PALLADIUM-CATALYZED INTRAMOLECULAR ARYL-PALLADATION VIA ULTRASONICS

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Abstract: Aryl halides containing α,β-unsaturated carbonyl groups can undergo a palladium-catalyzed intramolecular cyclization with the aid of ultrasound.

Key Words: Ultrasound, Palladium-catalyzed reaction, Intramolecular cyclization.

INTRODUCTION

A variety of organic reactions promoted by palladium compounds have been discovered in the past decades.\(^1\),\(^2\) Among them the alkenyl- or aryl-palladation of carbon-carbon double bonds, also known as Heck reaction, is a precious tool in forming the carbon-carbon bonds. This reaction has been shown to proceed in a two-stage process: cis-addition of an organopalladium complex followed by cis-elimination\(^3\) (Scheme I). Recently, we\(^4\) and others\(^5\) have reported that palladium-catalyzed intramolecular cyclization of alkenyl and aryl halides containing α,β-unsaturated carbonyl derivatives could give some stereo-defined exocyclic alkenes in reasonable yield (eq. 1). However, these reactions were all carried out at solvent reflux temperature (ca. 80°C) for at least 12 h. Usually it took more than 24 h for the reaction to reach the maximum yield. This was not only a time-consuming process but also led to other side reactions. In this paper, we describe a modification which utilizes ultrasound to achieve similar reactions efficiently and stereoselectively in less reaction time.

Scheme I. Mechanism for the Pd-Catalyzed Arylation of Carbon-Carbon Double Bond (Heck Reaction)
RESULTS AND DISCUSSION

Our results are summarized in Table I. The reactions were completed in 6 h. Longer reaction times in the presence of ultrasonic waves gave no improvement in the yield of these cyclic products. While comparable yields of the cyclized products were obtained as in the previous report, shorter reaction time and lower reaction temperature as well as less by-products are the obvious advantages to these ultrasound-promoted reactions. Without ultrasonic promotion, the reaction did not proceed at room temperature even after 48 h. The isomeric purities of these cyclized products were ≈98% as shown by their 13C-NMR spectra and GLC analyses. Assignment of the stereochemistry of the exocyclic alkenes in 1 and 2 was supported by their 2D-NOESY 1H-NMR spectra. Cyclic either 3 can also be obtained in good yield via this route. The ring fusion in 3 is assigned to be cis as judged by its 1H-NMR spectrum. The coupling constant of the doublet (J = 7.6 Hz, 1 H) at 84.36 ppm in 1H-NMR spectrum of 3 is in good agreement with the calculated value (J = 7.56 Hz for cis-fused structure and J = 10.68 Hz for trans-fused structure). Attempts to cyclize 3-(o-bromobenzyl)-1-methoxycarbonyl-1-cyclohexene 9 under the same conditions gave a complex mixture. Using Pd(PPh3)4 as the

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catalyst in the cyclization of 8 via ultrasonics for 12 h, we got 5-10% of hydro-debrominated compound along with 80% of recovered 8. However, the reaction of 8 with a catalytic amount of Pd(OAc)₂(PP₃)₂ and 2 equiv. of NaHCO₃ in DMF(9) in the presence of ultrasonic waves induced intramolecular cyclization to give product 4 with a shorter reaction time than that by the thermal method(3) (6 h vs. 36 h).

The above ultrasonic method provides an alternative and efficient procedure for the high regio- and stereoselective intramolecular arylpalladation to conjugated double bonds followed by dehydropalladation.

EXPERIMENTAL SECTION

Sonication was carried out with an ultrasonic laboratory cleaner (Branson B-220H, 50-60 Hz). Infrared spectra were recorded on a PE 882 or a PE 297 Infrared Spectrophotometer. A Bruker MSL 200 Nuclear Magnetic Resonance Spectrometer was used for ¹H-NMR spectra and 2D-NOESY spectra with tetramethylsilane as an internal standard. A HP 5995 GC/MS was used for mass spectra. High resolution mass spectra were obtained by a VG TS-250 Mass Spectrometer. Precoated silica gel 60F-254 aluminum plates made by EM reagents were used for thin layer chromatography. GLC analyses were performed on a Shimadzu GC-8A gas chromatograph, equipped with a 2 m x 3 mm column packed with SE-30 (5% on chromosorb W). GLC peak integrals were recorded by using a Shimadzu chromatopac C-R3A integrator. All reactions involving organometallic compounds were carried out in oven- and/or flame-dried glassware equipped with a side arm, gas outlet adapter and mercury bubbler for the purpose of maintaining an inert atmosphere.

Methyl (E)-5-(o-iodophenyl)-2-pentenoate 5. Propyne (0.42 g, 10.5 mmol) was slowly bubbled through a cooled (−60°C) stirred solution containing n-butyllithium (13.2 mL of 1.6 M solution in hexane, 2.1 mmol) and tetramethyleneethylenediamine (1.22 g, 10.5 mmol) (10). The cooling bath was then removed and the reaction mixture was stirred for 2 h at room temperature. The mixture containing 1,3-dilithiopropyne was then added dropwise to a solution of o-iodobenzyl bromide (2.97 g, 10 mmol) in THF (2 mL). Stirring was continued for 12 h. Addition of 3 M solution of hydrochloric acid (5 mL), followed by extraction with ether (3 x 10 mL) and distillation (b.p. 60-2°C/2 mmHg) gave 1.98 g (78%) of 4-(o-iodophenyl)-1-butene: GC purity > 95%. ¹H-NMR (CDCl₃, TMS) 1.99 (t, J = 2.6 Hz, 1 H), 2.49 (dt, J = 2.6, 7.4 Hz, 2 H), 2.95 (t, J = 7.4 Hz, 2 H), 6.8-7.0 (m, 1 H), 7.25-7.30 (m, 2 H), 7.81 (d, J = 7.7 Hz, 1 H) ppm. ¹3C-NMR (CDCl₃, TMS) 18.99, 39.52, 69.11, 83.04, 100.16, 128.17, 129.70, 139.39, 142.57 ppm. IR (neat) 3300 (s), 3050 (w), 2950 (w), 2120 (w), 1590 (w), 1560 (w), 1465 (m), 1450 (m), 1420 (m), 1260 (w), 1010 (s), 750 (s), 640 (s) cm⁻¹. MS m/z 256 (M⁺), 217, 129, 128, 127. Then, into a dry, nitrogen-flushed flask kept under a static pressure of nitrogen was added 4-(o-iodophenyl)-1-butene (529 mg, 2.1 mmol), n-hexane (10 mL), and disobutylaluminum hydride (2.3 mL of 1 M solution in n-hexane, 2.3 mmol). The solution was stirred at room temperature for 30 min, then heated at 90°C for 3 h. After cooling to room temperature, methyl chloroformate (0.62 mL, 8 mmol) was added at such a rate as to maintain the temperature during the addition below 20-25°C. The resulting reaction mixture was kept for an additional 1 h at room temperature before being poured slowly into a stirred mixture of 10% sulfuric acid (20 mL) and ice (50 g). The organic layer was separated, and the aqueous layer was extracted with ether (3 x 10 mL). The combined extract was washed with brine (2 x 10 mL), dried over MgSO₄, removed the solvent under reduced pressure, purified by column chromatography (silica gel, hexanes/ether = 4/1), and evaporated in vacuo to give 0.54 g (81%) of the title compound 5: ¹H-NMR (CDCl₃, TMS) 2.4-2.6 (m, 2 H), 2.87 (t, J = 7.2 Hz, 2 H), 3.74 (s, 3 H), 5.88 (dt, J = 15.6, 1.6 Hz, 1 H), 6.8-7.3 (m, 4 H), 7.82 (d, J = 7.9 Hz, 1 H) ppm. ¹3C-NMR
(CDCl₃, TMS) 32.50, 39.19, 51.39, 100.27, 121.56, 128.02, 128.36, 129.27, 139.52, 143.15, 147.65, 166.84 ppm. IR (neat) 1725 (s), 1660 (m), 1435 (m), 1270 (m), 1200 (m), 1010 (m), 750 (m) cm⁻¹. MS m/z 316 (M⁺), 285, 256, 217, 189, 157, 129. High resolution MS calc'd. for C₁₅H₁₉O₂: 315.9960, found: 315.9977.

(E)-1-Methoxy carbonylmethylenine 1. To a solution of methyl (E)-5-(oiodophenyl)-2-pentenoate 5 (159 mg, 0.5 mmol), in benzene (0.2 mL) and acetonitrile (0.2 mL), under an atmosphere of nitrogen, was added tetrakis (triphenylphosphine) palladium (58 mg, 0.05 mmol) and triethylamine (77 µl, 0.55 mmol). The reaction mixture was then irradiated in the water bath of an ultrasonic laboratory cleaner for 6 h. The cooled mixture was quenched with 1 N HCl (5 mL), and then extracted with ether (5 x 5 mL), washed with brine (2 x 5 mL), dried over MgSO₄, filtered, concentrated, purified by column chromatography (silica gel, hexanes/ether = 4/1), and concentrated in vacuo to give 72 mg (76%) of the title compound 1: 1H-NMR (CDCl₃, TMS) 3.05-3.15 (m, 2 H), 3.25-3.35 (m, 2 H), 3.77 (s, 3 H), 6.32 (t, J = 2.6 Hz, 1 H), 7.25-7.65 (m, 4 H) ppm. 13C-NMR (CDCl₃, TMS) 30.49, 31.09, 50.92, 107.14, 121.55, 125.55, 126.68, 130.81, 139.81, 149.45, 163.16, 167.85 ppm. IR (neat) 1702 (s), 1640 (s), 1441 (m), 1358 (m), 1286 (m), 1194 (m), 1167 (s), 871 (w), 764 (m) cm⁻¹. MS m/z 188 (M⁺), 173, 157, 129. High resolution MS calc'd. for C₁₂H₁₂O₂: 188.0838, found: 188.0814.

Ethyl (E)-5,5-dithiooxy carbonyl-6-(o-iodophenyl)-2-hexenoate 6. A 25 mL of round-bottomed flask is placed 8 mL of absolute alcohol and the there is added 46 mg (2 mmol) of clean sodium. The sodium ethoxide solution is stirred, and cooled to about 30°C, after which diethylmalonate (320 mg, 2 mmol) is added slowly to it. To the clean solution is added gradually o-tolobenzylbromide (594 mg, 2 mmol) in absolute alcohol (2 mL). The reaction mixture is stirred at room temperature for 12 h, concentrated under reduced pressure, added water (10 mL), extracted with ether (4 x 10 mL), washed with brine (2 x 10 mL), dried over MgSO₄, filtered, concentrated, purified by column chromatography (silica gel, hexanes/ether = 4/1), and evaporated in vacuo to give 692 mg (92%) of diethyl 2-(o-tolobenzyl)malonate: 1H-NMR (CDCl₃, TMS) 1.21 (t, J = 7.2 Hz, 3 H), 3.22 (d, J = 6.9 Hz, 2 H), 3.82 (t, J = 6.9 Hz, 1 H), 4.19 (q, J = 7.2 Hz, 2 H), 6.97-7.0 (m, 1 H), 7.27-7.3 (m, 2 H), 7.82 (d, J = 7.9 Hz, 1 H) ppm. 13C-NMR (CDCl₃, TMS) 13.89, 39.17, 51.62, 61.39, 100.30, 128.15, 128.53, 130.48, 139.55, 140.18, 168.41 ppm. IR (neat) 1750 (s), 1730 (s), 1470 (m), 1370 (m), 1300 (m), 1225 (m), 1150 (m), 1040 (m), 1010 (m), 750 (m) cm⁻¹. MS m/z 376 (M⁺), 285, 249, 221, 175, 147. High resolution MS calc'd. for C₁₄H₁₂O₄: 376.0172, found: 376.0180. Then, in a 25 mL of round-bottomed flask is placed 8 mL of absolute alcohol and 23 mg (1 mmol) of clean sodium. The sodium ethoxide solution is stirred, and cooled to about 30°C, after which diethyl 2-(o-tolobenzyl)malonate (376 mg, 1 mmol) is added slowly to it. To the clean solution is added gradually ethyl γ-bromocrotonate (232 mg, 1.2 mmol). The reaction mixture is stirred at room temperature for 12 h, concentrated under reduced pressure, added water (10 mL), extracted with ether (4 x 10 mL), dried over MgSO₄, filtered, concentrated, purified by column chromatography (silica gel, hexanes/ether = 4/1), and evaporated in vacuo to give 425 mg (87%) of the title compound 6: 1H-NMR (CDCl₃, TMS) 1.21 (t, J = 7.1 Hz, 6 H), 1.27 (t, J = 7.1 Hz, 3 H), 2.78 (dd, J = 7.5, 1.4 Hz, 2 H), 3.54 (s, 2 H), 4.14-4.3 (m, 6 H), 5.82 (dt, J = 15.6, 1.4 Hz, 1 H), 6.85-7.30 (m, 4 H), 7.83 (d, J = 7.5 Hz, 1 H) ppm. 13C-NMR (CDCl₃, TMS) 13.82, 14.17, 36.26, 42.84, 58.60, 60.17, 61.65, 102.91, 124.50, 128.12, 128.64, 130.11, 139.30, 139.89, 143.12, 165.79, 170.12 ppm. IR (neat) 1730 (s), 1655 (w), 1270 (m), 1180 (m), 1040 (m), 1010 (m), 860 (w), 750 (w) cm⁻¹. MS m/z 443 (M⁺), 397, 375, 361, 329, 287, 243, 217, 185, 169, 141. High resolution MS calc'd. for C₂₆H₂₅O₅: 488.0696, found: 488.0756.

(E)-1-Ethoxycarbonylmethylenine-3-dithioxy carbonyl tetralin 2. To a solution of ethyl (E)-5,5-dithioxy carbonyl-6-(o-iodophenyl)-2-hexenoate (244 mg, 0.5 mmol), in benzene (0.2 mL) and acetonitrile (0.2 mL), under an atmosphere of nitrogen, was added tetraakis-
(triphenylphosphine)palladium (58 mg, 0.05 mmol) and triethylamine (77 µl, 0.55 mmol). The reaction mixture was then irradiated in the water bath of an ultrasonic laboratory cleaner for 6 h. The cooled mixture was quenched with 1 N HCl (10 mL), and then extracted with ether (6 x 5 mL), washed with brine (3 x 5 mL), dried over MgSO₄, filtered, concentrated, purified by column chromatography (silica gel, hexanes/ether = 4/1), and concentrated in vacuo to give 124 mg (69%) of the title compound. ¹H-NMR (CDCl₃, TMS) 1.15 (t, J = 7.1 Hz, 6 H), 1.32 (t, J = 7.2 Hz, 3 H), 3.32 (s, 2 H), 3.71 (d, J = 1.9 Hz, 2 H), 4.12 (q, J = 7.1 Hz, 4 H), 4.22 (q, J = 7.2 Hz, 2 H), 6.39 (t, J = 1.9 Hz, 1 H), 7.20-7.65 (m, 4 H) ppm. ¹³C-NMR (CDCl₃, TMS) 13.81, 14.24, 33.53, 35.45, 53.85, 59.82, 61.53, 114.33, 124.42, 127.03, 129.22, 129.95, 133.08, 135.51, 150.02, 166.42 ppm. IR (neat) 1736 (s), 1698 (s), 1626 (m), 1599 (m), 1445 (m), 1369 (m), 1304 (m), 1262 (s), 1235 (s), 1164 (s), 1045 (s), 866 (m), 766 (m) cm⁻¹. MS m/z 360 (M⁺), 241, 213, 141. High resolution MS calc'd for C₆₀H₄₄O₈: 360.1573, found: 360.1600.

3-(o-Lodophenoxy)-1-methoxycarbonyl-1-cyclohexene 7. A mixture of N-bromosuccinimide (256 mg, 2 mmol), 1-carbomethoxy-1-cyclohexene (281 mg, 2 mmol) and dry carbon tetrachloride (3 mL) in a 25 mL round-bottomed flask was refluxed for 3 h; by this time all the solid should have risen to the surface of the liquid. Filtered off the succinimide, washed it with a little dry carbon tetrachloride, concentrated, purified by column chromatography (silica gel, hexanes/ether = 4/1), concentrated, and evaporated in vacuo to give 275 mg (63%) of 3-bromo-1-methoxycarbonyl-1-cyclohexene and 3-bromo-2-carbomethoxy-1-cyclohexene 66 mg (15%). 3-Bromo-1-methoxycarbonyl-1-cyclohexene: ¹H-NMR (CDCl₃, TMS) 1.7-2.6 (m, 6 H), 3.76 (s, 3 H), 4.8-5.0 (m, 1 H), 6.9-7.1 (m, 1 H) ppm. ¹³C-NMR (CDCl₃, TMS) 18.14, 23.71, 31.58, 45.93, 51.77, 132.03, 137.26, 167.00 ppm. IR (neat) 1720 (s), 1640 (w), 1440 (m), 1265 (s), 1245 (s), 1180 (m), 1090 (m), 750 (m), 730 (w) cm⁻¹. MS m/z 187 (M⁺—1), 139, 107, 79. High resolution MS calc'd for C₆₀H₄₄BrO₇: 217.9942, found: 217.9912. Then, a mixture of 2-lodophenol (210 mg, 1.05 mmol), 3-bromo-1-carbomethoxy-1-cyclohexene (241 mg, 1.1 mmol) and potassium carbonate (304 mg, 2.2 mmol) in acetone (1 mL) was stirred under a nitrogen atmosphere at reflux for 12 h. The cooled reaction mixture was diluted with water (15 mL), extracted with ether (4 x 10 mL), washed with 10% NaOH (3 x 10 mL), dried over MgSO₄, filtered, concentrated by column chromatography (silica gel, hexanes/ether = 4/1), and evaporated in vacuo to give 293 mg (78%) of the title compound. ¹H-NMR (CDCl₃, TMS) 1.6-2.5 (m, 6 H), 3.75 (s, 3 H), 4.8-5.0 (m, 1 H), 6.7-7.8 (m, 5 H) ppm. ¹³C-NMR (CDCl₃, TMS) 18.86, 24.24, 27.73, 51.76, 72.81, 88.20, 114.24, 123.01, 129.26, 134.12, 135.52, 139.69, 156.26, 167.30 ppm. IR (neat) 1715 (s), 1470 (s), 1440 (m), 1260 (s), 1240 (s), 1090 (m), 1020 (m), 750 (m) cm⁻¹. MS m/z 230 (M⁺), 139, 138, 137. High resolution MS calc'd for C₆₀H₄₄Br₂O₈: 358.0066, found: 358.0088.

cis-4-Methoxyxarbonyl-9-oxa-1,2,4,9a-tetrahydro-9H-fluorene 3. To a solution of 3-(o-lodophenoxy)-1-methoxycarbonyl-1-cyclohexene 7 (179 mg, 0.5 mmol) in benzene (0.2 mL) and acetonitrile (0.2 mL), under an atmosphere of nitrogen, was added tetraakis(triphenylphosphine)-palladium (58 mg, 0.05 mmol) and triethylamine (77 µl, 0.55 mmol). The reaction mixture was then irradiated in the water bath of an ultrasonic laboratory cleaner for 6 h. The cooled mixture was quenched with 1 N HCl (5 mL), and then extracted with ether (3 x 5 mL), washed with brine (3 x 5 mL), dried over MgSO₄, filtered, concentrated, purified by column chromatography (silica gel, hexanes/ether = 4/1), and concentrated in vacuo to give 73 mg (64%) of the title compound. ¹H-NMR (CDCl₃, TMS) 1.6-1.8 (m, 2 H), 2.2-2.5 (m, 2 H), 3.80 (s, 2 H), 4.36 (d, J = 7.6 Hz, 1 H), 5.11 (dt, J = 7.6, 4 Hz, 1 H), 6.75-6.85 (m, 2 H), 7.1-7.4 (m, 3 H) ppm. ¹³C-NMR (CDCl₃, TMS) 20.04, 24.70, 40.24, 51.58, 80.91, 109.53, 120.41, 126.15, 128.36, 129.83, 130.40, 140.78, 159.38, 166.93 ppm. IR (neat) 1710 (s), 1480 (m), 1460 (m), 1440 (m), 1260 (s), 1230 (m), 1080 (m), 1060 (m), 890 (m), 750 (m) cm⁻¹. MS m/z 230 (M⁺), 197, 171. High resolution MS...
calcd. for C_{15}H_{17}BrO_{2}: 230.0943, found: 230.0931.

3-(o-Bromobenzyl)-2-cyclohexenone 8. A solution of o-bromo-benzylmagnesium bromide in ether, prepared from o-bromobenzyl bromide (500 mg, 2 mmol) and magnesium turnings (48.6 mg, 2 mmol) in ether (1 mL), was sequentially added THF (2 mL) and 3-ethoxy-2-
cyclohexenone\(^{11}\) (238 mg, 1.7 mmol) at 0°C. The cooling bath was removed and the reaction mixture was stirred at room temperature for 5 h. The mixture was then quenched with water (10 mL), extracted with ether (5 x 10 mL), washed with brine (4 x 10 mL), dried over MgSO_{4}, filtered, concentrated, purified by column chromatography (silica gel, hexanes/ether = 4/1), and evaporated in vacuo to give 377 mg (84%) of the title compound. \(^1\)H-NMR (CDCl_{3}, TMS)
1.9-2.1 (m, 2 H), 2.3-2.4 (m, 4 H), 3.66 (s, 2 H), 5.67-5.69 (m, 1 H), 7.1-7.3 (m, 3 H), 7.56 (dd, J = 7.7, 1.1 Hz, 1 H) ppm. \(^13\)C-NMR (CDCl_{3}, TMS) 22.47, 29.57, 31.18, 43.83, 124.98, 126.84, 127.54, 128.56, 131.11, 132.97, 136.43, 163.22, 199.56 ppm. IR (neat 1670 (s),
1630 (m), 1470 (m), 1430 (m), 1025 (m), 760 (m), 750 (cm^{-1}). MS m/z 266, 264 (M^+),
238, 236, 185, 157, 129, 128.

1,2,3,9-Tetrahydro-4H-fluoren-4-one 4. A mixture of 3-(o-bromobenzyl)-2-cyclohexenone
(132.5 mg, 0.5 mmol), palladium acetate (11 mg, 0.05 mmol), triphenylphosphine (26.2 mg, 0.1 mmol) and sodium bicarbonate (84 mg, 1 mmol) in dry DMF (5 mL) was irradiated in the water bath of an ultrasonic laboratory cleaner for 6 h. The cooled mixture was quenched with 1 N HCl (5 mL), and then extracted with ether (5 x 5 mL), washed with brine (2 x 5 mL), dried over MgSO_{4}, filtered, concentrated, purified by column chromatography (silica gel, hexanes/ether = 12/1), and concentrated in vacuo to give 67 mg (72%) of the title compound which was in pale yellow color. \(^1\)H-NMR (CDCl_{3}, TMS) 2.17 (m, 2 H), 2.55 (t, J = 6.1 Hz, 2 H), 2.75
(t, J = 6.1 Hz, 2 H), 3.55 (s, 2 H), 7.2-7.4 (m, 3 H), 8.10 (d, J = 7.2 Hz, 1 H) ppm. \(^13\)C-NMR (CDCl_{3}, TMS) 23.65, 26.63, 38.58, 41.72, 122.36, 123.31, 125.18, 126.73, 136.47, 140.44,
140.66, 166.27, 196.32 ppm. IR (neat 1722 (w), 1663 (s), 1631 (s), 1605 (m), 1465 (m),
1175 (w), 770 (w), 730 (w) cm^{-1}. MS m/z 184 (M^+), 156, 155, 141, 129, 128, 115. m.p.
113.4°C (lit. 113°C)\(^{12}\).

3-(o-Bromobenzyl)-1-methoxy-carbonyl-1-cyclohexene 9. To a solution of o-bromobenzylmagnesium bromide in ether, prepared from o-bromobenzyl bromide (250 mg, 1 mmol) and magnesium turnings (24.3 mg, 1 mmol) in ether (1 mL), was added a solution of zinc chloride (136 mg, 1 mmol) in THF (1 mL) at 0°C. The resulting reaction mixture was stirred for an additional 1 h and then added a mixture of 3-bromo-1-carbomethoxy-1-cyclohexene (186 mg, 0.85 mmol) and tetrakis(triphenylphosphine) palladium (98 mg, 0.085 mmol) in THF (2 mL) at 0°C. The cooling bath was removed and the reaction mixture was stirred at room temperature for 4 h. The mixture was then quenched with water (20 mL), extracted with ether (3 x 10 mL), washed with brine (2 x 10 mL), dried over MgSO_{4}, filtered, concentrated, purified by column chromatography (silica gel, hexanes/ether = 4/1), and evaporated in vacuo to give 78 mg (30%) of the title compound. \(^1\)H-NMR (CDCl_{3}, TMS) 1.6-2.4 (m, 6 H), 2.75-3.05 (m, 2 H), 3.68
(s, 3 H), 7.0-7.6 (m, 5 H) ppm. \(^13\)C-NMR (CDCl_{3}, TMS) 15.18, 24.75, 25.90, 33.83, 38.96, 51.36, 124.90, 127.14, 127.46, 131.25, 132.58, 133.57, 140.40, 140.73, 167.78 ppm. MS m/z 308 (M^+), 277, 229, 197, 171, 169, 139, 138, 137. High resolution MS calcd. for C_{15}H_{17}BrO_{2}: 308.0412, found: 308.0463.

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REFERENCES

(6) For example, cyclization of 5 via the thermal procedure results in 71% of 1 and 20% of hydro-deiodinated product. While the ultrasonic procedure gives 76% of 1 along with less than 5% of the hydro-deiodinated product.
(7) The stereochemical study with molecular models showed that cis-fused and trans-fused structures of 3 have the dihedral angles of 30° and 160° between 4a-H and 9a-H, respectively, and hence the Karplus formula(8) gives J_{4a,9a} = 7.56 Hz for cis and 10.68 Hz for trans.

超音波用於鈀催化的分子內苯鈀加成反應

程 宇 �inflate 沃芬 壹

摘要

带有关于α,β-不饱和碳基的芳香烃卤化物可利用超音波来进行钯催化的分子内碳氢反应。