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Lewis Acid Mediated Thienium Cation Diels-Alder Reaction: A New Method for Regio- and Stereoselective Functionalization of 1,3-Dienes

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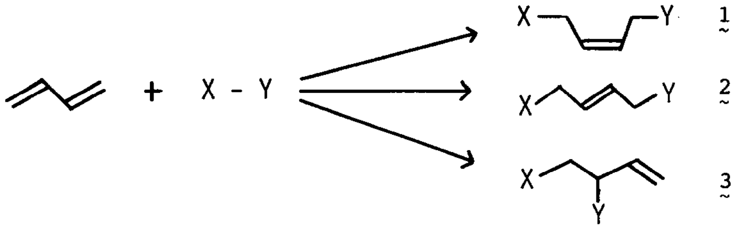
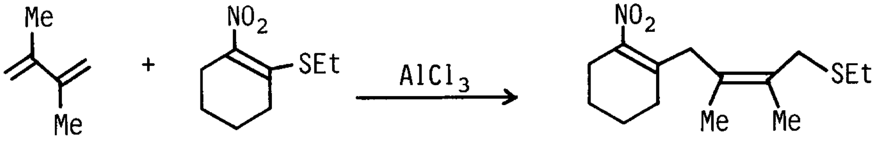
Summary: Under the influence of aluminum chloride the β-ethylthionitroolefin results in the formation of the thienium cation, which reacts with a variety of 1,3-dienes in the Diels-Alder sense. The cleavage of the resulting ring provides in one pot the 1,4-functionalized olefins in regio- and stereoselective manner.

The electrophilic addition reaction of 1,3-diene with an electrophile (XY) may lead to the formation of three types of products **1**, **2**, and **3** as shown in Scheme 1. Generally, 1,2-addition is the predominant mode in electrophilic additions to 1,3-dienes.[1] Moreover, steroselective formation of either isomer **1** or **2** is difficult to attain, even if 1,4-addition mode is successfully performed. The most prevailing method of choice for achieving Z-functionalization of 1,3-dienes in 1,4-fashion with complete regio- and stereoselectivity is the two-step process involving Diels-Alder cycloadditions with heterodienophiles[2] followed by the cleavage of the resulting ring.[3] Here, we wish to report totally regio- and stereoselective one-pot transformation of 1,3-dienes leading to Z-olefins such as **1**, where X is a β-nitroolefinic moiety and Y is the ethylthio group.

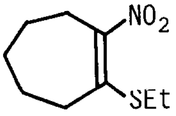
Scheme 1. Possible Products from the Electrophilic Addition of X-Y to 1,3-Dienes.



Reaction of the 1-ethylthio-2-nitrocyclohexene[4] (**4**) with 10 eq. of 2,3-dimethylbutadiene in the presence of aluminum chloride in dichloromethane at 0°C for 1 h afforded a single product in 84% yield. (based on the consumed nitroolefin), the structure of which was tentatively assigned to be as *Z*-olefin **8** based on the sprectral data. Optimum yields were obtained by using 2 eq. of aluminum chloride and 10 eq. of diene. The geometry of the olefin **8** was expected to be *Z* by its way of formation and this supposition was subsequently confirmed by detailed analysis of its 400 MHz ^{1}H-NMR spectrum[5] including decoupling and NOE experiments. Results obtained from the various combinations of dienes and nitroolefins **4** - **7** are listed in Table I.



4 **8**



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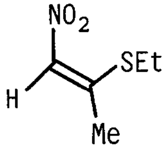

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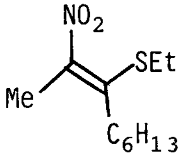

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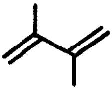
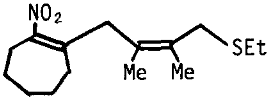
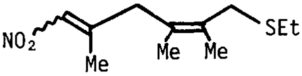
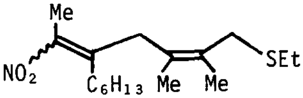
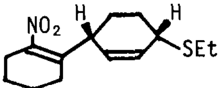
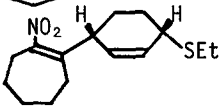
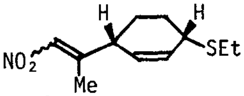
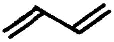
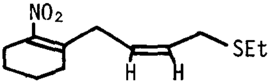
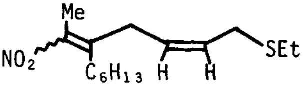
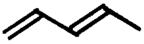
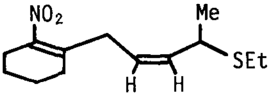
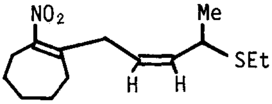
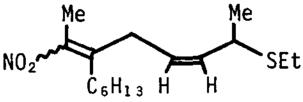
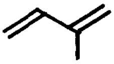
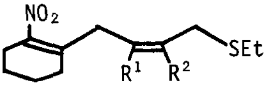
Several noteworthy features of this reaction are as follows. 1) Completely regioselective 1,4-addition of the ethylthio group and the nitroolefinic moiety to 1,3-diene takes place. 2) Steroselective formation of *Z*-olefin is observed in all cases. 3) Cyclohexadiene affords 1,4-cis-disubstituted cyclohexenes stereoselectively. 4) The nitroolefinic moiety predominantly adds to the electron-rich terminus in diene system, when an unsymmetrical diene is employed (entries 9 - 12).

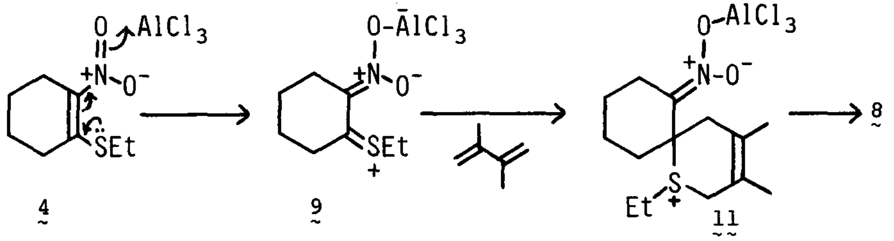
All the above mentioned remarkable features can be rationalized on the basis of the hard-hard interaction of aluminum chloride and the oxygen atom of nitro group in the β-ethylthionitroolefin **4** resulting in the formation of the thienium cation **9**. The addition of thienium cation **9** to dienes in the Diels-Alder sense affords adducts of type **10** (Scheme 2). Although there is no direct evidence for these processes, *in situ* opening of the resulting ring provides 1,4-addition products. Thus, the overall process completes the 1,4-functionalization of 1,3-dienes in highly selective manner.

Table 1. Reaction of Nitroolefins 4 - 7 with Dienes.

Entry	Diene	Nitroolefin	Product[a,b]	Isolated yield %
1		5		86
2	〃	6		65
3	〃	7		84(93)[c]
4		4		54
5	〃	5		58
6	〃	6		71
7		4		79
8	〃	7		58
9		4		61(83)[c]
10	〃	5		82
11	〃	7		63(73)[c]
12		4		68[d]

a) All new compounds have been fully characterized by spectral means and have satisfactory combustion analysis or high-resolution peak matching. b) Geometry represented by a wavy line was not determined. c) Numbers in parentheses are the yields based on the consumed starting material. d) A mixture of two isomers (R^1 = Me, R^2 = H and R^1 = H, R^2 = Me) in a 6:1 ratio.

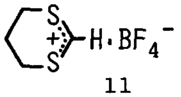
Scheme 2.



To our knowledge, the present reaction represents the second example of utilizing the thienium cation as a dienophile in the Diels-Alder cycloaddition reaction.[6,7] The work to explore the scope of this reaction in the synthesis of natural products is now in progress in our laboratory.

References and Notes

1. For example see: V. L. Heasley and S. K. Taylor, J. Org. Chem., 1969, 34, 2779.
2. For and extensive review, see: S. M. Weinreb and R. R. Staib, Tetrahedron, 1982, 38, 3087.
3. For an elegant application of this methodology to the natural product synthesis, see: S. M. Weinreb and R. S. Garigipati, J. Am. Chem. Soc., 1983, 105, 4499.
4. M. Node, T. Kawabata, M. Fujimoto, and K. Fuji, Synthesis, 1984, 234.
5. ^{1}H-NMR data for 8 at 400 MHz in $CDCl_3$: δ 1.25 (t, *J*=7.5 Hz, 3H), 1.58 (s, 3H), 1.60 (m, 2H), 1.73 (m, 2H), 1.79 (s, 3H), 2.09 (m, 2H), 2.48 (q, *J*=7.5 Hz, 2H), 2.59 (m, 2H), 3.18 (s, 2H), 3.23 (s, 2H).
6. Very recently, a $[2^+ + 4]$ polar cycloaddition of α-chlorosulfides with conjugated dienes has been reported: H. Ishibashi, Y. Kitano, H. Nakatani, M. Okada, M. Ikeda, M. Okura, and Y. Tamura, Tetrahedron Lett., 1984, 25, 4231.
7. 1,3-Dithienium fluoroborate (11) has been used as a dienophile in the Diels-Alder reaction.[8]



11

8. E. J. Corey and S. W. Walinsky, J. Am. Chem. Soc., 1972, 94, 8932.

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