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Triazene-Activated Donor–Acceptor Cyclopropanes: Ring-Opening and (3 + 2) Annulation Reactions

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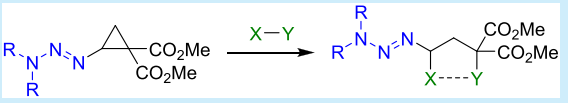
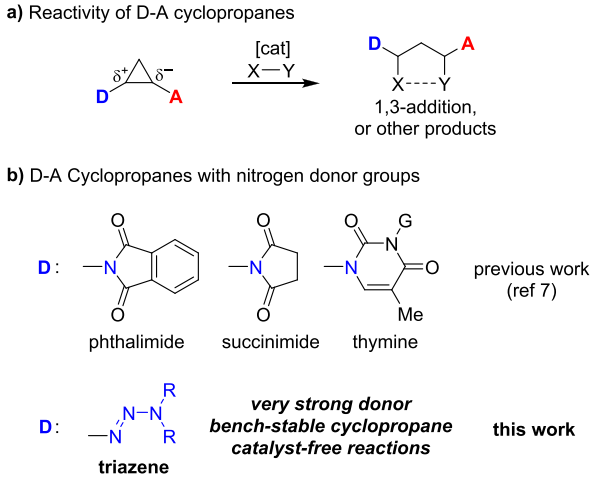
ABSTRACT: Donor–acceptor cyclopropanes substituted with 3,3-dialkyltriazenyl groups are described herein. The strong electron-donating character of the triazene renders the cyclopropanes highly reactive, allowing for catalyst-free ring-opening reactions with methanol and tetracyanoethylene under mild conditions. The triazene-substituted cyclopropanes could also be used as substrates in Lewis acid catalyzed (3 + 2) annulations with silyl enol ethers.



Cyclopropanes substituted with both electron-withdrawing and electron-donating groups in vicinal position display a high reactivity, which can be accentuated by using catalysts.[1,2] Typically, catalytic activation is achieved by coordination of a Lewis or Brønsted acid to the acceptor group.[2] The acid facilitates heterolytic C–C bond cleavage of the strained ring, allowing for reactions with electrophiles or nucleophiles, as well as cycloaddition and rearrangement reactions (Scheme 1a). Alternatively, formyl-acceptor groups can be activated by amine catalysts via iminium formation.[3] The catalytic activation of donor–acceptor (D–A) cyclopropanes via interaction of the donor group with Lewis bases is less common.[4] Examples of isolable D–A cyclopropanes, which are able to undergo ring-opening reactions without external catalysts, remain scarce.[5] The paucity of such cyclopropanes is related to the difficulty of finding donor/acceptor pairs, which provide the right amount of activation, while ensuring sufficient stability of the three-membered ring. Indeed, too much activation can result in spontaneous rearrangement of cyclopropanes into larger 5-membered heterocycles.[6]

Scheme 1. Reactivity of D–A Cyclopropanes (A) and Nitrogen-Based Donor Groups (B)[2−7]



A good balance between stability and reactivity has traditionally been realized with carbon- and oxygen-based donor groups, whereas nitrogen-based substituents were less investigated, despite their synthetic relevance.[2] To address this limitation, the Waser group has introduced phthalimide-, succinimide-, and nucleobase-substituted cyclopropanes (Scheme 1b).[2e,7] In this work, we introduce 3,3-dialkyltriazenes as new nitrogen-based donors. We show that triazenes provide an exceptional activation of the cyclopropane ring, allowing for ring-opening and -expansion reactions under mild conditions.

Over the last five years, we have studied the chemistry of 1-alkynyltriazenes.[8] These investigations have revealed that the triazene group is a very good electron donor, enabling an electrophilic attack to the triple bond. In view of these results, we were interested in exploring if triazenes could be used as donors in D–A cyclopropanes to expand the range of useful nitrogen substituents.

A common procedure for the synthesis of diester-substituted cyclopropanes is the Rh-catalyzed cyclopropanation of olefins with diazomalonates.[9] This approach could be implemented for the synthesis of cyclopropanes bearing triazene groups. The required vinyltriazenes starting materials **1a–1e** were accessed by coupling of vinyl Grignard reagents with nitrous oxide and lithium amides[8g,10] or by hydrogenation of alkynyltriazenes.[11]

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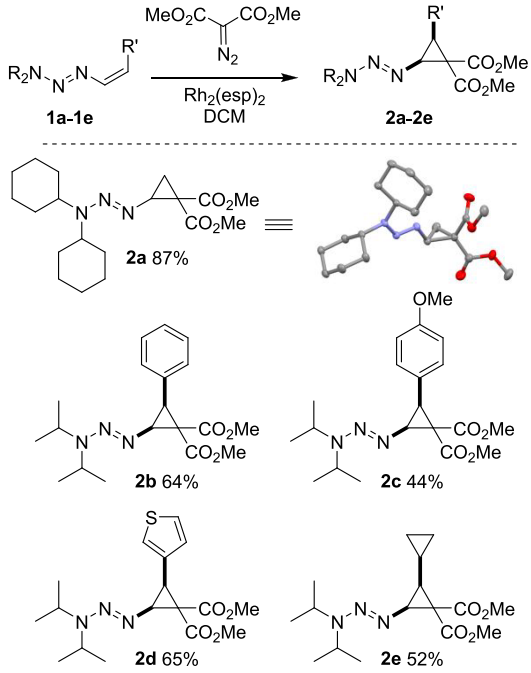
Cyclopropane **2a** could then be prepared by reaction of (*E*)-3,3-dicyclohexyl-1-vinyltriaz-1-ene (**1a**) with dimethyl diazomalonate (1.2 equiv) in the presence of commercially available $Rh_2(esp)_2$ (0.2 mol %) as catalyst (Scheme 2). The desired

Scheme 2. Synthesis of D−A Cyclopropanes with Triazene Groups[a]



[a]Reaction conditions: vinyltriazene (1 equiv), diazomalonate (1.2 equiv), $Rh_2(esp)_2$ (0.2−0.5 mol %), DCM (0.1 M), 0 °C to rt.

product was obtained in good yield, and the procedure was further optimized to gram scale with an isolated yield of 87%. Compound **2a** is a colorless crystalline solid, and its structure could be confirmed by single-crystal X-ray diffraction. Using this optimized procedure, we could prepare cyclopropanes **2b−2e** having additional phenyl, 4-anisyl, 2-thienyl, or cyclopropyl groups in C3 position from the corresponding *cis*-1,2-disubstituted vinyltriazenes **1b−1e**. The isolated yields of **2b−2e** varied from 52% to 65%. According to the ^1H NMR spectra, the *cis* stereochemistry is conserved in the products.

The ^{13}C NMR spectrum of cyclopropane **2a** in $CDCl_3$ shows a chemical shift for the C2 atom next to the triazene group at 55.6 ppm. Calculation of ^{13}C NMR chemical shifts for DFT-optimized structures of **2a** gave a similar value.[12] For comparison, the corresponding values for "standard" D−A cyclopropanes having aryl, cyclopropyl, or phthalimidyl donor groups lie in the range of 31−35 ppm, and cyclopropanes with poor donor groups such as *n*-butyl and hydrogen show a C2 signal at 24 and 17 ppm, respectively (Figure 1a).[13] The strongly shifted C2 signal of **2a** was a first indication for the pronounced electronic effect of the triazene group.

Further evidence for the strong electron-donating properties of the triazene group were obtained by calculating the relative stability of carbocations **A** and **B** (Figure 1b). This approach, which was developed by Werz,[14] allows comparison of the donor capabilities of different substituents. As a reference, we used the *p*-methoxyphenyl group, which is known to be one of the strongest donors among the reported stable D−A cyclopropanes, both from a thermodynamic[14] as well as a

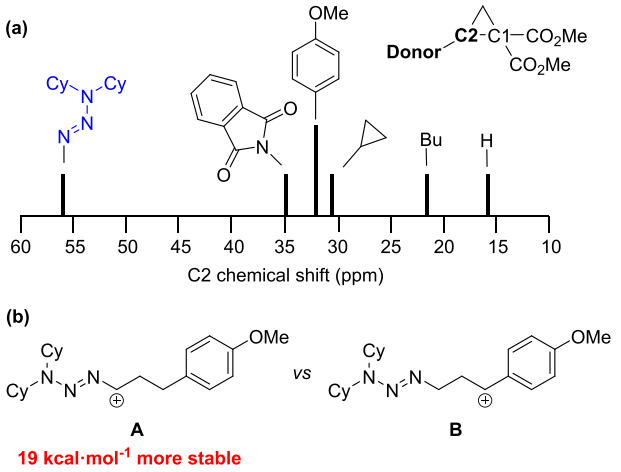
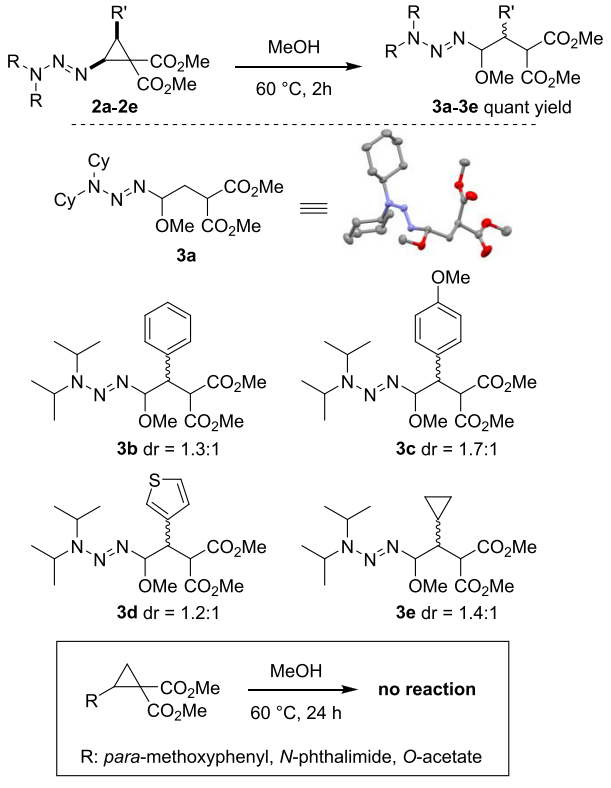


Figure 1. ^{13}C NMR chemical shifts of different D−A cyclopropanes (a) and (b) relative stability of carbocations (ΔG^{298} (kcal·mol^{-1})). The reference values were taken from the literature (ref 13). All spectra were measured in $CDCl_3$. The calculations for the carbocations were performed at the M06-2X/6-311+G(d,p) level.

kinetic[15] point of view. The calculations on M06-2X/6-311+G(d,p) level showed that carbocation **A** is 19 kcal·mol^{-1} more stable than **B**. Accordingly, the triazene group was expected to provide a very strong activation of the cyclopropane ring.

Diverse reactivity studies with these new cyclopropanes **2** were then carried out. When **2a** was dissolved in methanol, the ring-opened adduct **3a** (Scheme 3) could be isolated in quantitative yield after heating to 60 °C for 2 h, followed by evaporation of the solvent. The structure of **3a** could be confirmed by X-ray crystallography. Analogously, reaction of

Scheme 3. Methanol Addition Reactions



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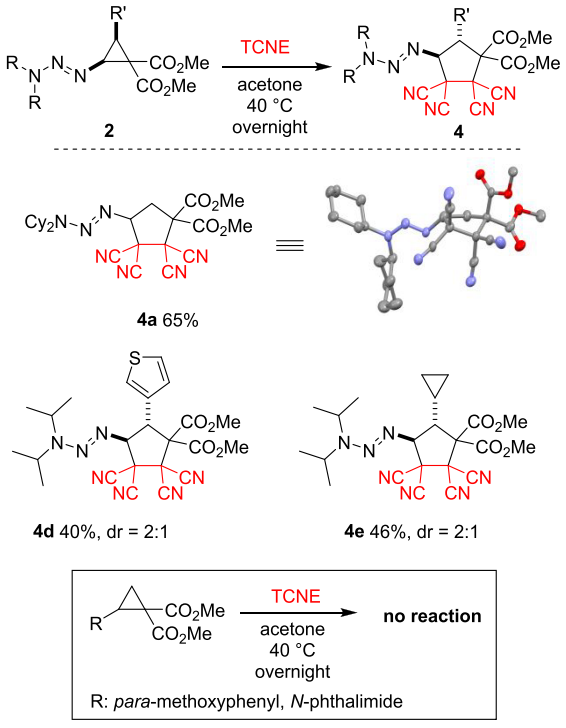
methanol with cyclopropanes **2b**–**2e** gave the addition products **3b**–**3e** in quantitative yields as a mixture of two diastereoisomers (ratio: ~1:1). In all cases, the bond between the triazene and the diester was broken, showing again that it was a better donor than a (hetero)arene or a cyclopropyl group. Preliminary mechanistic investigations indicate that methanol addition proceeds with participation of the ester group: more details are given in the Supporting Information.

For comparison, we have attempted reactions with methanol using three literature-known D–A cyclopropanes (donor = *p*-methoxyphenyl, *N*-phthalimide, or *O*-acetate). No reaction was observed, even after prolonged (24 h) heating at 60 °C. These results underline the unique donor properties of the triazene group.

Next, we have explored the reactivity of **2a** toward electrophiles. Ring-opening of D–A cyclopropanes with electrophiles is generally more challenging.[2] Cyclopropane **2a** reacted with tetracyanoethylene (TCNE) in a formal (3 + 2) cycloaddition reaction, in the absence of any external catalyst, to give the highly functionalized cyclopentane **4a** in 65% yield (Scheme 4).[16] Similarly, we were able to prepare the addition

Scheme 4. (3 + 2) Annulation with TCNE[a]



[a]Reaction conditions: **2a** (1 equiv), TCNE (1.2 equiv), acetone (0.1 M), 40 °C, 12 h.

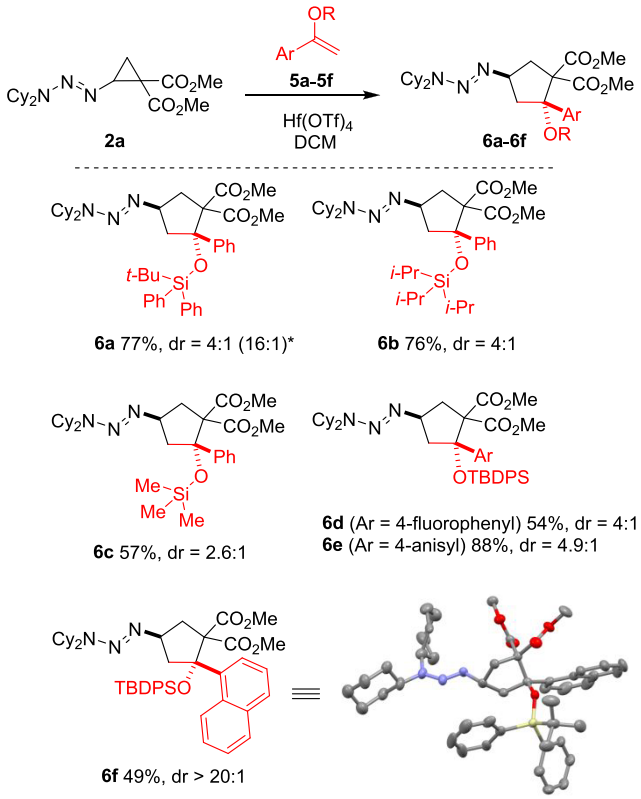
products **4d** and **4e**, albeit with reduced yields of 40% and 46%, respectively. The cyclopentanes **4d** and **4e** were isolated as mixtures of diastereoisomers, with prevalence of the *trans* isomer (dr = 2:1). As for the reactions with methanol, we found that D–A cyclopropanes with *p*-methoxyphenyl or *N*-phthalimide donor groups did not react with TCNE under these conditions.

After having established catalyst-free reactions with methanol and TCNE, we turned our attention to less reactive reaction partners, which require activation of the acceptor group by a catalyst. A priori, it was not clear if cyclopropanes bearing triazene groups could be activated by Lewis or Brønsted acids because the triazene groups are known to be acid sensitive.[17]

As a benchmark reaction, we have examined the addition of silyl enol ethers to cyclopropane **2a**. For D–A cyclopropanes with N-donor groups, this reaction is known to occur with a Lewis acid catalyst such as $SnCl_4$.[7] Screening of different LA catalysts and reaction conditions revealed that hafnium triflate[18] can catalyze the desired reaction between **2a** and silyl enol ethers at −40 °C (see the SI for details).

Using the optimized reaction conditions, we have tested different acetophenone-based silyl enol ethers (**5a**–**5c**, Scheme 5). Bulky TBDPS and TIPS groups allowed isolation of the

Scheme 5. (3 + 2) Annulation with Silyl Enol Ethers[a]



[a]Reaction conditions: **2a** (1 equiv), enol ether (1.2 equiv), $Hf(OTf)_4$ (10 mol %), DCM (0.1 M), −40 °C, 20 h. *After recrystallization from MeOH.

cyclopentanes **6a** and **6b** in good yields with a dr of 4:1. Recrystallization of **6a** from methanol improved the dr to 16:1. Analysis of **6a** by NOESY NMR spectroscopy revealed that the major diastereoisomer has a *trans* configuration of the triazene and the $OSiR_3$ group. The same selectivity had been observed for reactions with *N*-phthalimide D–A cyclopropanes.[7a] Utilization of a silyl enol ether with a less bulky TMS group (**5c**) gave cyclopentane **6c** in lower yield (57%) and a dr of 2.6:1. Next, we tested silyl enol ethers with different aryl groups. Electron-withdrawing 4-fluorophenyl and electron-donating 4-anisyl led to the formation of **6d** and **6e** in 54% and 88% yield, respectively. Interestingly, the dr of the products was only slightly influenced by the electronic properties of the aryl groups. On the other hand, using a substrate with a bulky 1-naphthyl substituent gave **6f** almost exclusively as one

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diastereoisomer (dr >20:1) in 49% yield. Cyclopentane **6f** was additionally characterized by single-crystal X-ray diffraction.

In conclusion, we report the first synthesis of D−A cyclopropanes substituted with dialkyltriazene groups by a simple Rh-catalyzed reaction of vinyltriazenes with dimethyl diazomalonate. The triazene group was found to provide an exceptionally strong activation of the cyclopropane ring, allowing for catalyst-free reactions with methanol and TCNE. Combined with the good stability of the new cyclopropanes, this type of reactivity is unique, as evidenced by the fact that "standard" D−A cyclopropanes with 4-methoxyphenyl or *N*-phthalimide donor groups do not react under these conditions. The usefulness of the new triazenyl cyclopropanes was further highlighted by their compatibility with Lewis acid catalysts in a (3 + 2) cycloaddition with silyl enol ethers, which delivered highly functionalized cyclopentanes. Taken together, our findings highlight the potential of the triazene group in activating cyclopropane ring systems. The results are also relevant from the more general perspective of triazene chemistry. So far, most investigations about triazenes have focused on 1-aryltriazenes,[19] with studies of 1-vinyl-[11,20] and 1-alkynyltriazenes[8] as recent additions. There are very few reports about 1-alkyltriazenes and no examples of alkyltriazenes with additional functional groups.[21] The D−A cyclopropane chemistry described above offers a means to prepare structurally and functionally complex alkyltriazenes. Further reactivity studies are ongoing in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01527.

Experimental details and analytical data of the new compounds (PDF)

Accession Codes

CCDC 1995157 and 1995416−1995418 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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(13) See the SI for an extended table of examples with references.

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