

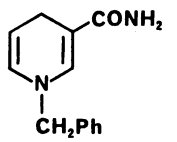
NAD(P)$^+$-NAD(P)H Models. 65. Photochemical Reductive Desulfonylation of β-Keto Sulfones with Hantzsch Ester

Masayuki Fujii,† Kaoru Nakamura, Hideyuki Mekata, Shinzaburo Oka, and Atsuyoshi Ohno*
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611
(Received August 26, 1987)

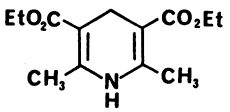
A new procedure for the reductive desulfonylation of β-keto sulfones is described. The reaction proceeds under a photochemical conditions with the Hantzsch ester in pyridine in the presence of ruthenium(II). Various functional groups are unaffected under the reaction conditions. Application of the procedure to the syntheses of certain natural products is also described.

NAD(P)H and its model compounds have been widely studied from the viewpoint of mimeses of biochemical transformations. As a consequence, it has been succeeded in reducing certain activated carbonyl compounds with excellent stereospecificity.

However, on the other hand, little attention has been paid to apply dihydropyridine derivatives as reductants in organic synthesis, and the functional groups susceptible to the reduction with the model compounds are limited. Since the reactivity of NAD(P)H or its analogs is quite low, biological systems employ appropriate enzymes as catalysts for the transformations. Therefore, it is reasonable to expect that a dihydropyridine derivative may be an interesting reductant in organic reactions if an appropriate catalyst is found. Along this idea, we have studied to extend the scope and limitation of the reduction with dihydropyridine derivatives. The use of a dihydropyridine derivative as an organic reductant introduces interesting specificities into organic reactions. For example, α,β-unsaturated aldehydes and ketones are reduced into the corresponding saturated aldehydes and ketones with the Hantzsch ester (HEH) in the presence of silica gel, whereas α,β-unsaturated esters and nitriles are not affected at all. We recently found that desulfonylation of β-keto sulfone undergoes with HEH in the presence of ruthenium(II) without influencing many other functional groups. Since the α-position of β-keto sulfone is highly susceptible to the attack by an electrophile, β-keto sulfones are hopeful candidate as building blocks for organic syntheses, and we studied the scope of this desulfonylation.[4] In this paper, we would like to describe the details of the reaction and its application to the syntheses of natural products.



BNAH

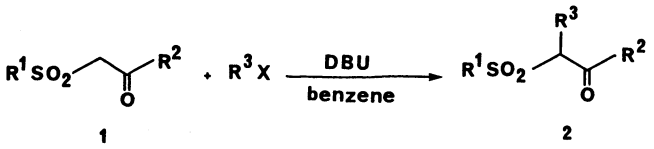


HEH

†Present address: Department of Industrial Chemistry, Faculty of Engineering, Kinki University, Iizuka, Fukuoka 820.

Results and Discussion

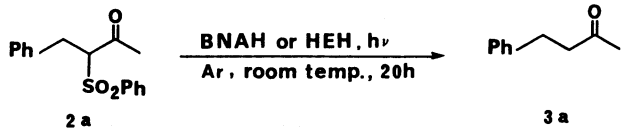
Alkylation. Alkylation of active methylene compounds has been studied extensively and many improved procedures have been reported.[5] Among these, it was found that the use of alkyl halide in benzene at room temperature in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is the best method for mono-alkylation of β-keto sulfones.[6] The results are summarized in Table 1.



1 2

(1)

Desulfonylation. It is reported that α-nitro sulfones can be desulfonylated by *N*-benzyl-1,4-dihydronicotinamide (BNAH) in DMF into the corresponding nitro compounds.[7] We have proposed that the reduction with a dihydropyridine derivative is initiated by an electron transfer from the reductant to the substrate.[8] Although a strongly electron-defficient substrate such as an α-nitro sulfone may be reduced without a catalyst, the electron defficiency of a β-keto sulfone is not sufficient enough to undergo the desulfonylation spontaneously. Photo-irradiation is a method to activate a dihydropyridine derivative[9] and we first examined the efficiency of BNAH-DMF/*hν* system for the reduction of 4-phenyl-3-phenylsulfonyl-2-butanone (**2a**). However, the yield from this system was found to be quite low as shown in Table 2.



2a 3a

(2)

After several attempts, it was found that BNAH is sensitive to the photo-irradiation and self-decomposition proceeds rapidly. Therefore, HEH, which is less sensitive to the photodecomposition, is superior to BNAH for the purpose. Finally, we came to a conclu-

Table 1. Alkylation of β-Keto Sulfones[a)]

Reactant/g	Halide/g	Product/g	Yield/%
1-Phenylsulfonyl-2-propanone **1a** (1.98)	Benzyl bromide (1.71)	4-Phenyl-3-phenylsulfonyl-2-butanone **2a** (1.83)	64
1-Phenylsulfonyl-2-propanone **1a** (1.98)	Hexyl iodide (2.12)	3-Phenylsulfonyl-2-nonanone **2b** (2.43)	86
1-Phenylsulfonyl-2-propanone **1a** (1.52)	Cinnamyl bromide (1.68)	3-Phenylsulfonyl-6-phenyl-5-hexen-2-one **2c** (2.04)	65
Phenylsulfonylmethyl phenyl ketone **1b** (2.60)	Allyl bromide (1.21)	1-Phenyl-2-phenylsulfonyl-4-penten-1-one **2d** (2.19)	73
Methyl phenylsulfonylacetate **1c** (1.26)	Benzyl bromide (1.80)	Methyl 3-phenyl-2-phenylsulfonylpropionate **2f** (1.92)	62
Phenylsulfonylacetonitrile **1d** (2.14)	Benzyl bromide (1.71)	3-Phenyl-2-phenylsulfonylpropionate **2g** (2.79)	69[b)]
p-Nitrophenylsulfonylacetone **1e** (1.56)	Benzyl bromide (1.48)	3-*p*-Nitrophenylsulfonyl-4-phenyl-2-butanone **2h** (1.72)	89

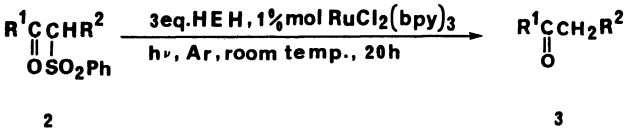
a) Solvent; benzene (50 ml). Base; DBU (1.52 g). b) Solvent; benzene (20 ml). Base; DBU (0.66 g).

Table 2. Photo-Reduction of 4-Phenyl-3-phenylsulfonyl-2-butanone (**2a**)

Reducing agent[a)]	$h\nu$[b)]	Catalyst[c)]	Solvent	Yield/%[d)]
BNAH	None	None	DMF	0
BNAH	A	None	DMF	13
BNAH	B	None	DMF	5
BNAH	A	None	CH_3CN	17
BNAH	A	+	DMF	14
BNAH	A	+	Pyridine	2
HEH	B	+	Pyridine	13
HEH	A	+	DMF	Trace
HEH	A	+	CH_3CN	2
HEH	A	+	Pyridine	68
HEH	B	+	Pyridine	97
HEH[e)]	B	+	Pyridine	59
HEH[f)]	B	+	Pyridine	83

a) Three equivalent amounts were used unless otherwise indicated. b) A: 600 W high-pressure mercury lamp with a Pyrex filter. B: USHIO HALOGEN LAMP JCD (100 V-650 W). c) 1% mol of $RuCl_2(bpy)_3$ was used. d) Determined on VPC (OV 330, 1 m, 130 °C). e) 1.5 equivalent amounts. f) 2.0 equivalent amounts.

sion that the use of 3 equivalent amounts of HEH in pyridine in the presence of 1% mole of $RuCl_2(bpy)_3$, as a photosensitizer, with irradiation of visible light under an inert atmosphere affords the best result as listed in Table 2. The procedure was applied to the desulfonylation from various β-keto sulfones as summarized in Table 3. Interestingly, while a sulfonyl group at the α-position to the keto group can be substituted by a hydrogen in food to excellent yields under the present reaction conditions, those at the α-positions of an ester and a cyano group are not affected at all.

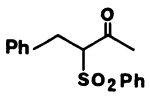
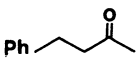
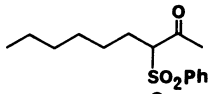
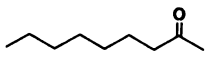
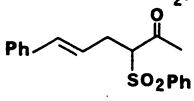
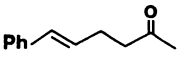
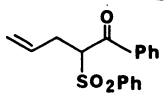
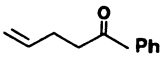
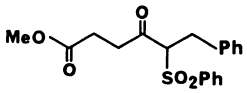
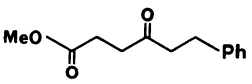
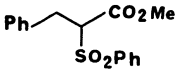
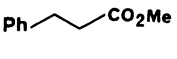
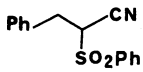
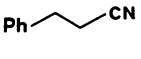
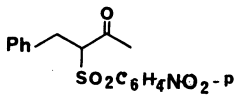
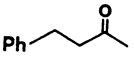


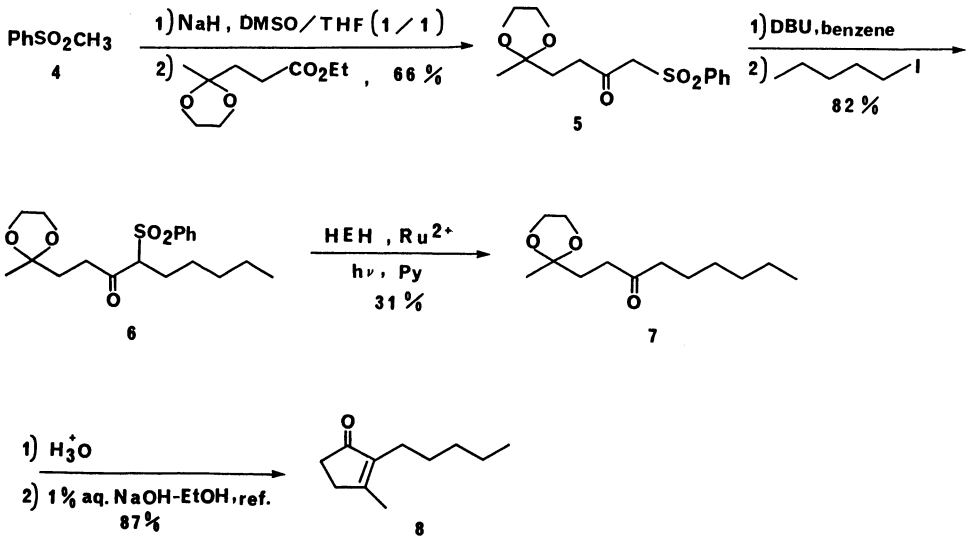
2 3 (3)

We believe that the present reaction proceeds through an electron-transfer from HEH to the substrate to form a radical ion intermediate and the process is mediated by the ruthenium complex. Indeed, it is known that Ru(II) is photochemically reduced into Ru(I)[10)] and Pac et al. proposed a Ru-mediated electron-transfer mechanism for the photochemical reduction of activated olefins with BNAH.[11)] As shown in the last example in Table 3, when the phenylsulfonyl group in the substrate is substituted by a *p*-nitrophenylsulfonyl group, the yield decreases remarkably to only 14%. Since the radical anion intermediate from the *p*-nitrophenylsulfonyl substrate is so stable under the reaction conditions due to the electron-withdrawing character of the *p*-nitro group that the cleavage of the C-S bond to form (probably) a carbon free radical and a sulfinate anion is inhibited here. Thus, the substituent on the sulfonyl group has to be electron-defficient but not too much in order to undergo the reaction smoothly.

Synthesis of Dihydrojasmone. Jasmones are im-

Table 3. Photo-Reduction of β-Keto Sulfones

	Substrate		Product	Yield/%
2a		3a		97
2b		3b		87
2c		3c		83
2d		3d		94
2e		3e		44
2f		3f		0
2g		3g		0
2h		3h		14

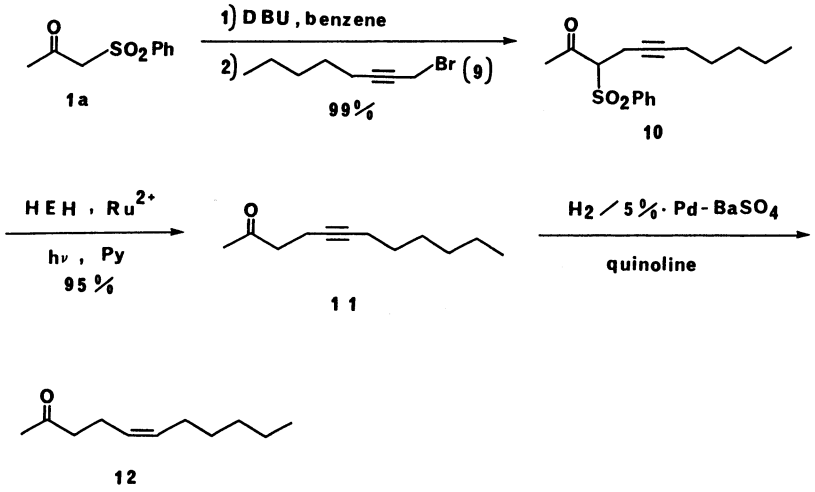


Scheme 1.

portant perfume components and have attracted a great attention of synthetic organic chemists.[12] We applied our alkylation-desulfonylation method to the synthesis of dihydrojasmone (**8**) along the process outlined in Scheme 1.

Methyl phenyl sulfone (**4**) was reacted with ethylene acetal of ethyl levulate in DMSO/THF (1/1) at 65 °C using sodium hydride as a base to afford the β-keto sulfone **5**, which was then alkylated with pentyl iodide in DBU/benzene system into the substituted β-keto sulfone **6**.

Desulfonylation of **6** was achieved with HEH in the presence of 1% mole of $RuCl_2(bpy)_3$ in pyridine under irradiation of visible light from a halogen lamp and the acetal **7** was isolated in 68% yield after purification on a column of silica gel. The acetal **7** was converted into dihydrojasmone (**8**) in 87% yield after an acid-catalyzed deprotection followed by reflux with 1% aq.



Scheme 2.

NaOH in EtOH.[13] Spectral data from **8** were identical with those reported in the literature[14] and the elemental analyses gave satisfactory results.

Synthesis of a Pheromone. (*Z*)-5-Undecen-2-one (**12**) was isolated as the principal volatile component of the pedal gland exudate of the bontebock, *Damaliscus dorcas dorcas*, by Burger et al.[15] They subjected the synthetic ketone **12** to the preliminary biological test as a mammalian pheromone and intense interest was shown by two captive animals. Application of our alkylation-desulfonylation method to the synthesis of this ketone provides a short (3 steps) and facile procedure and the ketone **12** was isolated in 79% overall yield (Scheme 2).

1-Phenylsulfonyl-2-propanone (**1a**) was regioselectively reacted with 1-bromo-2-octyne (**9**) in benzene with DBU to yield a β-keto sulfone **10** in 99% yield. Desulfonylation of **10** with the HEH-Ru(II)/*hν* system and subsequent purification on a column of silica gel afforded an acetylenic ketone, **11**, in 95% yield. Partial hydrogenation of **11** catalyzed by 5% Pd-$BaSO_4$ in the presence of quinoline gave the desired product **12** in 84% yield. The ^{1}H NMR spectrum indicated that the isolated product was consisted of the (Z)-isomer only. Other spectral data were also identical with those reported in the literature,[15] and the elemental analyses were satisfactory.

Experimental

Melting points were corrected with YANAGIMOTO MICRO MELTING POINT APPARATUS. Unless otherwise indicated, materials were purchaced from Nakarai Chemicals, Ltd.

Instruments. ^{1}H NMR spectra were measured at 100 MHz with a JEOL JN-FX100 fourier transform NMR spectrometer. IR spectra were recorded on a Hitachi EPI-S2 infrared spectrometer.

Elemental analyses were performed with a Yanaco MT-3 elemental analyzer. Gas chromatographic data were recorded on a Yanako G-1800 gas chromatograph (OV-330).

Alkylation: Preparation of 4-Phenyl-3-phenylsulfonyl-2-butanone (2a). A mixture of 1.98 g of 1-phenylsulfonyl-2-propanone (**1a**), 1.52 g of DBU, and 1.71 g of benzyl bromide in 50 ml of benzene was stirred at room temperature for 15 h. The reaction mixture was washed with three portions of each 50 ml of water and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by column chromatography on silica gel to give 1.83 g (64%) of 4-phenyl-3-phenylsulfonyl-2-butanone (**2a**), mp 92—93 °C.

^{1}H NMR ($CDCl_3$) δ=2.18 (s, 3H), 3.19 (q, 2H, *J*=14 Hz), 4.42, 4.45 (dd, 1H, *J*=11 Hz), 6.98—7.26 (m, 5H), and 7.52—7.90 (m, 5H). IR (KBr): 3000, 1723, 1320, and 1145 cm^{-1}. Found: C, 66.61; H, 5.52%. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59%.

2b—g were obtained similarly. Results are summarized in Table 1.

2b: ^{1}H NMR ($CDCl_3$) δ=0.87 (t, 3H, *J*=7 Hz), 1.04—1.32 (m, 8H), 1.91 (q, 2H, *J*=7 Hz), 2.42 (s, 3H), 4.08 (t, 1H, *J*=7 Hz), and 7.29—7.88 (m, 5H). IR (neat): 3075 (m), 2930 (s), 1725 (s), 1305, and 1150 cm^{-1}(s). Found : C, 64.05; H, 7.88%. Calcd for $C_{15}H_{22}O_3S$: C, 63.80; H, 7.85%.

2c: ^{1}H NMR ($CDCl_3$) δ=2.34 (s, 3H), 2.79 (t, 2H, *J*=7 Hz), 4.30 (t, 1H, *J*=7 Hz), 5.80, 5.95 (dt, 1H, *J*=15, 7 Hz), 6.36 (d, 1H, *J*=15 Hz), 7.20 (m, 5H), and 7.42—7.85 (m, 5H). IR (KBr): 3000, 1723, 1315, and 1150 cm^{-1}. Found: C, 66.28; H, 5.49%. Calcd for $C_{18}H_{18}O_3S$: C, 66.43, H; 5.60%.

2d: ^{1}H NMR ($CDCl_3$) δ=2.76 (t, 2H, *J*=7 Hz), 4.93—5.22 (m, 3H), 5.40—5.80 (m, 1H), and 7.32—7.96 (m, 10H). IR (KBr): 3000, 1674, 1305, and 1145 cm^{-1}. Found: C, 68.30; H, 5.51%. Calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37%.

2e: ^{1}H NMR ($CDCl_3$) δ=2.34—2.60 (m, 4H), 2.94—3.32 (m, 2H), 3.57 (s, H), 4.25 (q, 1H *J*=4 Hz), and 6.95—7.90 (m, 10H). IR (KBr): 3000 (m), 1740 (s, CO_2), 1715 (s, C=O), 1310, and 1140 cm^{-1} (s, SO_2). Found: C, 63.54; H, 5.54%. Calcd for $C_{19}H_{20}O_5S$: C, 63.32; H, 5.59%.

2f: Mp 92 °C. ^{1}H NMR ($CDCl_3$) δ=3.36 (d, 2H, *J*=4 Hz), 3.50 (s, 3H), 4.23 (dd, 1H, *J*=10, 4 Hz), 7.05—7.18 (m, 5H), and 7.48—7.97 (m, 5H). IR (Nujol): 2920 (s), 1735 (s, CO_2), 1310, and 1140 cm^{-1} (s, SO_2). Found: C, 63.06; H, 5.31%. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30%.

2g: Mp 76—78 °C. ^{1}H NMR ($CDCl_3$) δ=3.18 (q, 2H, *J*=12 Hz), 4.04, 4.10, (dd, 1H, *J*=4 Hz), 7.20—7.38 (m, 5H), and

7.54—8.14 (m, 5H). IR (Nujol): 2930 (s), 2220 (w, CN), 1320, and 1160 cm^{-1} (s, SO_2). Found: C, 66.71; H, 4.69; N, 5.03%. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16%.

Reductive Desulfonylation of β-Keto Sulfones: 4-Phenyl-2-butanone (3a). A solution of 288 mg (1 mmol) of **2a**, 750 mg of HEH (3 mmol) and 6.9 mg (0.01 mmol) of $RuCl_2(bpy)_3$ in 12 ml of pyridine was irradiated with visible light (USHIO HALOGEN LAMP JCD 100V-650W) at room temperature under an argon atmosphere for 20 h. The reaction mixture was poured into 100 ml of 2M hydrochloric acid (1 M=1 mol dm^{-3}) and extracted with ether. The organic layer was washed with water and brine, then dried on sodium sulfate. After removal of the solvent, the residue was chromatographed on silica gel with benzene as an eluent to give 143 mg (97%) of 4-phenyl-2-butanone (**3a**).

^{1}H NMR ($CDCl_3$) δ=2.12 (s, 3H), 2.60—3.04 (m, 4H), and 7.06—7.38 (m, 5H). IR (neat): 3000 (m) and 1715 cm^{-1} (s, C=O). Found: C, 80.94; H, 8.31%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

3b—e were obtained similarly. Results are summarized in Table 3.

3b: 87% yield. ^{1}H NMR ($CDCl_3$) δ=0.99 (t, 3H, *J*=6 Hz), 1.20—1.36 (m, 8H), 1.56 (t, 2H, *J*=7 Hz), 2.13 (s, 3H), and 2.43 (t, 2H, *J*=7 Hz). IR (neat): 3000 (s) and 1723 cm^{-1} (s, C=O). Found: C, 75.84; H, 12.91%. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.76%.

3c: 83% yield. ^{1}H NMR ($CDCl_3$) δ=2.16 (s, 3H), 2.40—2.68 (m, 4H), 6.08, 6.23 (dt, 1H, *J*=6 Hz), 6.41 (d, 2H), and 7.20—7.36 (m, 5H). IR (neat): 3000 (m), 1710 (s, C=O), and 1600 cm^{-1} (m, C=C). Found: C, 82.90; H, 8.16%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

3d: 94% yield. ^{1}H NMR ($CDCl_3$) δ=2.36—2.60 (m, 2H), 3.04 (t, 2H, *J*=7 Hz), 4.90—5.16 (m, 2H), 5.68—6.08 (m, 1H), and 7.32—8.00 (m, 5H). IR (neat): 3000 (m), 1685 (s, C=O), and 1600 cm^{-1} (m, C=C). Found: C, 82.41; H, 7.75%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

3e: 44% yield. ^{1}H NMR ($CDCl_3$) δ=2.52—3.02 (m, 8H), 3.64 (s, 3H), and 7.10—7.28 (m, 5H). IR (neat): 3000 (m), 1740 (s, CO_2), and 1720 cm^{-1} (s). Found: C, 71.06; H, 7.54%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.

Reduction of Methyl 3-Phenyl-2-phenylsulfonylpropionate (2f), 3-Phenyl-2-phenylsulfonylpropionitrile (2g), and 3-(*p*-Nitrophenylsulfonyl)-4-phenyl-2-butanone (2h). The reduction was carried out on 0.05 mmol scale of each substrate under the conditions as described for **2a**. The chemical yields of the corresponding reduction products were determined on GLC (OV330, 130 °C) employing hydroquinone dimethyl ether as an internal standard. No reduction product was detected from the reduction of **2f** and **2g**. 4-Phenyl-2-butanone was formed in 14% yield from **2h**.

Preparation of Dihydrojasmone (8) A mixture of 0.72 g (30 mmol) of sodium hydride, 4.68 g (30 mmol) of methyl phenyl sulfone (**4**) and 15 ml of dimethyl sulfoxide was heated to 65 °C with stirring until the evolution of hydrogen gas ceased (for about 30 min). The solution was cooled, diluted with 10 ml of tetrahydrofuran, and then a solution of 2.84 g (15 mmol) of ethyl levulate ethylene acetal in 5 ml of tetrahydrofuran was added. The resulting mixture was heated to 65 °C with stirring for 1 h, then cooled, poured into a mixture of ice and 2M hydrochloric acid, and extracted with six portions of chloroform. The combined organic extracts were washed successively with water, saturated aqueous sodium hydrogen carbonate, and brine, then dried and concentrated to leave the crude product which was column chromatographed on silica gel with hexane eluent to afford 2.60 g (66% yield) of 2-(4-phenylsulfonyl-3-oxobutyl)-2-methyl-1,3-dioxolane (**5**).

^{1}H NMR ($CDCl_3$) δ=1.28 (s, 3H), 2.00 (t, 2H, *J*=7 Hz), 2.73 (t, 2H, *J*=7 Hz), 3.85 (s, 4H), and 6.54—6.81 (m, 5H). IR (neat): 3000 (m), 1730 (s, C=O), 1310, and 1150 cm^{-1} (s, SO_2). Found: C, 56.63; H, 6.11%. Calcd for $C_{14}H_{18}O_5S$: C; 56.36, H; 6.08%.

A mixture of 2.12 g of **5**, 1.08 g of DBU and 1.40 g of pentyl iodide in 35 ml of dry benzene was stirred at room temperature for 15 h. The reaction mixture was worked up as described for **2a** to give 2.15 g (82%) of 2-methyl-2-(4-phenylsulfonyl-3-oxononyl)-1,3-dioxolane (**6**).

^{1}H NMR ($CDCl_3$) δ=0.81 (t, 3H, *J*=6 Hz), 1.15—1.36 (m, 6H), 1.28 (s, 3H), 1.74—2.09 (m, 4H), 2.72 (t, 2H, *J*=7 Hz), 3.88 (s, 4H), 4.15 (t, 1H, *J*=7 Hz), and 7.51—7.82 (m, 5H). IR (neat): 3000 (m), 1730 (s, C=O), 1310, and 1150 cm^{-1} (s, SO_2). Found: C, 61.82; H, 7.57%. Calcd for $C_{19}H_{23}O_5S$: C, 61.93; H, 7.66%.

A solution of 364 mg of **6**, 750 mg of HEH and 6.9 mg of $RuCl_2(bpy)_3$ in 12 ml of pyridine was irradiated with visible light at room temperature under an argon atmosphere for 20 h. The reaction mixture was worked up as described for **2a** to give 70 mg (31%) of 2-methyl-2-(3-oxononyl)-1,3-dioxolane (**7**).

^{1}H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=6 Hz), 1.20—1.68 (m, 11H), 1.96 (t, 2H, *J*=7 Hz), 2.41 (t, 2H, *J*=7 Hz), 2.48 (t, 2H, *J*=7 Hz), and 3.92 (s, 1H). IR (neat): 2980 (m) and 1730 (s) cm^{-1}. Found: C, 71.53; H, 6.56%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%.

A solution of 228 mg (1 mmol) of **7** in 10 ml of acetone and a few drops of 2M hydrochloric acid was stirred at room temperature for 5 h. The reaction mixture was condensed in vacuo, diluted with 10 ml of ethanol and 2 ml of 1% aq. NaOH and then heated at 80 °C for 3 h. The solution was poured into 2M hydrochloric acid, extracted with dichloromethane and washed with water and brine. The organic layer was dried on sodium sulfate, condensed in vacuo, and purified by column chromatography on silica gel with hexane-ethyl acetate (2 : 1) mixture as an eluent. Dihydrojasmone (**8**) was obtained in 87% yield (144 mg) and showed satisfactory spectra compared with those reported in the literature.[12]

^{1}H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=6 Hz), 1.20—1.36 (m, 6H), 2.04 (s, 3H), 2.20 (t, 2H, *J*=6 Hz), 2.34 (t, 2H, *J*=6 Hz), and 2.46 (t, 2H, *J*=7 Hz). IR (neat): 2930 (m), 1700 (s), and 1642 cm^{-1} (m). Found: C, 79.36; H, 11.03%. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91%.

Synthesis of a Pheromone, (*Z*)-5-Undecen-2-one (12). A mixture of 1.98 g of 1-phenylsulfonyl-2-propanone (**1a**), 1.52 g of DBU, 1.89 g of 1-bromo-2-octyne (**9**) in 50 ml of benzene was stirred at room temperature for 15 h. The reaction mixture was washed with water and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by column chromatography on silica gel to give 3.02 g (99%) of 3-phenylsulfonyl-5-undecyn-2-one (**10**).

^{1}H NMR ($CDCl_3$) δ=0.88 (t, 3H, *J*=6 Hz), 1.16—1.48 (m, 6H), 1.95—2.13 (m, 2H), 2.43 (s, 3H), 2.71—2.85 (m, 2H), 4.23 (t, 1H, *J*=8 Hz), and 7.44—7.91 (m, 5H). IR (neat): 2930 (s), 2212 (w), 1725 (s), 1310, and 1150 cm^{-1} (s). Found: C, 67.01; H, 7.27%. Calcd for $C_{17}H_{22}O_3S$: C, 66.63; H, 7.24%.

A solution of 305 mg (1 mmol) of **10**, 750 mg of HEH (3 mmol) and 6.9 mg (0.01 mmol) of $RuCl_2(bpy)_3$ in 10 ml of pyridine was irradiated with visible light at room temperature under an argon atmosphere for 20 h. The reaction mixture was poured into 100 ml of 2M hydrochloric acid and extracted with ether. The organic layer was washed with water and brine, and dried on sodium sulfate. After removal of the solvent, the residue was chromatographed on silica gel with benzene as an eluent to give 156 mg (95%) of 5-undecyn-2-one (**11**).

^{1}H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=6 Hz), 1.20—1.60 (m, 6H), 2.02—2.20 (m, 2H), 2.13 (s, 3H), 2.18—2.28 (m, 2H), and 2.36—2.42 (m, 2H). IR (neat): 3000 (m) and 1715 cm^{-1} (s). Found: C, 79.30; H, 10.87%. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

A mixture of 55 mg of **11**, 20 mg of 5% Pd/$BaSO_4$, 4 µl of quinoline in 10 ml of dry methanol under an atmosphere of hydrogen was stirred at room temperature for 6 h. The palladium catalyst was removed by filtration and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel with benzene as an eluent. The pure 5-undecen-2-one (**12**) was obtained in 84% yield and identified as the (*Z*)-isomer only by ^{1}H NMR analysis.

^{1}H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=6 Hz), 1.20—1.40 (m, 6H), 2.02 (q, 2H, J=6 Hz), 2.11 (s, 3H), 2.29 (q, 2H, J=6 Hz), 2.41 (t, 2H, J=6 Hz), and 5.28 (qAB, 2H, J=6 Hz). IR (neat): 3000 (s), 1720 (s), and 1680 cm^{-1} (m). Found: C, 78.81; H, 12.32%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

References

1) A. Ohno, S. Ushida, "Mechanistic Models of Asymmetric Reductions," Lecture Notes in Bio-Organic Chemistry, Vol. 1, Springer-Verlag, Heidelberg (1986).

2) K. Nakamura, M. Fujii, S. Oka, and A. Ohno, *Chem. Lett.*, **1985**, 523.

3) K. Nakamura, M. Fujii, H. Mekata, S. Oka, and A. Ohno, *Chem. Lett.*, **1986**, 87.

4) For other methods of reductive desulfonylation, see E. E. van Tamelen and E. A. Grant, *J. Am. Chem. Soc.*, **81**, 2160 (1950); E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1639 (1964); P. A. Grieco and Y. Masaki, *J. Org. Chem.*, **39**, 2135 (1974); J. B. Hendrickson, A. Giga, and J. Wareing, *J. Am. Chem. Soc.*, **96**, 2275 (1974); B. M. Trost, H. C. Arndt, D. E. Strege, and T. R. Verhoeven, *Tetrahedron Lett.*, **1976**, 3477.

5) For example, phase transfer method; E. V. Delmlow, *Angew. Chem., Int. Ed. Engl.*, **13**, 170 (1974); **13**, 493 (1977): and the method of ion pair extraction; A. Bröndstrom and U. Junggern, *Acta Chem. Scand.*, **23**, 2203 (1969); **23**, 2204 (1969); **23**, 3585 (1969); **25**, 1469 (1971).

6) N. Ono, T. Yoshimura, T. Saito, R. Tamura, R. Tanikaga, and A. Kaji, *Bull. Chem. Soc. Jpn.*, **52**, 1716 (1979).

7) N. Ono, R. Tamura, R. Tanikaga, and A. Kaji, *J. Chem. Soc., Chem. Commun.*, **1981**, 71.

8) A. Ohno, H. Yamamoto, and S. Oka, *J. Am. Chem. Soc.*, **103**, 2041 (1981).

9) Y. Ohnishi, M. Kagami, and A. Ohno, *Chem. Lett.*, **1975**, 125.

10) For a review on photoelectron transfer catalysis, see M. Julliard and M. Chanon, *Chem. Rev.*, **83**, 425 (1983).

11) C. Pac, M. Ihara, M. Yasuda, Y. Yamauchi, H. Sakurai, *J. Am. Chem. Soc.*, **103**, 6495 (1981); C. Pac, Y. Yamauchi, O. Ishitani, M. Ihara, M. Yasuda, and H. Sakurai, *J. Org. Chem.*, **49**, 26 (1984).

12) For reviews; R. A. Ellison, *Synthesis*, **1973**, 397; T.-L. Ho, Synth. *Commun.*, **4**, 265 (1974).

13) J. Tsuji and H. Yasuda, *Synth. Commun.*, **8**, 103 (1978).

14) F. Ogura, T. Otsubo, T. Sakamoto, and H. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **57**, 1691 (1984).

15) B. V. Burger, M. leRoux, C. F. Garbers, H. S. C. Spies, R. G. Bigalke, K. G. R. Pachler, P. L. Wessels, V. Christ, and K. H. Mourer, *Z. Naturforsch.*, **31C**, 21 (1976).