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A New Synthesis of (*Z*)-13-Eicosen-10-one and (*Z*)-12-Nonadecen-9-one, the Pheromones of Peach Fruit Moth

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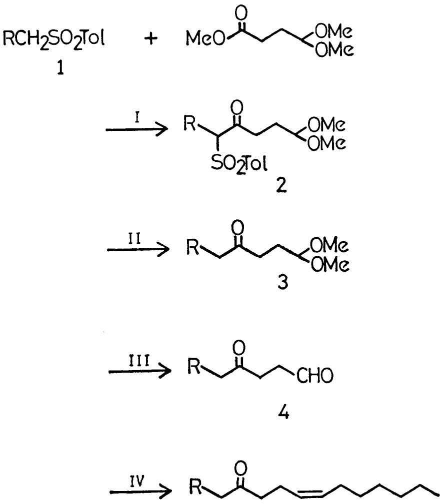
Synopsis. (*Z*)-13-Eicosen-10-one and (*Z*)-12-nonadecen-9-one were easily synthesized from starting 1-(*p*-tolylsulfonyl)nonane and 1-(*p*-tolylsulfonyl)octane *via* 4 steps, respectively.

It is known that (*Z*)-13-eicosen-10-one (**5a**) and (*Z*)-12-nonadecen-9-one (**5b**) are the pheromones of Japanese peach fruit moth (*Carposia niponensis* Walshingham),[1)] and that a mixture of **5a** and **5b** in the ratio of 20:1 has the strongest biological activity.[2)] Three examples for the preparation of the pheromones have been reported: (i) the addition of 4-undecynal prepared from 3-bromo-1-propanol to nonylmagnesium bromide;[1)] (ii) the addition of 3-decynenitrile to nonylmagnesium bromide;[3)] (iii) the alkylation of diethyl 3-oxoglutarate.[4)]

In previous papers, we reported the synthesis of the jasmonoids and 2,15-hexadecanedione using sulfones, such as *cis*-1-(*p*-tolylsulfonyl)-3-hexene,[5)] 1-(*p*-tolylsulfonyl)hexane,[5)] 1,1-ethylenedioxy-3-(*p*-tolylsulfonyl)cyclopentane,[6)] and 1,6-bis(*p*-tolylsulfonyl)hexane.[7)] In this paper, we wish to describe a new and simple synthesis of (*Z*)-13-eicosen-10-one (**5a**) and (*Z*)-12-nonadecen-9-one (**5b**) by the condensation of sulfones with ester,[8)] followed by desulfonylation[9)] and salt-free Wittig reaction.[10)]

The synthesis of the title compounds, **5a** and **5b**, were carried out as follows.



a: R = C_8H_{17}; b: R = C_7H_{15}

I: LDA, -78°C; II: Al(Hg), 10% aq THF; III; H_3O^+;
IV: hepthyltriphenylphosphonium bromide

The condensation of the dianion of 1-(*p*-tolylsulfonyl)nonane (**1a**) generated with two equivalents of lithium diisopropylamide (LDA) with methyl 4,4-dimethoxybutanoate gave 1,1-dimethoxy-5-(*p*-tolylsulfonyl)-4-tridecanone (**2a**) in quantitative yield. The treatment of the sulfone **2a** with aluminium amalgam in 10% aqueous THF afforded 1,1-dimethoxy-4-tridecanone (**3a**) in 69% yield. The acetal **3a** was acidified with 5% hydrochloric acid to give 4-oxotridecanal (**4a**) in 81% yield. The salt-free Wittig reagent prepared from heptyltriphenylphosphonium bromide and sodium amide was added to a solution of **4a** in benzene to give (*Z*)-13-eicosen-10-one (**5a**) in 54% yield. (*Z*)-12-Nonadecen-9-one (**5b**) was synthesized from 1-(*p*-tolylsulfonyl)octane (**1b**) in the same procedure. The resulting products, **5a** and **5b**, had no infrared absorption band at 970 cm^{-1} region due to disubstituted trans-alkene. The structure of these products was identified by comparing their IR and NMR spectra with those of the reported data.[3,4)] In conclusion, the method described above, compared with other methods, has various advantages: the starting sulfones are readily available, processes are short, simple, and easy, and the reaction proceeds smoothly to form the product in relatively good yield.

Experimental

Melting and boiling points are uncorrected. Melting points were taken on a Yanagimoto micro melting point apparatus. Infrared spectra were measured on a Shimazu IR-27G spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian EM-390 spectrometer at 90 MHz, using TMS (δ=0.00 ppm) as an internal standard.

*1-(*p*-Tolylsulfonyl)nonane (1a) and 1-(*p*-Tolylsulfonyl)octane (1b).* 1-Bromononane (20 g, 0.097 mol) was added to a stirred solution of sodium *p*-toluenesulfinate tetrahydrate (30 g, 0.12 mol) in methanol (100 ml). The mixture was stirred under reflux for 6 h. After the removal of methanol, the residue was poured onto 300 ml of water. The organic layer was extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulfate, and concentrated to give **1a** as a solid substance. Recrystallization from methanol–water afforded 26 g (95% yield) of **1a**, mp 51.4—51.5 °C. IR ($CHCl_3$): 2950, 1600, 1470, 1315, 1140 cm^{-1}. NMR (CCl_4): δ 0.75—1.05 (3H, br t, J=5.4 Hz), 1.1—1.5 (12H, br s), 1.5—1.8 (2H, br s), 2.47 (3H, s), 2.8—3.1 (2H, m), 7.38, 7.84 ppm (4H, an A_2B_2 pattern, J=7.5 Hz). Found: C, 68.37; H, 9.23%. Calcd for $C_{16}H_{26}O_2S$: C, 68.04; H, 9.26%. 1-(*p*-Tolylsulfonyl)octane (**1b**) was obtained from 1-bromooctane (20 g, 0.10 mol) and sodium *p*-toluenesulfinate tetrahydrate (30 g, 0.12 mol) in methanol (100 ml) in the same procedure, mp 34.4—34.5 °C. IR ($CHCl_3$) 2950, 1600, 1470, 1320, 1150 cm^{-1}. NMR (CCl_4) δ 0.7—1.05 (3H, br t, J=5.4 Hz), 1.1—1.8 (12H, br s), 2.43 (3H, s), 2.8—3.1 (2H, m), 7.31, 7.75 ppm (4H, an A_2B_2 pattern, J=7.5 Hz). Found: C, 67.88; H, 8.82%. Calcd for $C_{15}H_{24}O_2S$: C, 67.12; H, 9.00%.

*1,1-Dimethoxy-5-(*p*-tolylsulfonyl)-4-tridecanone (2a) and 1,1-Dimethoxy-5-(*p*-tolylsulfonyl)-4-dodecanone (2b).* To lithium diisopropylamide (LDA) prepared from *n*-BuLi (15%

hexane solution, 6.0 g, 0.014 mol) and diisopropylamine (1.5 g, 0.015 mol) in dry THF (15 ml) was added a solution of **1a** (2.0 g, 0.007 mol) in dry THF (15 ml) at −78 °C under nitrogen. After the mixture was stirred for 1 h, methyl 4,4-dimethoxybutanoate (1.3 g, 0.008 mol) in dry THF (15 ml) was added. The mixture was stirred for 1 h at −78 °C and for an additional 3 h at room temperature. The mixture was poured onto cold 2% sulfuric acid. The organic layer was extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulfate, and concentrated to give **2a** as a pale yellow viscous liquid in quantitative yield. The compound **2a** was purified by column chromatography over silica gel (60—80 mesh) with benzene as eluent to give white needles, mp 48.5—49.5 °C. IR (neat): 2900, 1720, 1600, 1470, 1320, 1150, 1080 cm^{-1}. NMR (CCl_4): δ 0.75—1.0 (3H, br t, J=5.4 Hz), 1.0—1.4 (12H, br s), 1.6—2.0 (4H, m), 2.35—3.15 (2H, m), 2.46 (3H, s), 3.35 (6H, s), 3.96 (1H, t, J=6.9 Hz), 4.33 (1H, t, J=6.0 Hz), 7.34, 7.66 ppm (4H, an A_2B_2 pattern, J=8.1 Hz). Found: C, 64.17; H, 8.73%. Calcd for $C_{22}H_{36}O_5S$: C, 64.05; H, 8.79%. 1,1-Dimethoxy-5-(*p*-tolylsulfonyl)-4-dodecanone (**2b**) was obtained from 1-(*p*-tolylsulfonyl)-octane (**1b**) (2.0 g, 0.007 mol) and methyl 4,4-dimethoxybutanoate (1.3 g, 0.008 mol) in quantitative yield, mp 41.5—42.5 °C. IR (neat): 2850, 1710, 1600, 1470, 1300, 1150, 1090 cm^{-1}. NMR (CCl_4): δ 0.75—1.0 (3H, br t, J=5.4 Hz), 1.0—1.4 (10H, br s), 1.6—2.0 (4H, m), 2.35—3.15 (2H, m), 2.45 (3H, s), 3.35 (6H, s), 3.96 (1H, t, J=6.9 Hz), 4.33 (1H, t, J=6.0 Hz), 7.34, 7.66 ppm (4H, an A_2B_2 pattern, J=8.1 Hz). Found: C 63.22; H 8.77%. Calcd for $C_{21}H_{34}O_5S$: C, 63.29; H, 8.60%.

1,1-Dimethoxy-4-tridecanone (3a) and 1,1-Dimethoxy-4-dodecanone (3b). To a stirred solution of **2a** (2.0 g, 4. 8mmol) in 10% aq. THF (60 ml) was added aluminium amalgam (1.5 g, 55.5 mmol). The mixture was stirred for 4 h at room temperature and then filtered. The filtrate was extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulfate, and concentrated to give **3a** as a pale yellow liquid. The compound **3a** was purified by column chromatography over silica gel (60—80 mesh) with benzene–hexane (7:3) as eluent to give 0.86 g (69% yield) of **3a** as a colorless liquid. IR (neat): 2950, 1720, 1470, 1360, 1190, 1130, 1060 cm^{-1}. NMR (CCl_4): δ 0.8—1.05 (3H, br t, J=5.4 Hz), 1.1—1.9 (16H, m), 2.2—2.5 (4H, m), 3.25 (6H, s), 4.27 ppm (1H, t, J=6.0 Hz). 1,1-Dimethoxy-4-dodecanone (**3b**) was obtained from **2b** (2.0 g, 5.0 mmol) in the same procedure. IR (neat): 2900, 1720, 1460, 1360, 1190, 1120, 1060 cm^{-1}. NMR (CCl_4): δ 0.75—1.1 (3H, br t, J=5.4 Hz), 1.2—1.95 (14H, m), 2.3—2.55 (4H, m), 3.28 (6H, s), 4.33 ppm (1H, t, J=6.0 Hz).

4-Oxotridecanal (4a) and 4-Oxododecanal (4b). The acetal **3a** (0.6 g, 2.3 mmol) was added to 5% hydrochloric acid (5 ml) and the mixture was stirred for 5 h at 50 °C. The organic layer was extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulfate, and concentrated to give **4a** as a pale yellow liquid. Compound **4a** was purified by column chromatography over silica gel (60—80 mesh) with benzene–hexane (5:5) as eluent to give 0.4 g (81% yield) of pure **4a** as a colorless liquid. IR (neat): 2900, 1730, 1710, 1470, 1410, 1090 cm^{-1}. NMR (CCl_4): δ 0.75—1.1 (3H, br t, J=5.4 Hz), 1.1—1.75 (14H, br s), 2.46 (2H, t, J=6.0 Hz), 2.73 (4H, s) 9.88 ppm (1H, s). 4-Oxododecanal (**4b**) was obtained from **3b** (1.0 g, 4.4 mmol) in the same procedure in 75% yield. IR (neat): 2900, 1730, 1710, 1470, 1400, 1090 cm^{-1}. NMR (CCl_4): δ 0.75—1.0 (3H, br t, J=5.4 Hz), 1.0—1.6 (12H, br s), 2.35 (2H, t, J=6.0 Hz), 3.60 (4H, s), 9.70 ppm (1H, s).

(Z)-13-Eicosen-10-one (5a) and (Z)-12-Nonadecen-9-one (5b). Sodium amide (0.1 g, 2.5 mmol) was added to a stirred solution of heptyltriphenylphosphonium bromide (0.4 g, 1.1 mmol) in dry benzene (50 ml) under nitrogen atmosphere. The temperature of the suspension was then slowly raised to the reflux temperature of benzene. The reaction mixture was stirred for 8 h under reflux. Stirring was discontinued and then the reaction mixture was cooled to room temperature. The upper layer (benzene phosphorane solution, Crystal Violet color) was separated by a syringe. The phosphorane was added to a stirred solution of (**4a**) (0.2 g, 0.87 mmol) in benzene (50 ml) over 0.5 h at room temperature. Stirring was continued for 15 h more at room temperature. Benzene was distilled under reduced pressure and hexane was poured onto the residue. The mixture was filtered and the filtrate was washed with 5% hydrochloric acid, brine, and dried over anhydrous sodium sulfate. Concentration of the hexane gave the crude product. This crude product was chromatographed over silica gel (60—80 mesh) with hexane–benzene (7:3) as eluent to give 0.14 g (54% yield) of **5a** as a pale yellow liquid. IR (neat): 2930, 1710, 1470, 1430, 1370, 1090 cm^{-1}. NMR (CCl_4): δ 0.7—1.0 (6H, br t, J=5.4 Hz), 1.1—1.7 (22H, br s), 1.9—2.15 (2H, m), 2.2—2.45 (6H, m), 5.2—5.45 ppm (2H, m). (*Z*)-12-Nonadecen-9-one (**5b**) was obtained from **4b** (0.2 g, 0.93 mmol) in the same procedure. IR (neat): 2950, 1710, 1460, 1370 cm^{-1}. NMR (CCl_4): δ 0.7—1.0 (6H, br t, J=5.4 Hz), 1.1—1.7 (20H, br s), 1.9—2.15 (2H, m), 2.2—2.45 (6H, m), 5.15—5.4 ppm (2H, m).

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