This article was downloaded by: [Northeastern University] On: 11 November 2014, At: 11:06 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/lsyc20

Synthesis of Ketones from Acyl Chlorides and Triorganoindium Reagents by Pd-Catalyzed Cross-Coupling

C. Croix ^a , A. Balland-Longeau ^a , A. Duchêne ^b & J. Thibonnet ^b ^a CEA Le Ripault, Materials Department , Monts, France

^b Laboratoire de Synthèse et Physicochimie Organique et Thérapeutique , Faculté des Sciences de Tours, Parc de Grandmont , Tours, France Published online: 24 Nov 2006.

To cite this article: C. Croix , A. Balland-Longeau , A. Duchêne & J. Thibonnet (2006) Synthesis of Ketones from Acyl Chlorides and Triorganoindium Reagents by Pd-Catalyzed Cross-Coupling, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 36:21, 3261-3270, DOI: <u>10.1080/00397910600910625</u>

To link to this article: http://dx.doi.org/10.1080/00397910600910625

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthetic Communications[®], 36: 3261–3270, 2006 Copyright © Taylor & Francis Group, LLC ISSN 0039-7911 print/1532-2432 online DOI: 10.1080/00397910600910625



Synthesis of Ketones from Acyl Chlorides and Triorganoindium Reagents by Pd-Catalyzed Cross-Coupling

C. Croix and A. Balland-Longeau CEA Le Ripault, Materials Department, Monts, France

A. Duchêne and J. Thibonnet

Laboratoire de Synthèse et Physicochimie Organique et Thérapeutique, Faculté des Sciences de Tours, Parc de Grandmont, Tours, France

Abstract: Triorganoindium reagents prepared from indium tribromide and 3 equiv of organolithium reagents react with acyl chlorides in palladium-catalyzed cross-coupling for preparation of new ketones.

Keywords: Indium, ketones, palladium catalyst, triorganoindium

The utilization of metals in organic synthesis, particularly to create carbon–carbon bond(s), is an important ongoing research theme. Transition-metal-catalyzed cross-coupling reactions of organic electrophiles with organo-metallic coupling partners represent one of the most powerful methods for the construction of carbon–carbon bonds.^[1] Since the emergence of indium-mediated organic reactions in aqueous media, indium has attracted considerable attention from organic chemists^[2] for various organic transformations such as conjugate addition,^[3] allylic substitution reactions,^[4] and allylation of carbonyl compounds.^[5] This interest is due to specific properties of indium, such as its low first oxidation potential, which makes it a very selective

Received in Poland April 4, 2006

Address correspondence to Jerome Thibonnet, Laboratoire de Synthèse et Physicochimie Organique et Thérapeutique, EA 3857, Faculté des Sciences de Tours, Parc de Grandmont, 37200 Tours, France. E-mail: jerome.thibonnet@univ-tours.fr



Scheme 1. Synthesis of triorganoindium reagents.

reagent.^[6] Furthermore, indium metal or salts such as InBr₃ are resistant to air and oxygen at an ambient temperature, as well as to boiling water and alkali solutions. Consequently, there is no need for specific activation of indium by heat, sonication, or acid catalysis as there is for other elements. Pérez et al. have recently reported the first Pd-catalyzed cross-coupling reactions of triorganoindium compounds with organic halides.^[7] On the basis of these cross-coupling reactions, it was found that a variety of organoindiums could be employed as nucleophilic coupling partners.^[8] This reaction was extended with indium reagents, such as tetraorganoindates^[9] in Pd-catalyzed carbonylative cross-coupling reactions. We describe here a successful Pd-catalyzed crosscoupling reaction with specific triorganoindium and acyl chlorides.

Triorganoindium compounds R_3 In were easily prepared as solutions in tetrahydrofuran (THF) by reaction of InBr₃ with 3 equiv of organolithium reagents (Scheme 1).^[10]

For the polymerization study,^[11] these organoindiums were characterized by ¹H NMR and ¹³C NMR. However, these compounds are unstable in water and insoluble after complete removal of solvents. After partial vacuum evaporation of THF, the triorganoindiums were introduced in THF- d_8 , where they could be characterized by ¹H and ¹³C NMR. The yields of these reactions were determined via iodolysis according to the following scheme, with 60–77% yields of the iodo compound derivatives (Scheme 2).

After characterization of the triarylindiums, we engaged them in crosscoupling reactions. The reaction of **In-1** with benzoylchloride (entry 1,



Scheme 2. Iodolysis.

Isolated yield Entry R₃In RCOCl Product^a No. (%) **1**^[12] 80 1 In-1 **2**^[13] 2 82 In-1 **3**^[1] 3 65 In-2 4 In-2 4 70 **5**^[15] 5 In-3 56 coci 6 In-3 6 40 **7**^[16] .coc 7 In-1 55 8 8 74 In-1 9 In-1 COC 9 52 .coci .coci 10 10 In-2 85 в в

Table 1. Results of the palladium-catalyzed cross-coupling reaction of triorganoindium reagents with acyl chlorides

^aAll products were identified by their ¹H NMR, ¹³C NMR, and MS spectral data.

Table 1) with 1% tetrakis(triphenylphosphine)palladium(0) allowed us to obtain the corresponding ketone (80% yield). Other acyl chlorides were engaged under similar conditions to determine the scope of the reaction (Scheme 3). Reactions of triorganoindium reagents (**In-1**, **2**, or **3**) with a

wide range of acyl chorides provided fair to good yields of corresponding ketones (Table 1, entries 2-8). The three styryl groups attached to the indium metal were transferred in all cases, in contrast with all other metals employed in cross-coupling reactions.

After the first series of reactions using triorganoindium, we decided to explore the use of the two reactional sites of 4-bromobenzoyl chloride in a one-pot Pd-catalyzed cross-coupling reaction to investigate whether it was possible to transfer the two tristyryl groups (Scheme 4). The results are reported in Table 1 (entries 9 and 10).

In conclusion, we describe the synthesis of new ketones by palladiumcatalyzed cross-coupling reaction with triarylindium compounds and acyl chlorides. The study of polymerization of tristyrylindium compounds is in progress in our laboratory.

EXPERIMENTAL

General Methods

All reactions were performed in oven-dried glassware under positive argon pressure. Toluene was dried and freshly distilled from sodium. ¹H NMR spectra were recorded at 200 MHz or at 300 MHz using CDCl₃ as solvent. reported using the residual proton resonance of CDCl₃ Results, $(\delta_{\rm H} = 7.25 \text{ ppm})$ as the internal reference, were as follows (in order): chemical shift (δ in ppm relative to Me₄Si), multiplicity (s, d, t, q, quint, m, b for singlet, doublet, triplet, quartet, quintuplet, multiplet, and broad), and coupling constants (J in Hz). ¹³C NMR spectra were recorded at 50 MHz or 75 MHz using CDCl₃ solvent peak at $\delta_{\rm C} = 77.0$ ppm as the reference. Electron impact mass spectra (EIMS) were measured at 70 eV by gas chromatography/mass spectrometry systems (GC/MS) or direct introduction mode. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer. Melting points were taken on a Büchi B-540 and are uncorrected. Standard column chromatography was performed on Merck silica gel (60 Å, 230-400 mesh silica gel) by flash column chromatography techniques. Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica-gel 60 F₂₅₄ plates.



Scheme 3. Palladium-catalyzed cross-coupling reaction of triorganoindium reagents with acyl chlorides.

Synthesis of Ketones from Acyl Chlorides and Triorganoindium



Scheme 4. Palladium-catalyzed twofold cross-coupling reactions with triorganoindium reagents.

Typical Procedure for the Preparation of Triorganoindium Reagents

BuLi (2.5 M) in hexane (2.88 mL, 7.20 mmol) was added to a solution of *p*-bromostyrene (1.29 g, 7.08 mmol) in dry THF (13 mL) at -78° C under an argon atmosphere. After 10 min of stirring, indium tribromide (0.84 g, 2.36 mmol) in dry THF (15 mL) was added dropwise, and the reaction mixture was allowed to warm to rt over 15 h. The mixture was not hydrolyzed, but 5–6 mL of this solution was concentrated in vacuo to obtain a viscous solution. The product obtained was then immediately mixed in solution in a minimum of THF- d_8 for NMR analysis.

Data

Tri(*p*-vinylphenyl)indium(III) (**In-1**). ¹H NMR (THF- d_8 , 200 MHz): δ 5.00 (dd, J = 11/1.3 Hz, 3H), 5.64 (dd, J = 17.7/1.3 Hz, 3H), 6.63 (dd, J = 11/1.7 Hz, 3H), 7.23 (d, J = 7.8 Hz, 6H_{Ar}), 7.66 (d, J = 7.8 Hz, 6H_{Ar}); ¹³C NMR (THF- d_8 , 50 MHz): δ 110.9 (3C), 124.8 (6C_{Ar}), 135.3 (3C), 139.3 (3C_{Ar}), 139.6 (6C_{Ar}), 160.1 (3C_{Ar}).

Tri(*m*-vinylphenyl)indium(III) (**In-2**). ¹H NMR (THF-*d*₈, 200 MHz): δ 5.00 (dd, J = 11/1.7 Hz, 3H), 5.60 (dd, J = 17.6/1.5 Hz, 3H), 6.64 (dd, J = 11/1.7 Hz, 3H), 7.09 (m, 6H), 7.59 (d, J = 6.4 Hz, 3H), 7.77 (bs, 3H); ¹³C NMR (CDCl₃, 50 MHz): δ 111.2 (3C), 123.8 (3C_{Ar}), 126.9 (3C_{Ar}), 135.8 (3C_{Ar}), 137.8 (3C), 139.1 (3C_{Ar}), 139.4 (3C_{Ar}), 159.0 (3C_{Ar}).

Tri(*o*-vinylphenyl)indium(III) (**In-3**). ¹H NMR (THF-*d*₈, 200 MHz): δ 4.76 (dd, J = 11/1.7 Hz, 3H), 5.41 (dd, J = 17.3/1.7 Hz, 3H), 6.91–7.13 (m, 6H_{Ar} + 3H), 7.45 (d, J = 8.6 Hz, 3H_{Ar}), 7.76 (d, J = 6.7 Hz, 3H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 110.4 (3C), 123.4 (3C_{Ar}), 126.1 (3C_{Ar}), 126.3 (3C_{Ar}), 140.7 (3C), 145.0 (3C_{Ar}), 146.3 (3C_{Ar}), 161.5 (3C_{Ar}).

General Procedure for the Preparation of Ketones

Approximately 0.1 M triarylindium in THF (16 mL, 1.6 mmol) was added to a solution of benzoyl chloride (4.8 mmol) in dry THF (18 mL) and Pd(PPh₃)₄

(56 mg, 0.05 mmol, 1 mol%) in an argon atmosphere. The reaction mixture was stirred at 65°C for 3 h. The reaction was quenched by the addition of ethanol (10 mL). The solvent was removed under reduced pressure, and the residue was diluted with Et_2O . The organic layer was washed successively with 5% aqueous HCl (20 mL), saturated aqueous NaHCO₃ (25 mL), and brine (20 mL). The organic layer was dried (MgSO₄) and the solvents removed in vacuo to give the crude product, which was purified by column chromatography (silica gel) using light petroleum ether (40–60°C)– Et_2O (90/10). Unknown compounds or compounds for which incomplete physical data were reported in the literature were characterized by FTIR, ¹H and ¹³C NMR, and MS spectral data.

Selected Data

Phenyl(*p*-vinylphenyl)ketone (1). Oil; IR (neat) $\nu = 3052$, 1646, 1602, 1448 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ 5.38 (dd, J = 11/0.7 Hz, 1H), 5.96 (dd, J = 17.6/0.7 Hz, 1H), 6.81 (dd, J = 11/17.6 Hz, 1H), 7.46–7.82 (m, 9H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 116.6, 126.7 (2C_{Ar}), 128.9 (2C_{Ar}), 130.4 (2C_{Ar}), 131.0 (2C_{Ar}), 132.8 (C_{Ar}), 137.0, 137.7 (C_{Ar}), 138.7 (C_{Ar}), 142.2 (C_{Ar}), 195.3; MS (EI, 70 eV): m/z (%) = 208 (M⁺, 69), 131 (100), 105 (33), 103 (23), 77 (51), 51 (14).

p-Bromophenyl(*p*-vinylphenyl)ketone (2). Solid; mp: $129-131^{\circ}$ C; IR (KBr) $\nu = 3088$, 3060, 1660, 1597, 1478 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ 5.36 (d, J = 11 Hz, 1H), 5.95 (d, J = 17.7 Hz, 1H), 6.82 (dd, J = 11/17.7 Hz, 1H), 7.58–7.78 (m, 8H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 116.7, 126.8 (2C_{Ar}), 127.5 (C_{Ar}), 130.9 (2C_{Ar}), 132.2 (2C_{Ar}), 132.3 (2C_{Ar}), 136.9, 137.2 (C_{Ar}), 137.9 (C_{Ar}), 142.5 (C_{Ar}), 194.3; MS (EI, 70 eV): m/z (%) = 288 (M⁺, 28), 286 (M⁺, 29), 207 (13), 185 (15), 183 (15), 157 (11), 155 (11), 131 (100), 103 (27), 77 (39).

Phenyl(*m***-vinylphenyl)ketone (3).** Oil; IR (neat) $\nu = 3089, 3065, 1645, 1602, 1479 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): <math>\delta 5.30$ (dd, J = 11/0.8 Hz, 1H), 5.85 (dd, J = 17.6/0.8 Hz, 1H), 6.74 (dd, J = 11/17.6 Hz, 1H), 7.45–7.68 (m, 6H_{Ar}), 7.78–7.85 (m, 3H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): $\delta 115.3, 128.4$ (C_{Ar}), 129.1 (2C_{Ar}), 129.3 (C_{Ar}), 130.0 (C_{Ar}), 130.4 (C_{Ar}), 130.7 (2C_{Ar}), 133.1 (C_{Ar}), 137.2, 138.7, 138.9, 139.2 (3C_{Ar}), 195.9; MS (EI, 70 eV): m/z (%) = 208 (M⁺, 100), 131 (55), 105 (43), 103 (20), 77 (74), 51 (33).

p-Bromophenyl(*m*-vinylphenyl)ketone (4). Solid; mp: 85–86°C; IR (KBr) $\nu = 3092, 3062, 1650, 1584, 1480 \text{ cm}^{-1}; {}^{1}\text{H} \text{ NMR} (\text{CDCl}_3, 200 \text{ MHz}): \delta$ 5.30 (dd, J = 11/0.5 Hz, 1H), 5.88 (dd, J = 17.6/0.6 Hz, 1H), 6.78 (dd, J = 11/17.6 Hz, 1H), 7.46 (t, $J = 7.6 \text{ Hz}, 1\text{H}_{\text{Ar}}$), 7.62–7.83 (m, 7H_{Ar}); ${}^{13}\text{C}$ NMR (CDCl₃, 50 MHz): δ 115.5, 127.9 (C_{Ar}), 128.4 (C_{Ar}), 129.4 (C_{Ar}), 130.0 (C_{Ar}), 130.7 (C_{Ar}), 132.5 (4C_{Ar}), 137.1, 137.6 (C_{Ar}), 138.8, 139.0 (2C_{Ar}), 195.0; MS (EI, 70 eV): m/z (%) = 288 (M⁺, 68), 286 (M⁺, 68), 207 (49), 185 (62), 183 (62), 157 (25), 155 (25), 131 (100), 103 (34), 77 (42), 51 (17).

Phenyl(*o*-vinylphenyl)ketone (5). Oil; IR (neat) $\nu = 3062, 3026, 1663, 1596, 1478 \text{ cm}^{-1}$; ¹H NMR (CDCl₃, 200 MHz): δ 5.17 (dd, J = 11/1.2 Hz, 1H), 5.73 (dd, J = 17.4/1.2 Hz, 1H), 6.76 (dd, J = 11/17.4 Hz, 1H), 7.33–7.58 (m, 6H_{Ar}), 7.73–7.79 (m, 3H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 116.4, 126.5 (C_{Ar}), 128.0 (C_{Ar}), 129.3 (2C_{Ar}), 129.6 (C_{Ar}); 130.9 (2C_{Ar}), 131.0 (C_{Ar}), 133.9 (C_{Ar}), 135.3, 137.4 (C_{Ar}), 138.8, 139.3 (2C_{Ar}), 197.6; MS (EI, 70 eV): m/z (%) = 208 (M⁺, 100), 207 (52), 179 (24), 178 (20), 103 (16), 77 (54), 51 (25).

p-Bromophenyl(*o*-vinylphenyl)ketone (6). Oil; IR (neat) $\nu = 3088, 3063, 1666, 1584, 1478 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ 5.19 (dd, <math>J = 11/1.1$ Hz, 1H), 5.72 (dd, J = 17.4/1.1 Hz, 1H), 6.77 (dd, J = 11/17.4 Hz, 1H), 7.34–7.36 (m, 2H_{Ar}), 7.45–7.52 (m, 1H_{Ar}), 7.66 (bs, 4H_{Ar}), 7.74 (d, J = 7.7 Hz, 1H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 116.8, 126.7 (C_{Ar}), 128.1, 128.9 (2C_{Ar}), 129.3 (C_{Ar}), 132.0 (C_{Ar}), 132.5 (2C_{Ar}), 132.6 (2C_{Ar}), 135.2, 137.5 (C_{Ar}), 137.7, 138.7 (2C_{Ar}), 196.6; MS (EI, 70 eV): m/z (%) = 288 (M⁺, 71), 287 (33), 286 (M⁺, 72), 285 (22), 208 (16), 207 (100), 206 (13), 179 (50), 178 (77), 157 (18), 155 (18), 131 (16), 103 (33), 77 (47), 76 (39), 75 (26), 51 (26), 50 (28).

Napht-2-yl(*p*-vinylphenyl)ketone (7). Solid; mp: $80-81^{\circ}$ C; IR (KBr) $\nu = 3054$, 1648, 1603, 1506, 1463 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ 5.39 (dd, J = 11/0.8 Hz, 1H), 5.97 (dd, J = 17.6/0.8 Hz, 1H), 6.85 (dd, J = 11/17.6 Hz, 1H), 7.55–7.65 (m, 4H_{Ar}), 7.83–7.97 (m, 6H_{Ar}), 8.31 (bs, 1H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 116.6, 126.9 (C_{Ar}), 127.0 (2C_{Ar}), 127.6 (C_{Ar}), 129.0 (C_{Ar}), 129.3 (C_{Ar}), 130.2, 131.2 (2C_{Ar}), 132.2 (1C), 133.5, 136.1, 136.3, 137.2 (4C_{Ar}), 138.0, 138.2 (C_{Ar}), 142.3 (C_{Ar}), 195.5; MS (EI, 70 eV): m/z (%) = 258 (M⁺, 100), 155 (61), 131 (60), 127 (57), 103 (27), 77 (44).

6-Bromohexyl(*p*-vinylphenyl)ketone (8). Solid; mp: 40–41°C; IR (KBr) $\nu = 3093, 3069, 2935, 1682, 1672, 1602, 1460 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): <math>\delta$ 1.46–1.57 (m, 2H), 1.65–1.76 (m, 2H₃), 1.81–1.88 (m, 2H₅), 2.98 (t, *J* = 7 Hz, 2H), 3.45 (t, *J* = 7 Hz, 2H), 5.34 (dd, *J* = 11/0.7 Hz, 1H), 5.90 (dd, *J* = 17.6/0.8 Hz, 1H), 6.78 (dd, *J* = 11/1.7.6 Hz, 1H), 7.51 (d, *J* = 6.7 Hz, 2H_{Ar}), 7.94 (d, *J* = 6.6 Hz, 2H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 24.1, 28.8, 33.8, 34.3, 38.7, 116.5, 127.0 (2C_{Ar}), 129.2 (2C_{Ar}), 137.1, 137.5 (C_{Ar}), 142.6 (C_{Ar}), 198.6; MS (EI, 70 eV): *m*/*z* (%) = 282 (M⁺, 2), 280 (M⁺, 2), 146 (70), 131 (100), 103 (29), 77 (24).

General Procedure for the Preparation of Ketones (Table 1, entries 9 and 10)

Approximately 0.1 M triarylindium in THF (32 mL, 3.2 mmol) was added to a solution of 4-bromo-benzoyl chloride (4.8 mmol) in dry THF (18 mL) and Pd(PPh₃)₄ (56 mg, 0.05 mmol, 1 mol%) in an argon atmosphere. The reaction mixture was stirred at 65°C for 3 h. The reaction was quenched by addition of ethanol (10 mL). The solvent was removed under reduced pressure and the residue was diluted with Et₂O. The organic layer was washed successively with 5% aqueous HCl (20 mL), saturated aqueous NaHCO₃ (25 mL), and brine (20 mL). The organic layer was dried (MgSO₄) and the solvents removed in vacuo to give the crude product, which was purified by column chromatography (silica gel) using light petroleum ether (40–60°C)–Et₂O (90/10). Unknown compounds or compounds for which incomplete physical data were reported in the literature were characterized by FTIR, ¹H and ¹³C NMR, and MS spectral data.

Selected Data

p-[(*p*-Vinylphenyl)phenyl](*p*-vinylphenyl)ketone (9). Solid; mp: 169–171°C (decomposition); IR (KBr) $\nu = 3085$, 3026, 1700, 1604 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ 5.26 (dd, J = 11/1 Hz, 1H), 5.38 (dd, J = 11/1 Hz, 1H), 5.86 (dd, J = 17.6/1 Hz, 1H), 5.96 (dd, J = 17.6/0.9 Hz, 1H), 6.71–6.92 (m, 2H), 7.53–7.90 (m, 12H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 114.5, 116.6, 126.9 (2C_{Ar}), 127.4 (2C_{Ar}), 127.5 (2C_{Ar}), 127.7 (2C_{Ar}), 131.1 (2C_{Ar}), 131.3 (2C_{Ar}), 137.2, 137.4 (2C), 137.6, 138.1, 138.6 (3C_{Ar}), 140.2 (C_{Ar}), 142.4 (C_{Ar}), 145.2 (C_{Ar}), 195.0; MS (EI, 70 eV): m/z (%) = 310 (M⁺, 100), 207 (62), 131 (43), 103 (25), 77 (26).

p-(*m*-Vinylphenyl)phenyl(*m*-vinylphenyl)ketone (10). Oil; IR (neat) $\nu = 3087, 3059, 1657, 1602, 1480 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz):$ δ 5.31 (dd, <math>J = 11/2.3 Hz, 2H), 5.88 (d, J = 17.6 Hz, 1H), 5.91 (dd, J = 17.6/0.8 Hz, 1H), 6.77–6.98 (m, 2H), 7.44–7.94 (m, 12H_{Ar}); ¹³C NMR (CDCl₃, 50 MHz): δ 114.7, 115.4, 126.1 (2C_{Ar}), 127.0 (C_{Ar}), 127.5 (C_{Ar}), 127.7 (2C_{Ar}), 128.4 (C_{Ar}), 129.3 (C_{Ar}), 130.0 (C_{Ar}), 130.4 (C_{Ar}), 131.4 (2C_{Ar}), 137.2, 137.5 (1C_{Ar}), 137.7 (1C), 138.8, 139.3, 139.4 (3C_{Ar}), 141.2 (C_{Ar}), 145.7 (C_{Ar}), 195.5; MS (EI, 70 eV): *m/z* (%) = 310 (M⁺, 94), 207 (100), 178 (48), 131 (24), 103 (22), 77 (21).

ACKNOWLEDGMENTS

We thank CEA Le Ripault for providing financial support and characterization.

REFERENCES

- (a) Heck, R. F. Palladium Reagents in Organic Synthesis; Academic Press: New York, 1985; (b) Trost, B. M.; Verhoeven, T. R. In Comprehensive Organometallic Chemistry; Wilkinson, G., Stone, F. G., Abel, E. W., Eds.; Pergamon: Oxford, UK, 1982; Vol. 8, pp. 799–938; (c) Farina, V. In Comprehensive Organometallic Chemistry II; Wilkinson, G., Stone, F. G., Abel, E. W., Eds.; Pergamon: Oxford, UK, 1995; Vol. 12, pp. 161–240; (d) Tsuji, J. Palladium Reagents and Catalyst; Wiley: Chichester, UK, 1995; Chapter 4; (e) Diederich, F.; Stang, P. J. Eds.; Metal-Catalyzed Cross-Coupling Reactions; Wiley-VCH: Weinheim, Germany, 1998; (f) Geissler, H. In Transition Metals for Organic Synthesis; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp. 158–183; Chapter 2.10; (g) Tsuji, J. Transition Metal Reagents and Catalysts; Wiley: Chichester, UK, 2000; pp. 27–108; Chapter 3; (h) Negishi, E. Organopalladium Chemistry; Wiley-Interscience: New York, 2002; Vol. I and II.
- (a) Cintas, P. Synthetic organoindium chemistry: What makes indium so appealing Synlett 1995, 1087; (b) Araki, S.; Ito, H.; Butsugan, Y. Indium in organic synthesis: indium-mediated allylation of carbonyl compounds. J. Org. Chem. 1988, 53, 1831;
 (c) Li, C.-J. Tetrahedron 1999, 55, 11149; (d) Li, C.-J.; Chan, T.-H. Organic Reactions in Aqueous Media; Wiley: New York, 1997; pp. 64–114; Chapter 4;
 (e) Paquette, L. A. In Green Chemistry: Frontiers in Benign Chemical Synthesis and Processing; Anastas, P. T., Williamson, T. C., Eds.; Oxford University Press: Oxford, UK, 1998; pp. 250–264; Chapter 15; (f) Podlech, J.; Maier, T. C. Indium in organic synthesis. Synthesis 2003, 633; (g) Loh, T. P. In Science of Synthesis, Category 1: Organometallic; Vol. 7: Compounds of Groups 13 and 2; Product Class 3: Indium Compounds; Yamamoto, H., Eds.; Thieme Chemistry: Stuttgart-New York, 2004; 413–452.
- 3. (a) Araki, S.; Shimizu, K.; Jin, S.-J.; Butsugan, Y. J. Application of indiumate complexes to synthetic chemistry: Selective conjugate addition to enones and coupling with allylic halides. J. Chem. Soc., Chem. Commun. 1991, 824; (b) Pérez, I.; Pérez Sestelo, J.; Maestro, M. A.; Mourino, A.; Sarandeses, L. A. First nickel-catalyzed 1,4-conjugate additions to α,β-unsaturated systems using triorganoindium compounds. J. Org. Chem. 1998, 63, 10074.
- 4. (a) Lee, P. H.; Sung, S.-Y.; Lee, K.; Chang, S. Palladium-catalyzed allylic substitution using in situ generated allylindium reagents. *Synlett* 2002;
 (b) Rodriguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. Copper-catalyzed regioselective allylic substitution reactions with indium organometallics. *J. Org. Chem.* 2003, 68, 2518; (c) Baker, L.; Minehan, T. Efficient palladium-catalyzed nucleophilic addition of triorganoindium reagents to carbocyclic derivatives. *J. Org. Chem.* 2004, 69, 3957.
- (a) Yi, X.-H.; Haberman, J. X.; Li, C.-J. Metal-mediated Barbier-type carbonyl allylation under solvent-free conditions. *Synth. Commun.* 1998, 28, 2999;
 (b) Pae, A. N.; Cho, Y. S. *Curr. Org. Chem.* 2002, 6, 715.
- 6. Li, C.-J.; Chan, T.-H. Organometallic reactions in aqueous media with indium. *Tetrahedron Lett.* **1991**, *32*, 7017.
- Pérez, I.; Pérez Sestelo, J.; Sarandeses, L. A. Palladium-catalyzed cross-coupling reactions of triorganoindium compounds with vinyl and aryl triflates or iodides. *Org. Lett.* **1999**, *1*, 1267.
- 8. (a) Pérez, I.; Pérez Sestelo, J.; Sarandeses, L. A. Atom-efficient metal-catalyzed cross-coupling reaction of indium organometallics with organic electrophiles.

J. Am. Chem. Soc. 2001, 123, 4155; (b) Pena, M. A.; Pérez, I.; Pérez Sestelo, J.; Sarandeses, L. A. Multifold and sequential cross-coupling reactions with indium organometallics. Chem. Commun. 2002, 2246; (c) Pena, M. A.; Pérez Sestelo, J.; Sarandeses, L. A. Palladium-Catalyzed Carbonylative Coupling Reactions Using Triorganoindium Compounds. Synthesis 2003, 780; (d) Pena, M. A.; Pérez Sestelo, J.; Sarandeses, L. A. New synthetic applications of indium organometallics in cross-coupling reactions. Synthesis 2005, 485; (e) Takami, K.; Yorimitsu, H.; Shnokubo, H.; Matsubara, S.; Oshima, K. Palladium-catalyzed cross-coupling reaction of organoindiums with aryl halides in aqueous media. Org. Lett. 2001, 3, 1997; (f) Rodriguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. Palladium-catalyzed cross-coupling reactions of allylic halides and acetates with indium organometallics. J. Org. Chem. 2004, 69, 8136.

- (a) Lee, S. W.; Lee, K.; Seomoon, D.; Kim, S.; Kim, H.; Kim, K.; Shim, E.; Lee, M.; Lee, S.; Kim, M.; Lee, P. H. Highly efficient Pd-catalyzed carbonylative cross-coupling reactions with tetraorganoindates. J. Org. Chem. 2004, 69, 4852;
 (b) Lee, P. H.; Lee, S. W.; Lee, K. Pd-catalyzed carbonylative cross-coupling reactions by triorganoindiums: Highly efficient transfer of organic groups attached to indium under atmospheric pressure. Org. Lett. 2003, 5, 1103;
 (c) Lee, P. H.; Lee, S. W.; Seomoon, D. Tetraorganoindates as nucleophilic coupling partners in Pd-catalyzed cross-coupling reactions. Org. Lett. 2003, 5, 4963.
- Clark, H. C.; Pickard, A. L. Organoindium chemistry: I. A convenient preparation of dimethylindium(III) derivatives. J. Organomet. Chem. 1967, 8, 421.
- Croix, C. Thesis: Synthese de nouveaux dérivés styrèniques organométalliques contenant de l'indium ou de l'or. Etude de leur comportement en polymérisation pour les cibles Laser, University Francois Rabelals, Tours, 2005.
- Uvarova, L. R.; Burykina, L. K.; Zubareva, M. M.; Polyanskii, I. D. Aromatic ketones with terminal vinyl groups. *Zh. Org. Khim.* 1988, 24, 1495.
- Pogosyan, G. M.; Zhamkochyan, G. A.; Matsoyan, S. G. Styrene derivatives, IX: Synthesis and polymerization of 4-acylstyrenes. *Armyanski Khimicheski Zhurnal* 1969, 22, 908.
- (a) Darses, S.; Michaud, G.; Genêt, J.-P. Potassium vinyltrifluoroborate: A stable and efficient vinylating agent of arenediazonium salts using palladium catalysts. *Tetrahedron Lett.* **1998**, *39*, 5045; (b) Ramminger, C.; Zim, D.; Lando, V. R.; Fassina, V.; Monteiro, A. L. Transition-metal catalyzed synthesis of ketoprofen. *J. Braz, Chem. Soc.* **2000**, *11*, 105.
- Gensler, W. J.; Healy, E. M.; Onshuus, I.; Bluhm, A. L. 2-Acylstyrenes from 3,4-Dihydroisoquinolines. J. Am. Chem. Soc. 1956, 78, 1713.
- Tsubakiyama, K.; Miyagawa, K.; Kaizaki, K.; Yamamoto, M.; Nishijima, Y. Photochemical reactions of 4-acylstyrenes: Effects of acyl substituents on photocyclodimerization via an excited triplet state. *Bull. Chem. Soc. Jpn.* **1992**, 65, 837.