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Cycloisomerization of 1,6-Dienes Mediated by Lewis Super Acids without Additives: Easy Access to Polysubstituted Six-Membered Carbocycles

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Dedicated to Professor Peter Vollhardt
on the occasion of his 60th birthday

Alkyl-substituted carbocycles are a common structural component in a number of naturally occurring and biologically active molecules.[1] One of the challenging problems in the synthesis of compounds containing five- and six-membered rings is the efficient control of the ring size during a cyclization or cycloaddition step. With innumerable applications, the Diels–Alder cycloaddition is the best established reaction leading to six-membered rings exclusively.[2] The advent of stereoselective transition-metal catalysts has stimulated new ways to catalytic cyclization[3] as another important approach for the construction of carbocyclic compounds.[4] Though often highly selective, none of these reactions are really ring-size specific.[5] The cycloisomerization of polyunsaturated substrates has been studied extensively and is well established as an efficient method for the synthesis of five-membered carbocycles.[6,7] Though many metals have been reported to achieve catalytic cycloisomerization reactions,[8] only a few examples are known that lead to the selective formation of six-membered rings. Cyclohexane derivatives have been obtained from 1,6-dienes (e.g. olefinic indoles) with palladium[9] and platinum[10] complexes without special additives. However, other systems require catalyst combinations such as bulky ethylenebis(tetrahydroindenyl)titanium dichloride in association with *n*BuMgBr,[11] $[Cp_2ZrCl_2]$/methylaluminoxane ($[Zr]:[Al] = 0.1$),[12] $[Cp_2^*ZrMe_2]/B(C_6F_5)_3/AlMe_3$ ($Cp^* = C_5Me_5$),[13] methylaluminoxane and butylmetallocene scandium hydride complexes.[14] These latter examples involve the use of highly sterically hindered catalysts in association with alkylation or reducing agents. No simple catalytic system has been yet reported for the cycloisomerization of 1,6-dienes to give highly substituted cyclohexane carbocycles.

In the presence of Lewis acids, the intramolecular ene reaction[15] of 1,6-dienes generally leads to five-membered-ring compounds.[16] In a particular example, an alkenylpentenolide was transformed in the presence of pure sulfuric acid into a cyclohexane ring, as a result of a Wagner–Meerwein transposition with the formation of a spirocyclic ring system.[17]

We have recently reported on Lewis acid catalyzed cycloisomerizations of nonactivated and differently substituted olefinic alcohols to give cyclic ethers.[18] We found that the catalyst, tin(IV) triflate, $Sn(OTf)_4$, is involved in the activation of both the hydroxy group and the double bond. The following order of reactivity was observed: trisubstituted $\approx$ 1,1-disubstituted $>$ 1,2-disubstituted $>$ monosubstituted olefins. It seemed to us that enhancing the electrophilicity of a double bond with a strong Lewis acid might also favor intramolecular C–C bond formation within dienes, in a process comparable to the olefin activation by cationic late transition metals.[19] However, in contrast to order of reactivity towards late transition metals, highly substituted double bonds were supposed to be much more reactive with Lewis acids. We now report on our preliminary results on the transformation of 1,6-dienes that are highly substituted at the alkene termini in the presence of catalytic amounts of tin(IV) bis(trifluoromethanesulfonyl)imide, $Sn(NTf)_4$, allowing the selective formation of highly substituted six-membered-ring carbocycles.

The active catalyst, $Sn(NTf_2)_4$, and other metal bis(trifluoromethanesulfonyl)imides and metal triflate salts were prepared by using a simple electrochemical procedure.[20] These metal salts can be considered as Lewis super acids owing to the strong acidity of $HNTf_2$ (pK_a in water estimated at 1.7).[21]

Treatment of diethyl diprenylmalonate (**1a**) in refluxing 1,2-dichloroethane with a 5 mol% $Sn(NTf_2)_4$ afforded the *gem*-dimethyl cyclohexane derivative **1b** in 60% yield (Table 1). The structure of the new compound was easily deduced from the ^1H and ^{13}C NMR spectra.[22] Indeed, the new carbon–carbon bond in cyclohexane derivative **1b** arises from cyclization of diene **1a** occurring nonsymmetrically at two different sites of the two identically substituted double bonds: the first double bond undergoes a nucleophilic attack by the second double bond with Markovnikov-type regiochemistry.

To examine the scope of this novel catalytic system, we investigated the reactions of **1a** using several SnX_n derivatives ($X = Cl$, OTf, NTf_2, $n = 2$ or 4; Table 1, entries 1–4). More classical Lewis acids such as $SnCl_4$ and $SnCl_2$ led to low conversion and low selectivity. The other metal triflates and bistriflimidates tested (e.g. with W^{VI}, Ni^{II}, Sm^{III}, Bi^{III}, Table 1, entries 5–8) were found to be inefficient. Only $Sn(OTf)_4$ and $Sn(NTf_2)_4$ showed interesting activities (Table 1, entries 1 and 4). $Sn(NTf_2)_4$ was by far the most efficient catalyst, since it

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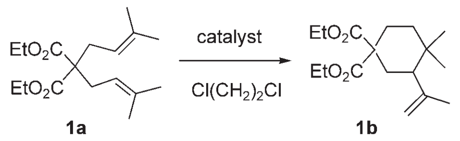
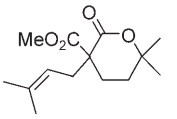
Table 1: Effect of Lewis acid catalysts in the cycloisomerization of **1a** to give **1b**.



Entry	Cat. (mol %)	*t*, *T*	Conv. [%]	Yield [%]
1	$Sn(OTf)_4$ (5)	71 h, 50 °C	78	60
2	$SnCl_4$ (5)	24 h, 40 °C	25	11
3	$SnCl_2$ (5)	28 h, 50 °C	28	14
4	$Sn(NTf_2)_4$ (2)	1.5 h, 50 °C	100	88
5	$Ni(OTf)_3$ (5)	24 h, 83 °C	32	24
6	$W(NTf_2)_6$ (5)	20 h, 83 °C	43	36
7	$Bi(OTf)_3$ (5)	7 h, 83 °C	31	23
8	$Sm(OTf)_3$ (5)	24 h, 83 °C	9	–

could be used in 2-mol % quantities under mild conditions. The rapid and selective cycloisomerization of **1a** led to **1b** in 88 % yield. To our knowledge, this is the first example of a selective Lewis acid catalyzed cycloisomerization of a highly (alkene-) substituted 1,6-diene.

A number of 1,6-dienes with different substitution patterns at the double bonds as well as at the homoallylic carbon were prepared from simple starting materials.[23] Table 2 summarizes some representative examples of this reaction using a variety of differently substituted substrates **1a**–**13a**. The conditions were optimized for the different substrates by using a catalytic amount of $Sn(NTf_2)_4$ (5 mol %). Two solvents, nitromethane and dichloroethane, turned out to be the best reaction media. The influence of the malonate unit was first studied with diprenyl-substituted derivatives **1a**–**6a** (Table 2, entries 1–6). In comparing ethyl and methyl malonates **1a** and **2a**, the reactions conducted under several experimental conditions led to similar selectivities and reactivities. Both cyclohexane derivatives **1b** and **2b** were obtained selectively in about 90 % yield under mild conditions (from room temperature to 40 °C). Under more severe reaction conditions, a cyclization involving one ester group became competitive. Thus, in refluxing dichloroethane (83 °C), the cycloisomerization of **2a** led to the corresponding cyclohexane derivative **2b** in lower yield (58 %), together with a by-product (10 % yield), which was identified as the δ-lactone **2c**. This lactone by-product is the result of an intramolecular cyclization involving one ester unit and one of the double bonds.[24] It is interesting to note that this reaction between an alkene and the ester moiety may become the dominant reaction when less substituted double bonds (with lower nucleophilicity) are present in the diene (see Table 2, entry 12).



2c

When one malonate ester group was replaced by a nitrile (Table 2, entry 3) or an ethyl ketone (entry 4), the corresponding cycloisomerization products were still obtained selectively in yields of 70–74 %. However, the malononitrile analogue (with two nitrile groups) was unreactive. This may indicate that the ester oxygen atom(s) play an important role in the mechanism of the cycloisomerization. Sulfone **5a** and phosphate **6a** (entries 5 and 6) also afforded the corresponding highly substituted cyclohexane structures **5b** and **6b**, respectively, arising from the head-to-tail diene cycloisomerization.

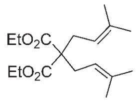
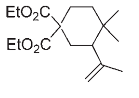
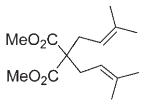
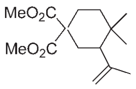
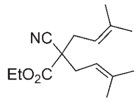
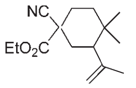
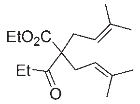
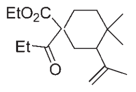
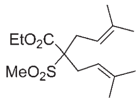
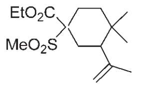
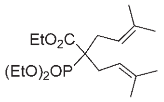
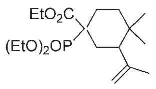
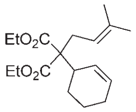
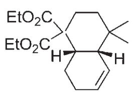
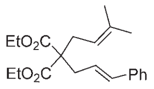
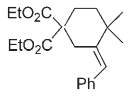
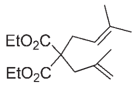
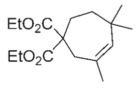
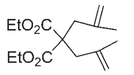
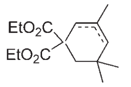
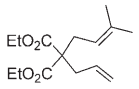
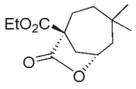
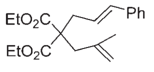
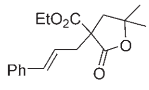
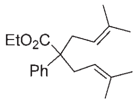
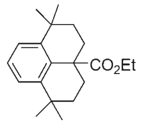
The influence of the double-bond substitution upon cycloisomerization was further examined with substrates **7a**–**12a** (Table 2, entries 7–12).[25] The transformation of these substrates proceeded with satisfactory yields and selectivities. The common structural feature of the cyclic products is the presence of the *gem*-dimethyl group at the cycloalkane skeleton, indicating that the C–C bond-forming step always occurs at the more substituted site of the double bond. It is also worth noting that the substitution pattern of the second (less substituted) double bond influences the cyclization in several ways: 1) When the second allyl group is substituted at the terminal alkene carbon, the usual cyclohexane structures are formed selectively (Table 2, entries 7–10). 2) Substrates with a terminal (mono- or disubstituted) double bond such as **9a** and **11a** (Table 2, entries 9 and 11) yielded cycloheptene and cycloheptane derivatives **9b**[26] and **11b**, respectively. Whereas the *gem*-dimethyl cycloheptene derivative **9b** was obtained selectively, in the case of **11a** the reaction was less efficient: instead of a single carbocyclic product, we could isolate only the bridged bicyclic lactone derivative **11b** in low yields (22 %) as the result of a cascade of C–C and C–O couplings, 3) With less substituted (less nucleophilic) double bonds such as in **12a** (Table 2, entry 12), C–C bond formation is disfavoured, and a C–O coupling reaction occurs between one of the double bonds and one of the ester groups (as mentioned before) to give **12b** in selectively 70 % yield.

Another point of interest was the competition between olefinic and aromatic double bonds in the C–C bond-forming step. When a phenyl group is present as in **13a** (Table 2, entry 13), a double cyclization occurs very selectively affording tricyclic compound **13b** in 78 % yield. Each of the double bonds of the diene reacts preferentially with an aromatic ring by C–H activation in a catalytic process (Table 2, entry 13).[27–28]

To evaluate whether other strong acids are also effective catalysts, the reaction of **1a** was carried out in the presence of $HNTf_2$. The cyclization giving **1b** occurred in 80 % yield;[29a] however, no conversion was observed with **3a.**[29b] With other olefins, the presence of this super acid led to partial or complete polymerization. These results indicate that the Lewis acid catalyst $Sn(NTf_2)_4$ has a different reactivity and is more effective than the protic acid $HNTf_2$ for the cycloisomerization of highly substituted 1,6-dienes. We tested a mixture of $Sn(NTf_2)_4/HNTf_2$ (1:1, 5 mol % each) for the cyclization of **1a** in a Brønsted acid assisted Lewis acid catalyzed process,[30] but the results were not better than those obtained with $Sn(NTf_2)_4$ alone.

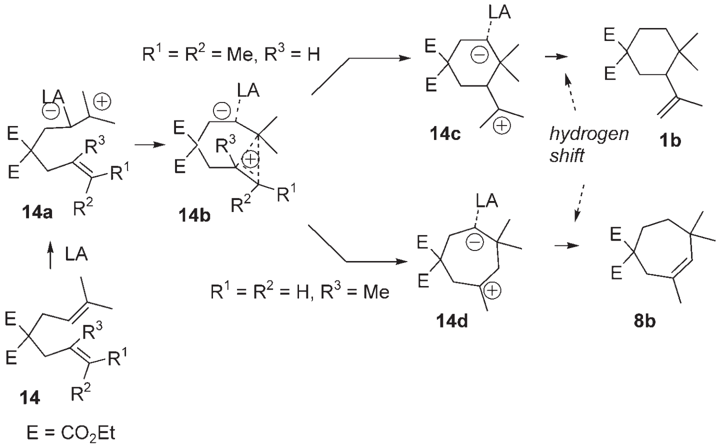
The possibility of a partial hydrolysis of $Sn(NTf_2)_4$ by reaction with traces of water was also considered. Preliminary kinetic studies carried out with **1a** and added water in distinct quantities. Whereas traces of water had almost no effect on either the reaction rate or the yield, the reaction rate decreased notably after the addition of greater amounts of water (up to 2 equiv H_2O with respect to the catalyst). At the

Table 2: Cycloisomerization of 1,6-dienes with $Sn(NTf_2)_4$ (5 mol%).

Entry	Substrate		*t* [h]	Solvent, *T* [°C]	Conversion [%]	Product (Yield [%])	
1		**1a**	4 2.5	$Cl(CH_2)_2Cl$, 40 CH_3NO_2, 25	100 100		**1b** (92) **1b** (92)
2		**2a**	5	$Cl(CH_2)_2Cl$, 40	100		**2b** (88)
3		**3a**	2	CH_3NO_2, 101	80		**3b** (70), 1 isomer
4		**4a**	5	CH_3NO_2, 25	90		**4b,c** (74), 2 diastereomers
5		**5a**	5	CH_3NO_2, 40	100		**5b** (74), 1 isomer
6		**6a**	5	CH_3NO_2, 101	59		**6b** (46), 1 isomer
7		**7a**	3	CH_3NO_2, 60	100		**7b** (88), 1 isomer
8		**8a**	5	$Cl(CH_2)_2Cl$, 60	100		**8b** (70)
9		**9a**	1	CH_3NO_2, 101	100		**9b** (61)
10		**10a**	1	CH_3NO_2, 101	100		**10b,c** (61), 0.69:1
11		**11a**	5	CH_3NO_2, 101	54		**11b** (22)
12		**12a**	6	CH_3NO_2, 101	75		**12b** (70)
13		**13a**	130	CH_3NO_2, 101	100		**13b** (78)

same time, the amount of by-products increased considerably. The importance of the acidity of the Sn^{IV} catalyst system was further demonstrated after the addition of 2,6-di-*tert*-butylpyridine as a highly hindered base ($Sn(NTf_2)_4$/base 1:1). Under these conditions, the cyclization of **1a** was completely inhibited.

We do not know yet the exact mechanism of these cycloisomerizations. However, all our results seem to point in favor of a carbocationic-type mechanism. The 1,6-dienes with the more substituted double bonds were the most efficient and selective substrates in the cyclization reaction. The product formation may be explained as the result of a first coordination of the Lewis acid to the more electron-rich double bond, followed by the coupling of the second less electron-rich olefin at the more substituted end of the first olefin (Scheme 1). The ester group present should also participate in the coordination to the Sn^{IV}. Thus, the electrophilic-type addition of the Lewis acid to the isobutenyl group of **14** gives an intermediate zwitterion **14a**, which is stabilized by the second alkene group in **14b**. The ring-closing step (C–C bond formation) is controlled by the stability of the carbocation intermediates **14c** and **14d**, which depends on the



Scheme 1. Cycloisomerization of 1,6-dienes and competition between the formation of six- and seven-membered rings (LA = Lewis acid).

substitution of the second olefin. Though in most reactions a six-membered ring formed, cycloheptanes were obtained in two cases. The ring-size specificity is explained by the predominance of the more stable (tertiary) cationic carbon center in **14c** and **14d**, respectively (Scheme 1).

This mechanistic proposition does not involve protic acids. However, the role of protons (from residual water) in the catalytic process cannot be completely excluded.[30] The combination of Brønsted and Lewis acids has been reported as a particularly useful tool in several efficient reactions in asymmetric catalysis.[31] Nevertheless, for the moment we have no experimental support for the direct interaction of protons in association with Lewis acids in the cycloisomerization of 1,6-dienes.

The enhancement of the electrophilic alkene activation in dimerization reactions by highly charged transition-metal complexes has been recently reported and is now well established.[19] However, the use of Lewis acids for this purpose is much less developed. The role of tin derivatives in olefin polymerization has also been emphasized.[32] Catalyst design is important since the action of strong Lewis acid anions (OTf$^-$, SbF$_5^-$) combined with cationic palladium complexes leads to quite uncontrolled isomerization processes in 1,6-dienes.[33]

In conclusion, we have found that Sn(NTf$_2$)$_4$ is a powerful catalyst for the cycloisomerization of malonate-type highly substituted 1,6-dienes. The present transformation provides simple and selective procedure for the preparation of highly functionalized six-membered-ring carbocyclic systems. Moreover, the development of new catalysts for diene cycloisomerization broadens the field of atom-economic cyclization processes.[34]

Experimental Section

General cyclization procedure: A mixture of the 1,6-diene (1 mmol) and Sn(NTf$_2$)$_4$ (0.05 mmol) was stirred under nitrogen at the reported temperature in distilled dichloroethane or nitomethane (5 mL). The progress of the reaction was monitored by GC analysis. The reaction products were hydrolyzed by addition of water (10 mL) and extracted with ether (3 × 10 mL). The combined organic phases washed with brine and dried over MgSO$_4$. After filtration and evaporation of the solvent, the products were purified by flash chromatography on silica gel. The compounds **1b**–**13b** were characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and high-resolution MS or elemental analysis. Compounds **3b**, **5b**, **6b**, and **7b** were obtained as single diastereomers. Compounds **4b,c** were obtained as a 1.2:1 mixture of diastereomers; the configuration could not be determined by NMR experiments. The *cis* configuration of **7b** was established according to the Karplus rules. The *E* configuration of **8b** was established by NOESY NMR experiments.

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Keywords: cyclization · dienes · Lewis acids · six-membered rings · tin

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of 1,7-dienes to give cyclohexanes, see Ref. [4]; c) For the conversion of 1,5-dienes to give cyclohexanes, see T. Kato, S. Kumazawa, Y. Kitahara, *Synthesis* **1972**, 573 – 575.

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[26] NMR data for **9b** : ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 5.08$ (1H, s), 4.11 (4H, q, $J = 7.3$ Hz), 2.55 (2H, s), 2.14 (2H, m), 1.67 (3H, s), 1.48 (2H, m), 1.18 (6H, t, $J = 7.4$ Hz), 0.93 ppm (6H, s); ^{13}C NMR (126 MHz, CDCl$_3$): $\delta = 172.38$ (2C), 136.44, 130.28, 61.56 (2C), 57.06, 44.98, 36.10, 35.94, 30.27 (2C), 29.96, 28.14, 14.39 ppm (2C); NOESY $\delta = 5.08$ ppm correlates with $\delta =$ 0.93 ppm.

[27] For transition-metal-catalyzed intramolecular hydroarylation of alkenes, see for example: S. W. Youn, S. J. Pastine, D. Sames, *Org. Lett.* **2004**, *6*, 581 – 584.

[28] These alkene arylation reactions will be developed in a separate research project.

[29] a) Reaction conditions: 5 mol% Tf$_2$NH, nitromethane, 2.5 h at 25 °C. b) Reaction conditions: 5 mol% Tf$_2$NH, nitromethane, 5 h at 101 °C.

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[32] We do not observe any reaction of **1a** with either concentrated HCl or *p*-toluene sulfonic acid in dichloroethane (60 °C, 3 h).

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