Stereoselective Synthesis of Vinylcyclopropanes from 2-Phenylsulfonyl-1,3-cyclohexadienes and Ketone Enolates or Nitrile Anion

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Michael addition of ketone enolates to 2-(phenylsulfonyl)-1,3-cyclohexadienes and subsequent cyclization affords vinylcyclopropanes in a highly stereoselective manner. In this process the enolate anion of the adduct displaces the allylic phenylsulfonyl group. The analogous reaction between the anion of benzyl cyanide and 2-(phenylsulfonyl)-1,3-cyclohexadiene afforded the corresponding vinylcyclopropane. An attempted synthesis of sesquicarene led to the sesquicarene derivative 3,endo-7-dimethyl-exo-7-(4-hydroxy-4-methylpentanoyl)-2-norcarene.

The organic chemistry of sulfones has undergone remarkable expansion over the last two decades and a number of synthetic transformations involving the sulfone functional group have been developed.[1] A variety of versatile sulfone-containing synthons are known today and among those, 2-arylsulfonyl 1,3-dienes have recently attracted attention.[2–7] Such 2-arylsulfonyl 1,3-dienes are useful Diels–Alder dienes,[6a,d,e,7] and, furthermore, they can be transformed into versatile synthetic intermediates via regioselective functionalization at either double bond.[2a,b,e,6b,c] Michael addition to these dienes is of particular interest since it produces an allylic sulfone, which can undergo further interesting functionalizations.
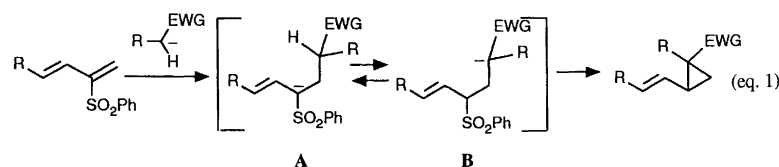
It is known that an allylic phenylsulfonyl group can act as a leaving group.[1b,c,8,9] A Michael addition of a carbon nucleophile to a 2-phenylsulfonyl 1,3-diene followed by intramolecular displacement of the allylic sulfonyl group would therefore be a possible route to vinylcyclopropanes [eqn. (1)]. In fact there is precedence for cyclization of an intermediate of type B to a vinylcyclopropane where B was generated via a different route.[8]

Vinylcyclopropanes occur as the structural unit in a number of natural products[10] and they are also important synthetic intermediates.[11] In connection with our previous studies on vinylcyclopropanes[2f,12] and our general interest in 2-phenylsulfonyl 1,3-dienes[2,6] we decided to study the possible synthetic route outlined in eqn. (1).
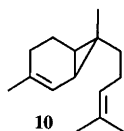
Results and discussion

Reaction of the enolates of ketones **2**, **3**, and **4** or the anion of nitrile **5** with 2-phenylsulfonyl-1,3-cyclohexadiene (**1**) at low temperature (−78 to −25°C) afforded the corresponding Michael adducts. These adducts were isolated and characterized in several cases. When the initially formed Michael adduct was stirred at an elevated temperature (20 to 50°C) without prior quenching, cyclization to a vinylcyclopropane took place (Table 1). The cyclization, in which the sulfone acts as a leaving group, was highly stereoselective and gave only one diastereoisomer of the corresponding cyclopropane. It was established by NOE measurements and other NMR data (see the Experimental) that the isomer formed has the large group *exo* in products **6**, **7**, **8**, and **9** (Table 1). It is conceivable that the Michael adduct initially produced undergoes an intramolecular anion exchange (A⇌B) followed by a cyclization with displacement of the sulfone. The high stereoselectivity in the formation of the cyclopropane to give the product with the large group *exo* can
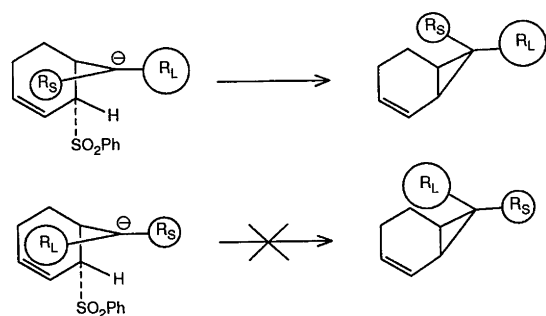

$$\text{(eq. 1)}$$

A   B

be explained by steric interaction in the transition state. Two approaches of the anion are possible one with the small group and one with the large group pointing towards the ring (Scheme 1). It is evident that steric interactions will be more severe in the latter approach.

Sesquicarene (10), is a hydrocarbon isolated from the essential oil of fruits of *Schisandra chinensis Baill.*[13] This naturally occurring hydrocarbon contains a vinylic cyclopropane which we attempted to synthesize with our new procedure.

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The strategy (Scheme 2) was to add the dianion of 6-hydroxy-6-methyl-3-heptanone[14] (12) to the sulfonyl diene 11 and subsequently raise the temperature to promote cyclization. Reduction of the carbonyl group followed by elimination of water to give the most highly substituted double bond[15] would lead to 10.

Addition of the dianion of 12 to 11 gave the corresponding Michael adduct 13. Attempts to cyclize the initially formed dianionic adduct simply by heating the reaction mixture prior to quenching failed. This is probably due to formation of a dianion in which the hydroxy group is always deprotonated. Apparently the alkoxide ion raises the pK_a of the proton α to the carbonyl group more than that of the proton α to the sulfonyl group,[16] and for this reason the anion required for cyclization was not formed. To avoid this effect the Michael adduct 13 was isolated and subsequently treated with one equivalent of base in THF. Under these conditions cyclization to vinylcyclopropane 14 occurred. The cyclization was again highly stereoselective. The anion responsible for the cyclization, which is in equilibrium with the two other possible anions, does have the OH group deprotonated in this case (Scheme 2). The yield obtained in THF was not satisfactory and therefore several other solvents or solvent systems were tried. Increasing the polarity by using DME decreased the yield of cyclized product and only a few percent of the product could be isolated. Reaction in

a less polar solvent increased the yield, and reaction in benzene resulted in an acceptable yield of the desired product (Table 2). This unexpected result is probably due to a different degree of cyclic hemiacetal formation in the Michael adduct. In the less polar solvent, benzene, the hemiacetal formation of the anion is suppressed compared with the situation in the more polar solvent THF. The analogous transformation of unsubstituted sulfonyl diene 1 into vinylcyclopropane 16 via 15 was also carried out under these reaction conditions (Table 2).

The next step was either to reduce the carbonyl group to a methylene group or to eliminate water. To avoid migration of the double bond to give an α,β-unsaturated ketone we decided to reduce the carbonyl group first. Several procedures for reduction of carbonyl groups are known.[17] Some of the methods tried include: (i) $N_2H_4 \cdot H_2O$, K_2CO_3–$(HOCH_2CH_2)_2O$;[18] (ii) thioacetal formation[19a,b] followed by Raney-Ni reduction;[19c] (iii) formation of a tosylhydrazone[20a] followed by $NaBH_3CN$ reduction.[20b] In all these cases cleavage of the cyclopropane occurred. To date we have not been able to reduce the carbonyl group to the required CH_2 group. Apparently the carbonyl group is too activated[11] and also too sterically hindered for successful reduction.
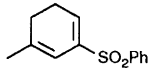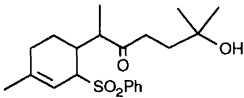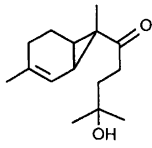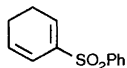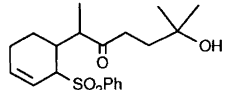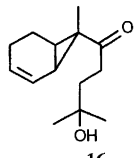
The present paper describes a procedure for the stereoselective transformation of 2-phenylsulfonyl-1,3-cyclohexadienes into vinylcyclopropanes. An attempted synthesis of sesquicarene (10) led to the sesquicarene derivative 14.

Scheme 1.

Table 1. One-step procedure. Formation of vinylcyclopropanes from conjugate addition of enolate and nitrile anions to 2-phenylsulfonyl 1,3-cyclohexadienes.

Entry	Sulfonyl diene	Nucleophile	Cyclopropane	Yield (%)[a]
1	1	2	6	62
2		3	7	66
3		4	8	64
4		5	9	64

[a] Isolated yield after flash chromatography.

Table 2. Two-step procedure. Formation of vinylcyclopropanes from conjugate addition of 6-hydroxy-6-methyl-3-heptanone to 2-phenylsulfonyl-1,3-cyclohexadienes.

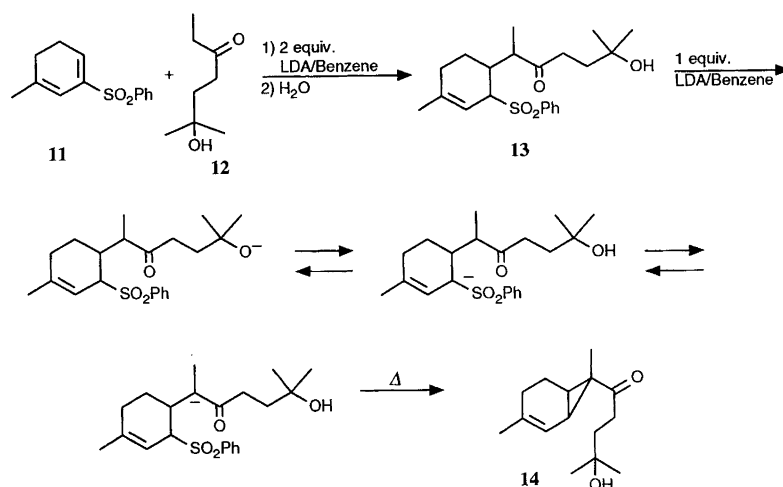| Entry	Sulfonyl diene	Adduct	Yield (%)[a]	Cyclopropane	Yield (%)[a]
1	11	13	59	14	70
2	1	15	60	16	57

[a] Isolated yield after flash chromatography.

Experimental

General methods. NMR spectra were recorded either on a Varian XL-300 MHz or a Varian Unity 400 MHz spectrometer: ^{1}H at 300 MHz or 400 MHz and ^{13}C at 74.5 MHz or 100.6 MHz, using $CDCl_3$ as the solvent and tetramethylsilane (0.0 ppm, ^{1}H) and $CDCl_3$ (77.0 ppm, ^{13}C) as internal standards. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer using a 0.1 mm KBr cell with $CDCl_3$ or CCl_4 as the solvent. Only the strongest and structurally most important peaks (v_{max}/cm^{-1}) are listed. Mass spectra were recorded on a Finnigan MAT INCOS 50 mass spectrometer. Elemental analyses were performed by *Analytische Laboratorien*, Engelskirchen, Germany. Reaction solvents were dried and distilled under nitrogen using standard procedures. Merck silica gel 60 (230–400 mesh) was employed for flash chromatography. 2-Phenylsulfonyl dienes

1 and **11** were prepared according to literature methods.[2a,c,d] Compounds **2–5** were purchased from Aldrich. 6-Hydroxy-6-methyl-3-heptanone (**12**) was prepared according to Ref. 14.

General procedure for the preparation of cyclopropanes (entries 1, 2 and 3, Table 1). A solution of lithium diisopropylamide (LDA) was prepared by addition of diisopropylamine (0.25 ml, 1.82 mmol) to an ice-cooled mixture of *n*-BuLi (1.14 ml, 1.6 M in hexane, 1.82 mmol) in dry THF (4.13 ml). The solution was stirred for 30 min. The ketone (1.82 mmol) was then added dropwise at – 25°C. The solution was stirred for 15 min, then the temperature was raised to 50°C and a solution of the sulfonyl diene **1** (200 mg, 0.91 mmol) in THF (1.00 ml) was added slowly (12 h) by use of a syringe pump. The reaction mixture was stirred at 50°C for the appropriate reaction time as indicated below. The reaction was quenched with

Scheme 2.

NH_4Cl (aq) and extracted with EtOAc ($\times 3$). The combined organic extracts were washed with H_2O ($\times 2$) and brine and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography (EtOAc–hexane) gave the pure product.

endo-7-*Methyl*-exo-7-*propionyl-2-norcarene* (6). The reaction was stirred for 3 days after completed addition of the sulfonyl diene. The crude product was purified by flash chromatography (EtOAc–hexane = 10:90) to give 92.5 mg (62%) of cyclopropane 6. IR ($CDCl_3$): 3155, 3032, 2979, 2937, 2880, 1678, 1459, 1379, 1350, 1218, 1191, 1124, 1032 cm^{-1}; ^1H NMR: δ 5.83 (dt, $J = 10$, 4.0 Hz, 1 H, $CH_2CH = CH$), 5.75 (dm, $J = 10$ Hz, 1 H, $CH_2CH = CH$), 2.55 (q, $J = 7$ Hz, 2 H, CH_3CH_2), 2.08 (m, 1 H, $CH_2CH = CH$), 1.97–1.86 (m, 2 H, $CH = CHCH$, CH_2CH_2CH), 1.86–1.72 (m, 2 H, CH_2CH_2CH, CH_2CH_2CH), 1.65 (m, 1 H, CH_2CH_2CH), 1.24 (s, 3 H, CH_3C), 1.03 (t, $J = 7$ Hz, 3 H, CH_3CH_2); ^{13}C NMR: δ 211.2, 129.0, 123.0, 38.5, 32.5, 25.8, 25.2, 21.5, 15.6, 9.6, 8.1.

Irradiation of the protons of the 7-methyl group gave an NOE for the olefin protons, which is consistent only with the 7-methyl group being endo.

endo-7-*Methyl*-exo-7-*benzoyl-2-norcarene* (7). The reaction was stirred for 20 h after completed addition of the sulfonyl diene. The crude product was purified by flash chromatography (EtOAc–hexane = 10:90) to give 127 mg (66%) of cyclopropane 7. IR ($CDCl_3$): 3066, 3031, 2929, 1665, 1598, 1580, 1448, 1265, 1002 cm^{-1}; ^1H NMR: δ 7.77–7.71 (m, 2 H), 7.54–7.39 (m, 3 H), 5.99–5.85 (m, 2 H), 2.13 (m, 1 H), 2.03 (m, 1 H), 1.99–1.75 (m, 4 H), 1.25 (s, 3 H); ^{13}C NMR: δ 203.4, 137.3, 131.8, 128.7, 128.5, 128.2, 122.7, 37.8, 21.9, 21.8, 21.8, 15.4, 12.0. Anal. calc. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.67; H, 7.75.

exo-7-*Benzoyl-2-norcarene* (8). The reaction was stirred for 20 h after completed addition of the sulfonyl diene. The crude product was purified by flash chromatography (EtOAc–hexane = 5:95) to give 115 mg (64%) of cyclopropane 8. IR ($CDCl_3$): 3038, 2932, 2852, 1660, 1598, 1580, 1449, 1415, 1345, 1292, 1221, 1039, 1024 cm^{-1}; ^1H NMR: δ 7.96 (m, 2 H, ArH), 7.58–7.42 (m, 3 H, ArH), 6.06 (ddd, $J = 10, 5, 3$ Hz, 1 H, $CH_2CH = CH$), 5.64 (ddd, $J = 10, 7, 2$ Hz, 1 H, $CH_2CH = CH$), 2.95 (t, $J = 4$ Hz, 1 H, $COCH$), 2.24 (m, 1 H, $CH = CHCH$), 2.19–1.70 (m, 5 H, CH_2CH_2CH); ^{13}C NMR: δ 198.6, 137.9, 132.6, 128.4, 127.9, 126.0, 125.4, 30.3, 27.4, 25.3, 20.7, 17.8; MS (70 eV): m/z 198 (M^+), 120, 105, 91, 77.

endo-7-*Cyano*-exo-7-*phenyl-2-norcarene* (9). To a solution of LDA (2.00 mmol) prepared as described above, was added benzyl cyanide (230 μl, 2.00 mmol) at $-78°C$ and the resulting mixture was stirred for 3 h.[9] 2-Phenylsulfonyl-1,3-cyclohexadiene (440 mg, 2.00 mmol) in THF (1.00 ml) was added at $-78°C$ over 5 min. The tem-

perature was maintained at $-78°C$ for 3 h and was then allowed to reach 20°C. After about 2 h a precipitate had formed and the reaction was quenched with NH_4Cl (aq). Work-up as above, followed by flash chromatography (EtOAc–hexane = 10:90) gave 250 mg (64%) of 9 as a colorless oil, which crystallized on standing. M.p. 89–91°C; IR (CCl_4): 2235 cm^{-1}; ^1H NMR: δ 7.40–7.20 (m, 5 H, ArH), 6.02 (m, 2 H, $CH = CH$), 2.40–2.07 (m, 6 H, aliphatic-H); ^{13}C NMR: δ 136.7, 130.0, 128.8, 127.3, 125.1, 120.6, 119.3, 30.0, 29.1, 28.6, 20.5, 17.0.

The measured coupling constants $^3J_{CH}$ between the cyano group and the bridgehead protons were found to be 0 Hz. This is consistent with the cyano group being endo.[9,21] Anal. calc. for $C_{14}H_{13}N$: C, 86.12; H, 6.71. Found: C, 85.95; H, 6.69.

4-(1,5-*Dimethyl-5-hydroxy-2-oxohexyl)-1-methyl-3-(phenylsulfonyl)cyclohexene* (13). A solution of LDA (115.1 mmol) was prepared as described above replacing THF with benzene. 6-Hydroxy-6-methyl-3-heptanone (12) (8.30 g, 57.56 mmol) was added to this solution at 0°C and the resulting mixture was stirred for 1 h. 1-Methyl-3-phenylsulfonyl-1,3-cyclohexadiene (11) (11.24 g, 47.97 mmol) in benzene (90.5 ml) was added over 3 h by the use of a syringe pump and the reaction mixture was stirred for another 45 min. The reaction was quenched with NH_4Cl (aq). Purification of the crude product by flash chromatography (EtOAc–hexane = 30:70) afforded 10.71 g (59%) of the pure adduct (13) as two stereoisomers. IR ($CDCl_3$): 3600, 3519, 3069, 2973, 2935, 1707, 1668, 1447, 1374, 1303, 1249, 1145, 1085 cm^{-1}. Major diastereoisomer: ^1H NMR: δ 7.88–7.82 (m, 2 H), 7.66 (m, 1 H), 7.60–7.52 (m, 2 H), 5.32 (m, 1 H), 3.43 (m, 1 H), 2.82 (m, 1 H), 2.70–2.43 (m, 3 H), 1.96–1.48 (m, 6 H), 1.73 (d, $J = 1.2$ Hz, 3 H), 1.22 (s, 3 H), 1.22 (s, 3 H), 1.08 (d, $J = 7$ Hz, 3 H); ^{13}C NMR: δ 214.2, 144.4, 137.5, 133.6, 129.2, 128.9, 111.5, 70.1, 64.6, 47.5, 36.5, 35.4, 32.6, 29.5, 29.4, 26.6, 24.1, 20.1, 13.1. Minor diastereoisomer: ^1H NMR: δ 7.91–7.85 (m, 2 H), 7.65 (m, 1 H), 7.60–7.52 (m, 2 H), 5.36 (m, 1 H), 3.66 (m, 1 H), 2.74–2.38 (m, 4 H), 1.92–1.50 (m, 6 H), 1.74 (s, 3 H), 1.21 (s, 6 H), 0.97 (d, $J = 7$ Hz, 3 H); ^{13}C NMR: δ 213.9, 144.2, 137.8, 133.6, 129.0, 129.0, 111.0, 69.9, 63.0, 46.9, 36.5, 36.3, 33.6, 29.5, 29.4, 26.4, 24.1, 21.6, 15.4.

3,endo-7-*Dimethyl*-exo-7-(4-*hydroxy-4-methylpentanoyl)-2-norcarene* (14). A solution of LDA (27.5 mmol) was prepared as described above replacing THF with benzene and the adduct 13 (10.00 g, 27.5 mmol) in benzene (40.00 ml) was added at 0°C. The temperature was raised to 80°C and the reaction mixture was stirred at this temperature for 16 h. The reaction was quenched with NH_4Cl (aq). Work-up as above followed by flash chromatography (EtOAc–hexane = 30:70) afforded 4.55 g (70%) of the cyclopropane 14. IR ($CDCl_3$): 3604, 3425, 2972, 2931, 1668, 1448, 1386, 1372, 1131 cm^{-1}; ^1H NMR: δ 5.44 (m, 1 H, $C = CH$), 2.67 (t, $J = 7$ Hz, 2 H, $COCH_2CH_2$), 2.02 (m, 1 H, $CH_2C = CH$), 1.99–1.91 (m, 2 H, $C = CHCH$,

CH_2CH_2CH), 1.83–1.56 (m, 3 H, CH_2CH_2CH, CH_2CH_2CH, CH_2CH_2CH), 1.75 (t, $J = 7$ Hz, 2 H, $COCH_2CH_2$), 1.70 (d, $J = 0.8$ Hz, 3 H, $CH_3C = CH$), 1.22 [s, 6 H, $C(CH_3)_2OH$], 1.20 (s, 3 H, CH_3CCO); ^{13}C NMR: δ 211.8, 137.3, 116.6, 70.0, 38.8, 36.8, 34.4, 29.4, 29.4, 28.1, 26.8, 24.9, 23.7, 16.6, 9.8.

4-(1,5-Dimethyl-5-hydroxy-2-oxohexyl)-3-(phenylsulfonyl)-cyclohexene (15). Prepared according to the same method as described above for **13**. 3-Phenylsulfonyl-1,3-cyclo-hexadiene (**1**) (10.57 g, 47.97 mmol) was used instead of the sulfonyl diene **11**. Work-up as above followed by flash chromatography (EtOAc–hexane = 40:60) afforded 10.50 g (60%) of the pure adduct **15** as two diastereo-isomers. IR ($CDCl_3$): 3690, 3605, 3550, 3040, 2973, 2932, 1705, 1602, 1448, 1373, 1305, 1146, 1086 cm^{-1}. Major diastereoisomer: ^1H NMR: δ 7.92–7.84 (m, 2 H), 7.66 (m, 1 H), 7.60–7.53 (m, 2 H), 6.15 (dm, $J = 10$ Hz, 1 H), 5.59 (dm, $J = 10$ Hz, 1 H), 3.47 (m, 1 H), 2.88 (quintet, $J = 8$ Hz, 1 H), 2.71–2.45 (m, 2 H), 2.57 (m, 1 H), 1.96–1.82 (m, 3 H), 1.80–1.65 (m, 2 H, CH_2, AB part of ABXY-system), 1.65–1.48 (m, 2 H, include OH), 1.23 (s, 3 H), 1.22 (s, 3 H), 1.10 (d, $J = 7$ Hz, 3 H); ^{13}C NMR: δ 214.1, 137.4, 136.0, 133.7, 129.2, 129.0, 117.6, 70.0, 63.8, 47.5, 36.5, 35.5, 33.0, 29.4, 29.4, 21.7, 19.7, 13.1. Minor diastereoisomer: ^1H NMR: δ 7.92–7.86 (m, 2 H), 7.66 (m, 1 H), 7.61–7.53 (m, 2 H), 6.16 (m, 1 H), 5.62 (m, 1 H), 3.67 (m, 1 H), 2.75 (m, 1 H), 2.66–2.45 (m, 3 H), 1.96 (m, 2 H), 1.80–1.68 (m, 3 H), 1.55 (s, 1 H, OH), 1.40 (m, 1 H), 1.21 (s, 6 H), 1.05 (d, $J = 7$ Hz, 3 H); ^{13}C NMR: δ 213.9, 137.7, 135.9, 133.7, 129.1, 129.1, 117.2, 70.0, 62.3, 46.9, 36.5, 36.3, 34.1, 29.5, 29.4, 21.5, 21.1, 15.4.

endo-7-Methyl-exo-7-(4-hydroxy-4-methylpentanoyl)-2-nor-carene (16). Prepared according to the same method as described above for **14**, using adduct **15** in place of **13**. The reaction mixture was stirred at 80°C for 2 days. Pu-rification of the crude product by flash chromatography (EtOAc–hexane = 30:70) afforded 3.48 g (57%) of the cy-clopropane **16**. IR ($CDCl_3$): 3400, 3033, 2973, 1671, 1448, 1387, 1372 cm^{-1}; ^1H NMR: δ 5.83 (dt, $J = 10$, 4 Hz, 1 H, $CH = CHCH$), 5.74 (dm, $J = 10$ Hz, 1 H, $CH = CHCH$), 2.67 (t, $J = 7$ Hz, 2 H, $COCH_2CH_2$), 2.07 (m, 1 H, $CH_2CH = CH$), 1.97–1.86 (m, 2 H, $CH = CHCH$, CH_2CH_2CH), 1.84–1.70 (m, 2 H, CH_2CH_2CH), 1.74 (t, $J = 7$ Hz, 2 H, $COCH_2CH_2$), 1.68–1.55 (m, 1 H, CH_2CH_2CH), 1.25 (s, 3 H, CH_3CCO), 1.21 [s, 6 H, $C(CH_3)_2OH$]; ^{13}C NMR: δ 211.5, 129.2, 122.9, 70.1, 38.9, 36.9, 34.4, 29.5, 29.4, 26.2, 25.6, 21.5, 15.7, 9.7.

Irradiation of the protons of the 7-methyl group gave an NOE for the olefin protons, which is consistent only with the 7-methyl being *endo*. Anal. calc. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.34; H, 9.82.

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16. This may be due to formation of a cyclic hemiacetal anion, or to the larger charge separation obtained when the second anion is α to the sulfonyl group.

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