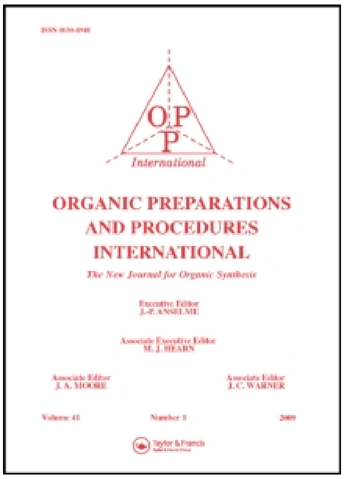

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A SHORT SYNTHESIS OF *ar*-TODOMATUIC ACID AND DIHYDRO-*ar*-TURMERONE BY THE HECK REACTION

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A SHORT SYNTHESIS OF *ar*-TODOMATUIC ACID AND DIHYDRO-*ar*-TURMERONE BY THE HECK REACTION

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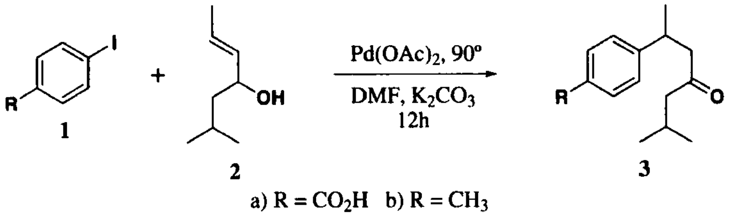
(Dedicated to the memory of the late Dr. Nitiraj R. Mane)

Sakai and Hirose[1] have reported the isolation of *ar*-todomatuic acid (**3a**) from the Douglas fir. *ar*-Juvabione, the methyl ester of *ar*-todomatuic acid (3, R=CO_2CH_3), which exhibits similar juvenile hormone activity as juvabione,[2,3] has attracted considerable attention as a third generation pesticide.[4] Three-step syntheses of **3a** have been reported by Mane *et al.*[2,3] and by Krishna Rao *et al.*[5] from 3-phenylbutyric acid and styryl isobutyl ketone in 14% and 10% yields, respectively. Dihydro-*ar*-turmerone (**3b**) was isolated from *Himalayan Cedar* wood by Bisarya and Sukh Dev.[6] Crawford *et al.*[7] have reported a three-step synthesis of **3b** from limonene in 45% overall yield. We report here a two-step, efficient synthesis of **3a** and **3b** by a Heck reaction.[8,9]

The Heck reaction[8] has been extended[9] to allylic alcohols to yield aldehydes, ketones or aryl-substituted allylic alcohols depending on whether the alcohol is primary, secondary or tertiary. The Heck reaction of 6-methyl-2-hepten-4-ol (**2**),[10] with 4-iodobenzoic acid (**1a**) or 4-iodotoluene (**1b**) using catalytic amounts of palladium acetate in DMF in the presence of potassium carbonate yielded *ar*-todomatuic acid (**3a**) and dihydro-*ar*-turmerone (**3b**) in 33% and 36% overall yields, respectively from crotonaldehyde.



a) R = CO_2H b) R = CH_3

EXPERIMENTAL SECTION

Melting points and boiling points are uncorrected. NMR spectra were recorded on Bruker AC 200F NMR spectrometer and chemical shifts are in δ units. The IR spectra were recorded on a Perkin-Elmer FT-spectrometer and peak positions are in wavenumbers (cm^{-1}).

_ar_-Todomatuic Acid (3a) and Dihydro-_ar_-turmerone (3b).- A mixture of 4-iodobenzoic acid (1.24 g, 5 mmol) or 4-iodotoluene (1.09 g, 5 mmol), 6-methyl-2-hepten-4-ol (0.8 g, 6.25 mmol), a catalytic amount of palladium acetate (4 mg, 0.015 mmol) and potassium carbonate (1.73 g, 12.5 mmol) in DMF (6 mL) was stirred at 90°C for 12 h.

For the isolation of ar-todomatuic acid, the reaction mixture was cooled, diluted with water (15 mL), acidified to pH 5 with conc. hydrochloric acid and extracted with ether (3 x 40 mL). The ethereal layer was extracted with saturated aqueous sodium bicarbonate and the bicarbonate layer acidified to yield an oily product which was extracted into ether (3 x 40 mL). The combined ethereal layer was washed with water and dried over anhydrous sodium sulfate. Removal of ether furnished *ar*-todomatuic acid (**3a**) which solidified upon the addition of a little pet. ether. Recrystallization from pet. ether afforded 0.82 g (66%) of a colorless solid, mp 78-79°C, *lit*[2] 77-78°C. IR (Nujol): 3500-2960 (br -COOH), 1691 (s br CO_2 CO), 1610 cm^{-1}. ^{1}H NMR ($CDCl_3$) : δ 0.86 [6 H, d, J = 7 Hz, $CH(CH_3)_2$], 1.29 (3 H, d, J = 7 Hz, $-CH_3$), 2.03 (3 H, m, $-CH_2$ and -CH), 2.65 (2 H, m, $-COCH_2$), 3.43 (1 H, sextet, J = 7 Hz, Ph-CH-), 7.31 (2 H, d, J = 8 Hz, Ar-H *meta* to CO group), 8.03 (2 H, d, J = 8 Hz, Ar-H *ortho* to CO group), 10.9 (1 H, br s, -COOH).

For the isolation of dihydro-ar-turmerone, the reaction mixture was cooled, diluted with water and extracted with ether (3 x 40 mL). The ethereal layer was washed with water and dried over anhydrous sodium sulfate. Removal of ether furnished dihydro-*ar*-turmerone (**3b**), which was purified by column chromatography [silica gel, pet. ether-ethyl acetate, 80:20] to give 0.78 g (72%) of a colorless liquid, bp. 112-114°C/1 mm, *lit.*[10] bp. 115°C/1 mm. IR (neat): 1712 cm^{-1} (C=O group). ^{1}H NMR: δ 0.84 [6 H, d, J = 7 Hz, $CH(CH_3)_2$], 1.22 (3 H, d, J = 7 Hz, $-CH_3$), 2.09 (3 H, m, $-CH_2$ and -CH), 2.29 (3 H, s, $Ar-CH_3$), 2.62 (2 H, m, - $COCH_2$), 3.27 (1 H, sextet, J = 7 Hz, Ph-CH-), 7.22 (2 H, d, J = 8 Hz, Ar-H *meta* to $-CH_3$), 7.38 (2 H, d, Ar-H *ortho* to CH_3).

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A CONVENIENT SYNTHESIS OF 1,1'- and 1,2'-DINAPHTHYLMETHANONES

Submitted by (11/15/02)
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Because of their increased ability to absorb UV radiation (4 times that of benzophenone), dinaphthylmethanones (DNMs) are considered a new generation of UV-absorbing agents.[1] In addition, because of their high electron density, favorable symmetry and stability, they are used to synthesize polyaryl ethers and ketones. They also serve as intermediates for the preparation of dyestuffs, electronic devices, coatings and other commercial products. Therefore, an effective synthesis for DNMs is needed and is a goal of our current research.

Larock *et al.*[2] investigated the synthesis of symmetrical divinyl and diaryl ketones *via* rhodium-catalyzed carbonylation of vinyl- and arylmercurials. Although they obtained diaryl methanones in excellent yields (up to 95%), relatively vigorous conditions including high carbon monoxide pressure (1000-1525 psi), expensive and toxic catalyst $[Rh(CO)_2Cl]_2$ and long reaction time (24 h) make their process inconvenient and economically unattractive. Cho *et al.*[3] synthesized diaryl methanones using the tetrakis(triphenylphosphine)palladium(0)-catalyzed reaction of an arylboronic acid with carbon monoxide, 1,1'-dinaphthylmethanone (1,1'-DNM) was obtained only in 27% yield. We now report that the reaction of naphthalene with oxalyl chloride in the presence of anhydrous aluminium chloride at room temperature provides an effective approach