Regioselective Preparation of Cyclohexadienes or Aromatic Nitro Compounds by Diels–Alder Reactions of β-Sulfonylnitroolefins or β-Sulfinylnitroethylene

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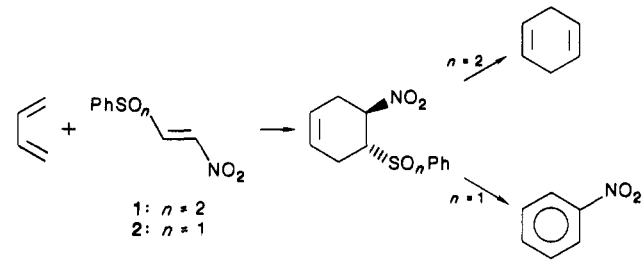
β-Sulfonylnitroolefins react with various dienes to give 4-nitro-5-(phenylsulfonyl)cyclohexenes under mild conditions, where the nitro group controls the direction of the addition more effectively than the sulfonyl group. Subsequent treatment of the adducts with Bu_3SnH results in the reductive elimination of the nitro and sulfonyl groups to give 1,4-cyclohexadienes. The Diels–Alder reaction of β-sulfinylnitroethylene with dienes and subsequent thermal elimination of sulfenic acid give 1-nitro-1,4-cyclohexadienes, which are readily aromatized to give nitrobenzene derivatives. Thus, β-sulfonylnitroolefins or β-sulfinylnitroethylene is regarded as alkynes or nitroacetylene equivalents for the Diels–Alder reaction, respectively.

Cyclohexene or 1,4-cyclohexadiene derivatives are important synthetic intermediates of the preparation of polycyclic compounds. The most direct approach to them is the Diels–Alder reaction of alkenes or alkynes to 1,3-dienes. Although the Diels–Alder reaction has been used extensively for the preparation of cyclic compounds,[1] simple alkenes or alkynes such as ethylene or acetylene have not been used frequently as dienophiles owing to the low reactivity of them.[2,3] Consequently, various synthetic equivalents of alkenes or acetylene have been explored so far.[4] For example, vinyl sulfones[5] and nitroolefins[6] serve as effective alkene equivalents, and (trimethylsilyl)vinyl sulfone,[5] ethynyl sulfone,[7] vinyl sulfoxide,[8] (*E*)- or (*Z*)-1,2-bis(phenylsulfonyl)ethylene,[9] maleic anhydride,[10] and 1,4-benzodithiin-1,1,4,4-tetraoxide[11] serve as effective acetylene equivalents. Although they can serve as acetylene equivalents, they cannot serve as general alkyne equivalents because of their low reactivity to the Diels–Alder reaction owing to steric factors. Thus, the discovery of general alkyne equivalents in the Diels–Alder reaction has been of interest.

In previous papers we reported the preparation of new types of electron-deficient olefins; β-sulfonylnitroolefins **1** and β-sulfinylnitroethylene **2**.[12] As they are activated by two strongly electron-withdrawing groups, they act as excellent dienophiles for the Diels–Alder reaction. Further, the Diels–Alder adducts of **1** or **2** have potentially useful functional groups, which may be converted into 1,4-cyclohexadienes or aromatic nitro compounds as shown in Scheme I.

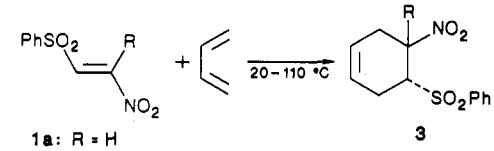
Scheme I



In this paper, we report the Diels–Alder reaction of **1** and **2** and the use of **1** or **2** as synthetic equivalents of alkynes or nitroacetylene, respectively.

Results and Discussion

Diels–Alder Reaction of 1. (*E*)-1-Nitro-2-(phenylsulfonyl)ethylene (**1a**) and alkyl-substituted β-sulfonylnitroolefins (**1b**, R = CH_3; **1c**, R = C_5H_{11}) were prepared by the oxidation of the corresponding sulfides. The Diels–Alder reaction of **1a**, **1b**, and **1c** with various dienes was carried out by stirring a mixture of **1** and dienes in an appropriate solvent at 20–110 °C (eq 1). Some of the



(1)

pure products were readily isolated from the reaction mixture by adding pentane and cooling the reaction mixture as described in the Experimental Section. The results are summarized in Table I. The Diels–Alder reaction of **1** proceeds under milder reaction conditions than that of other electron-deficient olefins which can act as acetylene equivalents.[5-11] It is noteworthy that the reaction of furan with **1a** proceeds at room temperature to give the Diels–Alder adducts **3b** in good yield. The intermolecular cycloaddition of furan is often encountered by the difficulty of the reversibility in cycloaddition reaction.[13] However, this problem is not serious in the reaction of **1a**, for **1a** is so reactive as dienophiles of the Diels–Alder reaction to

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(2) Bartlett, P. D.; Schueller, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 6071.

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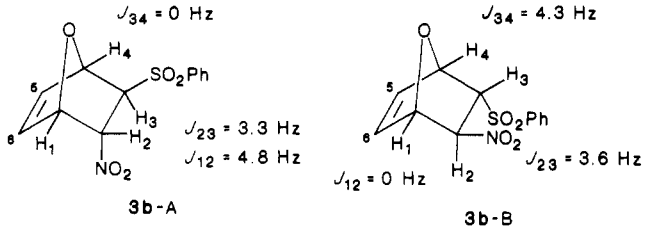
(11) Nakayama, J.; Nakamura, Y.; Hoshino, M. *Heterocycles* **1985**, *23*, 1119.

(12) Ono, N.; Kamimura, A.; Kaji, A. *J. Org. Chem.* **1986**, *51*, 2139. Ono, N.; Kamimura, A.; Kaji, A. *Tetrahedron. Lett.* **1986**, *27*, 1595.

(13) Viera, E.; Vogel, P. *Helv. Chim. Acta* **1982**, *65*, 1700. Klein, L. L.; Deeb, T. M. *Tetrahedron Lett.* **1985**, *26*, 3935.

0022-3263/88/1953-0251$01.50/0

Scheme II



give the adduct exclusively. More importantly, **1b** or **1c** which has an alkyl substituent at the C=C bond has still enough reactivity toward various dienes to give **3**. In general, the reactivity of olefins as dienophiles is greatly reduced by alkyl substituents. However, this reducing effect of the reactivity can be cancelled by two strongly activating group of the nitro and sulfonyl functions.

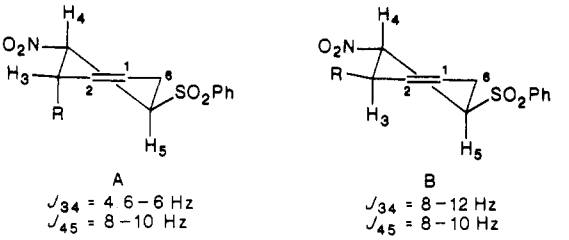
Stereo- and regiochemistry of the reaction of **1** are interesting problems; which of two groups controls them more effectively? To answer this question, the products were analyzed by HPLC or 400-MHz ^{1}H NMR. It was found that most of compounds **3** consisted of a pair of diastereoisomers except the case of **3d**, **3e**, and **3l**. The ratio of them was determined by ^{1}H NMR or HPLC as shown in Table I. The isomers were readily separated into each isomer by column chromatography (silica gel/benzene–hexane 7:3), and their structures were determined by 400-MHz ^{1}H NMR. As the α-protons to the nitro and sulfonyl groups show well-resolved resonances, they are especially helpful for the structural elucidation. They are summarized in Table II.

The reaction of **1** with cyclic dienes gives a pair of stereoisomers. For example, the reaction of **1a** with furan gave **3b**-A (mp 110–113 °C) and **3b**-B (mp 168–170 °C) in a ratio of 63:37. **3b**-A displays H_2 (C*H*-NO_2) as a doublet of doublets (J = 3.3 Hz, 4.8 Hz) at δ 5.38 and H_3 (C*H*-SO_2Ph) as a doublet (J = 3.3 Hz) at δ 3.82. As J_{34} in **3b**-A is 0 Hz, this suggests the nitro-endo structure of **3b**-A as shown in Scheme II.[14] The stereochemistries of other bicyclic adducts were determined in this way.

The reaction of **1** with acyclic dienes gave cyclohexene derivatives substituted by the nitro and sulfonyl groups. When **1a** and 1-substituted dienes were used as in entries 6–8, two isomers A and B were formed. As the α-hydrogen to the nitro in both A and B appears as a doublet of doublets or a triplet in ^{1}H NMR spectra, the nitro group should be located at the β-position of substituents such as $(CH_3)_3SiO$, CH_3, or C_7H_{15}. Thus, the direction of the addition is controlled mainly by the nitro group. Two isomers produced in this reaction should be the stereoisomers as shown in Scheme III. It is reasonable that the two large groups of the nitro and sulfonyl groups are assumed to be located at the pseudoequatorial positions. The stereochemistries of these adducts can be determined by comparing coupling constants (J_{34}) of isomer A with isomer B. The smaller coupling constant of A indicates that this isomer should be a 3,4-cis,4,5-trans isomer, and the larger one of B indicates that this isomer should be a 3,4,5-all-trans isomer.

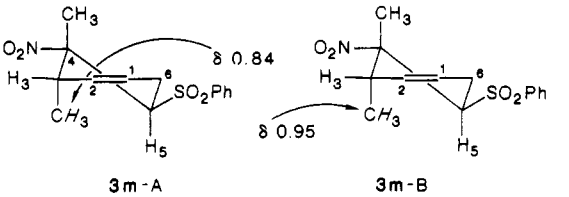
The reaction of **1b** or **1c** with acyclic dienes gave also two stereoisomers (entries 13, 14, 16). For example, the reaction of **1b** and (*E*)-1,3-pentadiene gave **3m**-A and **3m**-B in a ratio of 51:49. Pure **3m**-A and **3m**-B were separated by column chromatography. The structures of **3m**-A and

Scheme III[a]

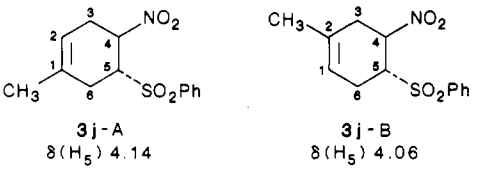


[a] R = $(CH_3)_3SiO$, CH_3, C_7H_{15}.

Scheme IV



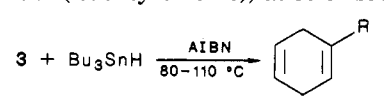
Scheme V



3m-B can be elucidated by the chemical shift of the methyl group at the C-3 position as shown in Scheme IV. Namely, the methyl group at the pseudoequatorial position should appear at a lower field than that of the opposite position due to the strong anisotropic effect of the nitro group.

The reaction of **1** with isoprene or myrcene gave a mixture of regioisomers, respectively. The structures of the adducts **1a** with isoprene are shown in Scheme V. Their structures are readily assigned by decoupling experiments. The α-proton to the sulfonyl group appeared at δ 4.14 and 4.06, respectively. When the proton at 4.14 was irradiated, the proton at C-6 turned to a singlet. On the other hand the proton became a doublet by irradiation at δ 4.06.

Reductive Elimination of 3. β-Nitro sulfones undergo reductive elimination to give corresponding alkenes on treatment with reducing agents such as sodium sulfide or tin radicals.[15] Then compounds **3** were treated with tributyltin hydride in the presence of catalytic amounts of AIBN (α,α-azobis(isobutyronitrile)) at 80 or 110 °C (eq 2).



(2)

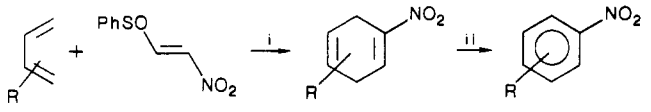
4

The results are summarized in Table III. When the nitro group was attached at the tertiary carbon, the elimination reaction took place at 80 °C, and elimination from the secondary nitro compounds required higher temperature. The overall reactions consisted of the Diels–Alder reaction of **1** and the reductive elimination with tin hydride to provide a useful method for the preparation of cyclic dienes as shown in Scheme I. Thus, **1** can be regarded as 1-alkyne equivalents and the direction of the addition is well controlled.

(14) Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie International Inc.: Deerfield Beach, FL, 1982.

(15) Ono, N.; Miyake, H.; Hamamoto, I.; Tamura, R.; Kaji, A. *Chem. Lett.* **1981**, 1139. Ono, N.; Kamimura, A.; Kaji, A. *Tetrahedron Lett.* **1984**, *25*, 5319.

Diels–Alder Reaction of 2. β-Sulfinylnitroethylene **2** was prepared by the oxidation of the corresponding sulfide with 1 equiv of *m*-CPBA.[12] The Diels–Alder reaction of **2** promises a potential utility as a nitroacetylene equivalent. Nitroacetylene itself is too unstable to be used in the Diels–Alder reaction.[16] Heating a mixture of **2** and dienes in an appropriate solvent at 110 °C gave cyclic nitro dienes **5**, where the Diels–Alder reaction and subsequent thermal elimination of sulfenic acid took place successively. Oxidation of **5** with DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) gave aromatic nitro compounds **6** (eq 3). The

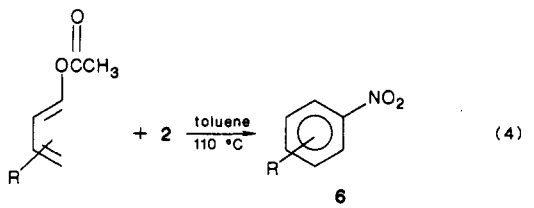


(3)

(i) toluene, 110 °C, 2 h; (ii) DDQ, benzene, 80 °C, 2 h

results are summarized in entries 1–4 of Table IV. Thus, *o*-alkyl-substituted nitrobenzenes can be prepared regioselectively by this method. However, the selectivity for the preparation of para-substituted nitrobenzenes by this method was very low, and it was very difficult to prepare meta-substituted ones by this method.

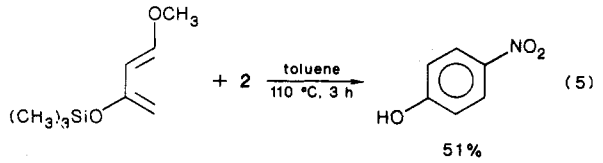
We have found a simple method for the preparation of meta- or para-substituted nitrobenzenes, which were difficult to be prepared by the reaction of eq 3. When 1-acetoxy-1,3-butadienes, which were readily prepared from α,β-unsaturated aldehydes, were used as dienes, the acetoxy group controlled the regiochemistry more effectively than the alkyl group, and the elimination of acetic acid took place in situ[17] to give meta- or para-substituted nitrobenzenes **6** regioselectively (eq 4). The results are



(4)

summarized in entries 5–9 in Table IV. The procedure is simple. Heating a mixture of **2** and 1-acetoxy-1,3-butadienes in toluene at 110 °C gave **6**, and oxidizing reagents such as DDQ were not required. It should be noted that not only para-substituted nitrobenzenes but also meta-substituted nitrobenzenes are obtained with perfect regioselectivity by this procedure.

When 1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene[18] was used as the diene, the reaction of this compound with **2** gave *p*-nitrophenol selectively (eq 5).



(5)

The present method for the preparation of aromatic nitro compounds starting from aliphatic substrates is complementary to the existing method by the nitration of aromatic compounds,[19] since, as well as being more regioselective, various kinds of nitro compounds and heteroatom-substituted dienes are available.[20]

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a JOEL-FX-400 spectrometer at 400 MHz. Alternatively a JEOL-PS-100 spectrometer at 100 MHz was used. Infrared spectra were recorded on a Hitachi 215 spectrometer. Mass spectra were recorded on a JEOL-DX-300/JMA-3100 mass spectrometer. High-performance liquid chromatography (HPLC) analyses were carried out with a Simadzu Model LC-6A chromatograph. GLC analyses were carried out on a Simadzu GC-8A chromatograph. Elemental analyses were performed in the microanalytical room, Institute for Chemical Research, Kyoto University. Compounds **1** and **2** were prepared by the previously reported method.[12]

Diels–Alder Reaction of 1. Prepration of 2-Nitro-3-(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (3a). Typical Procedure: A mixture of **1a** (0.26 g, 1.22 mmol) and freshly distilled cyclopentadiene (0.49 g, 7.42 mmol) in CH_2Cl_2 (7 mL) was stirred for 0.5 h at 25 °C. The reaction mixture was poured into pentane (30 mL) and cooled to −78 °C. A white precipitate was formed and collected by filtration to give **3a** (0.28 g, 82%). This **3a** was a mixture of **3a**-A and **3a**-B whose ratio was 75/25, which were separated into pure **3a**-A and **3a**-B by column chromatography (silica gel/benzene–hexane 3:7).

3a-A: mp 162 °C; NMR δ ($CDCl_3$) 8.10–7.40 (m, 5 H), 6.46 (d, d, J = 3.2 Hz, 5.5 Hz, 1 H), 6.12 (d, d, J = 2.7 Hz, 5.5 Hz, 1 H), 5.33 (t, J = 3.9 Hz, 1 H), 3.70 (d, d, J = 1.5 Hz, 3.9 Hz, 2 H), 3.50 (d, d, J = 1.5 Hz, 3.0 Hz, 1 H), 2.28 (d, J = 9.8 Hz, 1 H), 1.71 (d, d, d, J = 1.8 Hz, 3.9 Hz, 9.8 Hz, 1 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{13}H_{13}NO_4S$: C, 55.90; H, 4.69; N, 5.01. Found: C, 56.02; H, 4.68; N, 4.89. **3a-B**: mp 143.5–144.5 °C; NMR δ ($CDCl_3$) 8.10–7.40 (m, 5 H), 6.53 (d, d, J = 2.8 Hz, 5.5 Hz, 1 H), 6.31 (d, d, J = 3.7 Hz, 5.2 Hz, 1 H), 4.71 (d, d, J = 0.6 Hz, 3.7 Hz, 1 H), 4.36 (t, J = 3.5 Hz, 1 H), 3.51 (s, 1 H), 3.38 (s, 1 H), 1.89 (d, J = 9.8 Hz, 1 H), 1.77 (d, d, J = 0.6 Hz, 9.8 Hz, 1 H). Found: C, 56.37; H, 4.79; N, 4.84.

Preparation of 3-Methyl-4-nitro-5-(phenylsulfonyl)-cyclohexene (3g). Typical Procedure: A mixture of **1a** (0.43 g, 2.02 mmol) and (*E*)-1,3-pentadiene (0.6 mL, 6.0 mmol) in toluene (10 mL) was stirred at 110 °C for 4 h. The solvent was evaporated, and the residue was subjected to column chromatography (silica gel/benzene–hexane 3:7) to give two isomers of **3g**, **3g**-A, 0.26 g (46%), and **3g**-B, 0.28 g (49%).

3g-A: mp 62 °C; NMR δ ($CDCl_3$) 7.90–7.58 (m, 5 H), 5.71 (d, t, d, J = 1.8 Hz, 3.7 Hz, 10.1 Hz, 1 H), 5.64 (t, d, d, J = 1.8 Hz, 3.6 Hz, 10.0 Hz, 1 H), 5.21 (d, d, J = 6.1 Hz, 8.0 Hz, 1 H), 4.03 (q, J = 7.7 Hz, 1 H), 3.05–3.00 (m, 1 H), 2.63–2.60 (m, 2 H), 1.01 (t, J = 8 Hz, 3 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98. Found: C, 55.24; H, 5.32; N, 4.94. **3g-B**: mp 84 °C; NMR δ ($CDCl_3$) 7.91–7.58 (m, 5 H), 5.64 (t d d, J = 2.7 Hz, 4.9 Hz, 9.8 Hz, 1 H), 5.46 (q, d, J = 2.1 Hz, 10.1 Hz, 1 H), 4.52 (d, d, J = 9.5 Hz, 11.3 Hz, 1 H), 4.02 (d t, J = 6.7 Hz, 11.3 Hz, 1 H), 2.85–2.82 (m, 1 H), 2.63–2.45 (m, 2 H), 1.11 (d, J = 7.0 Hz, 3 H). Found: C, 55.55; H, 5.35; N, 4.97.

The Following compounds **3** were prepared by these procedures.

3b-A: mp 110–113 °C; NMR δ ($CDCl_3$) 7.96–7.48 (m, 5 H), 6.72 (d, d, J = 1.8 Hz, 5.8 Hz, 1 H), 6.43 (d, d, J = 1.8 Hz, 5.8 Hz, 1 H), 5.56 (d, d, J = 1.2 Hz, 1.8 Hz, 1 H), 5.52 (d, d, d, J = 1.2 Hz, 1.8 Hz, 4.8 Hz, 1 H), 5.38 (d, d, J = 3.3 Hz, 4.8 Hz, 1 H), 3.82 (d, J = 3.3 Hz, 1 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1280. Anal. Calcd for $C_{12}H_{11}NO_5S$: C, 51.24; H, 3.94; N, 4.98. Found: C, 51.52; H, 4.00; N, 4.74. **3b-B**: mp 168–170 °C; NMR δ ($CDCl_3$) 7.96–7.48 (m, 5 H), 6.86 (d, d, J = 1.5 Hz, 5.8 Hz, 1 H), 6.64 (d, d, J = 1.9 Hz, 5.8 Hz, 1 H), 5.54 (d, d, J = 0.9 Hz, 1.8 Hz, 1 H), 5.34 (d, d, d, J = 0.9 Hz, 1.4 Hz, 4.3 Hz, 1 H), 4.82 (d, J = 3.6 Hz, 1 H), 4.52 (d, d, J = 3.6 Hz, 4.3 Hz, 1 H). Found: C, 51.96; H, 4.08; N, 4.82.

3c-A: mp 153.5–155 °C; NMR δ ($CDCl_3$) 7.88–7.38 (m, 5 H), 6.56 (d, d, J = 2 Hz, 6 Hz, 1 H), 6.14 (d, d, J = 2 Hz, 6 Hz, 1 H),

(16) Jung, M. E.; Grove, D. D. *J. Chem. Soc., Chem. Commun.* **1987**, 753 and references therein.

(17) In this case, acetoxynitrocyclohexadiene was not detectable. See: Koreeda, M.; Ciufolini, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 2308.

(18) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807. Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400.

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Table I. Diels–Alder Reaction of β-Sulfonylnitroolefins 1

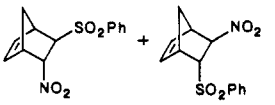
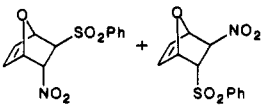
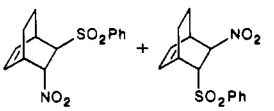
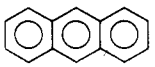
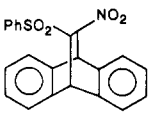
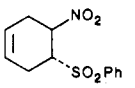
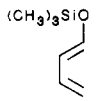
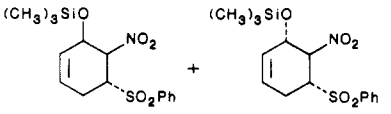
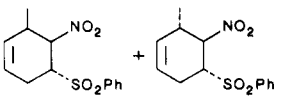
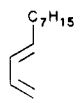
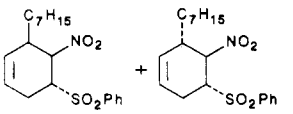
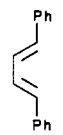
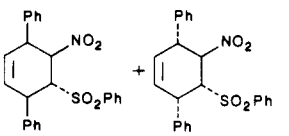
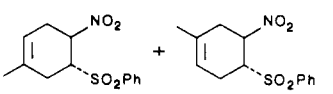
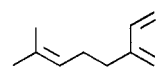
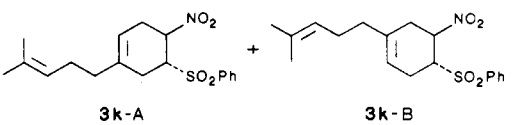
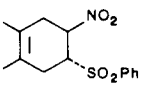
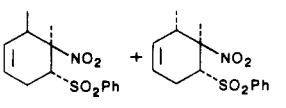
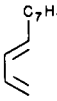
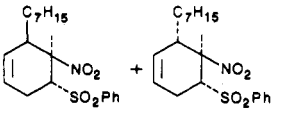
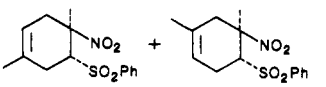
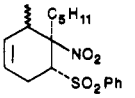
entry	1	dienes	conditions	adducts (3)	yield (%)[a]	A/B
1	**1a**		CH_2Cl_2, 20 °C, 0.5 h	 **3a**-A **3a**-B	82	75/25[b]
2	**1a**		CH_2Cl_2, 20 °C, 7 h	 **3b**-A **3b**-B	89	63/37[c]
3	**1a**		toluene, 110 °C, 6 h	 **3c**-A **3c**-B	94	59/41[d]
4	**1a**		toluene, 110 °C, 3 h	 **3d**	90	
5	**1a**		toluene, 110 °C, 6 h	 **3e**	60	
6	**1a**		toluene, 110 °C, 1.5 h	 **3f**-A **3f**-B	81	48/52[b]
7	**1a**		toluene, 110 °C, 4 h	 **3g**-A **3g**-B	95	43/57[b]
8	**1a**		toluene, 110 °C, 3 h	 **3h**-A **3h**-B	95	47/53[b]
9	**1a**		toluene, 110 °C, 18 h	 **3i**-A **3i**-B	91	*e*
10	**1a**		toluene, 110 °C, 3 h	 **3j**-A **3j**-B	99	60/40[b]
11	**1a**		toluene, 110 °C, 4 h	 **3k**-A **3k**-B	85	50/50[b]
12	**1a**		toluene, 110 °C, 1.5 h	 **3l**	97	
13	**1b**		toluene, 110 °C, 18 h	 **3m**-A **3m**-B	85	51/49[b]

Table I (Continued)

entry	1	dienes	conditions	adducts (3)	yield (%)[a]	A/B
14	**1b**		toluene, 110 °C, 40 h	 **3n-A** + **3n-B**	67	40/60[d]
15	**1b**		toluene, 110 °C, 20 h	 **3o-A** + **3o-B**	77	65/35[d]
16	**1c**		xylene, 140 °C, 10 h	 **3p**	78	*e*

[a] Isolated yield. [b] Determined by 400-MHz ^{1}H NMR. [c] Determined by 10/-MHz ^{1}H NMR. [d] Determined by HPLC. [e] Not determined.

Table II. ^{1}H NMR Data for the α-Proton to the Nitro or Sulfonyl Group of Cycloadducts 3

adducts	$CHNO_2$ (ppm)	$CHSO_2Ph$ (ppm)
3a-A	5.33 (t, J = 3.9 Hz)	3.70 (d, d, J = 1.5, 3.9 Hz)
3a-B	4.71 (d, d, J = 0.6, 3.7 Hz)	4.36 (t, J = 3.5 Hz)
3b-A	5.38 (d, d, J = 3.3, 4.8 Hz)	3.82 (d, J = 3.3 Hz)
3b-B	4.82 (d, J = 3.6 Hz)	4.52 (d, d, J = 3.6, 4.3 Hz)
3c-A	5.01 (d, d, J = 2.7, 4.8 Hz)	3.89 (t, d, J = 2.2, 4.4 Hz)
3c-B	4.75 (d, d, d, J = 1.5, 3.0, 5.5 Hz)	4.20 (d, d, J = 1.3, 5.5 Hz)
3d	5.10 (d, d, J = 2, 4 Hz)	4.36 nd, d, J = 2, 4 Hz)
3e	5.04 (q, J = 7.0 Hz)	4.11 (q, J = 6.6 Hz)
3f-A	5.01 (d, d, J = 4.6, 10.5 Hz)	4.34 (t, d, J = 8.2, 10.4 Hz)
3f-B	4.65 (d, d, J = 8.2, 11.9 Hz)	4.03 nd, t, J = 6.7, 11.6 Hz)
3g-A	5.21 (d, d, J = 6.1, 8.0 Hz)	4.03 (q, J = 7.7 Hz)
3g-B	4.52 (d, d, J = 9.5, 11.3 Hz)	4.02 (d, t, J = 6.7, 11.3 Hz)
3h-A	5.27 (t, J = 5.9 Hz)	4.01 (t, d, J = 6.4, 7.0 Hz)
3h-B	4.67 (t, J = 10.5 Hz)	4.01 (d, t, J = 6.7, 11.0 Hz)
3i-A	5.56 (d, d, J = 6.8, 10.2 Hz)	4.33 (d, d, J = 8.9, 10.2 Hz)
3i-B	5.26 (d, d, J = 10.0, 10.5 Hz)	4.41 (d, d, J = 5.5, 10.5 Hz)
3j-A	4.98 (q, J = 8 Hz)	4.15 (q, J = 8 Hz)
3j-B	5.06 (q, J = 8 Hz)	4.06 (q, J = 8 Hz)
3k-A	*a*	4.36 (q, J = 8 Hz)
3k-B	*a*	4.30 (q, J = 8 Hz)
3l	5.00 (q, J = 8 Hz)	4.10 (q, J = 8 Hz)
3m-A	(1.97 (s))[b]	4.28 (d, d, J = 7.0, 11.3 Hz)
3m-B	(1.74 (s))[b]	4.28 (d, d, J = 6.4, 11.6 Hz)
3n-A	(1.95 (s))[b]	4.31 (d, d, J = 7.3, 11.0 Hz)
3n-B	(1.72 (s))[b]	4.25 (d, d, J = 6.4, 11.3 Hz)
3o-A	(1.89 (s))[b]	4.37 (d, d, J = 6.4, 11.0 Hz)
3o-B	(1.90 (s))[b]	4.26 (d, d, J = 6.4, 11.0 Hz)

[a] Not specified. [b] δ (ppm) at H_3CCNO_2.

5.01 (d, d, J = 2.7 Hz, 4.8 Hz, 1 H), 3.89 (t, d, J = 2.2 Hz, 4.4 Hz, 1 H), 3.46 (t, d, J = 2.5 Hz, 3.2 Hz, 1 H), 3.36 (d, d, j = 2.9 Hz, 6.5 Hz, 1 H), 2.32 (t, d, d, J = 3.4 Hz, 9.8 Hz, 12.8 Hz, 1 H), 1.87 (d, d, d, d, J = 2.1 Hz, 5.1 Hz, 9.8 Hz, 12.9 Hz, 1 H), 1.53 (d, d, t, J = 3.7 Hz, 4.0 Hz, 12.6 Hz, 1 H), 1.17 (t, d, t, J = 2.3 Hz, 4.6 Hz, 12.6 Hz, 1 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{14}H_{15}NO_4S$: C, 57.32; H, 5.15; N, 4.78. Found: C, 57.76; H, 5.22; N, 4.80. **3c-B**: mp 129–131 °C; NMR δ ($CDCl_3$) 7.88–7.38 (m, 5 H), 6.48 (d, d, J = 2 Hz, 6 Hz, 1 H), 6.36 (d, d, J = 2 Hz, 6 Hz, 1 H), 4.75 (d, d, d, J = 1.5 Hz, 3.0 Hz, 5.5 Hz, 1 H), 4.20 (d, d, J = 1.3 Hz, 5.5 Hz, 1 H), 3.35 (d, d, J = 2.7 Hz, 6.4 Hz, 1 H), 3.21 (t, d, J = 1.5 Hz, 3.6 Hz, 1 H), 1.70 (t, d, d, J = 2.8 Hz, 9.8 Hz, 12.8 Hz, 1 H), 1.51 (d, d, t, J = 2.1 Hz, 4.3 Hz, 13.4 Hz, 1 H), 1.43 (t, t, J = 3.8 Hz, 12.5 Hz, 1 H), 1.26 (t m, J = 10.1 Hz, 1 H). Found: C, 57.26; H, 5.19; N, 4.72.

3d: mp 84–87 °C; NMR δ ($CDCl_3$) 7.85–7.10 (m, 13 H), 5.10 (d, d, J = 2 Hz, 4 Hz, 1 H), 5.06 (d, J = 2 Hz, 1 H), 5.00 (d, J = 2 Hz, 1 H), 4.36 (d, d, J = 2 Hz, 4 Hz, 1 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{22}H_{17}NO_4S$: C, 67.50; H, 4.38; N, 3.58. Found: C, 67.62; H, 4.43; N, 3.63.

3e: mp 91 °C; NMR δ ($CDCl_3$) 7.93–7.59 (m, 5 H), 5.71–5.65 (m, 2 H), 5.04 (q, J = 7 Hz, 1 H), 4.11 (q, J = 6.6 Hz, 1 H), 2.90–2.76 (m, 2 H), 2.53–2.50 (m, 2 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{12}H_{13}NO_4S$: C, 53.92; H, 4.90; N, 5.24. Found: C, 53.93; H, 4.87; N, 5.19.

3f-A: mp 111–112 °C; NMR δ ($CDCl_3$) 7.90–7.50 (m, 5 H), 5.90 (t, d, J = 4.0 Hz, 9.8 Hz, 1 H), 5.82–5.78 (m, 1 H), (d, d, J = 4.6 Hz, 10.5 Hz, 1 H), 4.70 (t, J = 4.6 Hz, 1 H), 4.34 (t, d, J = 8.2 Hz, 10.4 Hz, 1 H), 2.40 (d, d, d, J = 2.2 Hz, 3.6 Hz, 8.3 Hz, 2 H), 0.41 (s, 9 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{15}H_{21}NO_5SiS$: C, 50.68; H, 5.96; N, 3.94. Found: C, 50.40; H, 5.71; N, 4.00. **3f-B**: mp 143–144 °C; NMR δ ($CDCl_3$) 7.90–7.50 (m, 5 H), 5.67 (quintet, d, J = 2.4 Hz, 10.1 Hz, 1 H), 5.53 (d, d, d, J = 1.9 Hz, 4.3 Hz, 10.1 Hz, 1 H), 4.75 (d, t, d, J = 2.1 Hz, 3.0 Hz, 8.2 Hz, 1 H), 4.65 (d, d, J = 8.2 Hz, 11.9 Hz, 1 H), 4.03 (d, t, J = 6.7 Hz, 11.6 Hz, 1 H), 2.64 (t, d, d, d, J = 1.9 Hz, 4.5 Hz, 6.2 Hz, 18.0 Hz, 1 H), 2.46 (q, d, d, J = 2.9 Hz, 10.6 Hz, 18.0 Hz, 1 H), 0.72 (s, 9 H). Found: C, 51.00; H, 5.91; N, 3.93.

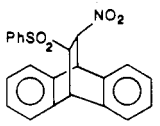
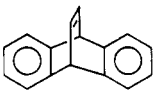
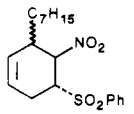
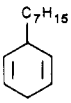
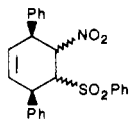
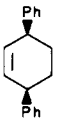
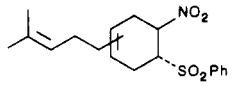
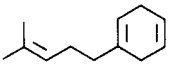
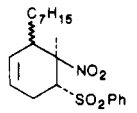
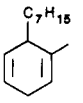
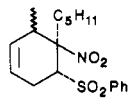
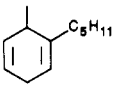
3h-A: mp 41–42 °C; NMR δ ($CDCl_3$) 7.91–7.59 (m, 5 H), 5.76 (d, d, d, J = 1.8 Hz, 3.6 Hz, 11.9 Hz, 1 H), 5.70 (d, d, d, J = 1.8 Hz, 3.6 Hz, 10.1 Hz, 1 H), 5.27 (t, J = 5.9 Hz, 1 H), 4.01 (t, d, J = 6.4 Hz, 7.0 Hz, 1 H), 2.84 (m, 1 H), 2.62 (d, d, J = 1.8 Hz, 3.6 Hz, 2 H), 1.64–1.25 (m, 12 H), 0.87 (t, J = 7.0 Hz, 3 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{19}H_{27}NO_4S$: C, 62.44; H, 7.45; N, 3.83. Found: C, 62.75; H, 7.83; N, 3.80. **3h-B**: mp 64–64.5 °C; NMR δ ($CDCl_3$) 7.91–7.57 (m, 5 H), 5.69–5.65 (m, 1 H), 5.57 (d, J = 10.0 Hz, 1 H), 4.67 (t, J = 10.5 Hz, 1 H), 4.01 (d, t, J = 6.7 Hz, 11.0 Hz, 1 H), 2.78 (m, 1 H), 2.61–2.45 (m, 2 H), 1.49–1.24 (m, 12 H), 0.87 (t, J = 7.5 Hz, 3 H). Found: C, 62.70; H, 7.66; N, 3.72.

3i-A: mp 197–199 °C; NMR δ ($CDCl_3$) 7.72–7.40 (m, 15 H), 5.91 (d, d, d, J = 1.0 Hz, 2.1 Hz, 10.0 Hz, 1 H), 5.87 (d, d, d, J = 2.1 Hz, 3.6 Hz, 10.1 Hz, 1 H), 5.56 (d, d, J = 6.8 Hz, 10.2 Hz, 1 H), 4.39 (d, d, d, J = 2.4 Hz, 4.5 Hz, 8.9 Hz, 1 H), 4.33 (d, d, J = 8.9 Hz, 10.2 Hz, 1 H), 4.36–4.31 (m, 1 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{24}H_{21}NO_4S$: C, 68.72; H, 5.05; N, 3.34. Found: C, 68.90; H, 5.16; N, 3.16. **3i-B**: mp 77–81 °C; NMR δ ($CDCl_3$) 7.72–7.16 (m, 15 H), 5.99 (d, d, d, J = 3.0 Hz, 5.0 Hz, 9.8 Hz, 1 H), 5.83 (t, d, J = 1.4 Hz, 9.8 Hz, 1 H), 5.26 (d, d, J = 10.0 Hz, 11.5 Hz, 1 H), 4.63 (t, J = 5.5 Hz, 1 H), 4.41 (d, d, J = 5.5 Hz, 10.5 Hz, 1 H), 4.09 (d, d, J = 1.5 Hz, 10.0 Hz, 1 H). Found: C, 68.32; H, 4.89; N, 3.27.

3j-A: mp 64–69 °C; NMR δ ($CDCl_3$) 7.92–7.58 (m, 5 H), 5.36 (m, 1 H), 4.98 (q, J = 8 Hz, 1 H), 4.15 (q, J = 8 Hz, 1 H), 2.80–2.73 (m, 2 H), 2.44–2.38 (m, 2 H), 1.68 (s, 3 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98. Found: C, 55.54; H, 5.41; N, 4.80. **3j-B**: NMR δ ($CDCl_3$) 7.92–7.58 (m, 5 H), 5.36 (m, 1 H), 5.06 (q, J = 8 Hz, 1 H), 4.06 (q, J = 8 Hz, 1 H), 2.73–2.68 (m, 2 H), 2.49–2.44 (m, 2 H).

3k-A: oil; NMR δ ($CDCl_3$) 8.00–7.44 (m, 5 H), 5.45–5.30 (m, 1 H), 5.20–4.70 (m, 2 H), 4.36 (q, J = 8 Hz, 1 H), 2.88–2.64 (m, 2 H), 2.64–2.38 (m, 2 H), 2.20–1.88 (m, 4 H), 1.66 (s, 3 H), 1.58 (s, 3 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1220. Anal. Calcd for $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63; N, 4.01. Found: C, 60.94; H, 6.42;

Table III. Preparation of 1,4-Cyclohexadienes 4

entry	3	conditions	products (4)	yield (%)[a]
1	 **3d**	Bu_3SnH (3.5 equiv), AIBN (0.8 equiv), toluene, 110 °C, 0.5 h	 **4a**	60
2	 **3h**	Bu_3SnH (3.5 equiv), AIBN 0.8 equiv), toluene, 110 °C, 0.5 h	 **4b**	79
3	 **3i**	Bu_3SnH (3.5 equiv), AIBN (0.8 equiv), toluene, 110 °C, 0.5 h	 **4c**	65
4	 **3k**	Bu_3SnH (3.5 equiv), AIBN (0.8 equiv), toluene, 110 °C, 0.5 h	 **4d**	63
5	 **3n**	Bu_3SnH (1.3 equiv), AIBN (0.3 equiv), benzene, 80 °C, 2 h	 **4e**	76
6	 **3p**	Bu_3SnH (1.3 equiv), AIBN (0.3 equiv), benzene, 80 °C, 2 h	 **4f**	79

[a] Isolated yield.

N, 3.66. **3k-B**: NMR δ ($CDCl_3$) 8.00–7.44 (m, 5 H), 5.45–5.30 (m, 1 H), 5.20–4.70 (m, 2 H), 4.30 (q, J = 8 Hz, 1 H), 2.88–2.64 (m, 2 H), 2.64–2.38 (m, 2 H), 2.20–1.88 (m, 4 H), 1.66 (s, 3 H), 1.58 (s, 3 H).

3l: mp 82–86 °C; NMR δ ($CDCl_3$) 8.00–7.48 (m, 5 H), 5.00 (q, J = 8 Hz, 1 H), 4.10 (q, J = 8 Hz, 1 H), 2.69 (d, J = 6.7 Hz, 2 H), 2.41–2.36 (m, 2 H), 1.61 (s, 6 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74. Found: C, 56.61; H, 5.80; N, 4.53.

3m-A: oil; NMR δ ($CDCl_3$) 7.97–7.53 (m, 5 H), 5.65–5.55 (m, 2 H), 4.28 (d, d, J = 7.0 Hz, 11.3 Hz, 1 H), 2.82 (d, d, d, J = 1.7 Hz, 11.3 Hz, 18.6 Hz, 1 H), 2.54–2.48 (m, 1 H), 2.48 (d, d, d, J = 3.5 Hz, 7.0 Hz, 18.0 Hz, 1 H), 1.97 (s, 3 H), 0.84 (d, J = 7 Hz, 3 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74. Found: C, 56.82; H, 5.84; N, 4.56. **3m-B**: mp 125–132 °C; NMR δ ($CDCl_3$) 7.97–7.53 (m, 5 H), 5.63 (t, t, J = 2.5 Hz, 7.6 Hz, 1 H), 5.36 (d, d, d, J = 1.8 Hz, 4.2 Hz, 10.0 Hz, 1 H), 4.28 (d, d, J = 6.4 Hz, 11.6 Hz, 1 H), 2.95–2.92 (m, 1 H), 2.77–2.67 (m, 1 H), 2.45–2.37 (m, 1 H), 1.74 (s, 3 H), 0.95 (d, J = 7 Hz, 3 H). Found: C, 56.82; H, 5.84; N, 4.56.

3n-A: oil; NMR δ ($CDCl_3$) 7.96–7.55 (m, 5 H), 5.67–5.64 (m, 2 H), 4.31 (d, d, J = 7.3 Hz, 11.0 Hz, 1 H), 2.86–2.36 (m, 3 H), 1.95 (s, 3 H), 1.39–1.10 (m, 12 H), 0.86 (t, J = 7 Hz, 3 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{20}H_{29}NO_4S$: C, 63.30; H, 7.70; N, 3.69. Found: C, 63.23; H, 7.75; N, 3.40. **3n-B**: NMR δ ($CDCl_3$) 7.96–7.55 (m, 5 H), 5.75 (m, 1 H), 5.54 (d, J = 10.1 Hz, 1 H), 4.25 (d, d, J = 6.4 Hz, 11.3 Hz, 1 H), 2.86–2.36 (m, 3 H), 1.72 (s, 3 H), 1.39–1.10 (m, 12 H), 0.86 (t, J = 7 Hz, 3 H).

3o-A: mp 121–126 °C; NMR δ ($CDCl_3$) 7.91–7.56 (m, 5 H), 5.31–5.30 (m, 1 H), 4.37 (d, d, J = 6.4 Hz, 11.0 Hz, 1 H), 2.78 (d, J = 17.9 Hz, 2 H), 2.25 (d, d, J = 6.7 Hz, 8.0 Hz, 2 H), 1.89 (s, 3 H), 1.68 (s, 3 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74. Found: C, 57.01; H, 5.83; N, 4.70. **3o-B**: NMR δ ($CDCl_3$) 7.91–7.56 (m, 5 H), 5.31–5.30 (m, 1 H), 4.26 (d, d J = 6.4 Hz, 11.0 Hz, 1 H), 2.65 (t, t, J = 4.1 Hz, 13.0 Hz, 2 H), 2.42 (d, d, J = 5.4 Hz, 7.0 Hz, 2 H), 1.90 (s, 3 H), 1.66 (s, 3 H).

3p: mp 123–130 °C; NMR δ ($CDCl_3$) 7.92–7.48 (m, 5 H), 5.60–5.32 (m, 2 H), 4.48 (dd, J = 7 Hz, 11 Hz), 4.38 (dd, J = 7 Hz, 11 Hz, 1 H), 3.00–2.00 (m, 5 H), 1.40–1.20 (m, 6 H), 1.04–0.80 (m, 6 H); IR cm^{-1} ($CHCl_3$) 1550, 1340, 1250. Anal. Calcd for $C_{18}H_{25}NO_4S$: C, 61.51; H, 7.17; N, 3.99. Found: C, 61.25; H, 7.18; N, 3.95.

Preparation of 4. Preparation of 5,6:7,8-Dibenzobicyclo-[2.2.2]octa-2,5,7-triene (4a). Typical Procedure. A mixture of **3d** (0.39 g, 1.00 mmol), Bu_3SnH (0.87 g, 3 mmol), and AIBN (0.13 g, 0.79 mmol) in toluene (3 mL) was stirred at 110 °C for 0.5 h. The solvent was evaporated, and the residue was subjected to column chromatography (silica gel/hexanee to give 0.12 g (60%) of **4a**: mp 121–123 °C (lit.[21] mp 119 °C); NMR δ ($CDCl_3$) 7.30 (d, d, J = 4 Hz, 6 Hz, 4 H), 7.08–6.90 (m, 6 H), 5.16 (d, d, J = 1 Hz, 3 Hz, 2 H).

The following 1,4-cyclohexadienes 4 were prepared by this method.

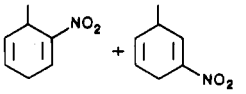
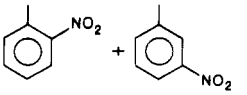
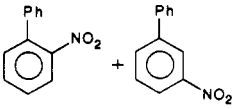
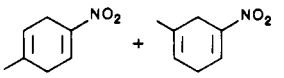
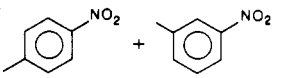
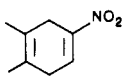
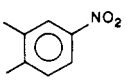
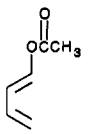
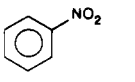
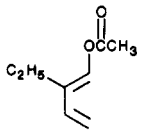
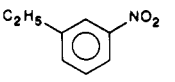
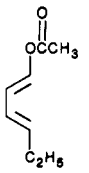
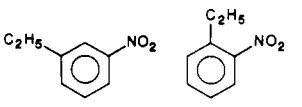
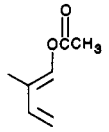
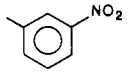
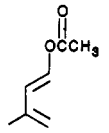
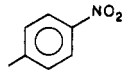
4b: colorless liquid; NMR δ ($CDCl_3$) 5.72–5.61 (m, 2 H), 5.48–5.40 (m, 2 H), 2.68–2.58 (m, 3 H), 1.50–1.08 (m, 12 H), 0.88 (t, J = 7 Hz, 3 H); MS, m/e (M^+) calcd for $C_{13}H_{22}$ 178.1721, obsd 178.1703.

4c: mp 45 °C; NMR δ ($CDCl_3$) 7.28 (s, 10 H), 5.79 (s, 4 H), 4.05 (s, 2 H); MS, m/e (M^+) calcd for $C_{18}H_{16}$ 232.1252, obsd 232.1253. Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.31; H, 6.97.

4d: colorless liquid; NMR δ ($CDCl_3$) 5.68 (s, 2 H), 5.44–5.36 (m, 1 H), 5.18–5.00 (m, 1 H), 2.68–2.50 (m, 4 H), 2.10–1.88 (m, 4 H), 1.66 (s, 3 H), 1.59 (s, 3 H); MS, m/e (M^+) calcd for $C_{12}H_{18}$ 162.1407, obsd 162.1361.

(21) Fireys, H. P.; Dralants, A. *Tetrahedron* **1972**, *28*, 1303.

Table IV. Diels–Alder Reaction of β-Sulfinylnitroethylene (2)

entry	dienes	conditions	adducts (5)	yield (%)[a]	aromatic nitro compounds 6	yield (%)[a]	6/6′ [b]
1		toluene, 110 °C, 2 h	 **5a** **5a′**	54	 **6a** **6a′**	81	90/10
2		toluene, 110 °C, 72 h	[c]		 **6b** **6b′**	31	98/2
3		toluene, 110 °C, 2 h	 **5c** **5c′**	68	 **6c** **6c′**	81	68/32
4		toluene, 110 °C, 2 h	 **5d**	80	 **6d**	87	
5		toluene, 110 °C, 2 h	[c]		 **6e**	52	
6		toluene, 110 °C, 3 h	[c]		 **6f**	60	100/0
7		toluene, 110 °C, 18 h	[c]		 **6f** **6f′**	60	75/25
8		toluene, 110 °C, 6 h	[c]		 **6g**	42	100/0
9		toluene, 110 °C, 5 h	[c]		 **6h**	65	100/0

[a] Isolated yield. [b] Determined by GLC. [c] Aromatized products were formed during the reaction conditions.

4e: colorless liquid; NMR δ ($CDCl_3$) 5.62–5.60 (m, 2 H), 5.47–5.36 (m, 1 H), 2.64 (m, 3 H), 1.64 (s, 3 H), 1.60–1.05 (m, 12 H), 0.86 (t, J = 8 Hz, 3 H); MS, m/e (M^+) calcd for $C_{14}H_{24}$ 192.1877, obsd 192.1863.

4f: colorless liquid; NMR δ ($CDCl_3$) 5.62–5.58 (m, 2 H), 5.40–5.34 (m, 1 H), 2.68–2.53 (m, 3 H), 2.05–1.88 (m, 2 H), 1.56–1.10 (m, 6 H), 1.04 (d, J = 7 Hz, 3 H), 0.88 (t, J = 8 Hz, 3 H); MS, m/e (M^+) calcd for $C_{12}H_{20}$ 164.1564, obsd 164.1517.

Diels–Alder Reaction of 2. Preparation of 3-Methyl-4-nitro-1,4-cyclohexadiene (5a). Typical Procedure. A mixture of **2** (0.42 g, 2.13 mmol) and (*E*)-1,3-pentadiene (0.68 g, 10 mmol) in toluene was stirred at 110 °C for 2 h. The reaction mixture was subjected to column chromatography (silica gel/hexane–benzene) to give 0.16 g (54%) of **5a**: yellow liquid; NMR δ ($CDCl_3$) 7.30–7.20 (m, 1 H), 5.78–5.64 (m, 2 H), 3.65–3.45 (m, 1 H), 3.10–2.90 (m, 2 H), 1.20 (d, J = 8 Hz, 3 H); IR cm^{-1} (neat) 1550; MS, m/e (M^+) calcd for $C_7H_9NO_2$ 139.0633, obsd 139.0641.

The following compounds **5** were prepared by this procedure.

5c: yellow liquid; NMR δ ($CDCl_3$) 7.40–7.28 (m, 1 H), 5.58–5.36 (m, 1 H), 3.36–2.80 (m, 4 H), 1.76 (s, 3 H for meta isomer), 1.72 (s, 3 H for para isomer); IR cm^{-1} (neat) 1550; MS, m/e (M^+) calcd for $C_7H_9NO_2$ 139.0633, obsd 139.0651.

5d: yellow liquid; NMR δ ($CDCl_3$) 7.30 (m, 1 H), 3.20–2.90 (m, 4 H), 1.70 (s, 6 H); IR cm^{-1} (neat) 1550.

Oxidation of 5 by DDQ. A mixture of **5** (1 mmol) and DDQ (0.27 g, 1.2 mmol) in benzene (5 mL) was heated at 80 °C for 2 h. The reaction mixture was subjected to column chromatography (silica gel/hexane–benzene) to give substituted nitrobenzenes **6**. The structural were determined by comparison with commercially available authentic samples of **6**. The isomer ratio was determined by GLC.

Diels–Alder Reaction of 2 with 1-Acetoxy-1,3-butadienes. Preparation of Nitrobenzene (6e). Typical Procedure. A mixture of **2** (0.40 g, 2.03 mmol) and 1-acetoxy-1,3-butadiene (0.40 g) in toluene (5 mL) was heated at 110 °C for 2 h. The reaction mixture was subjected to column chromatography (silica gel/hexane-benzene) to give nitrobenzene (**6e**). 0.13 g (52%). The structure of **6e** was determined by comparison with commercially available nitrobenzene.

The following substituted nitrobenzenes (**6f–h**) were prepared

by this method. All of structures were determined by comparison with commercially available authentic samples of **6**, and the isomeric purity was confirmed by GLC.

6f: yellow oil; MS, m/e (M^+) calcd for $C_8H_9NO_2$ 151.0634, obsd 151.0647.

6g: yellow oil; MS, m/e (M^+) calcd for $C_7H_7NO_2$ 137.0477, obsd 137.0501.

6h: mp 49–50 °C (lit.[22] mp 54.4 °C); MS, m/e (M^+) calcd for $C_7H_7NO_2$ 137.0477, obsd 137.0507.

Reaction of 2 with 1-Methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene. A mixture of **2** (0.94 g, 4.77 mmol) and the diene (1.12 g, 6.51 mmol) in toluene was heated at 110 °C for 3 h. The reaction mixture was subjected to column chromatography (silica gel/hexane–ethyl acetate) to give *p*-nitrophenol (0.34 g, 51%): mp 113–115 °C (lit.[23] mp 114 °C); NMR δ ($CDCl_3$) 8.20 (d, J = 8 Hz, 2 H), 7.00 (d, J = 8 Hz, 2 H), 6.85–6.70 (m, 1 H).

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Registry No. **1a**, 101933-29-3; **1b**, 101933-39-5; **1c**, 101933-45-3; **2**, 101933-28-2; **3a-A**, 101933-49-7; **3a-B**, 102043-92-5; **3b-A**, 106185-49-3; **3b-B**, 106248-46-8; **3c-A**, 106185-50-6; **3c-B**, 106248-47-9; **3d**, 106185-52-8; **3e**, 111905-19-2; **3f-A**, 111957-34-7; **3f-B**, 111957-35-8; **3g-A**, 101933-51-1; **3g-B**, 102043-93-6; **3h-A**, 111905-20-5; **3h-B**, 111957-36-9; **3i-A**, 111905-21-6; **3i-B**, 111957-37-0; **3j-A**, 111905-22-7; **3j-B**, 111905-23-8; **3k-A**, 111905-24-9; **3k-B**, 111905-25-0; **3l**, 106185-54-0; **3m-A**, 111957-38-1; **3m-B**, 111957-39-2; **3m-A**, 111905-26-1; **3n-B**, 111957-40-5; **3o-A**, 111905-27-2; **3o-B**, 111905-28-3; **3p**, 106185-57-3; **4a**, 2734-13-6; **4b**, 111905-29-4; **4c**, 38116-47-1; **4d**, 111905-30-7; **4e**, 111905-31-8; **4f**, 106185-58-4; **5a**, 101933-50-0; **5a'**, 111905-33-0; **5c**, 111905-34-1; **5c'**, 111905-35-2; **5d**, 111905-36-3; **6a**, 88-72-2; **6a'**, 99-08-1; **6b**, 86-00-0; **6b'**, 2113-58-8; **6c**, 99-99-0; **6c**, 99-51-4; **6e**, 98-95-3; **6f**, 7369-50-8; **6f'**, 612-22-6; CH_2=CHCH=CH_2, 106-99-0; (*E*)-TMSOCH=CHCH=CH_2, 63383-46-0; (*E*)-CH_2=CHCH=CHMe, 2004-70-8; (*E*)-CH_2=CHCH=CHC_7H_{15}, 79309-74-3; (*E,E*)-PhCH=CHCH=CHPh, 538-81-8; CH_2=C(Me)CH=CH_2, 78-79-5; $(Me)_2C$=$CH(CH_2)_2C$(=CH_2)CH=CH_2, 123-35-3; MeC(=CH_2)C(=CH_2)Me, 513-81-5; (*E*)-CH_2=CHCH=CHPh, 16939-57-4; (*E*)-CH_2=CHCH=CHOAc, 35694-20-3; (*E*)-CH_2=CHC(Et)=CHOAc, 111905-32-9; (*E,E*)-EtCH=CHCH=CHOAc, 91438-29-8; (*E*)-CH_2=CHC(Me)=CHOAc, 86400-08-0; (*E*)-CH_2=C(Me)CH=CHOAc, 52062-24-5; (*E*)-TMSOC(=CH_2)CH=CHOMe, 54125-02-9; *p*-$NO_2C_6H_4OH$, 100-02-7; cyclopentadiene, 542-92-7; furan, 110-00-9; cyclohexadiene, 592-57-4; anthracene, 120-12-7.

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Diisophorone and Related Compounds. 21.[1] Synthesis and Nucleophilic Reactions of 4,4,8- and 4,6,8-Tribromodiisophorones

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Halogenation of diisophorone (**1**) by 3 mol of bromine in acetic acid yields the 4,4,8-tribromo 3-ket-1-ol **2**, which is converted by Koch–Haaf carboxylation into the 4,4,8-tribromo 1-carboxylic acid **8**. The latter undergoes ring A contraction (to **10**) or ring A aromatization (to **11**) by the action of alkali or alkoxide, respectively. In contrast, tribromination in ether converts the parent ketol **1** predominantly into the 4,6,8-tribromo derivative **14**, which is also accessible unequivocally from the 4-mono and 4,8-dibromo analogues by the action of *N*-bromosuccinimide. Its interaction with nucleophiles proceeds by ring A aromatization, yielding 8-substituted 4-bromo-6-methyl-5-nordiisophora-2(7),3,5-triene-1,3-diols **19–22**. The structural assignments are in accord with the spectral properties of the new types of compounds, especially their carbon NMR and mass spectra.

Introduction

The controlled introduction of halogen substituents into the diisophorone structure provides reactive centers suitable for the investigation of further reactions at specific positions in this three-dimensional ring system. Both 4-[2] and 8-monobromo-[3-5] as well as 4,8-[6,7] and 6,8-dibromodiisophorones,[8] obtained by appropriate halogenation procedures, have been studied from this point of view. Their reactions with nucleophiles may involve simple replacements, with[5,6,9,10] or without[2,6] isomerization, or ring A contraction,[7] or ring A aromatization,[8,11] the preferred course depending on the number and position of the halogen substituents. We now close our account of this group of reactions with a report of the synthesis and behavior toward nucleophiles of 4,4,8- and 4,6,8-tribromodiisophorones, and with an attempt to correlate the sum of the available information.

The compounds now described are derivatives of tricyclo[7.3.1.$0^{2,7}$]tridecane, except **10**, which is a substituted tricyclo[6.3.1.$0^{2,6}$]dodecane. We continue to employ the simplified nomenclature and numbering that was originally

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