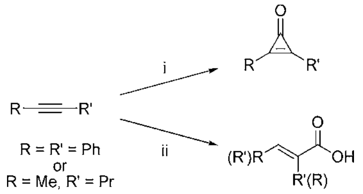
^{a}Unless otherwise noted, all reactions were performed in C_6H_6 at 23 °C for 16 h using equimolar concentrations of **1** ($[\mathbf{1}]_0$ = 0.2 M) and the alkyne shown. Abbreviations: ^{t}Bu = *tert*-butyl; Ph = phenyl; Cy = cyclohexyl; Bu = butyl; Pr = propyl; Et = ethyl. ^{b}Isolated yields of the corresponding cyclopropene products. ^{c}1 atm acetylene, $[\mathbf{1}]_0$ = 0.13 M, 8 h. ^{d}60 °C. ^{e}[alkyne]$_0$ = 0.4 M, 60 °C.

Scheme 1. Cyclopropene Formation Followed by Ring Expansion and Isomerization^{a}



^{a}Conditions: (i) DMAD (1 equiv), C_6H_6, 23 °C, 5 min, 97% yield; (ii) C_6H_6, 23 °C, 40 h, 41% yield from **1** (R = CO_2Me); (iii) C_6H_6, 60 °C, 12 h, 80% yield from **1**.

Scheme 2. Treatment of Various Alkynes with 1 Followed by Hydrolysis of the Resultant Cyclopropenes (e.g., 2e and 2g) under Acidic Conditions Enables Access to the Corresponding Cyclopropenone or *α*,*β*-Unsaturated Acid(s) Depending on the Reaction Temperature and Time^{a}



^{a}Conditions: (i) **1**, C_6H_6, 60 °C, 16 h then 50:50 v/v HCl/AcOH, 80 °C, 2 h (66–70% yield); (ii) **1**, C_6H_6, 60 °C, 16 h then 50:50 v/v HCl/AcOH, 100 °C, 48 h (32–43% yield).

all of the synthesized cyclopropenes were found to be high-melting-point solids (mp >140 °C) and stable to the ambient atmosphere. Regardless, in all cases, no competitive alkyne C–H insertion processes were observed, and the cyclopropenes formed constitute the first examples of their kind arising from alkynes and an isolable carbene.

While the aforementioned reactions afforded stable cyclopropenes as the sole products, the outcome of the reaction of **1** with an electron-deficient alkyne, dimethyl acetylenedicarboxylate (DMAD), was found to be time-dependent (Scheme 1). Stirring **1** with a stoichiometric quantity of DMAD in C_6D_6 at 23 °C for 5 min afforded the cyclopropene product **2i** (97% isolated yield), as evidenced in part by a diagnostic signal observed at 125.8 ppm in the ^{13}C NMR spectrum of this compound. However, when the same reaction was allowed to proceed for >30 min at 23 °C, a second product that exhibited upfield ^{1}H and ^{13}C NMR shifts (^{1}H, 5.98 and 6.14 ppm; ^{13}C, 119.58 and 121.05 ppm) gradually formed. The new spectroscopic signals were consistent with a loss of aromaticity and the formation of the fused cycloheptatriene **3**. The structural assignment was subsequently confirmed by single-crystal XRD [see the Supporting Information (SI)] following isolation of the product (41% yield). Additionally, heating either **2i** or **3** at 60 °C for 12 h resulted in the formation of a third product that displayed downfield ^{1}H NMR shifts [6.54 (2H) and 6.62 (2H) ppm] as well as a lack of olefinic ^{13}C NMR signals. In agreement with these data, single-crystal XRD (see the SI) of the isolated solid (80% yield based on **1**) revealed this compound to be the conjugated alkylideneamide **4**. We believe that the overall transformation of **2i** to **4** was driven by the ring-opening rearrangement of the cyclopropene to a norcaradiene derivative that underwent electrocyclic ring expansion to the corresponding cycloheptatriene **3**,[15] and ultimately isomerized to its more stable isomer **4**. This process represents a novel, metal-free C–C bond-forming reaction that involves the migration of a sterically hindered aryl group.

Considering that the carbene center in **1** is in the same oxidation state as the carbon atom in carbon monoxide, a gas reluctant to undergo [2 + 1] cycloaddition reactions,[16] we reasoned that hydrolysis of the aforementioned *N*,*N*-diamidocyclopropenes would provide a new synthetic route[11,17] to cyclopropenones, substrates desired for their utility in preparing heterocycles, cyclopropenylium ions, and other unsaturated carbonyl species.[17,18] To test this hypothesis, **2g** was heated to 80 °C in a 1:1 v/v mixture of glacial acetic acid and concentrated HCl for 2 h. Following purification over silica gel, 2,3-diphenylcyclopropenone was isolated in 66% yield (Scheme 2, route i). Although no ring-opened products were observed under these conditions, heating **2g** at 100 °C for 48 h in the same acid mixture followed by extraction afforded *trans*-α-phenylcinnamic acid, albeit in modest yield (32%; Scheme 2, route ii). Similarly, hydrolysis of **2e** afforded either 2-methyl-3-propylcyclopropenone (70%) or a 53:47 mixture of the isomeric ring-opened carboxylic acids *trans*-2-methylhex-2-enoic acid and *trans*-2-ethylidenepentanoic acid (43% overall yield), depending on the reaction conditions. As there are relatively few methods[17b,c] for the efficient preparation of dialkylcyclopropenones, especially in comparison with their diaryl analogues, the synthesis of 2-methyl-3-propylcyclopropenone in a single vessel and good yield is noteworthy and underscores the ability of DACs to serve as an equivalent to CO in useful cycloaddition reactions.

Having successfully demonstrated that the DAC **1** is a suitable [2 + 1] cycloaddition partner for alkynes, subsequent attention shifted toward studying the reaction of **1** with nitriles, another class of substates that contain triple bonds.[19] The addition of excess benzonitrile (2 equiv) to **1** in C_6D_6 ($[\mathbf{1}]_0$ = 0.09 M) at 23 °C for 2 h afforded a product that displayed NMR signals consistent with the formation of 2*H*-azirine **5a**. For example, ^{13}C NMR analysis of the above-mentioned reaction mixture revealed a signal at 167.6 ppm (C_6D_6) diagnostic[9,20] of a 1:1 cycloadduct of the nitrile and the DAC as opposed to an ylide.[21] To our surprise, attempts to isolate the azirine product by removing the residual solvent under vacuum followed by washing with pentane returned the starting material, **1**. Similar results were obtained with other functionalized derivatives of benzonitrile as well as acetonitrile. Collectively, these observations suggested to us that the interaction between the DAC and the aforementioned nitriles is reversible (see below). Nevertheless, the formation of a 2*H*-azirine product was later unequivocally determined by single-crystal XRD analysis of **5c** (see Figure 3 and the SI for details).

The equilibrium constants (K_{eq}) for the reversible reactions of **1** with various nitriles were measured in C_7D_8 by variable-temperature NMR spectroscopy and used to construct van't Hoff plots (see the SI). Linear fits of these data enabled the determination of ΔH and ΔS for each reaction investigated. These studies revealed that the [2 + 1] cycloaddition of **1** was more favored for electron-deficient nitriles, as evidenced by the larger K_{eq} and more negative ΔH values measured (Table 2). Treatment of **1** with acetonitrile was also found to afford the corresponding azirine **5d** (diagnostic ^{13}C NMR signal in C_6D_6 at 169.9 ppm) in a reversible manner (K_{eq} = 4 M^{-1} at 30 °C).[22] Although the K_{eq} for the reaction with the alkyl nitrile was lower than those measured for the aryl analogues, this result represents the first example of an isolable carbene undergoing a [2 + 1] cycloaddition with an alkyl nitrile as opposed to affording the formal C−H insertion product that is typically observed.[7,23]

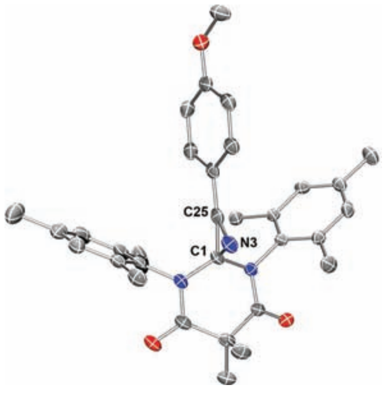
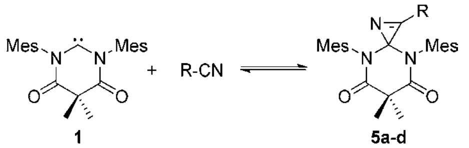


Figure 3. ORTEP diagram of **5c**, with thermal ellipsoids drawn at 50% probability and H atoms omitted for clarity. Selected distances (Å) and angles (deg): C1−C25, 1.436(2); C1−N3, 1.5184(18); N3−C25, 1.2753(19); N3−C25−C1, 67.81(10); C25−N3−C1, 61.15(10); C25−C1−N3, 51.05(9).

Table 2. Thermodynamic Data for the Reversible [2 + 1] Cycloadditions of 1 with Various Nitriles[a]



Product	R	ΔH ($kJ \cdot mol^{-1}$)	ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)	K_{eq}, 30 °C (M^{-1})
5a	Ph	-47.4	-129	26
5b	p-NO_2Ph	-50.0	-129	72
5c	p-MeOPh	-38.6	-101	23
5d[b]	CH_3	-36.8	-110	4

[a] Conditions: 1 equiv of RCN, C_7D_8, unless otherwise noted. [b] 10 equiv of CH_3CN.

In summary, we report a series of [2 + 1] cycloaddition reactions through the combination of a stable, isolable diamidocarbene (DAC) with various alkynes and nitriles to afford cyclopropenes and 2*H*-azirines, respectively. In all cases, the reactions proceeded under mild conditions (23−60 °C) and reached high conversions. The azirination reactions were found to be reversible at ambient temperature, which is more typical of given transition metals and a first for an organic compound,[24] and may complement known[25] methods for activating nitriles. Aside from being among the first examples of their kind, the aforementioned diamidocyclopropenes were hydrolyzed to afford either the corresponding cyclopropenones or ring-opened acids, depending on the conditions employed. Additionally, exposure of the DAC to electron-deficient substrates facilitated the discovery of new C−C bond-forming reactions. Collectively, these transformations underscore the ability of DACs to function as useful synthetic reagents in applications that extend beyond facilitating the formation of three-membered rings. We expect these results to broaden the utility of isolable carbenes in synthesis, structural analysis, and dynamic covalent chemistry.[26]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures; X-ray crystallographic data for **2a−c**, **3**, **4**, **5c**, and **6**; and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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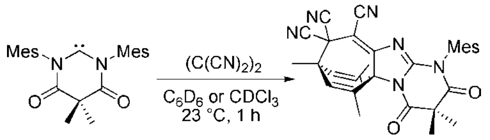
(21) In contrast, many electrophilic carbenes [e.g., fluorenylidene, tetrakis(trifluoromethyl)cyclopentadienylidene, and methylene], all of which must be generated in situ, are known to react with nitriles to form nitrile ylides. See: (a) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. Notable exceptions to these reactions are the adamantylidenes, which have been shown to afford 2*H*-azirines upon exposure to nitriles. See: (b) Knoll, W.; Mieusset, J.-L.; Arion, V. B.; Brecker, L.; Brinker, U. H. *Org. Lett.* **2010**, *12*, 2366.

(22) The observed pseudo-first-order rate constants for the formation of the following cyclopropenes were measured (conditions: 10 equiv of alkyne, $[\mathbf{1}]_0$ = 66 mM, C_6D_6, 50 °C; see the SI): **2b** (k_{obs} = 0.5026 min^{-1}) > **2d** (k_{obs} = 0.1215 min^{-1}) > **2f** (k_{obs} = 0.0487 min^{-1}) > **2e** (k_{obs} = 0.0055 min^{-1}). These data are consistent with a partial buildup of charge in the cycloaddition transition state. For detailed mechanistic discussions of cycloadditions involving carbenes, see: (a) Hoffman, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. (b) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770. (c) Xu, L.; Doubleday, C. E.; Houk, K. N. *J. Am. Chem. Soc.* **2011**, *133*, 17848.

(23) Treatment of **1** with tetracyanoethylene, an electron-deficient nitrile, afforded crystalline **6**, albeit in 17% isolated yield (see the SI for the solid-state structure). The overall transformation appeared to involve dearomatization with concomitant C–C bond formation followed by isomerization.



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