Efficient syntheses of four chiral phenylcyclopropanes

John E. Baldwin and Stephanie R. Singer

Abstract: An efficient four-step synthetic route from each of four crystalline isotopically labeled (1*R*)-menthyl (1*S*,2*S*)-(+)-2-phenylcyclopropanecarboxyates of better than 99% enantiomeric excess has provided multi-gram quantities of the corresponding chiral phenylcyclopropanes. The key transformation involved a bis[1,3-bis(diphenylphosphino)propane]rhodium chloride that catalyzed a highly stereoselective decarbonylation of a *trans*-2-phenylcyclopropanecarboxaldehyde.

Key words: cyclopropanes chiral thanks to isotopic substituents, catalytic decarbonylations of cyclopropanecarboxaldehydes.

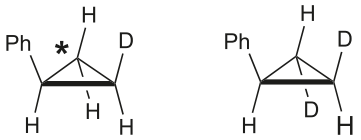
Résumé : Une méthode de synthèse efficace et en quatre étapes pour chacun des quatre (1*S*,2*S*)-(+)-2-phénylcyclopropanecarboxylates de (1*R*)-menthyle isotopiquement marqués avec un excès énantiomérique de plus de 99 % a permis de préparer des quantités supérieures au gramme des phénylcyclopropanes chiraux correspondants. La transformation clé implique une réaction très stéréosélective de décarbonylation d'un *trans*-2-phénylcyclopropanecarboxaldéhyde catalysée par un chlorure de bis[1,3-bis(diphénylphosphino)propane]rhodium.

Mots-clés : cyclopropanes chiraux en raison de substituants isotopiques, décarbonylation de cyclopropanecarboxaldéhydes.

[Traduit par la Rédaction]

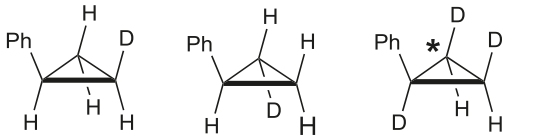
Introduction

This article reports the preparation of four chiral isotopically labeled phenylcyclopropanes (**1**-d_i). In the representations of structures **1**-d_i, and elsewhere, the asterisk symbol (*) denotes a carbon-13 atom.



1-d_1 **1**-d_2 **1**-d_3 **1**-d_3'

A long-standing interest in mechanistic questions posed by the thermal chemistry exhibited by relatively simple hydrocarbons, including cyclopropanes (1), led years ago to the preparation and utilization in mechanistic studies of **1**-d_3' and three other isotopically labeled chiral phenylcyclopropanes, (1*S*,2*R*)-**1**-d_1, (1*R*,2*R*)-**1**-d_1 and (1*R*,2*S*,3*R*)-**1**-d_3 (2). The present work extends, and greatly improves upon these earlier synthetic endeavors.



(1*S*,2*R*)-**1**-d_1 (1*R*,2*R*)-**1**-d_1 (1*R*,2*S*,3*R*)-**1**-d_3

To make multi-gram quantities of each of the **1**-d_i compounds (**1**-d_1, **1**-d_2, **1**-d_3, and **1**-d_3') with reasonable efficiency would require thrifty preparations of chiral intermediates of high enantiomeric purity, high stereochemical integrity, and high incorporations of the requisite labels. Once these demands were satisfied, a functional group temporarily used for securing a specific enantiomer of a given diastereomer of high stereochemical purity would need to be replaced by a hydrogen, or possibly a deuterium atom.

The first of these two desiderata has been achieved: each of the four crystalline (1*R*)-menthyl (1*S*,2*S*)-(+)-2-phenylcyclopropanecarboxyates (**2**-d_i) has been prepared efficiently on a 20 g scale (3). No trace of a (1*R*)-menthyl (1*R*,2*R*)-(+)-2-phenylcyclopropanecarboxyate was detected by capillary GC analyses in once recrystallized **2**-d_i compounds.

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In Memoriam, Professor Keith Yates (1928–2006).

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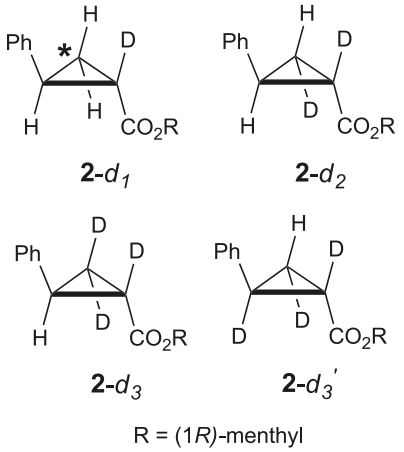


To satisfy the second requirement, a conventional reaction sequence was projected: hydroylysis of a menthyl ester to the corresponding carboxylic acid (4), reduction of the acid to a *trans*-2-phenylcyclopropanemethanol (5), oxidation of the alcohol to an aldehyde with PCC (pyridinium chlorochromate), and finally a Rh-catalyst-promoted decarbonylation. Not surprisingly, the first three steps were easily accomplished, while the decarbonylation proved challenging.

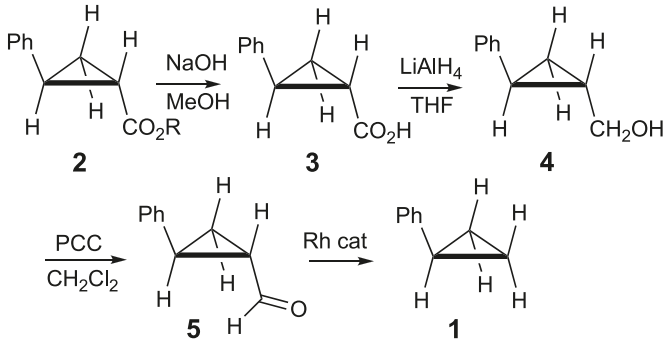
Results and discussion

The reaction sequence used to prepare chiral phenylcyclopropanes (**1**-d_1, **1**-d_2, **1**-d_3, and **1**-d_3') is summarized without full detail in Scheme 1 for unlabeled structures. Earlier preparations of chiral isotopically labeled phenylcyclopropanes, such as **1**-d_3' and stereoisomers (1*S*,2*R*)-**1**-d_1, (1*R*,2*R*)-**1**-d_1, and (1*R*,2*S*,3*R*)-**1**-d_3, depended on this scheme, though two limitations led to far from optimal overall yields (2, 5).

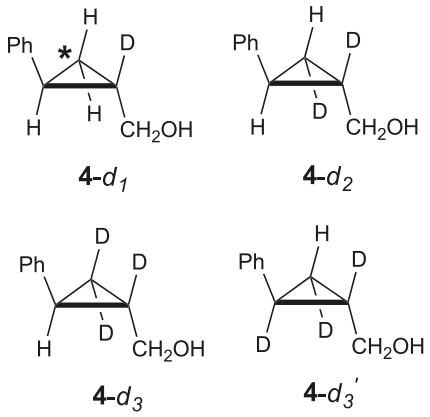
The first limitation was inherent in the presupposition of Scheme 1 that the starting material **2** or at least intermediates **3**, **4**, and **5** would be enantiomerically pure. One enantiomer of acid **3** may be secured through a chiral copper catalyst promoted diastereoselective and enantioselective condensation of racemic menthyl α-deuteriodiazoacetate and styrene or an isotopically labeled styrene, followed by a separation of cis and trans diastereomers, and then fractional crystallization of quinine salts of the trans acids (2, 5). This sequence of steps works, but it is both tedious and inefficient. This first limitation has been overcome by adopting and developing an efficient route to crystalline, enantiomerically pure esters (**2**-d_1, **2**-d_2, **2**-d_3, and **2**-d_3') (3).

The second limitation in earlier work was associated with the decarbonylation step: decarbonylations of *trans*-2-phenylcyclopropanecarboxaldehydes using stoichiometric amounts of chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst) (6–8) were realized (in 8 reactions) with yields ranging from 42% to 72% (55% ± 12% on average) on scales affording from 124 to 630 mg of a labeled phenylcyclopropane product (330 ± 164 mg on average). Given the investments required to secure 20 g amounts of intermediates **2**-d_1, **2**-d_2, **2**-d_3, and **2**-d_3', and the cost of commercial $RhCl(PPh_3)_3$, a catalytic and more efficacious decarbonylation reaction option seemed essential.

Scheme 1. Reaction sequence to convert (1*R*)-menthyl (1*S*,2*S*)-(+)-2-phenylcyclopropanecarboxyate to phenylcyclopropane (R = (1*R*)-menthyl).



The first three steps outlined in Scheme 1, starting with enantiomerically pure **2**-d_i esters, were implemented without difficulty and in high yields. The two-step hydrolysis-then-reduction sequence converting a **2**-d_i ester to the corresponding colorless distilled **4**-d_i alcohol was completed with an average overall yield of 92% ± 3%.

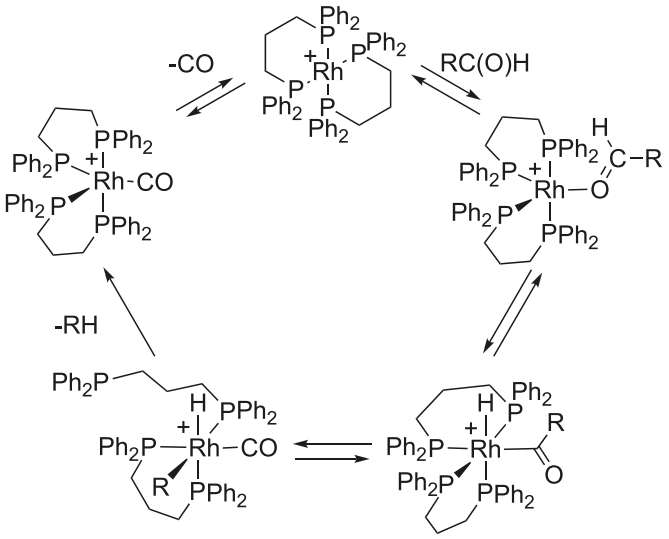


The oxidation of a **4**-d_i alcohol with PCC in CH_2Cl_2 afforded the related aldehyde, essentially quantitatively; it was typically stored briefly under argon and decarbonylated as promptly as possible. The all-important decarbonylation step was not so easily dispatched.

Decarbonylations of aldehydes using $RhCl(Ph_3P)_3$ in stoichiometric proportions are generally successful for aryl, alkenyl, and primary alkyl aldehydes at modest temperatures (8). They involve a reversible dissociation of the reagent to $RhCl(PPh_3)_2$ and PPh_3 as a key step, and usually take place with excellent stereochemical selectivity, with the retention of configuration (9). Other reactions may sometimes intervene, but are not of significant concern in the present context. The co-product of the decarbonylation reaction, $RhCl(CO)(PPh_3)_2$, is relatively stable thermally at normal reaction temperatures; the thermal dissociation of $RhCl(CO)(PPh_3)_2$ to give CO and $RhCl(PPh_3)_2$ is typically too slow to facilitate a catalytic decarbonylation process.

Primary alkyl aldehydes may be decarbonylated catalytically in high yields when combined with only 5% of Wilkinson's catalyst and a stoichiometric portion of diphenylphosphoryl azide, but more sterically crowded aldehydes are relatively inert (10).

Scheme 2. Catalytic decarbonylation of an aldehyde (R-C(O)H) by $[Rh(dppp)_2]^+$.



Bisdiphosphine complexes of Rh(I), such as [bis(1,3-bisdiphenylphosphino)propane]rhodium chloride or tetrafluoroborate, $[Rh(dppp)_2]Cl$ or $[Rh(dppp)_2]BF_4$ (11, 12), will decarbonylate an aldehyde following a mechanistic path much like one postulated for Wilkinson's catalyst mediated decarbonylations. The reductive elimination step gives a $[Rh(dppp)_2]^+CO$ complex that dissociates relatively easily to $[Rh(dppp)_2]^+$, and the process can continue, as schematized in the putative mechanistic model outlined in Scheme 2.

The $[Rh(dppp)_2]^+$ structure is probably not square planar but distorted so as to position the two P-Rh-P planes at a dihedral angle approximately midway between 0° and 90°, as has been found for $Rh(PMe_3)_4^+$ and [bis(1,4-bisdiphenylphosphino)butane]rhodium$^+$ (13, 14). The pentacoordinate complexes with CO or an aldehyde are approximately trigonal bipyramidal, though they exhibit considerable conformational flexibility. At room temperature (RT) all four phosphorous atoms are equivalent: $^{31}P\{^1H\}$ NMR spectra exhibit a simple doublet due to P-Rh spin–spin coupling, while at –80 °C an A_2B_2X pattern of multiplets is observed (15).

Kinetic evidence points toward the oxidative addition step being rate-limiting (12). The catalytic cycle is completed through a reverse migration followed by an irreversible reductive elimination to give the decarbonylation product and a carbon monoxide complex, one that can dissociate readily at modest temperatures.

Reported decarbonylations of aryl, alkenyl, and primary alkyl aldehydes with reagents providing a source of $[Rh(dppp)_2]^+$ are impressively efficient, but similar reactions of secondary alkyl aldehydes using these catalysts have not been entirely encouraging: 2-ethylbutanal and a catalytic amount of $[Rh(dppp)_2]BF_4$ at 110 °C for 36 h gave pentane in only 15% yield (12).

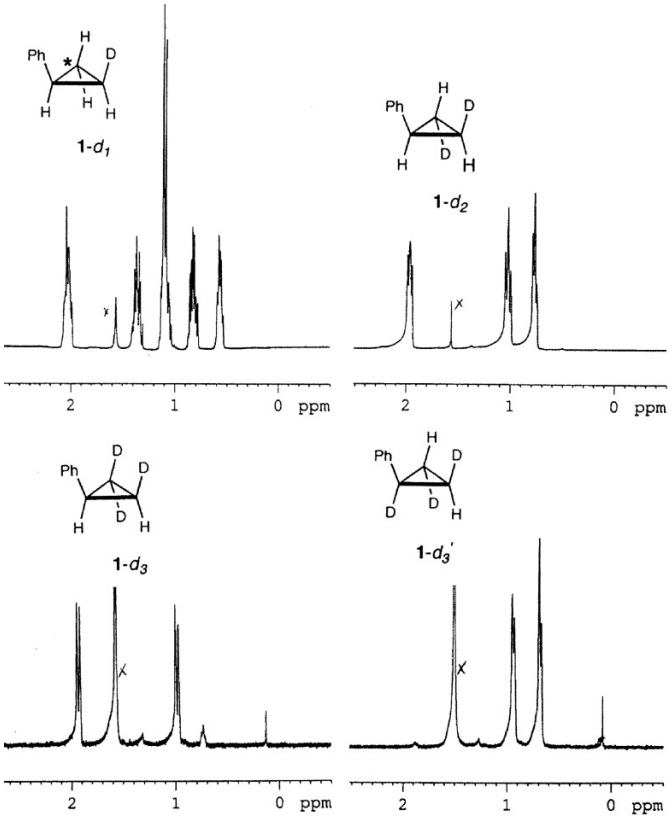
The $[Rh(dppp)_2]Cl$ or $[Rh(dppp)_2]BF_4$ catalysts may be prepared in crystalline form. A convenient alternative is to make the former in situ by combining $RhCl(CO)(PPh_3)_2$ with 1,3-bis(diphenylphosphino)propane in a 1:2 ratio, respectively (16). The present work opted for this option. When a labeled aldehyde, **5**-d_i, was combined with a catalyst prepared from 3.6 mol% of $Cl(CO)Rh(PPh_3)_2$ and 7.2 mol% of dppp in anhydrous, degassed toluene, and heated at reflux for about a day, analysis by capillary GC revealed that the decarbonylation reaction was progressing slowly. An additional increment of catalyst was prepared and added, and the reaction mixture was heated at reflux for another day. A third increment of catalyst was prepared and added. After another day at reflux, all of the aldehyde had reacted, according to GC analyses. Following workup, the labeled phenylcyclopropane was secured in good yields, with very little contamination by the side-product α-methylstyrene. In three of the eight decarboxylation reactions, two from each of the labeled phenylcyclopropanecarboxaldehydes, four or five increments of catalyst and additional days of heating the reaction mixture at reflux were invested, prompted by indications of incomplete reactions gained from GC analyses. The annoyingly inconsistent rates of decarbonylation may be associated with various intrusions of adventitious oxygen, which binds reversibly but tightly to $[Rh(dppp)_2]^+$, and stalls but does not shut down the catalytic cycle (17).

Proton NMR spectra of **1**-d_1, **1**-d_2, **1**-d_3, and **1**-d_3' were completely consistent with expectations. For **1**-d_2, for example, the three equal-intensity cyclopropyl H multiplet absorptions were observed at δ 1.97, 1.02, and 0.78 (Fig. 1). In **1**-d_3, the upfield absorption of the H cis to phenyl at δ 0.78 is nearly absent, and the two cyclopropyl H doublets for cis related hydrogens at C1 and C3 are separated by 0.95 ppm. In **1**-d_3', the spectrum has the expected pair of doublets for trans disposed hydrogens at C2 and C3 and no significant absorption intensity at δ 1.97. For **1**-d_1, the spectrum is complicated just as one might anticipate from ^{13}C-H spin–spin couplings.

The eight decarbonylation reactions (Scheme 3), two from each **5**-d_i isotopomer, gave phenylcyclopropanes **1**-d_i in 79% yields, on average, from the precursor alcohols **4**-d_i. The catalytic decarbonylation reactions were slow but effective. The four **1**-d_i chiral phenylcyclopropanes prepared, secured in quantities ranging from 5.4 to 5.9 g, should prove sufficient for projected stereochemical and mechanistic studies.

The synthetic project reported in this work realized its objective, but surely did not validate an optimal experimental protocol for the catalyzed decarbonylation reactions. The goal was to make useful amounts of the required chiral isotopically labeled phenylcyclopropanes efficiently, not to perfect the decarbonylation step. Work in that direction might well find that employing $[Rh(dppp)_2]Cl$ or $[Rh(dppp)_2]BF_4$ directly, rather than making a catalyst in situ, would bring better yields or shorter reaction times; perhaps another solvent at another reaction temperature rather than toluene at reflux would be preferred; perhaps different and more rigorous measures to keep oxygen from the catalyst at every stage would prove beneficial. A systematic optimization effort could be most useful, but even now an efficient (though slow) catalytic decarbonylation procedure for cyclopropanecarboxaldehydes, one that should work for other secondary aldehydes, has been exemplified. Especially for reactions on a multi-gram scale; it should prove a practical and valuable synthetic method, and in certain situations make possible mechanistic studies that otherwise would remain imagined but not undertaken.

Fig 1. ^{1}H NMR spectra of chiral phenylcyclopropanes **1**-d_1, **1**-d_2, **1**-d_3, and **1**-d_3' acquired on a 300 MHz spectrometer; × absorptions = H_2O.



Experimental section

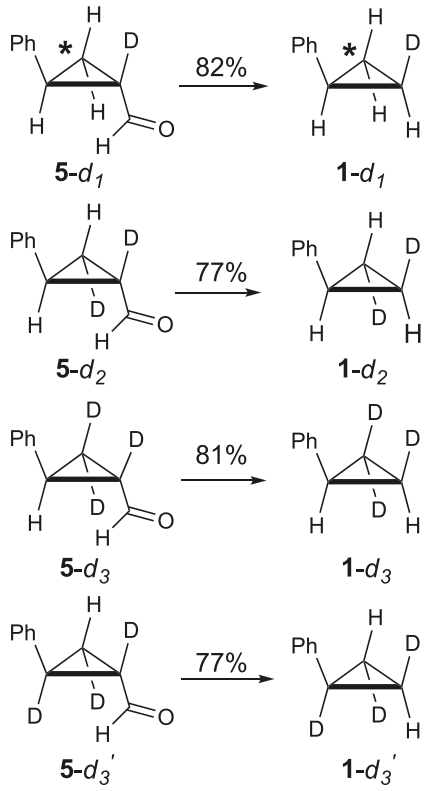
trans-2-Phenylcyclopropanemethanol

The following general procedures for the hydrolysis of (1*R*)-menthyl (1*S*,2*S*)-(+)-2-phenylcyclopropanecarboxylate was used to prepare acids **3**-d_1, **3**-d_2, **3**-d_3, and **3**-d_3' from esters **2**-d_1, **2**-d_2, **2**-d_3, and **2**-d_3', and to reduce these acids to **4**-d_1, **4**-d_2, **4**-d_3, and **4**-d_3'.

(1*R*)-Menthyl (1*S*,2*S*)-(+)-2-phenylcyclopropanecarboxylate (9.65 g, 31.9 mmol) suspended in 300 mL of CH_3OH was stirred for 30 min. Aqueous 25% NaOH (56 g) was added, and the reaction mixture was heated at reflux for 21 h. It was cooled to RT and concentrated by rotary evaporation. The white residue was dissolved in 225 mL of H_2O and the basic solution was extracted with ether (3 × 100 mL). The aqueous layer was separated, acidified with concd HCl (~30 mL), and extracted with ether (4 × 100 mL). The ether extracts were combined, dried ($MgSO_4$), and filtered. The colorless filtrate was concentrated by distillation to remove all but about 30 mL of the ether.

This concentrate was added dropwise by addition funnel along with anhydrous THF (~30 mL, used to rinse out the flask) to a suspension of $LiAlH_4$ (3.03 g, 79.8 mmol) in anhydrous THF (250 mL) under argon. The resulting gray suspension was heated at reflux for 42 h, cooled in an ice bath, and quenched with H_2O (3.0 g), 15% aqueous NaOH (3.03 g), and H_2O (9.09 g), with 5 min of stirring the quenched reaction mixture after each addition. The resulting mixture was stirred for an additional 30 min, dried over K_2CO_3, and filtered through Celite. The solid collected over Celite was washed with THF (~75 mL) and the filtrates were combined and concentrated by distillation. The colorless liquid remaining was purified by Kugelrohr distillation at 75–95 °C under reduced pressure. The colorless oil collected (4.45 g, 93% yield) had a ^{1}H NMR spectrum matching the reference data for *trans*-2-phenylcyclopropanemethanol (5). In **4**-d_2 and **4**-d_3' the C3-H cis to phenyl was seen at δ 0.95 (1H); in **4**-d_1, **4**-d_2, and **4**-d_3 the benzylic H was recorded at δ 1.81–1.85 (1H).

Scheme 3. Stereoselective Rh-catalyzed decarbonylation reactions.



trans-2-Phenylcyclopropanecarboxaldehydes

trans-2-Phenylcyclopropanecarboxaldehydes (**5**-d_i) were prepared as described in this specific example, starting from **4**-d_2. Alcohol **4**-d_2 (4.87 g, 32.4 mmol) in anhydrous CH_2Cl_2 (25 mL) was added dropwise by addition funnel to an orange suspension of PCC (11.18 g, 51.9 mmol) in 100 mL of anhydrous CH_2Cl_2. The flask containing **4**-d_2 and the addition funnel were rinsed with dry CH_2Cl_2 (3 × 5 mL). A dark brown suspension formed immediately, and the reaction mixture was stirred for 4 h at RT under argon. Ether (150 mL) was added and a light brown precipitate was formed. The mixture was stirred for 5 min and then filtered through a short column of Florisil. The reaction flask residue and the Florisil column were rinsed with additional ether (3 × 50 mL). All ethereal material was combined and concentrated by distillation under an aspirator vacuum, and then using a vacuum pump. The residue, a green oil of crude aldehyde **5**-d_2 (4.80 g, ≈100% yield), was stored briefly under argon and subjected to catalytic decarbonation without delay.

Labeled chiral 2-phenylcyclopropanes by catalytic decarbonylation of labeled chiral *trans*-2-phenylcyclopropanecarboxaldehydes

Labeled chiral 2-phenylcyclopropanes (**1**-d_i) by catalytic decarbonylation of labeled chiral *trans*-2-phenylcyclopropanecarboxaldehydes (**5**-d_i) were synthesized as described in this specific example, starting from the sample of crude **5**-d_2 prepared immediately above.

An argon atmosphere was established for an oven-dried 500 mL three-necked round-bottomed flask equipped with an addition funnel, condenser, and a specialized adapter to connect a septum to the flask through a stopcock to protect the septum from toluene at reflux. Then $RhCl(CO)(PPh_3)_2$ (0.78 g, 1.5 mmol) and 1,3-bis(diphenylphosphino)propane (dddp; 1.3 g, 2.5 mmol) were added quickly, and 160 mL of anhydrous, degassed toluene was added by syringe. The resulting mixture was heated to 70–90 °C for 1 h. To the orange solution in the reaction flask was added a yellow solution of **5**-d_2 (4.80 g, 32.4 mmol) in anhydrous, degassed toluene (20 mL) through an addition funnel. The small flask that had contained the aldehyde solution was rinsed with toluene (3 × 5 mL) and the washings were added to the reaction mixture, which was then heated to reflux for 21 h.

A mixture of $RhCl(CO)(PPh_3)_2$ (0.78 g, 1.5 mmol), dddp (1.03 g, 2.5 mmol), and toluene (40 mL) in a separate flask was heated for 1 h at 65–80 °C and then added to the reaction mixture. The small flask was rinsed with toluene (2 × 5 mL) and the washings were added to the reaction mixture, which was then heated to reflux for an additional 24 h. Analysis by GC showed that the aldehyde (**5**-d_2)/phenylcyclopropane (**1**-d_2) ratio was about 1:1. An additional 1.5 mmol of catalyst was prepared and added to the reaction mixture, which was heated to reflux for another 24 h. The (**5**-d_2)/(**1**-d_2) ratio was 0.46:1. Additional toluene (50 mL) was added, and the mixture was heated to reflux for 26 h. Another increment of catalyst (0.49 mmol) was prepared and added, and the reaction mixture was heated to reflux for an additional 44 h, by which time the reaction had gone to completion. Pentane (200 mL) was added to the cooled reaction mixture; the mixture was passed through a silica gel column, followed by 275 mL of pentane. The colorless, clear liquid collected was concentrated by distillation using an efficient teflon spinning band column (a B/R Instrument Corporation 36T 100 system rated at up to 200 theoretical plates with microprocessor controller). The dark yellow pot residue (9.69 g) was characterized by capillary GC: it contained the phenylcyclopropane **1**-d_2 (31.6 weight%, 3.06 g, 79% yield for the two steps from alcohol **4**-d_2), toluene (56.1%, 5.44 g) and α-methylstyrene (1.4%, 0.14 g). Further concentration using a micro spinning band distillation system (B/R 800), followed by a Kugelrohr distillation at 130 °C, afforded a colorless liquid. ^{1}H NMR δ: 0.78 (m, 1H), 1.02 (m, 1H), 1.97 (m, 1H), 7.15–7.37 (m, 5H). ^{13}C NMR δ: 9.25 (1:1:1 triplet), 15.63, 125.78, 126.09, 128.71.

This decarbonylation reaction utilized four additions of catalyst, 12 mol% in all, and 139 h of heating the reaction mixture at reflux. A second preparation of **1**-d_2 starting with 4.70 g of **4**-d_2 used three 3.5 mol% additions of catalyst and keeping the reaction mixture at reflux for 73 h gave 2.83 g (75% yield) of the d_2-phenylcyclopropane.

Other labeled **1**-d_i phenylcyclopropanes were prepared from **4**-d_i alcohols in like fashion. For the eight preparations, times at reflux ranged from 66 to 146 h. Five reactions took three portions of catalyst (10.5% in all); three took four portions (12.5 mol% in total); the 146 h reaction required five portions of catalyst (4 × 3.5% + 2%).

Pure **1**-d_i samples could be secured easily by preparative GC using an Apiezon L column at 125 °C. Under the conditions employed, the retention times for toluene, α-methylstyrene, and a phenylcyclopropane were 2.66, 9.16, and 11.83 min, respectively.

Acknowledgments

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