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Diels–Alder cycloadditions: 3-(*p*-toluenesulfonyl)-2-propenal as dienophile

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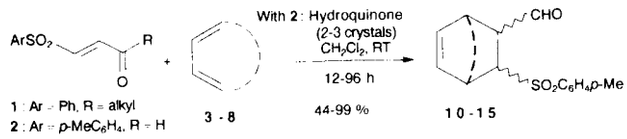
Abstract. The cycloadditions of 3-(*p*-toluenesulfonyl)-2-propenal with cyclopentadiene, 1,3-cyclohexadiene, 1-methoxy-1,3-cyclohexadiene, 1-(trimethylsilyloxy)-1,3-butadiene, or 1,3-diphenylisobenzofuran have been easily carried out at room temperature in the absence of catalyst. In contrast, furan has led to a Michael-type addition. The basic elimination of the sulfonyl moiety of a cycloadduct has shown that this dienophile is a synthetic equivalent of propynal.

Some years ago, we reported palladium-mediated formations of β-(*p*-toluenesulfonyl) α,β-unsaturated carbonyl compounds from allylic sulfones[1]. These compounds are versatile synthons[2]. We then decided to examine their use in [4 + 2] cycloadditions. A recent paper concerning Diels–Alder reactions with enones **1** as dienophiles[3] prompted us to present results we have obtained with the enal **2**.



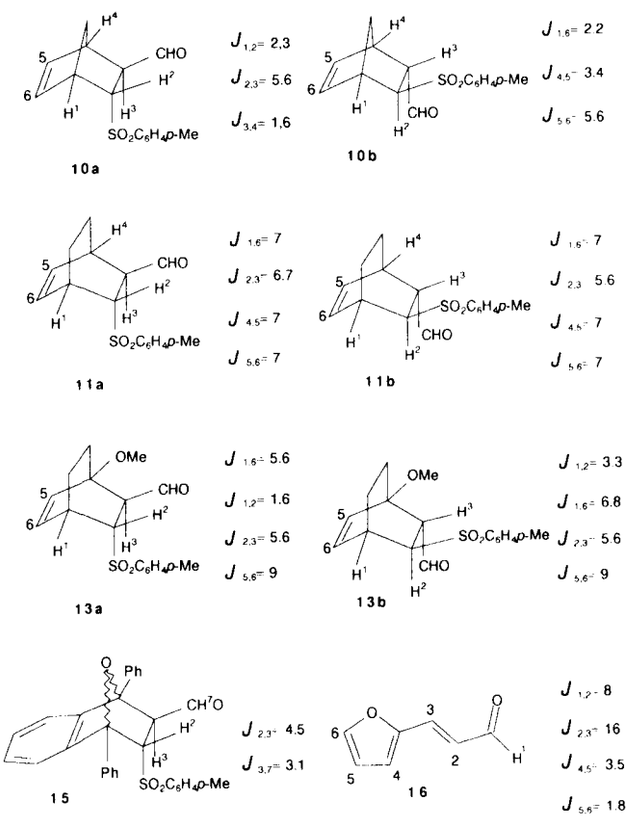
The results of reactions of **2** with cyclopentadiene (**3**), 1,3-cyclohexadiene (**4**), (*E*)-1,3-pentadiene (**5**), 1-methoxy--1,3-cyclohexadiene (**6**), 1-(trimethylsilyloxy)-1,3-butadiene (**7**), 1,3-diphenylisobenzofuran (**8**), and furan (**9**) are shown in Table I. With dienes **3**, **4**, **6**, **7** and **8**, cycloaddition proceeded cleanly at room temperature. In contrast, **5** led to degradation products under these conditions. On decreasing the temperature to −20°C, the cycloaddition of **2** with **5** required the presence of a Lewis-acid catalyst.

The adducts have been purified by chromatography. Although **12** and **14** were homogeneous by TLC, their NMR spectra showed the presence of small amounts (about 5%) of an isomeric cycloadduct. Stereo- and regiochemistry of the reaction of **2** have been studied from the 300-MHz ^{1}H NMR spectra of the adducts and comparisons with pub-

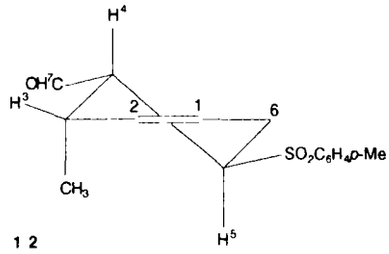
Table I Reaction of **2** *with dienes* **3** *to* **9**.

Dienes	Reaction time (h)	Adducts (isolated yields)
3	12	**10a** (56%), **10b** (34%)
4	90	**11a** (64%), **11b** (25%)
5	96[a]	**12** (44%)
6	38	**13a** (77%), **13b** (8%)
7	28	**14** (95%)
8	15	**15** (99%)
9	48	**16** (53%)

[a] Reaction carried out at −20°C in the presence of 2 drops of $BF_3 \cdot Et_2O$.

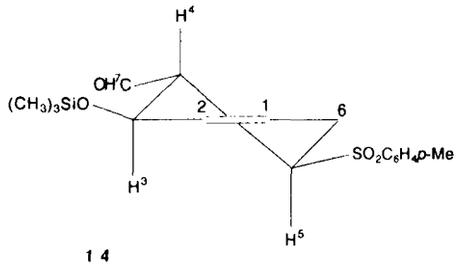


lished data[4]. The NMR signal of the aldehydic proton of **12** and **14** is a doublet. This assignment showed that the proton geminal to an aldehydic group is more shielded than the proton geminal to a sulfonyl group (Table II). This difference allowed us to assign the position of the corresponding protons of **10a**, **10b**, **11a**, **11b**, **13a**, **13b**, and **15**. The assignment of the *endo/exo* position of the sulfonyl group of the bicyclic adducts, except **15**, was made by reference to the position of the vinylic protons, since it appears[4] that these protons are "deshielded" by a sulfonyl group in the *endo* position. Following these remarks, the stereochemical assignments have been easily established, except for **15**[5].



1 2

$J_{1,2}$= 11
$J_{3,4}$= 6
$J_{4,5}$= 7
$J_{4,7}$= 2.7
$J_{5,6}$= 7



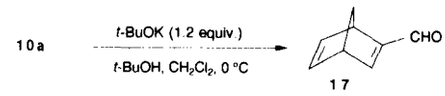
1 4

$J_{3,4}$= 8.7
$J_{4,5}$= 12.7
$J_{4,7}$= 4.2
$J_{5,6}$= 6 and 11

Table II Characteristic ^1H chemical shifts (300 MHz, $CDCl_3$, δ in ppm) of the Diels–Alder adducts.

Adduct	CHCO	CHTol	–CH=CH–
10a	2.94	4.11	6.38
10b	3.35	3.35	6.13, 6.22
11a	2.97	3.85	6.31, 6.40
11b	3.15	3.50	6.09, 6.34
12	2.87	3.80	5.58, 5.68
13a	3.30	3.97	6.28, 6.47
13b	3.36	3.63	6.15, 6.31
14	2.70	3.72	5.54–5.68
15	3.72	4.90	

Comparison of the results obtained with the dienes used with both **1** and **2** leads to the following comments: First, similar yields have been obtained but a slightly better stereoselectivity can be attained from **2**. Second, **2** is more reactive than **1**: at room temperature, the Diels–Alder reactions from **2** did not require the presence of a catalyst. Third, **9** led to a cycloadduct with **1**, whereas a Michael-type addition followed by elimination of the arylsulfonyl group was observed with **2**. Similar addition–elimination reactions have already been reported from **9** and either *E*-4-(phenylsulfinyl)-3-buten-2-one[6] or 3-(phenylsulfonyl--3-buten-2-one[7].



17

Finally, the use of **2** as a propynal equivalent has been shown by the basic elimination of the sulfonyl moiety of **10a** leading to **17**[8], which, however, slowly decomposed even at $-20°C$. In contrast, the starting material **10a** is stable for months at room temperature. Since good stability has also been observed for the other cycloadducts described in this paper, the use of **2** as a stable masked propynal for Diels–Alder reactions is clearly established.

Experimental

The ^1H NMR spectra (δ ppm, J Hz) were recorded with TMS as internal reference, in $CDCl_3$ solution in using a Bruker AC300 spectrometer. The IR spectra (cm^{-1}) were recorded in $CHCl_3$ solution on a Philips SP3-300 spectrometer. The melting points were determined with a Büchi apparatus. Combustion analyses were performed by the microanalysis section of the University of Champagne-Ardenne.

The preparation[1] and characteristics[1a] of **2** have been previously described[1]. **2** has also been prepared from the corresponding alcohol[9] which was oxidized by activated MnO_2[10]. The diene **7** has been prepared from (*E*)-2-butenal[11]. Other dienes are commercial products. Methylene chloride was distilled over CaH_2 under an argon atmosphere.

General procedure of the cycloaddition reactions

2 (1 eq.) was added in one portion to a stirred solution of the diene (4 eq.) in methylene chloride (10 ml/mmol) containing a few crystals of hydroquinone. The mixture was stirred at room temperature under an argon atmosphere during the time indicated in Table I. The solvent was then evaporated under reduced pressure. Flash chromatography of the residue on silica gel (EtOAc/petroleum-ether) led to isolation of the products with yields indicated in Table I. Crystallisation was carried out from methylene-chloride/petroleum-ether mixtures.

3-endo-*(p-Toluenesulfonyl)-5-norbornene-2*-exo-*carbaldehyde* (**10a**). M.p. 98–99°C. NMR: 1.30 (d, *J* 9, CH); 1.50 (dd, *J* 9, 2.2, CH); 2.45 (s, *p*-CH_3); 2.94 (dd, *J* 5.6, 1.6, CHC=O); 3.20 (m, 1H); 3.28 (m, 1H); 4.11 (dd, *J* 5.6, 2.3, $CHSO_2$); 6.38 (m, CH=CH); 7.26 (d, *J* 7.9, 2H); 7.75 (d, *J* 7.9, 2H); 9.66 (s, CHO). IR: 2950, 1730, 1320, 1310, 1155, 1090. Anal. calcd. for $C_{15}H_{16}SO_3$ (276.35): C 65.19, H 5.84; found: C 65.45, H 5.97%.

3-exo-*(p-Toluenesulfonyl)-5-norbornene-2*-exo-*carbaldehyde* (**10b**). M.p. 92–93°C. NMR: 1.58 (dd, *J* 9, 1.6, CH); 2.20 (d, *J* 9, CH); 2.45 (s, *p*-CH_3); 3.35 (m, 2H); 3.45 (m, 2H); 6.13 (dd, *J* 5.6, 2.2, CH=C); 6.22 (dd, *J* 5.6, 3.4, C=CH); 7.36 (d, *J* 8, 2H); 7.79 (d, *J* 8, 2H); 9.37 (s, CHO). IR: 2950, 1730, 1318, 1150, 1100. Anal. calcd. for $C_{15}H_{16}SO_3$ (276.35): C 65.19, H 5.84; found: C 65.43, H 6.01%.

3-endo-*(p-Toluenesulfonyl)bicyclo[2.2.2]-oct-5-ene-2*-exo-*carbaldehyde* (**11a**). M.p. 101–103°C. NMR: 1.1–1.53 (4H); 2.45 (s, *p*-CH_3); 2.97 (br d, *J* 6.7, CHC=O); 3.07 (m, 1H); 3.15 (m, 1H); 3.85 (br d, *J* 6.7, $CHSO_2$); 6.31 (dd, *J* 7, 7, CH=C); 6.40 (dd, *J* 7, 7, C=CH); 7.36 (d, *J* 9, 2H); 7.74 (d, *J* 9, 2H); 9.54 (s, CHO). IR: 2950, 1730, 1345, 1150. Anal. calcd. for $C_{16}H_{18}SO_3$ (290.38): C 66.18, H 6.25; found: C 66.07, H 5.98%.

3-exo-*(p-Toluenesulfonyl)bicyclo[2.2.2]-oct-5-ene-2*-endo-*carbaldehyde* (**11b**). M.p. 96–97°C. NMR: 1.16 (m, 1H); 1.47 (m, 1H); 1.88 (m, 1H); 2.43 (s, *p*-CH_3); 2.45 (1H, m); 3.10 (m, 2H); 3.15 (d, *J* 5.6, CHC=O); 3.50 (br d, *J* 5.6, $CHSO_2$); 6.09 (dd, *J* 7, 7, CH=C); 6.34 (dd, *J* 7, 7, C=CH); 7.34 (d, *J* 8, 2H); 7.75 (d, *J* 8, 2H); 9.25 (s, CHO). IR: 2950, 1730, 1340, 1290, 1090. Anal. calcd. for $C_{16}H_{18}SO_3$ (290.38): C 66.18, H 6.25; found: C 66.25, H 6.02%.

1-Methoxy-3-endo-*(p-toluenesulfonyl)bicyclo[2.2.2]-oct-5-ene-2*-exo-*-carbaldehyde* (**13a**). Oil. NMR: 1.31–1.64 (4H); 2.44 (s, *p*-CH_3); 3.01 (m, 1H); 3.30 (dd, *J* 5.6, 2.2, CHC=O); 3.50 (s, OMe); 3.97

(dd, *J* 5.6, 1.6, $CHSO_2$); 6.28 (dd, *J* 9, 5.6, C=CH–); 6.47 (d, *J* 9, CH=C); 7.34 (d, *J* 9, 2H); 7.71 (d, *J* 9, 2H); 9.70 (s, CHO). IR: 2950, 1730, 1320, 1310, 1295, 1160. Anal. calcd. for $C_{17}H_{20}SO_4$ (320.41): C 63.73, H 6.29; found: C 63.54, H 6.17%.

*1-Methoxy-3-*exo*-(p-toluenesulfonyl)bicyclo[2.2.2]-oct-5-ene-2-*endo*-carbaldehyde* (**13b**). Oil. NMR: 1.30 (m, 1H); 1.69 (dt, *J* 12.5, 4.5, CHCOMe); 2.0 (dt, *J* 11.3, 4.5, HCCOMe); 2.43 (s, *p*-CH_3); 2.54 (m, 1H); 3.23 (dd, *J* 6.8, 3.3, =C–CH); 3.36 (d, *J* 5.6, CHC=O); 3.45 (s, OCH_3); 3.63 (m, $CHSO_2$); 6.15 (d, *J* 9, CH=C); 6.31 (dd, *J* 9, 6.8, C=CH); 7.33 (d, *J* 9, 2H); 7.72 (d, *J* 9, 2H); 9.48 (s, CHO). IR: 2950, 1730, 1320, 1310, 1160. Anal. calcd. for $C_{17}H_{20}SO_4$ (320.41): C 63.73, H 6.29; found: C 63.94, H 6.37%.

6t-(p-Toluenesulfonyl)-2t-trimethylsilyloxy)-cyclohex-3-ene-1r-carbaldehyde (**14**). Oil. NMR: 0.1 (s, $OSi(CH_3)_3$; 2.15–2.55 (CH_2); 2.47 (s, *p*-CH_3-Me); 2.70 (ddd, *J* 12.7, 8.7, 4.2, CHCO); 3.72 (ddd, *J* 12.7, 11, 6, $CHSO_2$); 4.60 (br d, *J* 8.7, CHOSi); 5.54–5.68 (CH=CH); 7.39 (d, *J* 7.9, 2H); 7.74 (d, *J* 7.9, 2H); 9.90 (d, *J* 4.2, CHO). IR: 2950, 1730, 1320, 1150, 1090. Anal. calcd. for $C_{17}H_{24}SO_4$ (324.44): C 62.94; H 7.46; found: C 62.76, H 7.34%.

1,4-Diphenyl-3t-(p-toluenesulfonyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene-2r-carbaldehyde (**15**). M.p. 171–172°C. NMR: 2.4 (s, *p*-CH_3); 3.72 (dd, *J* 4.5, 3.1, CHC=O); 4.90 (d, *J* 4.5, $CHSO_2$); 7.2–8.0 (18H); 9.20 (d, *J* 3.1, CHO). IR: 2950, 1730, 1320, 1150, 1090. Anal. calcd. for $C_{28}H_{28}SO_4$ (480.58): C 74.98, H 5.03; found: C 74.70, H 4.90%.

(E)-3-(2-Furyl)-2-propenal (**16**). M.p. 53–55°C (litt.[12] m.p. 54°C.). NMR: 6.54 (dd, *J* 3.5, 1.8, 1H); 6.6 (dd, *J* 16, 8, CHC=O); 6.77 (d, *J* 3.5, 1H); 7.22 (d, *J* 16, CH=CC=O); 7.57 (d, *J* 1.8, 1H); 9.62 (d, *J* 8, CHO). IR: 3000, 1670, 1110, 1010, 960.

Cycloaddition of (E)-1,3-pentadiene with **2**. **2** (65 mg, 0.3 mmol) was added in one portion to a cooled solution (–20°C) of **5** (100 mg, 1.2 mmol) in methylene chloride (10 ml) and 2 drops of $BF_3 \cdot Et_2O$ were then added. The solution was stirred under an argon atmosphere for 28 h. Water was then added and the mixture was allowed to warm to room temperature. After extraction, the organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was flash chromatographed on silica gel (EtOAc/petroleum-ether: 25–75) to give **12** (38 mg).

2c-Methyl-6t-(p-toluenesulfonyl)-cyclohex-3-ene-1r-carbaldehyde (**12**). Oil. NMR: 1.23 (d, *J* 7, CMe); 2.32 (m, CH_2); 2.47 (s, *p*-CH_3); 2.87 (ddd, *J* 7, 6, 2.7, CHC=O); 2.93 (m, CHMe); 3.80 (ddd, *J* 7, 7, 7, $CHSO_2$); 5.58 (m, CH=C); 5.68 (br d, *J* 11, C=CH); 7.38 (d, *J* 9, 2H); 9.91 (d, *J* 2.7, CHO). IR: 2950, 1730, 1320, 1310, 1150, 1090. Anal. calcd. for $C_{15}H_{18}SO_3$ (278.37): C 64.72, H 6.52; found: C 64.56, H 6.42%.

Basic elimination of sulfonyl moiety. Potassium *tert*-butylate (15 mg, 1 equiv.) was added to a cooled solution (0°C) of **12a** (30 mg) in *t*-BuOH (3 ml) and CH_2Cl_2 (5 ml). The mixture was stirred at 0°C for 30 min. The solvent was then evaporated under reduced pressure. The residue was immediately chromatographed on silica gel plates eluted with EtOAc/petroleum-ether (10–90) to give **17** (12 mg, homogeneous in TLC).

Norbornadiene-2-carbaldehyde (**17**)[8]. Unstable oil. NMR: 0.90 (m, 1H); 1.55 (m, 1H); 2.98 (m, 1H); 3.10 (m, 1H); 5.80–6.25 (m, CH=CH); 6.85 (d, *J* 2.3, CH=CC=O); 9.75 (s, CHO). IR: 1650, 1605.

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