New Routes to *cis*-Jasmone and Dihydrojasmone via 1,4-Diketones Exploiting the Mobile Activating Sulfonyl Group

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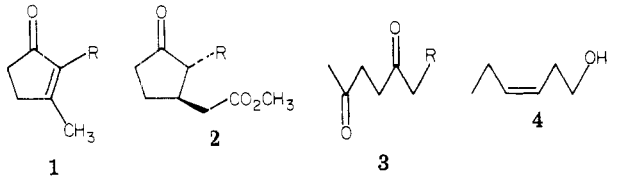
cis-Jasmone (**1a**) and dihydrojasmone (**1b**) are synthesized starting from *cis*-3-hexen-1-yl phenyl sulfone (**6a**) and *n*-hexyl phenyl sulfone (**6b**), respectively, through 1,4-diketones **3a,b**. The key intermediates in these syntheses are the diketo sulfones **7a,b**, which are prepared by two methods. The reaction of dilithio sulfones **12a,b** with γ-valerolactone in tetrahydrofuran in the presence of hexamethylphosphoramide at −78 °C gives the hydroxy keto sulfones **13a,b** in satisfactory yields and the successive oxidation of these compounds with Jones reagent in acetone affords **7a,b** in very good yields. On the other hand, the reaction of **12a,b** with ethyl levulinate ethylene ketal gives the partially protected diketo sulfones **17a,b**, from which **7a,b** are obtained by removal of the protecting group. Cleavage of the carbon–sulfur bond in **7a,b**, accomplished by aluminum amalgam in aqueous tetrahydrofuran, affords **3a,b** which are then cyclized to **1a,b** by heating over basic alumina in benzene.

Undiminished efforts are currently devoted to the synthesis of saturated and unsaturated five-membered cyclic ketones, since a large number of biologically active natural products possess this moiety as a structural feature. Among them *cis*-jasmone (**1a**) and methyl jasmonate **2a**,



1 **2** **3** **4**

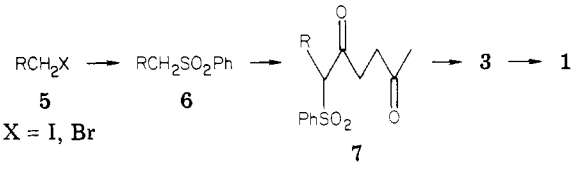
a, R = *cis*-$CH_3CH_2CH{=}CHCH_2$; b, R = *n*-C_5H_{11}

primary odorous principles of the flower oils of several varieties of Jasminum, are raw materials in the perfume industry. Dihydrojasmone (**1b**) and racemic methyl dihydrojasmonate (**2b**) are more easily available by synthesis and so are conveniently used as substitutes for the natural products, although they have inferior olfactory properties.

The most common method to obtain the correctly 2,3-disubstituted cyclopentenones **1a,b** is based on the preliminary preparation of 1,4-unsymmetrically substituted 1,4-diketones **3a,b**,[1-3] since the base-catalyzed cyclization of these compounds is completely regioselective. On the other hand the cis double bond in the lateral chain of *cis*-jasmone is often derived from *cis*-3-hexen-1-ol (**4**), a naturally occurring compound known as "leaf alcohol", through its derivatives, generally the bromide.[1,3]

Starting from **4**, commercially available with more than 97% stereochemical purity, we prepared *cis*-3-hexen-1-yl phenyl sulfone (**6a**) through the iodide **5a** (X = I) and

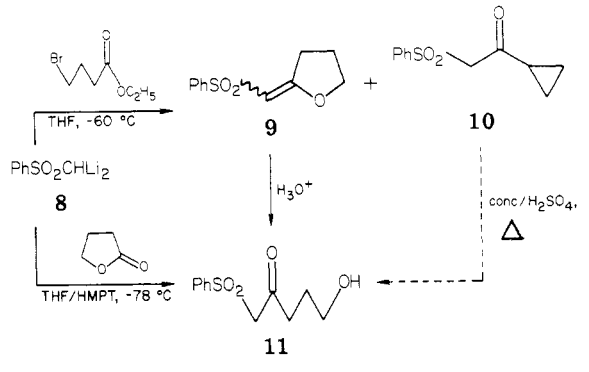
Scheme I



5 X = I, Br; **6**; **7**

a, R = *cis*-$CH_3CH_2CH{=}CHCH_2$; b, R = *n*-C_5H_{11}

Scheme II



8 **9** **10** **11**

exploited the mobile activating sulfonyl group[4] to achieve new syntheses of *cis*-jasmone,[5] following Scheme I. Similarly we prepared dihydrojasmone from *n*-hexyl phenyl sulfone (**6b**).

The crucial point in this scheme is of course the obtainment of the diketo sulfones **7a,b** from sulfones **6a,b**, since the successive step, which involves the cleavage of the carbon–sulfur bond, can be accomplished readily by aluminum amalgam.[6] Hence we have developed different methods to prepare **7a,b** by simple reaction sequences involving in the first step the condensation of sulfones **6a,b** with easily available substrates possessing a suitable 1,4-bifunctionality.

Recently we have described the reaction of dilithioalkyl phenyl sulfones with ethyl 4-bromobutyrate:[7] for example, dilithiomethyl phenyl sulfone (**8**) reacts with this ester in

(1) Synthetic methods to cyclopentenones have been reviewed: R. A. Ellison, *Synthesis*, 397 (1973); T. L. Ho, *Synth. Commun.*, **4**, 265 (1974); *ibid.*, **7**, 351 (1977).

(2) S. Torii, H. Tanaka, and Y. Tomotaki, *Bull. Chem. Soc. Jpn.*, **50**, 537 (1977); S. Takano, T. Sugahara, M. Ishiguro, and K. Ogasawara, *Heterocycles*, **6**, 1141 (1977); P. Bazukis and M. L. F. Bazukis, *J. Org. Chem.*, **42**, 2362 (1977); E. Keinan and Y. Mazur, *J. Am. Chem. Soc.*, **99**, 3861 (1977); P.-E. Sum and L. Weiler, *Can. J. Chem.*, **56**, 2301 (1978); G. Stork, A. Ozorio, and A. Y. W. Leong, *Tetrahedron Lett.*, 5175 (1978); M. Bellassoued, F. Dardoize, and M. Gaudemar, *J. Organomet. Chem.*, **177**, 35 (1979); A. Barco, S. Benetti, G. P. Pollini, P. G. Baraldi, M. Guarneri and G. B. Vicentini, *J. Org. Chem.*, **44**, 105 (1979); J. Tsuji, *Synth. Commun.*, **8**, 103 (1978); T. Takahashi, H. Nagashima, and J. Tsuji, *Tetrahedron Lett.*, 799 (1978).

(3) Y. Ito, T. Konoike, T. Harada, and T. Saegusa, *J. Am. Chem. Soc.*, **99**, 1487 (1977); S. Murata and I. Matsuda, *Synthesis*, 221 (1978); J. Nokami, T. Yamamoto, M. Kawada, M. Izumi, N. Ochi, and R. Okawara, *Tetrahedron Lett.*, 1047 (1979); S. Torii, H. Tanaka, J. Nokami, and M. Kawata, *Bull. Chem. Soc. Jpn.* **52**, 1553 (1979); C. S. Subramaniam, P. J. Thomas, V. R. Mamdapur, and M. S. Chadha, *J. Chem. Soc., Perkin Trans. 1*, 2346 (1979).

(4) The wide applicability of sulfones in organic synthesis has been recently reviewed: P. D. Magnus, *Tetrahedron*, **33**, 1 (1978); B. M. Trost, *Chem. Rev.*, **78**, 363 (1978); L. Field, *Synthesis*, 713 (1978).

(5) The use of sulfur-substituted organolithium compounds to achieve syntheses of jasmonoids, rethrolonoids, and prostanoids via 1,4-dicarbonyl compounds is part of a review: B. T. Grobel and D. Seebach, *Synthesis*, 357 (1977).

(6) E. J. Corey and M. Chaykowsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965); H. O. House and J. K. Larsson, *J. Org. Chem.*, **33**, 61 (1968).

(7) M. C. Mussatto, D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, 260 (1980).

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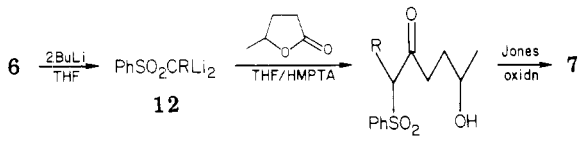
Scheme III



a, R = *cis*-$CH_3CH_2CH{=}CHCH_2$; b, R = *n*-C_5H_{11}

tetrahydrofuran at −60 °C to give (tetrahydro-2-furylidene)methyl phenyl sulfone (**9**), as a mixture of *E* and *Z* isomers, together with (phenylsulfonyl)methyl cyclopropyl ketone (**10**; Scheme II).

Both these compounds can be converted by hydrolysis to the same hydroxy keto sulfone **11**, although under different conditions. In fact, as described for simple five-membered cyclic vinyl ethers,[8] we converted **9** to **11** in 97% yield by means of aqueous dilute hydrochloric acid in tetrahydrofuran at room temperature,[9] whereas **10** would require previous rearrangement in concentrated sulfuric acid on heating.[10]

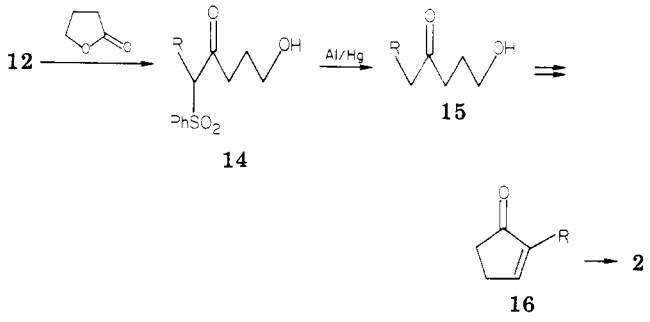
We have found that a more convenient and direct route to benzenesulfonyl-substituted γ-hydroxy ketones is provided by the use of γ-lactones as masked 1,4-bifunctional compounds. To our knowledge only reactions of sulfonyl-stabilized carbanions with nonenolizable lactones have been reported in the literature;[11] nevertheless by the reaction of dilithiomethyl phenyl sulfone (**8**) with γ-butyrolactone at −78 °C in tetrahydrofuran in the presence of a small amount of hexamethylphosphoramide we obtained **11** in 65% yield (Scheme II).

We then applied this method to achieve the synthesis of diketo sulfones **7a,b** and hence of jasmones **1a,b**, starting from sulfones **6a,b** and γ-valerolactone (Scheme III).

cis-3-Hexen-1-yl phenyl sulfone (**6a**) was prepared from *cis*-3-hexen-1-ol (**4**) in three steps in 67% overall yield. Treatment of the alcohol with *p*-toluenesulfonyl chloride in pyridine gave the corresponding tosylate. Subsequent iodide ion displacement in acetone afforded the iodide **5** (X = I),[12] which was converted to the sulfone by the reaction with polymer-supported benzenesulfinate anion in refluxing toluene.[13] With the same supported reagent and 1-bromohexane we obtained the sulfone **6b** in 92% yield.

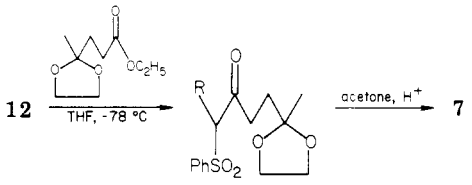
The addition of 2 equiv of *n*-butyllithium to **6a,b** dissolved in tetrahydrofuran gave the soluble dilithio derivatives **12a,b** to which a small amount of hexamethylphosphoramide and then the stoichiometric amount of γ-valerolactone were added at −78 °C. Quenching with aqueous ammonium chloride, usual workup, and column chromatography of the crude reaction mixture afforded the expected products **13a,b** in 63 and 65% yields, respectively. Considerable amounts of unreacted starting materials (about 20% sulfones) were recovered, probably

Scheme IV



a, R = *cis*-$CH_3CH_2CH{=}CHCH_2$; b, R = *n*-C_5H_{11}

Scheme V



a, R = *cis*-$CH_3CH_2CH{=}CHCH_2$; b, R = *n*-C_5H_{11}

owing to the occurrence of a concomitant reaction, i.e., the abstraction of the relatively acidic α-hydrogen atom of the lactone by the sulfonyl carbanions.[14]

The oxidation of **13a,b** was accomplished with Jones reagent[15] in acetone to give the diketo sulfones **7a,b** in very good yields. Then desulfonation with aluminum amalgam[6] in aqueous tetrahydrofuran afforded the 1,4-diketones **3a,b** in approximately 90% yields, pure by VPC analysis.[16]

The final cyclization of **3a,b** can be carried out readily by various described procedures.[1-3] We used basic alumina, which is not only useful as a heterogeneous base or as a reagent support[17] but also permits easy separation of the soluble reaction products by filtration. With this reagent in refluxing toluene we obtained the cyclopentenones **1a,b** in about 60% yields after purification by chromatography on silica gel. *cis*-Jasmone appeared pure by ^1H and ^{13}C NMR spectroscopy. In the infrared spectrum the absorption at 970 cm^{-1}, characteristic of the trans isomer,[18] was almost negligible. However VPC analysis on a Carbowax column showed a cis/trans ratio of 95.5:4.5.[16]

(8) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, 520 (1950); A. Kankaampera, E. Taskinen, and P. Salomaa, *Acta Chem. Scand.*, **21**, 2487 (1967).

(9) Unpublished result from our laboratory.

(10) The hydrolysis of *n*-hexyl 2-methylcyclopropyl ketone to the corresponding γ-hydroxy ketone has been exploited to achieve the synthesis of dihydrojasmone: T. Nakai, E. Wada, and M. Okawara, *Tetrahedron Lett.*, 1531 (1975).

(11) H. O. House and J. K. Larsson, *J. Org. Chem.*, **33**, 61 (1968); L. J. Dolby, S. Esfandiari, C. A. Elliger, and K. S. Marshall, *ibid.*, **36**, 1277 (1971); H. O. House, D. G. Melillo, and F. J. Sauter, *ibid.*, **38**, 741 (1973); P. A. Bartlett, F. R. Green III, and E. H. Rose, *J. Am. Chem. Soc.*, **100**, 4852 (1978).

(12) The one-step preparation of *cis*-1-bromo-3-hexene (**5a**; X = Br) from the alcohol **4** has been performed in lower yield: L. Crombie, S. H. Harper, R. E. Stedman, and D. Thompson, *J. Chem. Soc.*, 1715 (1950); G. Buchi and H. Wuest, *J. Org. Chem.*, **31**, 977 (1966).

(13) F. Manescalchi, M. Orena, and D. Savoia, *Synthesis*, 445 (1979).

(14) For the same reason the reaction of **12a,b** with α-angelica lactone (4-hydroxy-3-pentenoic acid lactone), which would give directly the diketo sulfones **7a,b**, proved to be unsatisfactory since large amounts of unreacted sulfones **6a,b** were recovered. It has been reported, however, that α-angelica lactone undergoes attack of Grignard reagents to give tertiary alcohols through a ring-opening reaction, as is normally done by saturated lactones: R. Chiron and Y. Graff, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **276**, 1207 (1973).

(15) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); R. G. Curtis, I. M. Heilbron, E. R. H. Jones, and G. F. Woods, *ibid.*, 457 (1953).

(16) A single symmetric peak was recorded by VPC analysis of the cis diketone **3a** on a 15% Carbowax column at 170 °C, whereas a strongly unsymmetrical peak was observed under the same experimental conditions for a cis–trans mixture of the same compound prepared from cis–trans 3-hexen-1-yl phenyl sulfone (see Experimental Section). The cyclization of the cis–trans sample with 3% sodium hydroxide in ethanol–water at 80 °C gave a sample of cis–trans jasmone in an approximate 1:1 ratio; the two isomers were almost completely separated on the Carbowax column at 160 °C, as well as on a 5% FFAP column at the same temperature.

(17) G. H. Posner, *Angew. Chem., Int. Ed. Engl.*, **17**, 487 (1978); G. Bram and T. Fillenbeen-Khan, *J. Chem. Soc., Chem. Commun.*, 522 (1979); S. L. Regen, S. Quici, and S.-J. Liaw, *J. Org. Chem.*, **44**, 2029 (1979); S. Quici and S. L. Regen, *ibid.*, **44**, 3436 (1979); D. Savoia, E. Tagliavini, C. Trombini, and A. Umani-Ronchi, *J. Org. Chem.*, **45**, 3227 (1980); D. Savoia, E. Tagliavini, C. Trombini, and A. Umani-Ronchi, *J. Organomet. Chem.*, in press.

(18) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 869 (1952).

A similar reaction sequence, developed by starting from γ-butyrolactone, leads to the 2-substituted cyclopentenones **16a,b**, which are the precursors of methyl jasmonates **2a,b**[19] (Scheme IV).

In fact the reaction of **12b** with γ-butyrolactone by the usual procedure gave the hydroxy keto sulfone **14b** in 60% yield. Cleavage of this compound with aluminum amalgam afforded the known γ-hydroxy ketone **15b** in 85% yield. The conversion of **15b** to the cyclopentenone **16b**, by oxidation with the chromium trioxide–pyridine complex and successive cyclization in base, has already been reported in the literature.[10]

Levulinic acid derivatives are also suitable substrates for the conversion to 1,4-diketones. We developed another route to the diketo sulfones **7a,b**, as shown in Scheme V, in which the first step is the reaction of dilithio sulfones **12a,b** with ethyl levulinate ethylene ketal to give the partially protected diketo sulfones **17a,b**. Removal of the protecting group by treatment with a catalytic amount of *p*-toluenesulfonic acid in excess acetone afforded **7a,b** in more than 55% yields.

Levulonitrile ethylene thioketal has already been employed to synthesize jasmones **1a,b** through the reaction with the proper Grignard reagents, followed by hydrolysis of the formed imines and removal of the protecting group with ceric ammonium nitrate.[20] However, we believe that our route from ethyl levulinate should be considered an improvement on both the economic and workup points of view, because levulonitrile is less readily available[21] than the ester and requires a less convenient protection of the carbonyl group.

Experimental Section

General. Infrared spectra (IR) were recorded on a Perkin-Elmer 710B spectrometer and the frequencies are given in reciprocal centimeters. ^1H and ^{13}C NMR spectra were determined in $CDCl_3$ on Perkin-Elmer R12B and Varian FTXL-100 spectrometers, respectively, and the chemical shifts are expressed as δ values in parts per million from internal tetramethylsilane. Mass spectra were taken on a Varian MAT 111 instrument (70 eV). Vapor-phase chromatography (VPC) was performed on a Perkin-Elmer SIGMA 3 instrument using 0.25 in. × 6 ft columns of 5% FFAP on 80–100 mesh silanized Chromosorb G and 15% Carbowax 20M on 80–100 mesh Chromosorb W. Thin-layer chromatography (TLC) was performed on silica gel sheets (IB2-F, Baker) and column chromatography on silica gel 60 (70–230 mesh, Merck).

Tetrahydrofuran (THF) was obtained anhydrous and oxygen-free by distillation over sodium benzophenone ketyl under argon. Pyridine was distilled over calcium hydride and hexamethylphosphoramide (HMPTA) from lithium aluminum hydride under reduced pressure of argon. Ethylene glycol was obtained pure by spinning-band distillation using a Perkin-Elmer 251 Auto Annular apparatus.

γ-Butyrolactone (99.5%) and γ-valerolactone (98%) were purchased from Fluka, and ethyl levulinate (98%) was purchased from Aldrich. *cis*-3-Hexen-1-ol (**4**) was available from Aldrich and was 97.3% pure by VPC analysis on a 5% FFAP column at 150 °C. Under these conditions it was possible to separate three components having relative retention times of 0.66 (0.4%), 0.90 (2.3%, probably the trans isomer), and 1.00 (97.3%). Melting points (mp) are uncorrected.

***cis*-3-Hexen-1-yl Phenyl Sulfone (6a).** *p*-Toluenesulfonyl chloride (14.7 g, 77 mmol) dissolved in dry pyridine (30 mL) was added at 0 °C with magnetic stirring to a solution of *cis*-3-hexen-1-ol (**4**; 7.0 g, 70 mmol) in pyridine (20 mL). After 3 h the white precipitate was filtered off, 20% aqueous HCl was added until an acidic pH was reached, and the organic phase was extracted, with ethyl acetate. The collected extracts were washed with brine and dried over sodium sulfate, and the solvent was distilled under reduced pressure. TLC of the crude residue (hexane–ethyl acetate, 70:30) showed the presence of a small amount of unreacted alcohol; the NMR spectrum was indicative of the tosyl derivative: δ 7.55 (AA′BB′, 4 H, aromatic), 5.3 (m, 2 H, vinylic), 3.95 (t, 2 H, CH_2OTs), 2.4 (s, 3 H, *p*-CH_3), 2.6–1.7 (m, 4 H, allylic), 0.9 (t, 3 H, CH_3).

Sodium iodide (15 g, 0.1 mol) was added to the solution of the tosylate in dry acetone (100 mL) and the mixture was stirred at reflux for 6 h, then cooled, and filtered. Acetone was distilled under reduced pressure, dry benzene (80 mL) was added, and the small amount of solid precipitated was filtered off and washed with benzene (20 mL). A sample of the benzene solution was concentrated and analyzed. TLC (hexane–ethyl acetate, 50:50) revealed small amounts of **4** and the tosylate accompanying the major product. The NMR spectrum showed essentially the signals attributable to *cis*-1-iodo-3-hexene (**5a**) (X = I): δ 5.4 (m, 2 H, vinylic), 3.1 (t, 2 H, CH_2I), 2.8–1.7 (m, 4 H, allylic), 0.95 (t, 3 H, CH_3). VPC on a 5% FFAP column at 80 °C revealed an impurity (relative retention time 0.92), probably the trans isomer, not perfectly separated from the cis isomer; the areas of the two components were in an approximate ratio 2:98, which is comparable to the isomer ratio in the starting alcohol **4**.

Amberlyst A-26, benzenesulfinate form[13] (28.2 g, 0.1 equiv), was added to the benzene solution of the iodide and the mixture was stirred at reflux for 4 h. The resin was then filtered off and washed with dichloromethane (50 mL). Distillation of the solvent gave the crude sulfone (11.4 g), which was chromatographed on a silica gel column (hexane–ether, 96:4), eluting at first *cis*-3-hexen-1-yl benzenesulfinate[22] (0.69 g, 3.08 mmol, 4.4%) and successively *cis*-3-hexen-1-yl phenyl sulfone (**6a**) (10.6 g, 47.3 mmol, 67.6% overall yield from **4**).

***cis*-3-Hexen-1-yl phenyl sulfone 6a** was an oil: NMR 7.4–8.1 (m, 5 H, aromatic), 5.3 (m, 2 H, vinylic), 3.1 (m, 2 H, CH_2SO_2), 2.45 (m, 2 H, allylic), 1.95 (dq, 2 H, allylic), 0.9 (t, 3 H, CH_3); IR (neat) 1590 (vw), 1310 (s), 1145 (s), 1005 (w); mass spectrum, *m/e* 224 (M^+). Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.27; H, 7.19; S, 14.27. Found: C, 64.44; H, 7.32; S, 14.14.

***cis*-3-Hexen-1-yl benzenesulfinate** was an oil: NMR 7.6 (m, 5 H, aromatic), 5.3 (m, 2 H, vinylic), 4.3–3.3 (complex pattern, 2 H, CH_2O), 2.35 (m, 2 H, allylic), 2.0 (dq, 2 H, allylic), 0.9 (t, 3 H, CH_3); IR (neat) 1135 (s), 985 (s), 940 (s), 875 (s).

A cis–trans mixture of 3-hexen-1-yl phenyl sulfone was obtained by distillation of the crude cis isomer **6a** at 200 °C (20 mmHg). In fact the IR spectrum showed an absorption band at 970 cm^{-1}. We carried out the reaction sequence described for the cis isomer in Scheme III on this sample to obtain *cis*- and *trans*-jasmone in a ratio of about 1:1.

Condensation of Sulfones with γ-Lactones. General Procedure. *n*-Butyllithium (1.8 M, Fluka, 22.5 mL, 40 mmol) was added at 0 °C with stirring under argon to a solution of sulfone (20 mmol) in THF (70 mL). After 30 min, HMPTA (5 mL) and the lactone (20 mmol) were added at −78 °C. The reaction was stirred for 3 h, then allowed to reach room temperature, and quenched with aqueous NH_4Cl. The organic phase was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude reaction product was chromatographed on a silica gel column, eluting with hexane–ethyl acetate (95:5) to separate at first the unreacted sulfone (about 20%) and successively with hexane–ethyl acetate (80:20) to obtain pure hydroxy keto sulfones.

1-(Phenylsulfonyl)-5-hydroxypentan-2-one (**11**; 3.15 g, 65%) was an oil. The NMR spectrum showed that it was a mixture of the open-chain and cyclic semiketalic forms, as reported for

(19) G. Buchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971); A. I. Meyers and N. Nazarenko, *ibid.*, **38**, 175 (1973); U. Ravid and R. Ikan, *ibid.*, **39**, 2637 (1974); H. J. Monteiro, *ibid.*, **42**, 2324 (1977); J. Tsuji, Y. Kobayashi, and I. Shimizu, *Tetrahedron Lett.*, 39 (1979).

(20) H. C. Ho, T.-L. Ho, and C. M. Wong, *Can. J. Chem.*, **50**, 2718 (1972).

(21) G. D. Buckley, T. J. Elliott, F. G. Hunt, and A. Lowe, *J. Chem. Soc. C*, 1505 (1947).

(22) The obtainment of this ester in relatively high amount is due in part to the presence of a small amount of unreacted tosylate in the crude iodide **5a**; in fact it is known that methyl tosylate gives comparable amounts of O- and S-alkylation products in the reaction with *p*-toluenesulfinate anion in methanol: J. S. Meek and J. S. Fowler, *J. Org. Chem.*, **33**, 3422 (1968).

5-hydroxypentan-2-one,[23] in a ratio of about 35:65, respectively: NMR 7.5–8.1 (m, 5 H, aromatic), 4.2 (s, $SO_2CH_2C{=}O$), 3.6 (s, SO_2CH_2, cyclic form), 3.8 (m, 2 H, CH_2O), 2.8 (t, $CH_2C{=}O$); IR (neat) 3500 (m), 1720 (s), 1310 (s), 1080 (s), 1045 (s); mass spectrum, *m/e* 242 (M^+). Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.54; H, 5.83; S, 13.21. Found: C, 54.80; H, 5.92; S, 12.85.

(*Z*)-6-(Phenylsulfonyl)-2-hydroxyundec-8-en-5-one (13a; 4.10 g, 63%) was an oil which crystallized on standing: mp 43 °C (from hexane–benzene); NMR 7.5–8.0 (m, 5 H, aromatic), 5.25 (m, 2 H, vinylic), 4.1 (t, 1 H, $CHSO_2$), 3.7 (m, 1 H, CHOH), 2.3–2.9 (m, 4 H), 2.5 (s, 1 H, OH), 1.5–2.1 (m, 4 H), 1.15 (d, 3 H, CH_3CHOH), 0.9 (t, 3 H, CH_3); IR (Nujol) 3500 (m), 1720 (s), 1310 (s), 1080 (s); mass spectrum, *m/e* 324 (M^+). Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.95; H, 7.46; S, 9.87. Found: C, 63.10; H, 7.60; S, 9.80.

6-(Phenylsulfonyl)-2-hydroxyundecan-5-one (13b; 4.24 g, 65%) was an oil: NMR 7.5–8.1 (m, 5 H, aromatic), 4.2 (t, 1 H, $CHSO_2$), 3.8 (m, 1 H, CHOH), 2.8 (m, 2 H, $CH_2C{=}O$), 2.7 (s, 1 H, OH); IR (neat) 3500 (m), 1720 (s), 1310 (s), 1150 (s), 1080 (s); mass spectrum, *m/e* 326 (M^+). Anal. Calcd for $C_{17}H_{26}O_4S$: C, 62.56; H, 8.03; S, 9.80. Found: C, 62.72; H, 8.11; S, 9.85.

5-(Phenylsulfonyl)-1-hydroxydecan-4-one (14b; 3.73 g, 59%) was an oil: NMR 7.5–8.0 (m, 5 H, aromatic), 4.2 (t, 1 H, $CHSO_2$), 3.7 (t, 2 H, CH_2OH), 2.9 (s, 1 H, OH), 2.8 (m, 2 H, $CH_2C{=}O$); IR (neat) 3400 (m), 1720 (s), 1310 (s), 1150 (s), 1080 (s); mass spectrum, *m/e* 312 (M^+). Anal. Calcd for $C_{16}H_{24}O_4S$: C, 61.52; H, 7.75; S, 10.25. Found: C, 61.79; H, 7.91; S, 10.00.

Oxidation of Hydroxy Keto Sulfones 13a,b. Preparation of Diketo Sulfones 7a,b. The oxidation of the hydroxy keto sulfones **13a,b** was accomplished by slow addition of aqueous 8 N chromic acid solution[15] to the sulfone (10 mmol) in acetone (10 mL, freshly distilled from $KMnO_4$), until completion of the reaction, at 0 °C. After addition of 2-propanol (1 mL), the reaction mixture was filtered, the solid was washed with acetone, and most of the solvent was removed in vacuo. Aqueous 10% $NaHCO_3$ solution (20 mL) was added and the organic phase was extracted with ethyl acetate, then washed with brine, dried, and evaporated to give diketo sulfones **7a,b** in a good state of purity.

(*Z*)-6-(Phenylsulfonyl)-8-undecene-2,5-dione (7a; 2.94 g, 92%) was an oil which crystallized on standing: mp 56–57 °C (from hexane–ether); NMR 7.5–8.1 (m, 5 H, aromatic), 5.2 (m, 2 H, vinylic), 4.05 (t, 1 H, $CHSO_2$), 2.2–3.0 (m, 6 H), 2.05 (s, 3 H, $CH_3C{=}O$), 1.9 (dq, 2 H), 0.9 (t, 3 H, CH_3); IR (Nujol) 1720 (s), 1310 (s), 1150 (s), 1080 (s); mass spectrum, *m/e* 322 (M^+). Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.34; H, 6.88; S, 9.92. Found: C, 63.52; H, 7.12; S, 9.57.

6-(Phenylsulfonyl)undecane-2,5-dione (7b; 3.04 g, 94%) was an oil: NMR 7.5–8.1 (m, 5 H, aromatic), 4.2 (t, 1 H, $CHSO_2$), 2.5–3.2 (m, 4 H, $CH_2C{=}O$), 2.1 (s, 3 H, $CH_3C{=}O$); IR (neat) 1720 (s), 1310 (s), 1150 (s), 1080 (s); mass spectrum, *m/e* 324 (M^+). Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.95; H, 7.46; S, 9.87. Found: C, 62.65; H, 7.51; S, 9.57.

Ethyl Levulinate Ethylene Ketal. The mixture of ethyl levulinate (7.2 g, 50 mmol), anhydrous ethylene glycol (20 mL), ethyl orthoformate (20 mL), *p*-toluenesulfonic acid (200 mg), and benzene (100 mL) was heated at reflux for 3 h. After cooling, the reaction mixture was washed with two portions of 10% aqueous $NaHCO_3$ and then with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column, eluting with hexane–ether (90:10) to give ethyl levulinate ethylene ketal (7.7 g, 82%): NMR 4.5 (q, 2 H, CH_2O), 3.85 (s, 4 H, OCH_2CH_2O), 2.1 (m, 4 H), 1.2 (s, 3 H, CH_3), 1.2 (t, 3 H, CH_3); IR (neat) 1735 (s); mass spectrum, *m/e* 188 (M^+).

Condensation of Sulfones 6a,b with Ethyl Levulinate Ethylene Ketal. Preparation of Diketo Sulfones 7a,b. *n*-Butyllithium (1.8 M, 22.5 mL, 40 mmol) was added at 0 °C with stirring under argon to a solution of **6a,b** in THF (70 mL). After 30 min, HMPTA (5 mL) and the ester were added at −78 °C. The reaction was stirred for 3 h, then allowed to reach room temperature, and quenched with aqueous NH_4Cl. The organic phase was extracted with ethyl acetate, washed with brine, dried (Na_2SO_4), and evaporated to give a residue containing the partially protected diketo sulfones **17a,b**. Only **17a** was isolated from the crude reaction product by column chromatography (silica gel, hexane–ethyl acetate, 80:20): NMR 7.5–8.0 (m, 5 H, aromatic), 5.2 (m, 2 H, vinylic), 4.0 (t, 1 H, $CHSO_2$), 3.85 (s, 4 H, OCH_2CH_2O), 2.55 (m, 4 H), 1.9 (m, 4 H), 1.2 (s, 3 H, CH_3), 0.9 (t, 3 H, CH_3); IR (neat) 1720 (s), 1310 (s), 1150 (s); mass spectrum, *m/e* 354 (M^+). Removal of the protecting group was quantitatively accomplished by treating **17a** overnight with a catalytic amount of *p*-toluenesulfonic acid in excess acetone (30 mL). The solvent was then evaporated, 10% aqueous $NaHCO_3$ (20 mL) was added, and the organic phase extracted with ethyl acetate, washed with brine, dried (Na_2SO_4), and evaporated in vacuo to obtain the diketo sulfone **7a** (3.76 g, 58%) in quite pure state. The same deprotection procedure on the crude reaction mixture containing **17b**, followed by column chromatography (silica gel, hexane–ethyl acetate 80:20), afforded pure **7b** (3.60 g, 55%).

Cleavage of β-Keto Sulfones. Aluminum amalgam (2.7 g of Al, 0.1 mol), prepared according to Corey,[6] was added to a solution of β-keto sulfone (8 mmol) in THF–H_2O (9:1, 150 mL) and the mixture was heated at reflux for 2 h, then cooled, and filtered. The solid phase was washed with THF. Most of the solvent was removed in vacuo, ether (100 mL) was added, the aqueous phase was separated, and the organic phase was dried (Na_2SO_4) and concentrated in vacuo at room temperature to give ketones in a good state of purity after chromatography on a short column of silica gel (pentane–ether, 80:20).

(*Z*)-8-Undecene-2,5-dione (3a; 1.30 g, 90%, from **7a**) was a single compound at VPC analysis on a 15% Carbowax column at 170 °C:[16] NMR 5.3 (m, 2 H, vinylic), 2.6 (s, 4 H, $CH_2C{=}O$), 2.1 (s, 3 H, $CH_3C{=}O$), 0.95 (t, 3 H, CH_3); IR (neat) 1710 (s); mass spectrum, *m/e* 182 (M^+). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.70; H, 9.85.

Undecane-2,5-dione (3b; 1.36 g, 92%, from **7b**): NMR 2.55 (s, 4 H, $CH_2C{=}O$), 2.35 (t, 2 H, $CH_2C{=}O$), 2.1 (s, 3 H, $CH_3C{=}O$), 0.95 (t, 3 H, CH_3); IR (neat) 1705 (s); mass spectrum, *m/e* 184 (M^+).

1-Hydroxydecan-4-one (15b; 1.16 g, 85%, from **14b**): NMR 3.7 (s, 1 H, OH), 3.55 (t, 2 H, CH_2OH), 2.4 (m, 4 H, $CH_2C{=}O$), 1.2–2.1 (m, 10 H), 0.9 (t, 3 H, CH_3); IR (neat) 3420 (m), 1710 (s); mass spectrum, *m/e* 172 (M^+).

Cyclization of Diketones 3a,b. Preparation of Cyclopentenones 1a,b. A solution of diketone (5 mmol) in benzene (30 mL) was stirred at reflux for 3 h over basic alumina (Merck, Brockmann activity I, 3 g). The solid was then filtered and washed with ether and the organic phase was concentrated under reduced pressure at room temperature. TLC of the residue with hexane–ether (60:40) showed pure cyclopentenones **1a,b**.

***cis*-Jasmone (1a;** 0.50 g, 60%) contained 4.5% of the trans isomer, as evaluated by VPC analysis on a 15% Carbowax column at 160 °C.[16] The trans isomer had a relative retention time of 0.92 with respect to the cis isomer: NMR 5.25 (m, 2 H, vinylic), 2.85 (d, 2 H, allylic), 1.9–2.7 (6 H), 2.05 (s, 3 H, CH_3), 0.95 (t, 3 H, CH_3); IR (neat) 1700 (s), 1645 (s); mass spectrum, *m/e* 164 (M^+); ^{13}C NMR 208.8 (s), 170.0 (s), 139.5 (s), 132.3 (d), 125.2 (d), 34.3 (t), 31.7 (t), 21.2 (t), and 20.6 (t) (allylic methylene carbons in the lateral chain), 17.3 (q), 14.2 (q) [in the spectrum of cis–trans jasmone[16] the signals of the methylene allylic carbons of the trans isomer fell at 26.1 (t) and 25.4 (t)].

Dihydrojasmone (1b; 0.51 g, 61%) was a pure compound by VPC analysis: NMR 1.9–2.7 (6 H), 2.1 (s, 3 H, CH_3), 0.9 (t, 3 H, CH_3); IR (neat) 1700 (s), 1645 (s); mass spectrum, *m/e* 166 (M^+).

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Registry No. 1a, 488-10-8; **1a** trans isomer, 6261-18-3; **1b**, 1128-08-1; **3a**, 4868-21-7; **3b**, 7018-92-0; **4**, 928-96-1; **4** tosylate, 34019-85-7; **5a** (X = I), 21676-03-9; **6a**, 74420-26-1; **6b**, 16823-63-5; **7a**, 74420-27-2; **7b**, 74420-28-3; **8**, 74420-29-4; **11**, 74420-38-5; **12a**, 74420-36-3; **12b**, 74420-37-4; **13a**, 74420-30-7; **13b**, 74420-31-8; **14b**, 74420-32-9; **15b**, 55882-40-1; **17a**, 74420-33-0; **17b**, 74420-34-1; *cis*-3-hexen-1-yl benzenesulfinate, 74420-35-2; *trans* 3-hexen-1-yl phenyl sulfone, 74432-09-0; phenyl methyl sulfone, 3112-85-4; γ-valerolactone, 108-29-2; α-butyrolactone, 96-48-0; ethyl levulinate, 539-88-8; ethyl levulinate ethylene ketal, 6413-10-1.

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