Journal of Organometallic Chemistry 693 (2008) 3441–3445

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Indium(I) bromide-promoted stereoselective preparation of cyclopropanes via sequential aldol-type coupling/elimination/Michael-induced ring closure reaction from α,α-dichloroacetophenone and aldehydes

Clovis Peppe *, Rafael Pavão das Chagas, Robert Alan Burrow

Laboratório de Materiais Inorgânicos, Departamento de Química, Universidade Federal de Santa Maria, Santa Maria-RS 97105-900, Brazil

ARTICLE INFO

Article history:
Received 10 June 2008
Received in revised form 6 August 2008
Accepted 7 August 2008
Available online 12 August 2008

Keywords:
Indium(I)
Aldol-type coupling
Elimination reaction
Michael-induced ring closure reaction
Sequential chemical reactions

ABSTRACT

The indium enolate generated from indium(I) bromide and α,α-dichloroacetophenone reacts with aldehydes to produce (*syn* + *anti*)-2-chloro-3-hydroxy-propan-1-ones which can be converted to their *trans*-prop-2-en-1-ones derivatives upon reaction with an extra equivalent of InBr. The enones undergo Michael-induced ring closure reactions with an extra equivalent of the initial enolate to afford the corresponding cyclopropane derivatives, according to a sequenced reaction mechanism.

1. Introduction

Recent work from this laboratory demonstrated that the organoindium(III) compounds, **1** derived of the oxidative insertion of indium(I) bromide [1] into one of the carbon-halogen bonds of geminal dihalides, RR^1CX_2 (**1a**, R = C_6H_5CO, R^1 = H, X = Cl [2]; **1b**, R = CN, R^1 = H, X = Br [3]; **1c,** R = CN, R^1 = X = Cl [4]) couple with carbonyl compounds, particularly aldehydes, R^2CHO (R^2 = alkyl, aryl) to afford initially the corresponding indium(III) alkoxides, **2** which undergo elimination to alkenes, **3** in a sequential fashion upon reaction with an extra equivalent of indium(I) bromide (Scheme 1) [5].

The organoindium(III) compounds **1** contain a nucleophilic alkyl substituent bearing a leaving group and therefore they are expected to give rise to Michael-induced ring closure (MIRC) reactions with an electrophilic alkene, **4** to produce the corresponding cyclopropane, **5** (Scheme 2).

Cyclopropanes have always attracted the attention of chemists because of the bonding aspects associated with their strained ring and/or their versatility as synthetic intermediates in organic synthesis [6]. Cyclopropanes are found as a basic structural unit in a variety of naturally occurring compounds and they have been used as building blocks for the synthesis of natural and artificial substances [7]. The cyclopropanation of electron-deficient olefins by pyridinium, sulfonium, selenonium, and phosphonium ylides was rather well studied [8]. Michael-initiated ring closure (MIRC), reaction involving ylides and electron-deficient olefins, is one of the most important methods for the preparation of cyclopropanes. The stereoselectivity of the MIRC reactions depends on how fast is the ring closure process related to rotation around the single bond in the intermediate, and therefore mixtures of stereoisomers are expected [9]. The finding of new reagents capable of forming the three-membered ring, particularly those leading to a high degree of stereoselectivity under mild reaction conditions is highly desirable [7a,9].

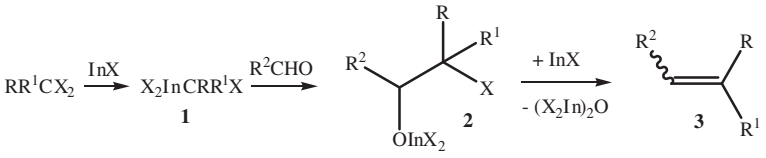
We now show that the organoindium compound obtained from InBr and α,α-dichloroacetophenone, Br(Cl)InCHClCOPh, **1a** is able to react with selected electron deficient alkenes to produce the corresponding cyclopropyl-phenyl-methanone, **6** (Table 1).

2. Results and discussion

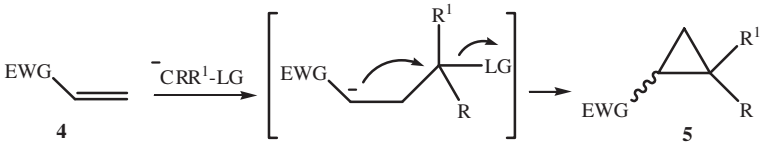
The alkene to cyclopropane transformations were realized independently by two different methods. The first (method A) involves the direct reaction of the electron deficient alkene and **1a**. Optimum reaction conditions were determined from experiments with (*E*)-3-(4-chlorophenyl)-1-phenyl-2-propen-1-one (entry b), which produced a 4:1 mixture of the cyclopropanes *c*-1,*t*-2-dibenzoyl-*r*-3-(4′-chlorophenyl)cyclopropane (**6b**) and

* Corresponding author. Tel.: +55 55 3220 8868; fax: +55 55 3220 8031.
E-mail address: peppe@quimica.ufsm.br (C. Peppe).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.08.011

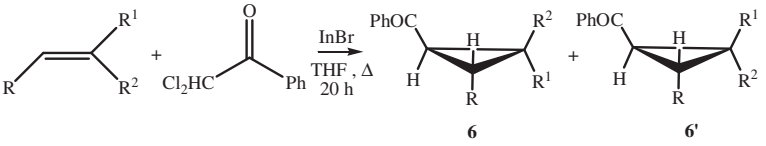


Scheme 1. Indium(I) halide-promoted sequential intermolecular aldol-type coupling/elimination reactions from $RR'CX_2$ compounds and aldehydes.



Scheme 2. Michael-induced ring closure (MIRC) reactions.

Table 1
Indium(I) bromide-promoted sequential intermolecular aldol-type coupling/elimination/MIRC reactions of α,α-dichloroacetophenone and aldehydes



	R	R^1	R^2	**6 + 6′** (%)[a]	**6**:**6′**
a	C_6H_5	PhCO	H	71 (37)	3:1(5:2)
b	*p*-Cl-C_6H_4	PhCO	H	75 (55) [53][b]	4:1(4:1)
c	*p*-Br-C_6H_4	PhCO	H	–(40)	–(2:1)
d	*o*-Br-C_6H_4	PhCO	H	–(30)	–(>98:1)[c]
e	*p*-CH_3-C_6H_4	PhCO	H	48 (27)	5:2(2:1)
f	*p*-CH_3O-C_6H_4	PhCO	H	40	>98:1[c]
g	*n*-C_3H_7	PhCO	H	62	>98:1[c]
h	C_6H_5	CN	CN	61	>98:1[c]
i	*p*-Cl-C_6H_4	CN	CN	77	>98:1[c]
j	*p*-CH_3O-C_6H_4	CN	CN	33	>98:1[c]
k	*p*-Cl-C_6H_4	CN	H	0	–

Optimal reaction conditions (stoichiometric ratio, temperature and time) were determined from experiments involving (*E*)-3-(4-chlorophenyl)-1-phenyl-2-propen-1-one (entry **b**): alkene:$PhCOCHCl_2$:InBr = 2:1:2 (Method A)

[a] Yields in parenthesis correspond to experiments starting from the aldehyde RCHO, $PhCOCHCl_2$ and InBr in the molar ratio 2:1:3 (Method B).

[b] Yields in brackets corresponds to experiment starting from the alkene, $PhCOCHCl_2$ and InBr in the molar ratio 1:1:1.

[c] Evaluated by ^1H NMR spectroscopy, the minor isomer was not isolated.

t-1,*t*-2-dibenzoyl-*r*-3-(4′-chlorophenyl)cyclopropane (**6′b**) in 75% of yield, when the reaction is carried out in the stoichiometric ratio alkene:$PhCOCHCl_2$:InBr of 1:1:2. A substantial decrease in the yield to 55% was observed decreasing the amount of InBr to a 1:1:1 ratio. Poorer and similar yield was again observed using method B, when the enone was generated from *p*-chlorobenzaldehyde, α,α-dichloroacetophenone and InBr in the molar ratio 2:1:3.

Alkenes reactivity follows closely the expected pattern for MIRC reactions. Accordingly, the more electron withdrawing ability of the alkene R group, the higher is the reaction yield as it was in fact observed for both the enone (entries a–g) and 1,1-dicyanoethylene (entries h–j) series. The stereochemistry of the three-membered rings was readily determined by ^1H NMR spectroscopy (see Section 4) and in two cases – namely *c*-1,*t*-2-dibenzoyl-*r*-3-(4′-chlorophenyl)cyclopropane (**6b**) and *trans*-2-benzoyl-3-(4′-chlorophenyl)-1,1-dicyanocyclopropane (**6i**) – was confirmed by X-ray single crystal analysis. Cyclopropanation of 2-aryl-1,1-dicyanoethylenes (entries h–j) leads to *trans*-products with a high degree of stereoselectivity (*trans*:*cis* > 98:1) as imposed by the transition state model depicted at Fig. 1 which has been proposed for cyclopropanations with tellurium ylides [9a]; steric hindrance between the aromatic R group of the alkene and the benzoyl group of the nucleophile determines the *trans* relationship.

The trans stereochemistry relating the incoming benzoyl and the alkene R group in the cyclopropane ring so being determined, we now address the stereochemistry of the alkene R^1 and R^2 groups present in the enone series (entries a–g; R^1 = PhCO, R^2 = H). In these reactions, we clearly lose the initial *trans*-stereochemistry of the enone leading to a mixture of cyclopropanes **6** and **6′.** Loss of stereochemistry relating the R and R^1 groups in enones during MIRC-type cyclopropanations has been interpreted in terms of rotation around the single bond in the intermediate (see Fig. 2). Such a phenomenon seems to be operative in these reactions promoted by the indium enolate. Fig. 2 indicates which transition state is favoured in terms of the minimum interaction between the bulky groups of the two possibilities generated by the single bond rotation. The preferential formation of cyclopropanes, **6** as indeed is observed clearly requires the minimum energy.

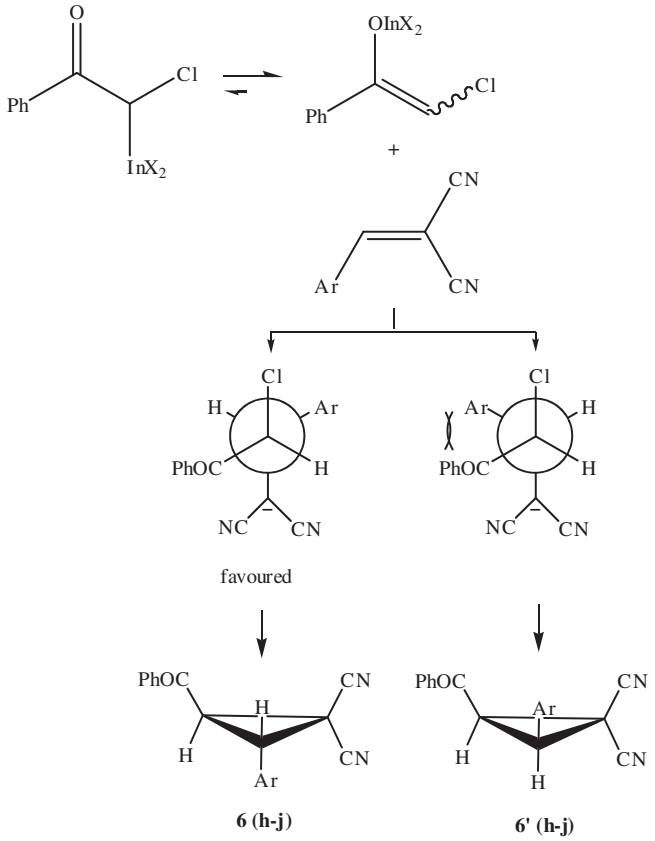


Fig. 1. Transition state models for cyclopropanation of 2-aryl-1,1-dicyanoethylenes.

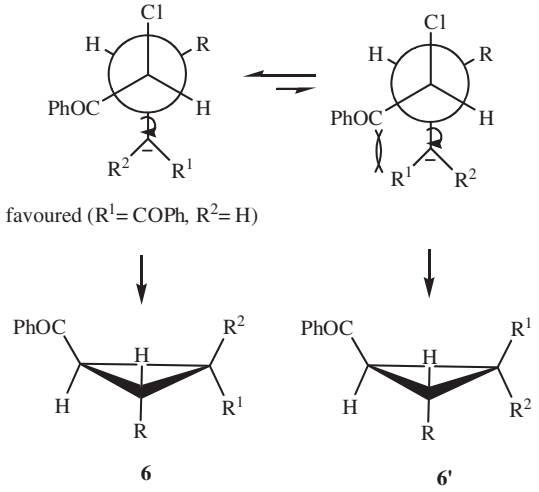


Fig. 2. Transition state models for cyclopropanation of enones.

3. Conclusion

The indium enolate obtained from the oxidative insertion of InBr into one of the carbon-chlorine bonds of α,α-dichloroacetophenone effectively promotes the cyclopropanation of alkenes bearing electron withdrawing groups, such as enones and 1,1-dicyano-2-aryl-ethenes. The reactions follow closely the MIRC proposed mechanisms and transition state models allowing a complete understanding of their effectiveness and stereoselectivity were proposed. Moreover, this is the final step of a series of reactions which can be carried out sequentially leading to formation of up to three new carbon-carbon bonds. The complete sequence is illustrated at Scheme 3 which shows the following properties of the enolate: it couples with a second molecule of the dichloroketone to produce, after reduction with excess of indium monobromide, the corresponding 1,4-butanediones, **7** [2a]; alternatively, the enolate condenses with an aldehyde to give the corresponding 2-chloro-3-hydroxy-propan-1-one derivative, **8** which can be easily converted into the *trans*-epoxide, **9** by treatment with a convenient base [2b] or transformed into the respective chalcone, **10** by elimination with an extra equivalent of InBr [5a]. The final step of the sequenced process is the formation of the cyclopropane rings by the action of enolate **1a** in the chalcone following a MIRC reaction pathway.

Throughout the sequence, mechanistic descriptions and transition state models that satisfactorily explain reaction details, particularly stereochemical features, have been proposed. We expect, therefore, that this knowledge will shed some light to organic chemists planning to use indium monohalides as promoters of organic reactions.

4. Experimental

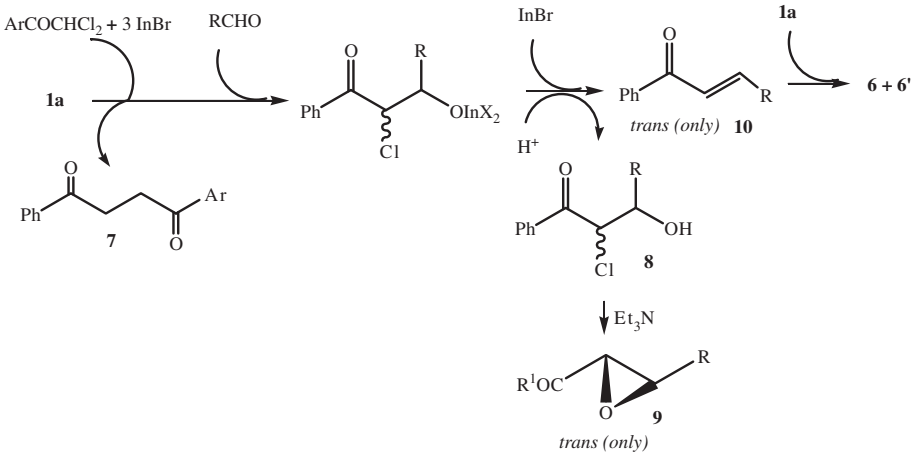
4.1. General data

Indium monobromide, α,α-dichloroacetophenone, aldehydes and solvents were prepared or treated as described in previous work [2,5a]. All the chalcones (Table 1, entries a–f) were prepared by the Claisen–Schmidt reaction: An ethanol solution (20 mL) of acetophenone (20 mmol) was added to a 10% KOH solution (60 mL); the resulting solution was cooled to 0 °C and the aromatic aldehyde (20 mmol) dissolved in EtOH (5 mL) was added; the resulting mixture was stirred at room temperature (25 °C) for 4 h; the precipitated chalcone was filtered, washed with H_2O and ethanol and recrystallized from hot ethanol; this procedure affords the chalcones in yields varying from 60% to 80%. (*E*)-1-phenyl-2-hexen-1-one (entry g) [5a], the 1,1-dicyano alkenes (entries h–j) [10a,b] and the alkenenitrile (entry k) [10c] were prepared according to literature methods. ^1H and ^{13}C NMR spectra were acquired on spectrometers Bruker DPX 200 and 400. Mass spectra were registered in a HP 6890 GC (equipped with a split–splitless injector and a cross-linked HP-5 capillary column measuring 30 m and with internal diameter of 0.32 mm) connected to a HP 5973 MSD spectrometer, with helium as the carrier gas.

4.2. Indium(I) bromide-promoted stereoselective preparation of cyclopropanes via sequential aldol-type coupling/elimination/Michael-induced ring closure reactions from α,α-dichloroacetophenone and aldehydes

Method A: A Schlenk test tube equipped with a condenser, truly dried under high vacuum, was charged with 3 mL of dry (sodium) THF, 150 mg (0.75 mmol) of the red solid InBr, 95 mg (0.50 mmol, 71 μL) of α,α-dichloroacetophenone and 0.75 mmol of the corresponding alkene (entries a–k – Table 1). The reaction was kept under reflux for 20 h (monitored by TLC), under a dry nitrogen atmosphere. At the end of this period, the reaction was quenched with water. The organics were extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated to dryness. The cyclopropanes **6** and **6′** were separated by column chromatography with hexanes–ethyl acetate mixtures.

Method B: In the same apparatus, 3 mL of dry (sodium) THF, 293 mg (1.50 mmol) of the red solid InBr, 189 mg (1.00 mmol, 142 μL) of α,α-dichloroacetophenone and 0.50 mmol of the corresponding aldehyde were heated under reflux in a dry N_2 atmosphere for 20 h. Similar work up produced cyclopropanes **6** and



Scheme 3. Indium(I) bromide-promoted sequential intermolecular aldol-type coupling/elimination reactions from α,α-dichloroacetophenone and aldehydes.

6′. Yields of reactions are given in Table 1, analytical and spectroscopic data for products **6** and **6′** are as follows:

c-1,t-2-Dibenzoyl-r-3-phenylcyclopropane (***6a***) [11]: Colorless solid; m.p. 115–117 °C (lit. 113–114 °C). ^{1}H NMR ($CDCl_3$): δ = 3.47 (dd, *J* = 6.0, 10 Hz, 1H), 3.69 (dd, *J* = 5.0, 10 Hz, 1H), 4.17 (dd, *J* = 5.0, 6.0 Hz, 1H), 7.00–7.22 (m, 5H), 7.25–7.58 (m, 6H), 7.84–7.94 (m, 2H), 8.01–8.12 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 29.75, 37.40, 37.99, 127.23, 128.22, 128.27, 128.40, 128.57, 128.68, 128.73, 133.18, 133.50, 134.27, 137.02, 137.44, 193.64, 197.32. MS (EI, 70 eV): *m*/*z* (%) = 326 $[M]^+$ (1), 221 (100), 203 (11), 143 (5), 115 (35), 105 (100), 77 (100).

t-1,t-2-Dibenzoyl-r-3-phenylcyclopropane (***6′a***) [11]: Colorless solid; m.p. 148–150 °C (lit. 150–151 °C). ^{1}H NMR ($CDCl_3$): δ = 3.31 (d, *J* = 6.0 Hz, 2H), 3.47 (t, *J* = 6.0 Hz, 1H), 7.17–7.49 (m, 11H), 7.88–7.97 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 31.25, 36.86, 126.59, 128.33, 128.53, 128.85, 127.21, 133.02, 137.40, 138.59, 194.17. MS (EI, 70 eV): *m*/*z* (%) = 221 (100), 203 (6), 115 (22), 105 (94), 77 (63).

c-1,t-2-Dibenzoyl-r-3-(4′-chlorophenyl)cyclopropane (***6b***): Colorless solid; m.p. 140–141 °C. ^{1}H NMR ($CDCl_3$): δ = 3.43 (dd, *J* = 6.0, 9.9 Hz, 1H), 3.69 (dd, *J* = 5.0, 9.9 Hz, 1H), 4.13 (dd, *J* = 5.0, 6.0 Hz, 1H), 7.10 (s, broad, 4H), 7.27–7.60 (m, 6H), 7.80–7.96 (m, 2H), 8.00–8.11 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 29.85, 36.97, 37.26, 128.26, 128.40, 128.42, 128.67, 128.79, 130.05, 132.85, 133.11, 133.37, 133.62, 136.91, 137.32, 193.46, 196.95. MS (EI, 70 eV, for ^{35}Cl): *m*/*z* (%) = 255 (67), 220 (9), 192 (6), 115(10), 105 (100), 77 (72). Anal. Calc. for $C_{23}H_{17}ClO_2$: C, 76.56; H, 4.75. Found: C, 76.31; H, 4.52%.

t-1,t-2-Dibenzoyl-r-3-(4′-chlorophenyl)cyclopropane (***6′b***): Colorless solid; m.p. 158–160 °C. ^{1}H NMR ($CDCl_3$): δ = 3.29 (d, *J* = 6.2 Hz, 2H), 3.44 (t, *J* = 6.2 Hz, 1H), 7.13–7.52 (m, 10H), 7.83–7.95 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 30.33, 36.79, 127.87, 128.28, 128.58, 128.94, 132.95, 133.23, 136.95, 136.98, 193.91. MS (EI, 70 eV, for ^{35}Cl): *m*/*z* (%) = 255 (86), 220 (23), 192 (8), 115 (11), 105 (100), 77 (67). Anal. Calc. for $C_{23}H_{17}ClO_2$: C, 76.56; H, 4.75. Found: C, 76.74; H, 4.62%.

c-1,t-2-Dibenzoyl-r-3-(4′-bromophenyl)cyclopropane (***6c***) [12]: Colorless solid; m.p. 161–163 °C (lit. 165 °C). ^{1}H NMR ($CDCl_3$): δ = 3.42 (dd, *J* = 6.0, 10.0 Hz, 1H), 3.69 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.13 (dd, *J* = 5.0, 6.0 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 7.24–7.60 (m, 8H), 7.85–7.94 (m, 2H), 8.01–8.10 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 29.79, 37.03, 37.22, 121.26, 128.27, 128.41, 128.68, 128.80, 130.40, 131.36, 133.36, 133.40, 133.64, 136.89, 137.29, 193.45, 196.95. MS (EI, 70 eV, for ^{79}Br): *m*/*z* (%) = 299 (50), 220 (14), 192 (15), 115 (16), 105 (100), 77 (59).

t-1,t-2-Dibenzoyl-r-3-(4′-bromophenyl)cyclopropane (***6′c***): Colorless solid; m.p. 170–172 °C. ^{1}H NMR ($CDCl_3$): δ = 3.28 (d, *J* = 6.3 Hz, 2H), 3.44 (t, *J* = 6.3 Hz, 1H), 7.07–7.15 (m, 2H), 7.31–7.51 (m, 8H), 7.88–7.92 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 30.41, 36.76, 121.00, 128.24, 128.30, 128.60, 131.93, 133.25, 136.99, 137.56, 193.89. MS (EI, 70 eV, for ^{79}Br): *m*/*z* (%) = 299 (47), 220 (25), 192 (16), 115 (15), 105 (100), 77 (63).

c-1,t-2-Dibenzoyl-r-3-(2′-bromophenyl)cyclopropane (***6d***): Colorless solid; m.p. 144–146 °C. ^{1}H NMR ($CDCl_3$): δ = 3.53 (dd, *J* = 6.4, 9.5 Hz, 1H), 3.87 (dd, *J* = 4.6, 9.5 Hz, 1H), 4.14 (dd, *J* = 4.6, 6.4 Hz, 1H), 6.96–7.06 (m, 1H), 7.15–7.60 (m, 9H), 7.96–8.10 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 31.43, 36.45, 38.95, 126.03, 129.98, 128.47, 128.49, 128.63, 128.80, 128.85, 130.64, 132.59, 133.24, 133.63, 133.92, 136.93, 137.24, 193.81, 196.80. MS (EI, 70 eV, for ^{79}Br): *m*/*z* (%) = 325 (15), 299 (29), 220 (13), 192 (13), 115 (12), 105 (100), 77 (58). Anal. Calc. for $C_{23}H_{17}BrO_2$: C, 68.16; H, 4.23. Found: C, 68.50; H, 4.27%.

c-1,t-2-Dibenzoyl-r-3-(4′-methylphenyl)cyclopropane (***6e***): Colorless solid; m.p. 135–136 °C. ^{1}H NMR ($CDCl_3$): δ = 2.15 (s, 3H), 3.44 (dd, *J* = 6.0, 9.9 Hz, 1H), 3.68 (dd, *J* = 4.9, 9.9 Hz, 1H), 4.15 (dd, *J* = 4.9, 6.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.27–7.56 (m, 6H), 7.84–7.94 (m, 2H), 8.01–8.11 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 21.01, 29.89, 37.44, 37.91, 128.29, 128.40, 128.55, 128.57, 128.73, 128.96, 131.21, 133.14, 133.46, 136.86, 137.08, 137.54, 193.79, 197.43. MS (EI, 70 eV): *m*/*z* (%) = 340 $[M]^+$ (1), 235 (100), 129 (6), 115 (12), 105 (92), 77 (49). Anal. Calc. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.91; H, 5.33%.

t-1,t-2-Dibenzoyl-r-3-(4′-methylphenyl)cyclopropane (***6′e***): Colorless solid; m.p. 153–155 °C. ^{1}H NMR ($CDCl_3$): δ = 2.29 (s, 3H), 3.28 (d, *J* = 6.0 Hz, 2H), 3.43 (t, *J* = 6.0 Hz, 1H), 7.05–7.15 (m, 4H), 7.30–7.37 (m, 4H), 7.42–7.48 (m, 2H), 7.88–7.94 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 21.06, 31.10, 36.85, 126.41, 128.32, 128.53, 129.50, 133.07, 135.40, 136.94, 137.21, 194.43. MS (EI, 70 eV): *m*/*z* (%) = 340 $[M]^+$ (1), 235 (100), 129 (8), 115(14), 105 (85), 77 (52).

c-1,t-2-Dibenzoyl-r-3-(4′-methoxyphenyl)cyclopropane (***6f***): Colorless solid; m.p. 93–96 °C. ^{1}H NMR ($CDCl_3$): δ = 3.42 (dd, *J* = 6.1, 9.8 Hz, 1H), 3.62 (s, 3H), 3.67 (dd, *J* = 5.0, 9.8 Hz, 1H), 4.12 (dd, *J* = 5.0, 6.1 Hz, 1H), 6.62–6.68 (m, 2H), 7.02–7.11 (m, 2H), 7.30–7.55 (m, 6H), 7.84–7.93 (m, 2H), 8.00–8.08 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 29.97, 37.46, 37.58, 55.05, 113.64, 126.20, 128.24, 128.36, 128.55, 128.69, 129.71, 133.12, 133.43, 137.05, 137.50, 158.64, 193.78, 197.37. MS (EI, 70 eV): *m*/*z* (%) = 356 $[M]^+$ (1), 251 (100), 115 (8), 105 (77), 77 (43). Anal. Calc. for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 81.31; H, 5.02%.

c-1,t-2-Dibenzoyl-r-3-n-propylcyclopropane (***6g***): Yellowish oil. ^{1}H NMR ($CDCl_3$): δ = 0.75 (t, J = 7.2 Hz, 3H), 1.13–1.33 (m, 2H), 1.41–1.55 (m, 2H), 2.18–2.26 (m, 1H), 3.42 (dd, J = 4.6, 9.6 Hz, 1H), 3.48 (dd, J = 4.6, 5.8 Hz, 1H), 7.35–7.41 (m, 4H), 7.44–7.50 (m, 2H), 7.95–7.99 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 13.63, 22.48, 27.87, 31.57, 35.10, 35.28, 128.17, 128.19, 128.52, 128.53, 133.09, 133.15, 137.04, 137.57, 195.76, 197.78. MS (EI, 70 eV): m/z (%) = 292 $[M]^+$ (3), 187 (100), 170 (8), 145 (6), 105 (100), 77 (100).

trans-2-Benzoyl-3-phenyl-1,1-dicyanocyclopropane (***6h***) [13,14]: Colorless solid; m.p. 129–130 °C (lit. 134–135 °C) ^{1}H NMR ($CDCl_3$): δ = 3.83 (d, J = 8.1 Hz, 1H), 3.99 (d, J = 8.1 Hz, 1H), 7.28–7.70 (m, 8H), 8.01–8.05 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 15.20, 35.49, 38.62, 111.54, 112.14, 128.29, 128.70, 129.27, 129.28, 129.41, 129.77, 135.04, 135.34, 188.84. MS (EI, 70 eV): m/z (%) = 140 (8), 105 (100), 77 (89).

trans-2-Benzoyl-3-(4′-chlorophenyl)-1,1-dicyanocyclopropane (***6i***) [13]: Colorless solid; m.p. 179–180 °C (decomposition) (lit. 179–180 °C). ^{1}H NMR ($CDCl_3$): δ = 3.81 (d, J = 8.1 Hz, 1H), 3.95 (d, J = 8.1 Hz, 1H), 7.22–7.71 (m, 7H), 7.98–8.07 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 15.18, 35.53, 37.76, 111.25, 111.97, 127.93, 128.74, 129.37, 129.60, 129.68, 135.19, 135.23, 136.02, 188.48. MS (EI, 70 eV, for ^{35}Cl): m/z (%) = 165 (3), 105 (100), 77 (49).

trans-2-Benzoyl-3-(4′-methoxyphenyl)-1,1-dicyanocyclopropane (***6j***) [13]: Colorless solid; m.p. 160–162 °C (decomposition) (lit. 161–162 °C).^{1}H NMR ($CDCl_3$): δ = 3.76 (s, 3H), 3.79 (d, J = 8.0 Hz, 1H), 3.94 (d, J = 8.0 Hz, 1H), 6.87–6.93 (m, 2H), 7.19–7.27 (m, 2H), 7.49–7.71 (m, 3H), 8.00–8.06 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 15.31, 35.70, 38.52, 55.37, 111.64, 112.35, 114.71, 121.11, 128.70, 129.29, 129.56, 135.02, 135.39, 160.61, 188.93. MS (EI, 70 eV): m/z (%) = 302 $[M]^+$ (1), 105 (100), 77 (34).

Acknowledgments

C.P. thanks CNPq for financial support, and R.P.D. for the award of a scholarship.

References

[1] For a discussion on the oxidative insertion reactions of indium(I) compounds see: C. Peppe, Curr. Org. Synth. 1 (2004) 227.
[2] (a) C. Peppe, R.P. das Chagas, Synlett (2004) 1187;
(b) C. Peppe, R.P. das Chagas, Synlett (2006) 605.
[3] J.A. Nóbrega, S.M.C. Gonçalves, C. Peppe, Tetrahedron Lett. 41 (2000) 5779.
[4] J.A. Nóbrega, S.M.C. Gonçalves, C. Peppe, Tetrahedron Lett. 42 (2001) 4745.
[5] (a) For **1a** see: C. Peppe, R.P. das Chagas, J. Organomet. Chem. 691 (2006) 5856;
(b) For **1b** see: C. Peppe, P.D. Mello, R.P. das Chagas, J. Organomet. Chem. 691 (2006) 2335.
[6] H.N.C. Wong, M.-Y. Hon, C.-W. Tse, Y.-C. Yip, J. Tanko, T. Hudlicky, Chem. Rev. 89 (1989) 165.
[7] (a) W.A. Donaldson, Tetrahedron 57 (2001) 8589;
(b) R.E. Taylor, F.C. Engelhardt, M.J. Schmitt, Tetrahedron 59 (2003) 5623.
[8] A.-H. Li, L.-X. Dai, V.K. Aggarwal, Chem. Rev. 97 (1997) 2341.
[9] (a) For a discussion about the stereoselective preparation of cyclopropanes see: H. Lebel, J.-F. Marcoux, C. Molinaro, A.B. Charette, Chem. Rev. 103 (2003) 977;
(b) H. Pellissier, Tetrahedron 64 (2008) 7041.
[10] (a) M.L. Deb, P.J. Bhuyan, Tetrahedron Lett. 46 (2005) 6453;
(b) F. Bigi, M.L. Conforti, R. Maggi, A. Piccinno, G. Sartori, Green Chem. 2 (2000) 101;
(c) S.A. DiBiase, B.A. Lipisko, A. Haag, R.A. Wolak, G.W. Gokel, J. Org. Chem. 44 (1979) 4640.
[11] Y. Matano, J. Chem. Soc., Perkin Trans. 1 (1994) 2703.
[12] M. Hetschko, J. Gosselck, Chem. Ber. 106 (1973) 996.
[13] Z. Ren, W. Cao, W. Ding, Y. Wang, Synthesis (2005) 2718.
[14] S. Kojima, M. Suzuki, A. Watanabe, K. Ohkata, Tetrahedron Lett. 47 (2006) 9061.