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β-SULFONYLNITROOLEFINS AS VERY REACTIVE ALKYNE-EQUIVALENTS IN DIELS-ALDER REACTIONS

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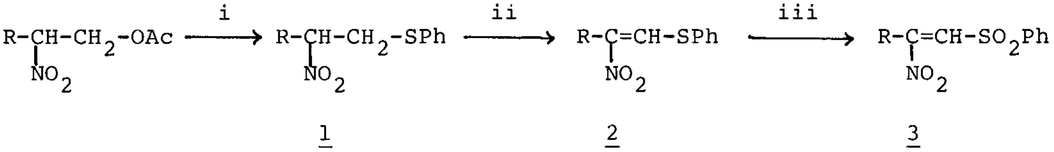
Summary: Very reactive dienophiles, β-sulfonylnitroolefins, are prepared starting from β-nitro alcohols. The high activation due to the nitro and the sulfonyl groups promotes the Diels-Alder reaction to various dienes under mild conditions. Reductive elimination of the adduct with Bu_3SnH gives cyclic 1,4-dienes.

As alkenes and alkynes are generally poor dieophiles, activated equivalents of alkenes and alkynes are often required to get cyclic olefins or cyclic 1,4-dienes, especially polycyclic compounds by the Diels-Alder reaction. Various synthons, for example, nitroolefins,1) vinyl sulfoxide,2) vinyl sulfone,3) (E)- or (Z)-1,2-bis(phenylsulfonyl)ethylene,4) maleic anhydride,5) and 1,4-benzodithiin 1,1,4,4-tetraoxide6) have been used for this purpose. Among them 1,2-bis(phenylsulfonyl)ethylene has been used as the most useful acetylene-equivalent for the preparation of complex polycyclic compounds.7) In this paper we wish to report the preparation of a more reactive alkyne-equivalent, β-sulfonylnitroolefin (3). This compound was prepared by oxidation of β-phenylthionitroolefin (2), which was prepared by chlorination of β-nitro sulfide (1) and the subsequent elimination of HCl. Procedures are shown in Scheme 1 and the results are summarized in Table 1. As the present method starts from β-nitro alcohols, various kinds of 3 can be prepared by this method.8)

The Diels-Alder reaction of 3 with various dienes was carried out under the conditions listed in Table 2. In all cases, the thermal reaction proceeds very smoothly without any catalysts to afford the corresponding cycloadducts in good yields as shown in Table 2. Thus, 3 displays very high reactivity and regio-selectivity toward various dienes. For example, 3a reacts with furan at room temperature and the reaction is complete within 7 h to give the adduct in 89% yield. The intermolecular cycloaddition of furans is generally difficult owing to the reversible nature of this reaction.[9)] High reactivity of 3 overcomes this difficulty.

When unsymmetrical dienes are used, the reaction proceeds regioselectively as shown in entry 6, 7, 9, 10, and 11. Namely, the nitro group controls the direction of the addition more effectively than the sulfonyl group.

Scheme 1. Preparation of β-Sulfonylnitroolefins (3)



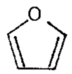
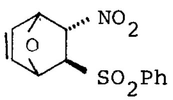
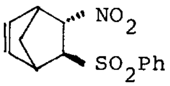
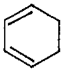
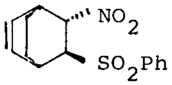
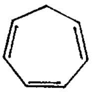
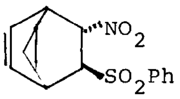
(i) PhSH, Et_3N, CH_3CN, 0 °C, 2 h (ii) SO_2Cl_2, CH_2Cl_2, 0 °C, 10 min; Et_3N, 0 °C, 30 min (iii) m-Chloroperbenzoic acid (2 equiv), $CHCl_3$, 60 °C, 3 h

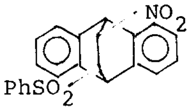
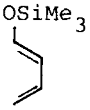
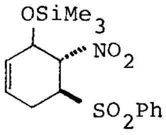
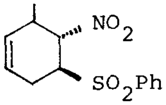
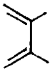
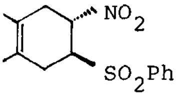
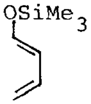
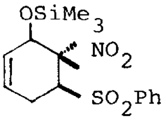
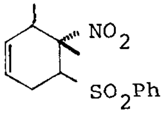
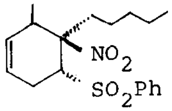
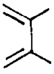
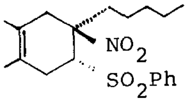
Table 1. Preparation of 1, 2, and 3

	R	1, yield, %[a)]	2, yield, %[a)] (E/Z)[b)]	3, yield, %[a)] (E/Z)[b)]
a	H	96	87 (1/0)	53 (1/0)
b	Me	95	88 (1/1)	88 (1/1)
c	n-C_5H_{11}	90	88 (1/1)	87 (1/1)

(a) Yield after purification by colum chromatography (b) Determined by NMR[10)]

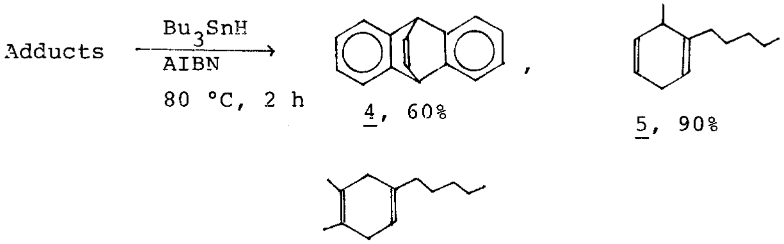
Table 2. Diels-Alder Reaction of 3

entry	Dienophile	Conditions	Diene	Product[a)]	yield, %[b)]
1	3a	20 °C, 7 h CH_2Cl_2			89
2	3a	20 °C, 0.5 h CH_2Cl_2			82
3	3a	110 °C, 6 h toluene			94
4	3a	110 °C, 12 h toluene			93

5	3a	110 °C, 3 h toluene			90
6	3a	110 °C, 1.5 h toluene			76
7	3a	110 °C, 4 h toluene			95
8	3a	110 °C, 1.5 h toluene			97
9	3b	110 °C, 3 h toluene			78
10	3b	110 °C, 18 h toluene			85
11	3c	140 °C, 9 h xylene			78
12	3c	110 °C, 24 h toluene			75

(a) The nitro group is located at the endo or exo position whose ratio is about 1 : 1. (b) Yield after isolation by recrystallization.

Adducts were readily converted into the corresponding dienes on treatment with Bu_3SnH in the presence of azobisisobutyronitrile (AIBN, 0.2 equiv) at 80 °C for 2 h,11) or other reducing agents such as sodium sulfide.12) Hydrocarbons, 3, 5, and 6 were prepared by elimination of the nitro and the sulfonyl groups from the adduct of entry 5, 11, and 12, respectively, with Bu_3SnH. It should be emphasized that 5 can be prepared regioselectively. Thus, 3 (R = H) can be regarded as a regio-cotrolled equivalent of alkynes in the Diels-Alder reaction.



4, 60%

5, 90%

6, 81%

References and notes

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8) The present paper is the first preparation of β-sulfonylnitroolefins. The preparation of β-alkylthionitroolefins starting from α-nitro ketones was reported recently, however, compounds 2 can not be prepared by this method, see, M. Node, T. Kawabata, M. Fujimoto, K. Fuji, Synthesis, 234 (1984).

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10) Vinylic protons of (E)-2 and (E)-3 are strongly deshielded by anisotropic effect of the nitro group. So the E/Z ratio was readily determined.

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