251. A Novel Pentannulation Sequence

Facile Access to Key Intermediates for the Synthesis of *Exaltone*® and Muscone

by **Charles Fehr**

Firmenich SA, Research Laboratories, CH-1211 Geneva 8

(23. VIII. 83)

Summary

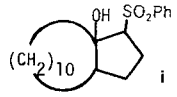
Treatment of the sulfonyl ketones **1a** and **1b** with potassium *t*-butoxide in toluene or with potassium hydroxide in toluene/dimethyl sulfoxide affords in high yield the bicyclic dienes **3a** and **3b**, important precursors for *Exaltone*® and (±)-muscone. An application of this novel pentannulation sequence is demonstrated for the sulfonyl ketones **6**, **10**, and **14**. An intermolecular variant is exemplified by the synthesis of diene **22**.

The preceding paper [2] described a new synthesis of (±)-muscone based on the intramolecular condensation of a sulfonyl lactone followed by reductive removal of the sulfonyl group. We now report the analogous intramolecular reaction of the sulfonyl ketones **1a** and **1b**, leading to the bicyclo[10.3.0]pentadecenes **4a** and **4b**, which are key intermediates for the synthesis of *Exaltone*® and (±)-muscone [3] *(Scheme 1)*.

The intramolecular cyclization of the readily available sulfonyl ketone **1a** [1] [2] using *t*-BuOK (1.5 equiv.) in toluene at 50° [2]) gave the β,γ-unsaturated sulfone **2a** in 88% yield *(Scheme 1)* [3]). Sulfone **2a** may be directly reduced to **4a** (*cf.* [5]) but for convenience we preferred to exploit the allylic nature of the sulfonyl group for its possible elimination [4]). Accordingly, when sulfonyl ketone **1a** was treated with an excess of *t*-BuOK in toluene at reflux, the allylic sulfone **2a** formed *in situ* was directly transformed to the diene **3a** (9:1 isomeric mixture) in 83% yield. Alternatively, NaOMe or KOH in hot toluene containing a small amount of DMSO effected the same conversion; in the absence of DMSO, the reaction stopped at the bicyclic sulfone **2a**.

---

[1]) The part of this work concerned with *Exaltone*® and muscone was presented at the Swiss Chemical Society Meeting in Berne, October 16, 1981. For a preliminary account, see [1].

[2]) 

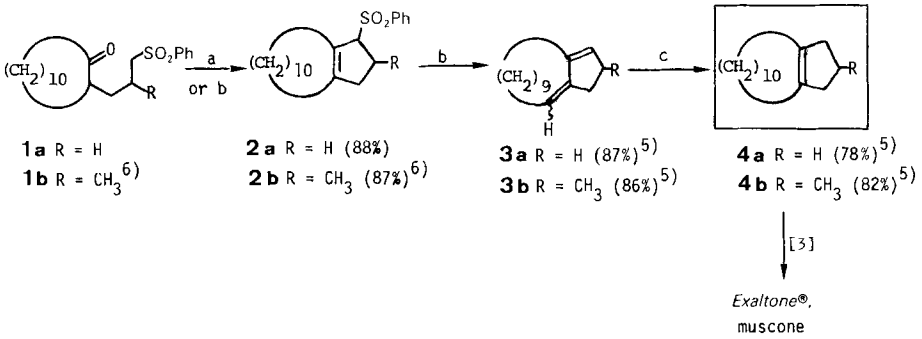
i

At 25° hydroxy sulfone **i** (mixture of diastereomers) was formed.

[3]) Presumably, dehydration of **i** leads to the α,β-unsaturated sulfone which readily isomerizes to **2a** (*cf.* [4]).

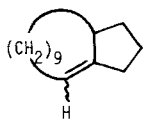
[4]) Saturated sulfones undergo elimination only under more stringent conditions [6].

Scheme 1

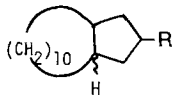


Reagents: a) *t*-BuOK (1.5 equiv.), toluene/50°/1 h or KOH (7 equiv.), toluene/110°/30 min; b) *t*-BuOK (2.5 equiv.), toluene/110°/1 h or KOH (6.5 equiv.), toluene, DMSO (2.8 equiv.)/110°/15 h [7]; c) H_2/Pd/C, toluene/100°/45 min.

The hydrogenation of **3a** (Pd/C, toluene/100°) gave a mixture of the desired alkene **4a** and its isomer **ii**; the latter was converted into **4a** [3] (78% from **1a**) using a prolonged reaction time (45 min), a small amount (7%) of fully hydrogenated product **iii** was also formed [8]).



ii



iii R = H
iv R = CH_3

The same sequence was applied to the sulfonyl ketone **1b** affording diene **3b** (86%, 93 : 7 isomeric mixture). Hydrogenation gave **4b** (82% from **1b**), together with **iv** (5%). In comparison with the classical synthesis of **4b** [3], this sequence represents a substantial improvement in yield and simplicity [9]).

To investigate the scope of this novel pentannulation sequence [10]), we prepared the bicyclic dienes **8**, **12**, and **16**, free from any C, C-double bond isomers, in one operation from the corresponding sulfonyl ketones **6**, **10**, and **14**. The latter were readily obtained from the corresponding allyl ketones **5**, **9**, and **13** by the usual sequence [2] of radical-initiated thiophenol addition and peracid oxidation of the intermediate thioether *(Scheme 2)*. The intermolecular variant of this sequence is also feasable; thus

[5]) Yield based on **1a** and **1b**.

[6]) Diastereomeric mixture.

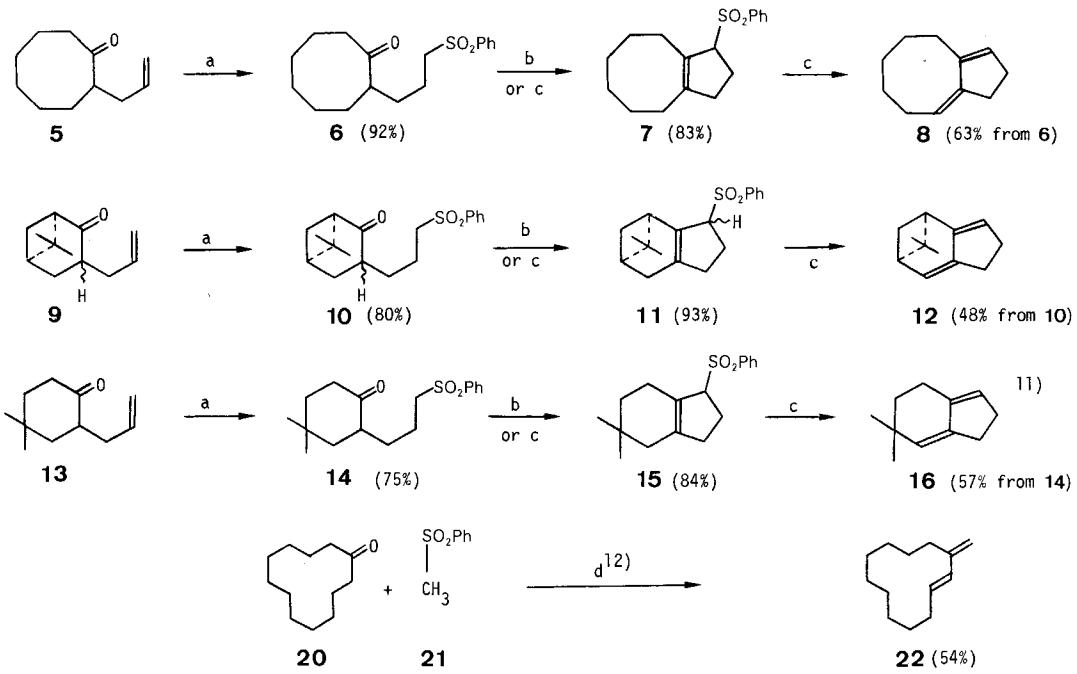
[7]) Other reaction conditions which effect the transformation **1a** to **3a** include: $NaOCH_3$, toluene, DMSO; NaH, $H_2N(CH_2)_2NH_2$; $NaOC(CH_3)_2C_2H_5$, toluene, DMSO.

[8]) When the hydrogenation was performed at 20°, the amount of **iii** increased to 15%.

[9]) 71% yield (76% based on consumed material) in three steps from 2-(2-methylallyl)cyclododecanone (*cf.* [2] and [7]). After completion of our work [1], an alternative approach to intermediate **4b** was reported [7].

[10]) To our knowledge, the combination of an intramolecular sulfonyl ketone condensation with subsequent elimination of sulfinic acid has not been reported. For intramolecular sulfonyl ketone condensations, see [8]; for examples of sulfinate eliminations, see [9].

Scheme 2



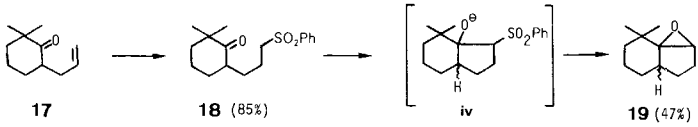
Reagents: a) PhSH (1 equiv.)/α, α'-azoisobutyronitrile/80°/12 h, then CH_3CO_3H (2 equiv.), toluene/30°; b) KOH (10 equiv.), toluene/110°/1 h; c) KOH (10 equiv.), toluene, DMSO/110°/15 h; d) *t*-BuOK (2.5 equiv.), toluene/110°/24 h.

(*E*)-3-methylenecyclododecene (**22**) was obtained in 54% yield from cyclododecanone (**20**) and methyl phenyl sulfone (**21**)[13]).

In conclusion, a novel pentannulation sequence with concomitant regioselective formation of a diene has been developed. The synthetic versatility of the bicyclic allylic sulfones, together with the possibility of analogous formation of other ring systems, further increases the preparative value of this sequence which is confidently expected to find application for elaboration of structurally more complex systems.

---

[11]) Unexpectedly, the cyclization of **18** led to epoxide **19**. Apparently, steric constraints in the intermediate alkoxy sulfone **iv** favor epoxide formation over dehydration. A similar type of reaction starting from oxo-sulfonium compounds has recently been reported [11].



[12]) When reaction conditions c) were used, **22** was obtained together with two unidentified isomeric dienes.

[13]) For a related reaction, see [10].

Experimental Part

General Remarks. See [2]. Specific rotations: *Perkin-Elmer 141* polarimeter ($CHCl_3$-solutions, 20°). UV: *Unicam SP 700 A* (EtOH-solutions, λ max. in nm ε in parentheses. ^{1}H-NMR: *Bruker WH 360* (360 MHz), *Bruker HX 90* (90 MHz). ^{13}C-NMR: *Bruker WH 360* (90.5 MHz), *Bruker HX 90* (22.63 MHz).

13-Phenylsulfonylbicyclo[10.3.0]pentadec-1(12)-ene (**2a**). A solution of *2-[3-(phenylsulfonyl)propyl]-cyclododecanone* (**1a**) [2] (728 mg, 2.0 mmol) and *t*-BuOK (336 mg, 3.0 mmol) in toluene (8 ml) was heated at 50° for 1 h. Addition of H_2O and extraction (Et_2O) afforded 673 mg of a crystalline product. Recrystallization (Et_2O/PE) gave pure **2a** (612 mg, 88%), m.p. 94–99°. The same result was obtained by heating a suspension of **1a** (728 mg, 2.0 mmol) and KOH (760 mg, 14.0 mmol) in toluene (8 ml) at reflux for 1 h. IR ($CDCl_3$): 2920, 1460, 1440, 1300, 1285, 1125, 1080. ^{1}H-NMR (90 MHz): 0.95–1.95 (*m*, 18 H); 2.00–2.70 (*m*, 6 H); 4.20 (br. *d*, *J* = 7, 1 H); 7.40–7.95 (*m*, 5 H). ^{13}C-NMR (22.63 MHz): 22.1 (*t*); 22.4 (*t*); 23.4 (*t*); 23.9 (*t*); 24.3 (*t*); 24.7 (*t*); 25.0 (*t*); 25.2 (*t*); 32.5 (*t*); 73.2 (*d*); 128.6 (2 *d*); 128.9 (2 *d*); 130.3 (*s*); 133.4 (*d*); 137.7 (*s*); 147.3 (*s*). MS: 219 (15), 218 (8), 147 (7), 133 (7), 119 (14), 107 (17), 105 (15), 95 (35), 91 (24), 81 (21), 77 (19), 55 (19), 40 (100).

14-Methyl-13-phenylsulfonylbicyclo[10.3.0]pentadec-1(12)-ene (**2b**)[6]. Heating *2-[2-methyl-3-(phenylsulfonyl)propyl]cyclododecanone* (**1b**) [2] (756 mg, 2 mmol) with KOH (760 mg, 14.0 mmol) in toluene (8 ml) at 50° for 1 h afforded, after bulb-to-bulb distillation (200°/0.01 Torr, **2b**[6]) (627 mg, 87%). IR ($CDCl_3$): 2945, 1470, 1445, 1300, 1140, 1080. ^{1}H-NMR (90 MHz): 0.90–1.80 (*m*, 22 H); 2.20–3.00 (*m*, 4 H); 3.78 (br. *s*, 1 H); 7.35–7.96 (*m*, 5 H). MS: 360 (0.5, M^+), 220 (9), 219 (48), 149 (9), 147 (12), 133 (13), 123 (13), 119 (24), 109 (22), 107 (33), 94 (71), 81 (62), 69 (44), 55 (50), 41 (56), 40 (100).

Bicyclo[10.3.0]pentadeca-1,12-diene (**3a**)[14]. A mixture of **2a** (728 mg, 2.0 mmol) and *t*-BuOK (560 mg, 5.0 mmol) in toluene (8 ml) was heated at reflux for 1 h, in a *Dean-Stark* apparatus. The resulting thick slurry was cooled at 10° and treated with H_2O. Extraction (Et_2O) and bulb-to-bulb distillation (140°/0.02 Torr) furnished **3a** (340 mg, 83%). In another experiment, a suspension of **2a** (10.92 g, 30.0 mmol), KOH (11.0 g, 197 mmol), toluene (40 ml) and DMSO (6.6 g (6.0 ml), 84.5 mmol) was heated at reflux for 15 h, in a *Dean-Stark* apparatus[15]. Extraction and bulb-to-bulb distillation afforded **3a** (5.32 g, 87%). UV: 246 (16880). IR (neat): 2910, 1460, 1440, 925, 915, 845. ^{1}H-NMR (360 MHz): 1.10–1.70 (*m*, 14 H); 2.12 (*t d*, *J* = 7.5 and 5, 2 H); 2.32 (*t*, *J* = 7, 2 H); 2.38 (*m*, 2 H); 2.52 (*m*, 2 H); 5.47 (*t t*, *J* = 7.5 and 2.5, 1 H); 5.72 (br. *s*, 1 H). MS: 205 (15), 204 (84, M^+), 175 (8), 161 (34), 148 (60), 147 (78), 134 (42), 133 (100), 119 (62), 106 (42), 105 (57), 93 (47), 91 (81), 79 (70), 67 (58).

14-Methylbicyclo[10.3.0]pentadeca-1,12-diene (**3b**)[14]. Sulfone **2b** (11.35 g, 30.0 mmol) was converted to **3b** (5.61 g, 86%), b.p. 150° (bath)/0.05 Torr, using the procedure for the synthesis of **3a** (with KOH). UV: 247 (16280). IR (neat): 2920, 1460, 1440, 835. ^{1}H-NMR (90 MHz): 1.00 (*d*, *J* = 7, 3 H); 1.08–1.73 (*m*, 14 H); 1.80–2.40 (*m*, 5 H); 2.55–2.91 (*m*, 2 H); 5.40 ('*t*', *J* = 7.5, 1 H), 5.60 (br. *s*, 1 H). MS: 219 (16), 218 (93, M^+), 203 (80), 175 (30), 161 (70), 147 (100), 133 (92), 112 (68), 107 (60), 106 (44), 105 (68), 94 (55), 93 (72), 91 (75), 79 (55), 67 (32), 55 (38).

Bicyclo[10.3.0]pentadec-1(12)-ene (**4a**). A solution of crude **3a** (6.06 g), obtained from **1a** (10.92 g, 30.0 mmol) in toluene (40 ml) was hydrogenated at 100° in the presence of 10% Pd/C (600 mg). After 15 min the H_2-absorption was complete (740 ml) and GC analysis indicated the absence of **3a** and the formation of two new products. Isomerization was effected by shaking the mixture under H_2 until disappearance of one of the two GC, peaks (30 min). The mixture was cooled to 20°, filtered *(Celite)*, evaporated and the residue distilled at 140° (bath)/0.02 Torr to give **4a** (5.20 g (93% pure), 78%)[5], identical in all respects with an authentic sample [3].

14-Methylbicyclo[10.3.0]pentadec-1(12)-ene (**4b**). The crude **3b** (6.48 g) obtained from **1b** (11.34 g, 30.0 mmol) was hydrogenated as described above for **4a** to give **4b** (5.69 g, (95% pure), 82%)[5], b.p. 150° (bath)/0.02 Torr, which was identical in all respects to an authentic sample [3].

Preparation of 2-allylcyclooctanone (**5**) [12], *(1R,5R)-3-allyl-6,6-dimethylbicyclo[3.1.1.]heptan-2-one* (**9**)[6], *2-allyl-4,4-dimethylcyclohexanone* (**13**) and *6-allyl-2,2-dimethylcyclohexanone* (**17**). The general procedure is given for **9**. A solution of allyl chloride (535 mg (= 0.50 ml), 7.0 mmol) in toluene (10 ml) was added dropwise over a period of 15 min to a stirred suspension of KOH (560 mg, 10.0 mmol), *t*-BuOK (1.12 g, 10.0 mmol) and (1*R*, 5*R*)-nopinone [13] (1.38 g, 10.0 mmol) in toluene (8 ml) at 60° in an apparatus equipped with an efficient reflux condenser. Stirring was continued for 30 min at 60°, the mixture was cooled to 20°, treated with H_2O and then extracted with Et_2O. Bulb-to-bulb distillation (120°/0.1 Torr) afforded a *ca.* 1:1 mixture (1.50 g) of (1*R*,

---

[14]) The configuration at the C(1), C(2)-double bond was not determined (**3a** 9:1 mixture, **3b** 93:7 mixture of stereoisomers).

[15]) The use of larger amounts of KOH (13.5 g, 240 mmol) or DMSO (12 ml) reduces the reaction time to 30–60 min.

5 *R*)-nopinone and allyl-nopinone **9**[6]) together with a minor amount (*ca.* 10%) of diallylated product. Chromatography (silica gel) with cyclohexane/AcOEt 98 : 2 afforded recovered (1 *R*, 5 *R*)-nopinone (680 mg, 49%) and pure **9**[6]) (705 mg, 78% based on consumed (1 *R*, 5 *R*)-nopinone). IR (neat): 2950, 2880, 1705, 1645, 920. – ^{1}H-NMR (60 MHz): 0.73 and 0.92 (2 *s*, ≈ 4 : 1, together 3 H), 1,33 (*s*, 3 H), 1.35–3.00 (*m*, 9 H), 4.90–5.20 (*m*, 2 H), 5.50–6.20 (*m*, 1 H). MS: 178 (13, M^+), 163 (14), 137 (33), 109 (26), 95 (100), 83 (98), 67 (49), 55 (67), 41 (82).

Using the above procedure, the ketones **5** [12] (80%, conversion 55%), **13** (76%, conversion 50%) and **17** (81%, conversion 58%) were prepared.

Data for **13**. IR (neat): 2950, 2880, 1710, 1640, 920. ^{1}H-NMR (60 MHz): 1.00 (*s*, 3 H); 1.20 (*s*, 3 H); 1.50–2.85 (*m*, 9 H); 4.88 (*m*, 1 H); 5.10 (*m*, 1 H); 5.50–6.20 (*m*, 1 H). MS: 151 (1), 122 (6), 109 (17), 95 (20), 81 (22), 69 (41), 67 (34), 55 (83), 43 (49), 41 (100).

Data for **17**. IR (neat): 2950, 2875, 1710, 1645, 1430, 995, 920. ^{1}H-NMR (60 MHz): 1.03 (*s*, 3 H); 1.19 (*s*, 3 H); 1.30–2.80 (*m*, 9 H); 4.88 (*m*, 1 H), 5.11 (*m*, 1 H); 5.30–6.15 (*m*, 1 H). MS: 166 (44, M^+), 151 (8), 123 (13), 109 (13), 95 (34), 82 (100), 67 (41), 55 (51), 41 (57).

Preparation of 2-[3-(phenylsulfonyl)propyl]cyclooctanone (**6**), *(1 R, 5 R)-6,6-dimethyl-3-[3-(phenylsulfonyl)propyl]bicyclo[3.1.1]heptan-2-one* (**10**)[6]), *4,4-dimethyl-2-[3-(phenylsulfonyl)propyl]cyclohexanone* (**14**) and *2,2-dimethyl-6-[3-(phenylsulfonyl)propyl]cyclohexanone* (**18**). The sulfonyl ketones **6**, **10**, **14**, and **18** (for yields see *Scheme 2*) were prepared by radical-initiated addition of PhSH and subsequent oxidation of the resulting thio ethers with CH_3CO_3H at 10–20° as described for **1a** [2]. Purification was effected by chromatography (silica gel) with cyclohexane/AcOEt 92 : 8 or by recrystallization (Et_2O).

Data for **6**. IR (neat): 2950, 2870, 1700, 1450, 1310, 1150, 1090. ^{1}H-NMR (60 MHz): 1.10–2.70 (*m*, 17 H); 3.10 ('*t*', *J* ≈ 7, 2 H); 7.50–8.10 (*m*, 5 H).

Data for **10**[6]). IR (neat): 2950, 2880, 1710, 1450, 1310, 1150, 1090. ^{1}H-NMR (60 MHz): 0.67 and 0.87 (2 *s*, *ca.* 4 : 1, together 3 H); 1.30 (*s*, 3 H); 1.20–2.70 (*m*, 11 H); 3.16 ('*t*', *J* = 7.5, 2 H); 7.50–8.10 (*m*, 5 H).

Data for **14**. M.p. 67–70°. IR ($CDCl_3$): 2950, 2880, 1705, 1450, 1310, 1150, 1090. ^{1}H-NMR (60 MHz): 0.99 (*s*, 3 H); 1.19 (*s*, 3 H); 1.30–2.70 (*m*, 11 H); 3.10 ('*t*', *J* ≈ 7, 2 H); 7.50–8.10 (*m*, 5 H).

Data for **18**. IR (neat): 2950, 2880, 1705, 1450, 1310, 1150, 1090. ^{1}H-NMR (60 MHz): 1.00 (*s*, 3 H); 1.16 (*s*, 3 H); 1.30–2.70 (*m*, 11 H); 3.11 ('*t*', *J* ≈ 7, 2 H); 7.50–8.10 (*m*, 5 H).

Preparation of 9-phenylsulfonylbicyclo[6.3.0]undec-1(8)-ene (**7**), *(1 R, 8 R)-9,9-dimethyl-3-phenylsulfonyltricyclo[6.1.1.0^{2,6}]dec-2(6)-ene* (**11**)[6]) and *3,3-dimethyl-7-phenylsulfonylbicyclo[4.3.0]non-1(6)-ene* (**15**). The sulfones **7**, **11**, and **15** (for yields, see *Scheme 2*) were prepared from the ketones **6**, **10**, and **14** (10 mmol), respectively, using KOH (10 equiv.) in toluene (40 ml) as described for the preparation of **2a**. Purification was effected by chromatography (silica gel) using cyclohexane/AcOEt 19 : 1.

Data for 7. IR ($CDCl_3$): 2950, 2865, 1450, 1300, 1140, 1090. ^{1}H-NMR (60 MHz): 1.20–2.70 (*m*, 16 H); 4.10 (*m*, 1 H); 7.40–8.00 (*m*, 5 H).

Data for **11**[6]). IR ($CDCl_3$): 2950, 1450, 1310, 1150, 1090. ^{1}H-NMR (60 MHz): 0,69 and 0.98 (2 *s*, *ca.* 3 : 2, together 3 H); 1.25 (*s* + *m*, 3 + 1 H); 2.00–2.70 (*m*, 9 H); 4.14 (*m*, 1 H); 7.40–8.00 (*m*, 5 H).

Data for **14**. IR (neat): 2950, 1450, 1310, 1150, 1090. ^{1}H-NMR (60 MHz): 0.90 (2 *s*, 6 H); 1.36 (*t*, *J* = 6, 2 H); 1.60–2.50 (*m*, 8 H); 4.11 (*m*, 1 H); 7.40–8.00 (*m*, 5 H).

Preparation of bicyclo[6.3.0]undeca-1,8-diene (**8**), *(1 R, 8 S)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-2,6-diene* (**12**) and *3,3-dimethylbicyclo[4.3.0]nona-1,6-diene* (**16**). The dienes **8**, **12**, and **16** (for yields, see *Scheme 2*) were prepared from the sulfonyl ketones **6**, **10**, and **14** (10 mmol), respectively, using KOH (10 equiv.) and DMSO (4 ml) in toluene (40 ml) as described for the preparation of **3a** and purified by bulb-to-bulb distillation (120°/4 Torr).

Data for **8**. UV: 249 (12160). IR (neat): 3050, 2930, 2855, 1480, 1445, 1275, 1015, 930, 795. ^{1}H-NMR (360 MHz): 1.55 (*m*, 4 H); 1.63 (*m*, 2 H); 2.36 (*m*, 4 H); 2.59 (*m*, 4 H); 5.28 (*t*, *J* = 8, 1 H); 5.71 (br. *s*, 1 H). ^{13}C-NMR (90.5 MHz): 22.7 (*t*); 25.3 (*t*); 27.9 (*t*); 29.0 (2 *t*); 29.9 (*t*); 31.7 (*t*); 114.2 (*d*); 135.8 (*d*); 145.4 (*s*); 149.7 (*s*). MS: 148 (61, M^+), 133 (38), 119 (100), 105 (74), 91 (96), 79 (55), 77 (30), 41 (27).

Data for **12**. $[\alpha]_D = 0$, $[\alpha]_{436} = +13$ (*c* = 0.16). UV: 256 (9200). IR (neat): 3050, 2950, 460, 1370, 840, 780. ^{1}H-NMR (360 MHz): 0.78 (*s*, 3 H); 1.34 (*s*, 3 H); 1.40 (*d*, *J* = 8.5, 1 H); 2.23 (*dt*, *J* = 6 and 6, 1 H); 2.51 (*m*, 5 H); 2.73 (*t*, *J* = 6, 1 H); 5.50 (*m*, 1 H); 5.81 (br. *d*, *J* = 6, 1 H)[16]). ^{13}C-NMR (22.63 MHz): 22.7 (*q*); 25.6 (*t*); 26.4 (*q*); 32.5 (*t*); 35.7 (*t*); 43.3 (*d*); 43.9 (*s*); 45.5 (*d*); 121.4 (*d*); 123.9 (*d*); 144.5 (*s*); 150.0 (*s*). MS: 160 (16, M^+), 145 (12), 128 (7), 117 (100), 115 (25), 91 (14), 77 (7).

Data for **16**. UV: 243 (14200). IR (neat): 3050, 2950, 2870, 1450, 1370, 920, 810. ^{1}H-NMR (360 MHz): 1.00 (2 *s*, 6 H); 1.44 (*t*, *J* = 6.5, 2 H); 2.33–2.47 (*m*, 6 H); 5.21 (*m*, 1 H); 5.57 (*m*, 1 H). ^{13}C-NMR (22.63 MHz): 22.0 (*t*);

[16]) For an ^{1}H-NMR interpretation of similar systems, see [14].

27.6 (*t*); 29.6 (2 *q*); 30.5 (*t*); 32.4 (*s*); 37.4 (*t*); 125.7 (*d*); 127.5 (*d*); 141.3 (*s*); 143.4 (*s*). MS: 148 (21, M^+), 133 (100), 115 (7), 105 (25), 91 (26), 77 (21).

10,10-Dimethyl-2-oxatricyclo[4.4.0.0^{1,3}]decane (**19**)[6]. A solution of the sulfonyl ketone **18** (955 mg, 3.10 mmol) and KOH (1.51 g, 27.0 mmol) in toluene (5 ml) was heated at reflux for 8 h. Extraction (Et_2O) and bulb-to-bulb distillation (130°/4 Torr) afforded **19**[6]) (2:1, 240 mg, 47%). IR (neat): 3040, 2950, 2875, 1460, 1390, 1370, 905, 870. ^{1}H-NMR (60 MHz): 0.77 (*s*, 3 H); 1.07 (*s*, 3 H); 0.90–2.20 (*m*, 11 H); 3.39 (*s*, 1 H). MS: 166 (24, M^+), 151 (39), 133 (28), 122 (67), 109 (47), 81 (25), 67 (38), 55 (35), 41 (100).

(E)-3-Methylenecyclododecene (**22**). A suspension of cyclododecanone (**20**) (3.64 g, 20.0 mmol), methyl phenyl sulfone (**21**) [15] (3.12 g, 20.0 mmol) and *t*-BuOK (5.60 g, 50.0 mmol) in toluene (120 ml) was heated at reflux for 24 h. Extraction (Et_2O) and chromatography (silica gel) with cyclohexane afforded **22** (1.93 g, 54%) containing *ca.* 5% of isomeric products and unreacted **20** (404 mg, 11%). UV: 231 (12800). IR (neat): 3085, 2930, 2870, 1605, 1470, 1445, 980, 890. ^{1}H-NMR (360 MHz): 1.20–1.57 (*m*, 14 H); 2.15 (*dt*, J = 7.5 and 6, 2 H); 2.26 (*t*, J = 6.5, 2 H); 4.78 (*m*, 1 H); 4.90 (*d*, J = 2.5, 1 H); 5.86 (*dt*, J = 16 and 7.5, 1 H); 5.97 (*d*, J = 16, 1 H). MS: 178 (25, M^+), 163 (7), 149 (13), 135 (33), 121 (30), 107 (41), 93 (69), 79 (100), 67 (98), 55 (56), 41 (100).

REFERENCES

[1] *C. Fehr* (Firmenich SA), Eur. Pat. Appl. EP 37, 116 (7.10.1981); CH Appl. 80/2, 535 (31.3.1980); Chem. Abstr. *96*, 122291 y (1982).

[2] *C. Fehr*, Helv. Chim. Acta *66*, 2512 (1983).

[3] *G. Ohloff, J. Becker & K. H. Schulte-Elte*, Helv. Chim. Acta *50*, 705 (1967); *J. Becker, K. H. Schulte-Elte & G. Ohloff* (Firmenich et Cie), US Pat. 3,778,483 (11.12.1973); Swiss Pat. 513,791 (30.11.1971); Chem. Abstr. *76*, 99222 c (1972).

[4] *P. D. Magnus*, Tetrahedron *33*, 2019 (1977).

[5] *B. M. Trost, H. C. Arndt, P. E. Strege & T. R. Verhoeven*, Tetrahedron Lett. *1976*, 3477 and references cited therein.

[6] *A. Schöberl & A. Wagner*, in Houben-Weyl, 'Methoden der organischen Chemie', Vol. IX, Georg Thieme, Stuttgart, 1955, p. 244.

[7] *M. Baumann* (BASF AG), Ger. Offen. DE 2,916,418 (6.11.1980); Chem. Abstr. *94*, 156 417 t (1981).

[8] *D. A. Chass, D. Buddhasukh & P. D. Magnus*, J. Org. Chem. *43*, 1750 (1978); *H. O. House & J. K. Larson*, ibid. *33*, 61 (1968).

[9] *G. L. Olson, H.-C. Cheung, K. D. Morgan, C. Neukom & G. Saucy*, J. Org. Chem. *41*, 3287 (1976); *S. Torii, K. Uneyama & H. Ichimura*, ibid. *44*, 2292 (1979); *Q. Branca & A. Fischli*, Helv. Chim. Acta *60*, 925 (1977).

[10] *Ae. de Groot, B. J. M. Jansen, J. T. A. Reuvers & E. M. Tedjo*, Tetrahedron Lett. *1981*, 4137; *S. G. Traynor, B. J. Kane, M. F. Betkouski & L. M. Hirschy*, J. Org. Chem. *44*, 1557 (1979).

[11] *J. K. Crandall, H. S. Magaha, M. A. Henderson, R. K. Widener & G. A. Tharp*, J. Org. Chem. *47*, 5372 (1982); *M. E. Garst, B. J. McBride & A. T. Johnson*, ibid. *48*, 8 (1983).

[12] *H. C. Araújo & J. R. Mahajan*, Synthesis *1978*, 228.

[13] *T. Inokuchi, G. Asanuma & S. Torii*, J. Org. Chem. *47*, 4622 (1982) and references cited therein.

[14] *A. F. Thomas, W. Thommen & J. Becker*, Helv. Chim. Acta *64*, 161 (1981).

[15] *M. Julia & D. Uguen*, Bull. Chem. Soc. Fr. *1976*, 513; *B. M. Trost & D. P. Curran*, Tetrahedron Lett. *1981*, 1287.