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Synthesis and Consecutive Double Diels-Alder Cycloadditions of 3-Methylene-5-phenylsulfinyl-1-pentene as a Synthetic Equivalent of Parent Cross-conjugated Triene, 3-Methylene-1,4-pentadiene

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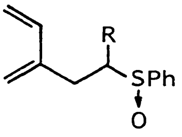
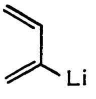
3-Methylene-5-phenylsulfinyl-1-pentene undergoes stepwise double Diels-Alder cycloadditions with two different dienophiles to afford hydronaphthalene skeletons. This sequence corresponds to cross type of diene-transmissive Diels-Alder cycloaddition of parent 3-methylene-1,4-pentadiene.

Since the first demonstration of diene-transmissive Diels-Alder reaction of 3-benzylidene-2,4-bis(trimethylsilyloxy)-1,4-pentadiene,1) a variety of cross-conjugated trienes and triene equivalents have been dedicated to this reaction system.2) Although parent cross-conjugated triene, 3-methylene-1,4-pentadiene, has been long known, the Diels-Alder reaction of this ready-to-polymerize molecule is too intractable to be utilized in organic synthesis.3) There is so far no example known for the cross type of diene-transmissive Diels-Alder reaction of the parent triene or its synthetic equivalent.4)

The present communication describes the efficient synthesis of 3-methylene-5-phenylsulfinyl-1-pentene (1) as a synthetic equivalent of parent 3-methylene-1,4-pentadiene and its consecutive Diels-Alder cycloadditions with two different dienophiles. This is the first example of reaction equivalents for the cross type of diene-transmissive Diels-Alder reaction of 3-methylene-1,4-pentadiene.

Although the triene equivalent 1 could be prepared by the Michael addition of 2-lithio-1,3-butadiene (3)5) to phenylsulfinylethene (4), a comparable amount of 3-methylene-5,7-bis(phenylsulfinyl)-1-heptene (2) was always accompanied under all the examined conditions. Consequently, the yield of 1 never exceeded 38% even under the optimized conditions.6,7) The inevitable formation of 2 has resulted


1: R = H
2: R = CH_2CH_2SOPh
6: R = $SiMe_3$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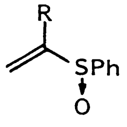
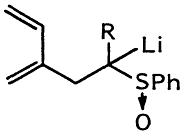
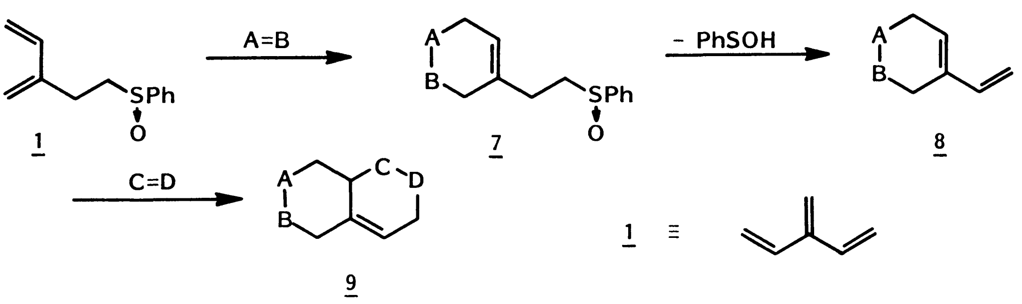

4: R = H
5: R = $SiMe_3$


A: R = H
B: R = $SiMe_3$

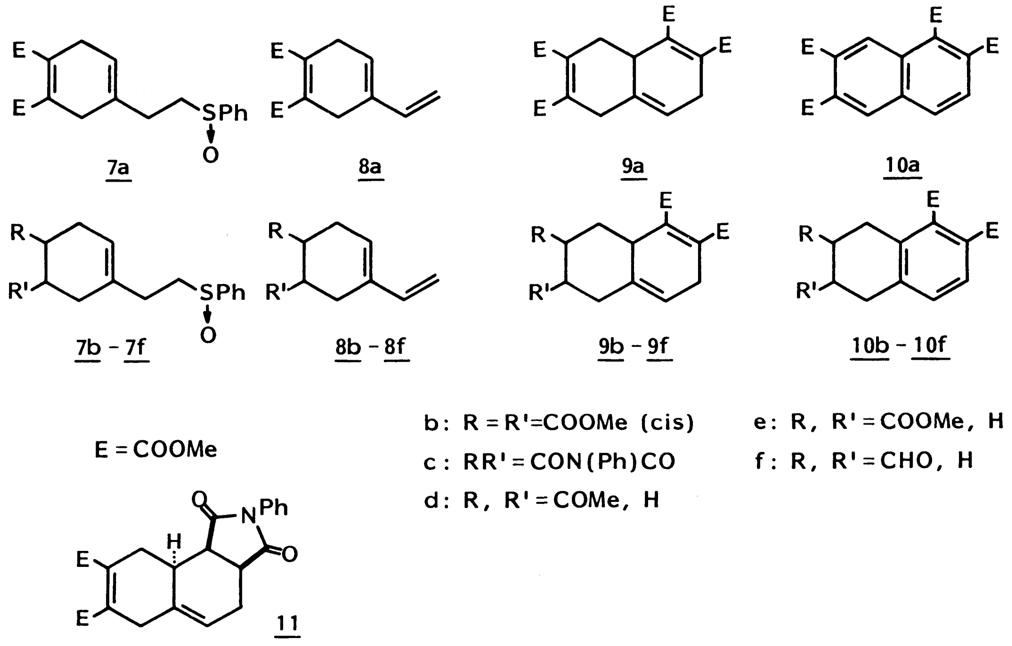


Scheme 1.

from the competitive Michael addition of 5-lithio-3-methylene-5-phenylsulfinyl-1-pentene (A) as the initial adduct with 4.

In the hope of the inhibition of this undesired reaction, 1-phenylsulfinyl-1-trimethylsilylethene (5) was employed instead of 4. The expected 1:1 adduct, 5-lithio-3-methylene-5-phenylsulfinyl-5-trimethylsilyl-1-pentene (B), bears a sterically hindered nucleophilic center so that the further Michael addition of B may become extremely unfavorable. In this case, however, it is necessary to solve a newly arising problem that the hydrolyzed 1:1 adduct 6 might undergo sila-Pummeler rearrangement losing the phenylsulfinyl moiety.8) Fortunately, smooth desilylation of 6 took place on its treatment with a fluoride anion in aqueous medium. Thus, the reaction of 3 with an equimolar amount of 5 was carried out in dry THF at -78 °C for 40 min and then quenched with a solution of tetrabutylammonium fluoride (TBAF) in aqueous THF at the same temperature. This procedure gave 73% yield of 1 after chromatographic purification on silica gel.

With the desired triene equivalent 1 in hand, its double Diels-Alder reaction sequence was next examined as shown in Scheme 1: The initial Diels-Alder reaction



b: R = R'=COOMe (cis)
c: RR' = CON(Ph)CO
d: R, R' = COMe, H
e: R, R' = COOMe, H
f: R, R' = CHO, H

Scheme 2.

with a dienophile (A=B) produces monocycloadduct 7. Thermal elimination of benzenesulfinic acid from 7 reveals a diene moiety 8 whose second Diels-Alder reaction with another dienophile (C=D) gives cross biscycloadduct 9.

As it was found later that benzenesulfinic acid was slowly eliminated when the monocycloadduct 7 was heated under reflux in benzene, the initial Diels-Alder reaction has to be conducted around 50-60 °C or below. But, the Diels-Alder reaction of 1 under these conditions was impractically slow. Use of a certain Lewis acid is necessary, while there is no example known for the Lewis acid-catalyzed Diels-Alder reactions of the dienes or dienophiles carrying a sulfinyl substituent.[9]

Among the catalysts tested, ethylaluminum dichloride and stannyl chloride were found to accelerate the cycloaddition to a significant extent. Thus, the reaction of 1 with a variety of dienophiles proceeded smoothly under mild conditions in the presence of the Lewis acid catalysts to give cycloadducts 7a-7f (Table 1 and Scheme 2). However, the regioselectivity in the reactions with unsymmetrical olefins was not so high as expected (para:meta=94:6 to 80:20).[10]

Table 1. Double Diels-Alder Cycloaddition of 1

Diene	Dienophile	Catalyst[a] (equiv.)	Solvent[b]	Temp/°C	Time/h	Product	Yield/%[c]
1	DMAD	-	BZ	50	54	7a	75
		AL (2.0)	DCM	rt	24		52[d]
1	dimethyl maleate	AL (2.0)	DCM	rt	7	7b	75
1	N-phenylmaleimide	AL (2.0)	DCM	rt	3	7c	83
1	3-buten-2-one[e]	SN (2.0)	DCM	rt	2	7d	93[f]
		SN (3.0)	DCM	-78	5		85[g]
		SN (5.0)	DCM	-78	15 min		55[h]
1	methyl acrylate[e]	AL (2.0)	DCM	rt	24	7e	69[i]
1	acrolein[e]	SN (2.0)	DCM	rt	1	7f	86[j]

Precursor	Diene generation[b]	Cycloaddition with DMAD[b]	Products (yield/%)[k]	
7a	reflux in T, 22 h	one-pot	-	10a (68)[l]
7b	reflux in T, 24 h	reflux in T, 25 h	9b (81)	10b (80)
7c	reflux in T, 22 h	one-pot	9c (82)	10c (100)
7d	reflux in T, 24 h	reflux in BZ, 72 h	9d (84)	10d (73)
7e	reflux in T, 23 h	reflux in T, 28 h	9e (59)	10e (81)
7f	reflux in T, 24 h	reflux in T, 24 h	9f (24)	-

a) AL: ethylaluminum dichloride; SN: stannyl chloride. b) BZ: benzene; DCM: dichloromethane; T: toluene. c) Isolated yield. d) 28% of 1 was recovered. e) The meta:para ratios in the reactions without catalyst: 7d (50 °C, 7 d, 96%, 70:30); 7e (50 °C, 14 d, 85%, 69:31); 7f (50 °C, 54 h, 75%, 70:30). f-j) The meta:para ratios are as follows: f: 87:13; g: 91:9; h: 94:6; i: 80:20; j: 92:8. k) The yields of 9 and 10 are based on 7 and 9, respectively. Aromatization was carried out by heating 9 with chloranil in toluene for 1 to 3 d. l) Based on 7a. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was used.

The cycloadducts 7 eliminated benzenesulfinic acid when heated under reflux in toluene, and the dienes 8a-8f generated were trapped by dimethyl acetylenedicarboxylate (DMAD) to give cross biscycloadducts 9a-9f (Scheme 2 and Table 1). As the sulfinic acid readily adds to DMAD and the resulting adduct is hardly separable from 9, we first removed the sulfinic acid by filteration of the reaction mixture through a column packed with silica gel and then the crude dienes 8a-8f were subjected to the second cycloaddition. These cross biscycloadducts 9 were dehydrogenated with chloranil or DDQ to give naphthalene 10a, or tetrahydronaphthalene derivatives 10b-10f in good yields.

The second Diels-Alder reaction can be carried out as well with an olefinic dienophile. For example, the stereoselective cross biscycloadduct 11 was obtained in the one-pot reaction of 7a with N-phenylmaleimide in 76% yield.

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2) a) O. Tsuge, E. Wada, S. Kanemasa, and H. Sakoh, Bull. Chem. Soc. Jpn., 57, 3221 (1984); b) O. Tsuge, S. Kanemasa, H. Sakoh, and E. Wada, ibid., 57, 3234 (1984); c) O. Tsuge, E. Wada, and S. Kanemasa, Chem. Lett., 1984, 469 and 709; d) S. Kanemasa, H. Sakoh, E. Wada, and O. Tsuge, Bull. Chem. Soc. Jpn., 58, 3312; e) S. Kanemasa, H. Sakoh, E. Wada, and O. Tsuge, ibid., 59, 1869 (1986).
3) A. T. Blomquist and J. A. Verdol, J. Am. Chem. Soc., 77, 81 (1955); W. J. Bailey and J. Economy, ibid., 77, 1133 (1955); W. J. Bailey, C. H. Cunov, and L. Nicholas, ibid., 77, 2787 (1955).
4) It was orally presented that 3-methylene-5-phenylthio-1-pentene could be serve as a synthetic equivalent of 3-methylene-1,4-pentadiene (H. Sano, Y. Ueno, and M. Okawara, The 45th Annual Meeting of Chemical Society of Japan (Tokyo), Preprint II, p. 973 (1982)).
5) 2-Lithio-1,3-butadiene 3 is readily available from 2-chloro-1,3-butadiene by its conversion to 2-tributylstannyl-1,3-butadiene and the subsequent transmetallation (E. Wada, S. Kanemasa, I. Fujiwara, and O. Tsuge, Bull. Chem. Soc. Jpn., 58, 1942 (1985)).
6) The yield was based on 4 which was used in half an equimolar amount of 3.
7) A diluted solution of the Michael acceptor 4 in THF (60 ml per 3 mmol of 4) was slowly added, in a period of 6 h at -78 °C, to the Michael donor 3 (two equiv. in THF). The mixture was allowed to react for 1 h at this temperature. Usual hydrolytic work-up gave 1 (38%) and 2 (38%) (yields based on 4).
8) The sulfoxide 6 undergoes facile sila-Pummeler rearrangement when kept to stand at room temperature.
9) The efficient use of ethylaluminum dichloride in the Diels-Alder reaction of the diene bearing a sulfonyloxy substituent with 3-butene-2-one is known (Ref. 2e).
10) As Lewis acid-catalyzed Diels-Alder reactions: T. C. Ehlert and J. L. Margrave, J. Am. Chem. Soc., 86, 3899 (1964); T. Inukai and T. Kojima, J. Org. Chem., 31, 1121, 2032 (1966), and ibid., 35, 1342 (1970).

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