SHORT COMMUNICATION

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Intermolecular Metal-Free Cyclopropanation of Alkenes Using Tosylhydrazones

José Barluenga,*[a] Noelia Quiñones,[a] María Tomás-Gamasa,[a] and María-Paz Cabal*[a]

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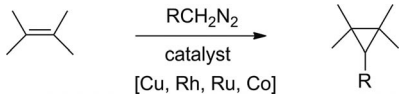
We describe the first general method for the metal-free cyclopropanation of alkenes by using *N*-tosylhydrazones as an in situ source of diazo compounds. This new method works with a wide variety of alkenes (styrene derivatives, dienes, enynes, and electron-deficient alkenes) by using *N*-tosylhydrazones derived from various ketones or aldehydes (aromatic, aliphatic, enones). The reaction is performed with the use of K_2CO_3 as a base to form the diazo species and is compatible with a wide array of functional groups.

Introduction

The cyclopropane unit is found as a basic structural element in many biologically important compounds.[1] Its unique reactivity enables the cyclopropane ring to be used as a versatile building block or intermediate in the synthesis of molecules with increased complexity.[2] Among the methods commonly used for its construction, the most general are transition-metal-catalyzed decomposition of diazo compounds in the presence of an olefin, a process involving metal carbene intermediates derived from Cu, Rh, Ru, Co, and other metal catalysts (Scheme 1).[3]



Scheme 1. Cyclopropanation by transition-metal-catalyzed decomposition of diazo compounds.

It has been proposed that highly reactive metal carbene reagents are required to overcome the ring strain generated in the newly formed cyclopropane unit.[4] Most of the examples involve diazo compounds stabilized by electron-withdrawing groups such as diazoketones or diazoesters. Aryl diazomethanes generally perform less effectively due to their greater tendency to dimerize in the absence of nucleophilic alkenes. However, metal-catalyzed reactions may also present problems associated with the high cost of precious metals and ligands and the need to dispose of or to eliminate the sometimes toxic metals. For this reason, metal-free reactions that could exhibit the same levels of efficiency and selectivity are highly desirable.

The limitation of this method is the need to synthesize and handle potentially toxic, and in some cases explosive, diazo compounds.[5] To solve this problem, sulfonylhydrazones are versatile synthetic intermediates that have been used as an in situ source of diazo compounds in different types of transition-metal-catalyzed processes, such as olefination, epoxidation, C–H and N–H insertion reactions, and cyclopropanations.[6]

In the last five years our group has demonstrated that in the presence of a Pd catalyst, tosylhydrazones can be used as a general source of diazo compounds without any limitation in the structure of the carbonyl precursor, and these compounds have found utility in important transformations such as cross-coupling reactions, oxidative cross-couplings, and cascade reactions.[7] We have also discovered that the same strategy can be applied in the absence of a metal catalyst; thus, we have recently reported new metal-free carbon–carbon (Scheme 2a) and carbon–oxygen (Scheme 2b) bond-forming reactions between tosylhydrazones and boronic acids or alcohols, respectively.[8] In continuing with our interest in metal-free processes employing tosylhydrazones, the synthesis of cyclopropanes from alkenes has emerged as an attractive synthetic transformation (Scheme 2c).

As far as we know, two examples of cyclopropanations have been reported in the literature for the thermal decomposition of sulfonylhydrazones in the presence of alkenes without a metal catalyst present: Aggarwal reported an intermolecular cyclopropanation of dehydroamino acids,[6b] and Taber developed an intramolecular cyclopropanation reaction between ketones and dienes.[9]

Here, we describe a new and general procedure for the synthesis of cyclopropanes by base-promoted decomposition of tosylhydrazones in the presence of alkenes. An at-

[a] Instituto Universitario de Química Organometálica "Enrique Moles". Unidad Asociada al CSIC, Universidad de Oviedo
c/ Julián Clavería 8, 33006 Oviedo, Spain
Fax: +34-98-510-3446
E-mail: barluenga@uniovi.es
pcabal@uniovi.es

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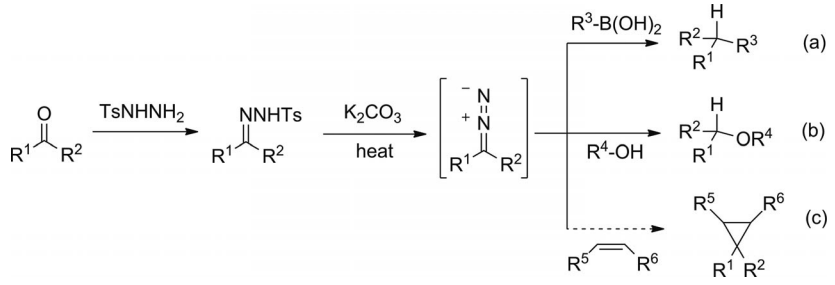


Scheme 2. Free-metal C–C and C–O bond-forming reactions from tosylhydrazones.

tractive feature is that the reaction is general and allows the use of tosylhydrazones readily prepared from simple, non-stabilized, carbonyl compounds.

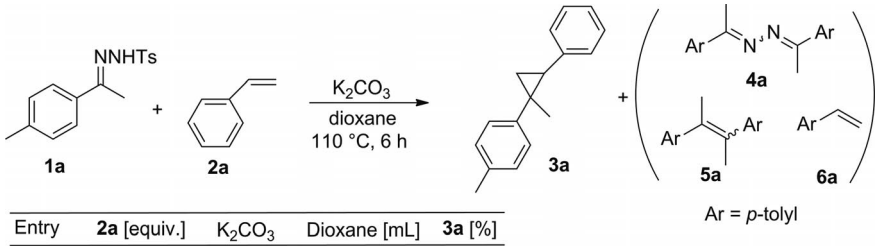
Results and Discussion

We first focused on the reaction of the tosylhydrazone derived from *p*-tolyl methyl ketone (**1a**) and styrene (**2a**, Scheme 3). Our first attempts gave encouraging results. The reaction run in the presence of K_2CO_3 with the use of dioxane as the solvent at 110 °C afforded aryl cyclopropane **3a** as a diastereomeric mixture (*cis*/*trans* = 0.4:1) in 71% yield (Scheme 3, Entry 1). The cyclopropanation is dependent on the concentration of the reagents, with the optimal being 2 equiv. of styrene, 1.5 equiv. of K_2CO_3, and 3 mL of dioxane, to afford adduct **3a** in 87% yield (Scheme 3, Entry 2). Several additional bases were screened, including Na_2CO_3, K_3PO_4, KOH, and NaO*t*Bu, but none of them provided desired cyclopropane **3a**. The reaction proceeds with $CsCO_3$ and LiO*t*Bu, albeit with a decrease in yield (67 and 58%, respectively). Similar results were obtained when the reaction time was doubled from 6 to 12 h. The reaction also proceeds at lower temperatures (70–90 °C) but with a substantial decrease in the yield due to the formation of side products such as azine **4a** and alkenes **5a** and **6a**, resulting from the dimerization and elimination (Bamford–Stevens reaction),[10] respectively, of the starting tosylhydrazone. At higher temperatures (150 °C) with the use of microwave irradiation (MW), the yield was not improved (69%), and an increase in the formation of byproduct **4a** was found in the crude product mixture.

The scope of the process was studied under the optimized reaction conditions shown in Scheme 3. The transformation proceeds very efficiently with a wide range of tosylhydrazones derived from ketones or aldehydes having aromatic, heteroaromatic, or alkyl substituents (Table 1). Hydrazones derived from aryl ketones afford the desired products in high yields, regardless of steric or electronic variations (Table 1, Entries 1–11). Hydrazones derived from aliphatic ketones afford more moderate yields (Table 1, Entries 12 and 13). Hydrazones derived from aromatic and heterocyclic aldehydes proceed with high conversions when electron-withdrawing substituents are located at the *meta* or *para* positions (Table 1, Entries 19–22). It is important to point out that the reaction takes place even with *p*-nitro- and *p*-fluoroaryl tosylhydrazones (Table 1, Entries 9 and 19), which are not accessible by other methodologies.[6d]

With regard to the aryl-substituted alkene, there is a broad substrate tolerance, which allows the reaction to be carried out even with electron-deficient benzene derivatives (Table 1, Entries 3–5, 11, 16–17, and 22) as well as highly hindered 1,1-disubstituted aryl substrates (Table 1, Entry 23).

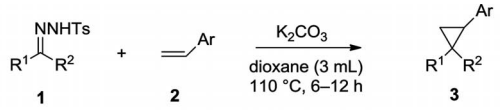
We next investigated the cyclopropanation reaction by using aliphatic substituted alkenes. Unfortunately, under the same reaction conditions previously used for the aryl alkenes, a complex mixture of products was obtained. Thus, a new optimization of the reaction conditions was carried out. The influence of the temperature was also investigated, and it was confirmed that reactions run at 150 °C gave the best results. The microwave-promoted reactions are advantageous in this particular transformation when compared



Entry	**2a** [equiv.]	K_2CO_3	Dioxane [mL]	**3a** [%]
1	3	3	2	71
2	2	1.5	3	87

Scheme 3. Influence of the reagent concentrations in the synthesis of **3a**.

Table 1. Synthesis of arylcyclopropanes **3**.[a]



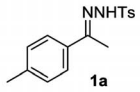
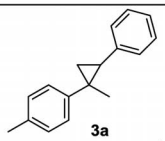
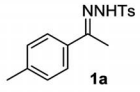
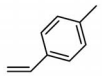
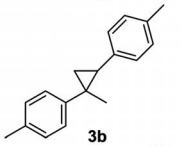
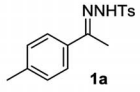
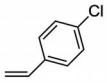
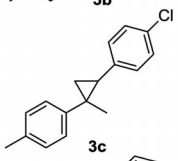
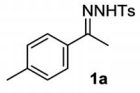
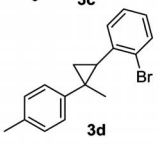
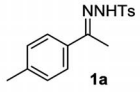
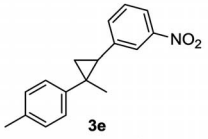
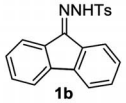
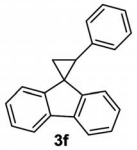
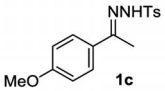
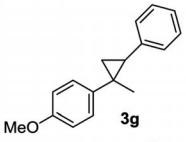
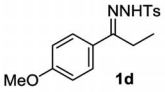
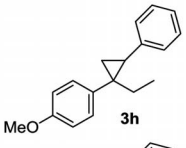
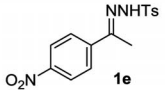
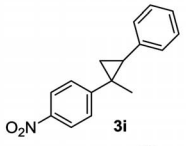
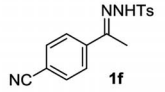
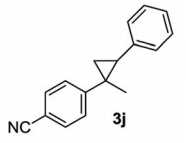
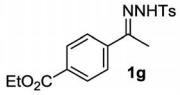
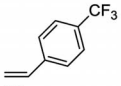
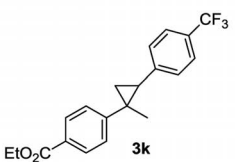
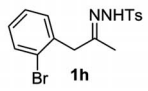
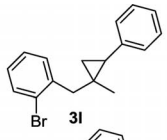
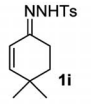
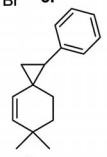
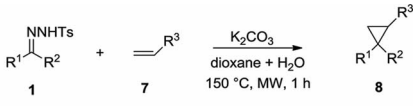
Entry	Hydrazone **1**	Alkene **2**	Cyclopropane **3**	Yield[b] [%]
1	 **1a**	 **2a**	 **3a**	85
2	 **1a**	 **2b**	 **3b**	70
3	 **1a**	 **2c**	 **3c**	91
4	 **1a**	 **2d**	 **3d**	64
5	 **1a**	 **2e**	 **3e**	89
6	 **1b**	 **2a**	 **3f**	62
7	 **1c**	 **2a**	 **3g**	73
8	 **1d**	 **2a**	 **3h**	71
9	 **1e**	 **2a**	 **3i**	67
10	 **1f**	 **2a**	 **3j**	36
11	 **1g**	 **2f**	 **3k**	84

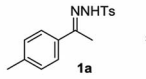
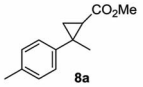
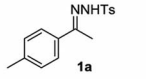
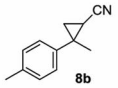
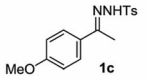
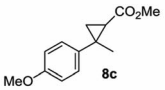
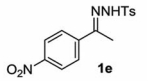
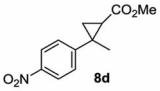
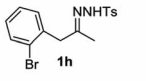
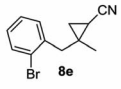
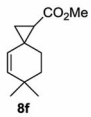
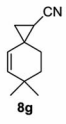
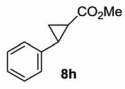
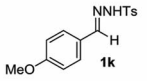
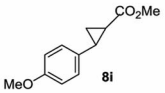
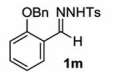
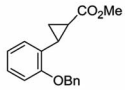
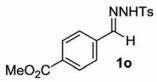
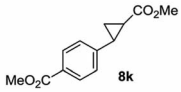
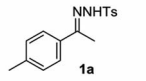
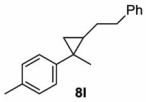
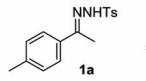
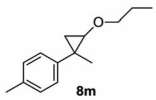
Table 1. *(continued)*

12	 **1h**	 **2a**	 **3l**	54
13	 **1i**	 **2a**	 **3m**	45
14	**1j**	**2a**	**3n**	64
15	**1k**	**2a**	**3o**	48
16	**1k**	**2e**	**3p**	32
17	**1l**	**2d**	**3q**	22
18	**1m**	**2a**	**3r**	45
19	**1n**	**2a**	**3s**	64
20	**1o**	**2a**	**3t**	63
21	**1p**	**2a**	**3u**	72
22	**1p**	**2g**	**3v**	75
23	**1a**	**2h**	**3w**	52

[a] Reaction conditions: Tosylhydrazone **1** (0.3 mmol), aryl alkene **2** (0.6 mmol), K_2CO_3 (0.45 mmol), dioxane (3 mL), 110 °C, 6–12 h. [b] Yield of isolated cyclopropane **3** as a mixture of diastereoisomers (*cis*/*trans* = 0.3–0.7:1).

Table 2. Synthesis of alkylcyclopropanes **8**.[a]



Entry	Hydrazone **1**	Alkene **7**	Cyclopropane **8**	Yield[b] [%]
1	 **1a**	 **7a**	 **8a**	74
2	 **1a**	 **7b**	 **8b**	59
3	 **1c**	 **7a**	 **8c**	80
4	 **1e**	 **7a**	 **8d**	60
5	 **1h**	 **7b**	 **8e**	70
6	 **1i**	 **7a**	 **8f**	66
7[c]	 **1i**	 **7b**	 **8g**	58
8	 **1j**	 **7b**	 **8h**	54
9	 **1k**	 **7a**	 **8i**	56
10	 **1m**	 **7a**	 **8j**	61
11	 **1o**	 **7a**	 **8k**	57
12	 **1a**	 **7c**	 **8l**	25[d]
13	 **1a**	 **7d**	 **8m**	15[d]

[a] Reaction conditions: Tosylhydrazone **1** (0.3 mmol), alkyl alkene **7** (0.3 mmol), K_2CO_3 (1.5 equiv.), dioxane (1.5 mL), H_2O (10 μL), 150 °C (MW), 1 h. [b] Yield of isolated cyclopropane **8** as a mixture of diastereoisomers (*cis*/*trans* = 0.3–0.8:1). [c] Alkene **7b** (0.6 mmol), K_2CO_3 (3 equiv.), 110 °C, 6 h. [d] Yield of the crude reaction mixture.

Table 3. Synthesis of alkenyl- and alkynylcyclopropanes **10**.[a]

Entry	Hydrazone **1**	Diene **9**[b]	Cyclopropane **10**	Yield[c] [%]
1	**1c**	**9a**	**10a**	37
2	**1c**	**9b**	**10b**	72
3	**1c**	**9c**	**10c**	62
4	**1e**	**9c**	**10d**	60
5	**1g**	**9c**	**10e**	67
6	**1r**	**9c**	**10f**	80
7	**1h**	**9c**	**10g**	43
8[d]	**1i**	**9c**	**10h**	41
9	**1k**	**9c**	**10i**	40
10	**1n**	**9c**	**10j**	21
11	**1o**	**9c**	**10k**	38
12	**1c**	**9d**	**10l**	57
13	**1p**	**9d**	**10m**	62

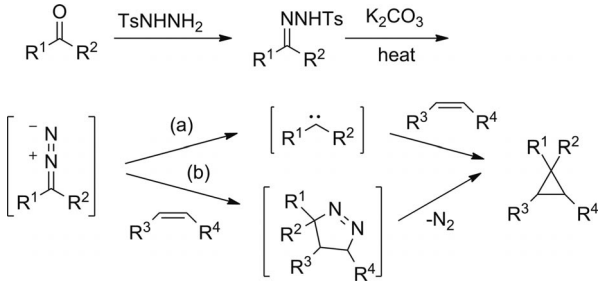
[a] Reaction conditions: Tosylhydrazone **1** (0.3 mmol), diene **9a**–**c** or enyne **9d** (1.5 mmol), K_2CO_3 (1.5 equiv.), dioxane (2 mL), 110 °C, 6 h. [b] Dienes **9a** and **9c** are a *Z*/*E* mixture of diastereoisomers. [c] Yield of isolated cyclopropane **10** as a mixture of diastereoisomers (*cis*/*trans* = 0.4–0.6:1). [d] K_2CO_3 (3 equiv.), 12 h.

to conventional heating: the higher reaction temperature allowed the process to take place faster and with higher yields (Table 2). Also, an excess amount of the alkene was not required to deliver the highest conversion. Again the reaction was general for tosylhydrazones derived from aromatic ketones (Table 2, Entries 1–4), aliphatic ketones (Table 2, Entries 5–7), or aromatic aldehydes (Table 2, Entries 8–11). Good results were obtained when electron-withdrawing substituents on the alkene were used, but neutral or electron-donating substituents afforded poor yields (Table 2, Entries 12 and 13).

Moreover, the cyclopropanation reaction is not restricted to aryl-substituted alkenes or aliphatic-substituted alkenes, as it can be successfully applied to conjugated dienes and enynes, provided that an excess amount of the substrate (5 equiv.) is used (Table 3). Under MW irradiation, lower yields were obtained, but with conventional heating at 110 °C, the cyclopropanes were obtained in fair to good yields. The regioselectivity of the reaction is sensitive to temperature, as at higher temperatures (150 °C, MW) the cyclopropanation occurs at both double bonds, but at 110 °C the reaction is regioselective for the terminal alkene. The reaction is general for *N*-tosylhydrazones derived from aromatic ketones with electron-donating (Table 3, Entries 1–3) or electron-withdrawing substituents (Table 3, Entries 4–6), as well as with aliphatic ketones (Table 3, Entries 7 and 8) and aryl aldehydes (Table 3, Entries 9–11).

Furthermore, 1-buten-3-ynes are good substrates, and the reaction occurred regioselectively to afford high yields of the alkynylcyclopropanes by using tosylhydrazones derived from ketones or aldehydes (Table 3, Entries 12 and 13).

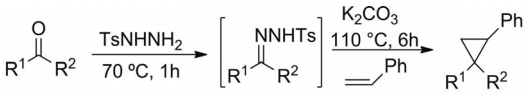
In Scheme 4, we consider two alternative pathways for these cyclopropanation reactions: (path a) carbene addition to the double bond or (path b) 1,3-dipolar cycloaddition followed by N_2 extrusion.



Scheme 4. Synthesis of cyclopropanes from tosylhydrazones by 1,3-dipolar cycloaddition.

Path b has been proposed in the literature for the formation of cyclopropanes in non-metal-catalyzed reactions.[11] In this case, the reaction is postulated to proceed through diastereoselective construction of a pyrazoline ring followed by extrusion of nitrogen, with retention of the configuration of the pyrazoline stereocenters.[12]

Lastly, we examined the possibility of generating the hydrazones in situ from carbonyl compounds to develop a one-pot cyclopropanation procedure (Scheme 5). Therefore, after heating carbonyl compound **13a** or **13b** and tosylhydrazine for 60 min at 70 °C, the base and the alkene were then added, and the mixture was heated for an additional 6 h. Cyclopropanes **3g** and **3s** were isolated in 66 and 34% yield, respectively.



	R^1	R^2	Yield [%]	*dr* (*trans*:*cis*)
3g	PMP	Me	66	(1:0.4)
3s	4-FC_6H_5	H	34	(1:0.3)

Scheme 5. One-pot procedure for the synthesis of cyclopropanes.

Conclusions

The results presented above show that the reaction of tosylhydrazones with alkenes is a very general method for the creation of cyclopropane products. The methodology can be applied to aryl and aliphatic alkenes, as well as conjugated dienes and enynes. The high functional group tolerance allows the reaction to be carried out on substrates not normally compatible with other methodologies. For instance, the reaction proceeds successfully in the presence of esters and nitriles. Moreover, halogen substitution on the aromatic ring is also tolerated and enables further derivatization through metal-catalyzed cross-coupling techniques. Also, the cyclopropanation reaction can be carried out directly from the carbonyl compound by generating the tosylhydrazone in situ, in a multicomponent fashion.

In summary, we have described a new procedure for the synthesis of cyclopropanes by base-promoted decomposition of tosylhydrazones in the presence of alkenes. Notably, the starting materials are readily available and stable; tosylhydrazones are easily synthesized from carbonyl compounds on a large scale and can be stored at room temperature without decomposition. The major advantages of this procedure are the operational simplicity, the preclusion of an inert atmosphere or ultra-dry solvents, and the high functional group tolerance. In this study we demonstrate for the first time that electron-deficient alkenes react with non-stabilized diazo compounds to overcome the limitation of previously reported metal-catalyzed intermolecular reactions between diazoesters and electron-deficient alkenes.[6b] We believe that this new methodology may become a useful tool in organic synthesis.

Supporting Information (see footnote on the first page of this article): Experimental procedures and spectroscopic data for cyclopropanes **3**, **8**, and **10**.

Acknowledgments

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