DOI: 10.1002/ejoc.200600037

Indium Triflate Catalyzed Rearrangement of Aryl-Substituted Cyclopropyl Carbinols to 1,4-Disubstituted 1,3-Butadienes

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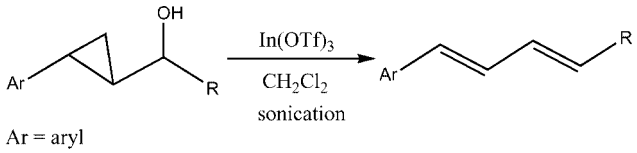
Keywords: Carbinols / Homogeneous catalysis / Indium / Rearrangement / Sonication

Aryl-substituted cyclopropyl carbinol derivatives undergo a facile stereoselective rearrangement catalyzed by $In(OTf)_3$ in dichloromethane under sonication to produce the substituted conjugated *all-trans*-butadienes.

Introduction

The importance of indium reagents in organic synthesis has been well demonstrated through novel protocols for carbon–carbon bond formation, rearrangements and a variety of other useful transformations over the past few years,[1] and interest in this area is continuing.[2] Indium(III) halides, including indium(III) triflate,[3c,3d] have also been used as potential Lewis acids in a variety of useful reactions.[3] As part of our activities in indium-mediated reactions[4] we are constantly looking for new indium reagents[5] for novel applications in organic synthesis. We demonstrate here the use of indium triflate as an efficient Lewis acid catalyst for the rearrangement of cyclopropyl carbinol derivatives, leading to the stereoselective synthesis of conjugated butadienes (Scheme 1).



Ar = aryl
R = aryl / alkyl

Scheme 1. Rearrangement of cyclopropyl carbinols.

Results and Discussion

Although cyclopropyl carbinols have been reported to undergo rearrangement to conjugated butadienes on treatment with an acid catalyst, $KHSO_4$ at elevated temperature and pressure[6a] or heating under reflux in DMSO for 5 h,[6b] to the best of our knowledge there is no report of this rearrangement with a Lewis acid under ambient conditions; this protocol meets this requirement. The experimental procedure for this transformation is very simple. The cyclopropyl carbinol was sonicated in the presence of a catalytic amount (10 mol-%) of $In(OTf)_3$ in dichloromethane for a set period of time (TLC). The product was then isolated by extraction with diethyl ether.

A variety of structurally diverse aryl-substituted cyclopropyl carbinol derivatives undergo this facile rearrangement catalyzed by $In(OTf)_3$ to provide the aryl-substituted *all-trans*-butadienes. The results are summarized in Table 1. The *trans* configuration of both the double bonds was established by the coupling constant (*J*) values of the olefinic protons. All these products (except two) are crystalline solids and the observed melting points of these compounds are also in good agreement with the reported values of known *trans* isomers. Various substituents like Cl, OMe, dioxymethylene, thiomethyl and benzyl remained unaffected under the reaction conditions. Sensitive molecules such as furan and thiophene derivatives (Entries 11 and 12) also survived in the reaction medium. However, the reactions with alkyl (2-alkyl cyclopropyl) carbinols are messy and lead to a mixture of unidentified products; these reactions have not been pursued further.

In general, the reactions are reasonably fast (25–45 min), and 10 mol-% of $In(OTf)_3$ is sufficient to push the reaction forward. The reactions can also be accomplished by stirring at room temperature for a longer time (4–6 h). However, in the absence of $In(OTf)_3$ the reaction did not proceed at all either under sonication or stirring at room temperature. Thus, for the best result in terms of reaction time sonication was the obvious choice. Methylene chloride was found to be most suitable for this reaction among other solvents (THF, CH_3CN). The widely used indium trichloride also failed to initiate this reaction. The products were obtained in high

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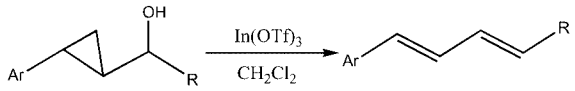
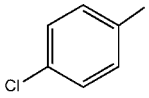
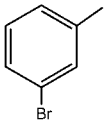
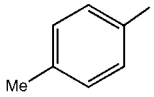
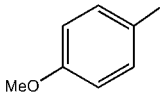
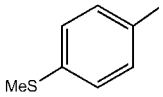
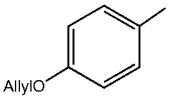
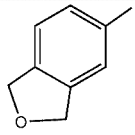
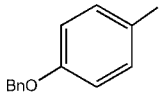
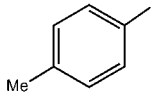
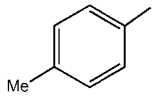
Table 1. $In(OTf)_3$-catalyzed rearrangement of cyclopropyl carbinols to butadienes.



Entry	Ar	R	Time/ min	Yield (%)[a]	Ref.
1	Ph	Ph	25	95	[10]
2		Ph	25	92	[11]
3		Ph	30	90	[12]
4		Ph	30	90	[13]
5		Ph	35	88	[10]
6		Ph	35	89	
7		Ph	40	85	
8		Ph	35	88	
9		Ph	25	90	
10	Ph		30	88	[13]
11		Ph	40	80	[11]
12		Ph	40	82	[11]
13	Ph	Me	45	85	[14]
14		Me	45	82	[15]

[a] Yields refer to those of pure isolated products characterized spectroscopically (IR, ^1H and ^{13}C NMR).

yields and purity after just a short filtration followed by chromatography or recrystallization of the crude products. No side-product was isolated in any reaction.

Presumably, indium triflate, which is a Lewis acid, polarizes the C–O bond of the cyclopropyl carbinol derivative and thus facilitates cleavage of the cyclopropyl moiety to produce the benzylic carbonium ion, which eventually leads to the diene through a similar path to that observed by Julia.[7]

Stereodefined conjugated dienes are of great importance in organic synthesis[8] as they constitute a common structural motif in natural products[8a] and are used as important synthons in Diels–Alder reactions.[8b] A number of methods for the preparation of conjugated dienes are available in the literature.[9] Among these methods, the most widely employed are those based on the cross-coupling reaction of alkenylmetals with haloalkenes in the presence of a transition metal complex and olefin cross-metathesis reactions. However, many of these are associated with significant limitations with regard to stability, easy accessibility and toxicity of the catalysts used, stereoselectivity and yields of dienes, and operational simplicity. However, the present procedure is free from these disadvantages.

Conclusion

The present procedure using indium(III) triflate as a catalyst for the rearrangement of cyclopropyl carbinol derivatives provides a novel protocol for the synthesis of substituted conjugated *all-trans*-butadiene systems. This procedure offers marked improvements with regard to operational simplicity, stereoselectivity (exclusively *trans*) and high isolated yields (80–95%) of products, considerably fast reaction time (25–45 min), and milder reaction conditions.

Experimental Section

General: NMR spectra were recorded with a DPX 300 instrument at 300 MHz for ^1H and at 75 MHz for ^{13}C. IR spectra were measured with a FT 8300 Shimadzu spectrometer. Melting points were determined on a glass disk with an electrical bath (Reichert, Austria) and are uncorrected. Dichloromethane was dried with P_2O_5 and distilled before use. The cyclopropyl carbinols were prepared by standard cyclopropanation procedures using diazomethane followed by reduction with sodium borohydride.

General Procedure for the Preparation of Cyclopropyl Carbinols. Preparation of Phenyl (2-phenylcyclopropyl)carbinol (Entry 1): A di-

ethyl ether solution of diazomethane was added dropwise to a stirred solution of 1,3-diphenylprop-2-ene-1-one (208 mg, 1 mmol) and $Pd(OAc)_2$ (10 mg) in diethyl ether (6 mL) at 0 °C and the reaction mixture was kept as such for 10 h. It was then filtered through a short column of silica gel to provide the crude cyclopropyl ketone (222 mg, 100%). This crude compound was then stirred with $NaBH_4$ (58 mg, 1.5 mmol) in MeOH (10 mL) at 0 °C for 2 h. The mixture was then quenched with water and diluted with diethyl ether (10 mL). This mixture was filtered through a short plug of silica gel and the filtrate was evaporated to provide the crude alcohol, which was then purified by a short column chromatography over silica gel (diethyl ether/hexane, 1:5) to furnish the desired carbinol (212 mg, 95%) as a mixture of diastereoisomers. IR (neat): $\tilde{\nu}$ = 3450, 1445, 1010 cm^{-1}. ^1H NMR (60 MHz, CCl_4): δ = 0.84–1.00 (m, 2 H), 1.81–1.98 (m, 1 H), 2.47–2.56 (m, 1 H), 4.52–4.78 (m, 1 H), 6.99–7.89 (m, 10 H) ppm.

This procedure was followed for the preparation of all carbinols (obtained as mixture of diastereoisomers) listed in Table 1.

General Procedure for Cyclopropyl Carbinol Rearrangement. Representative Example of Conversion of Phenyl (2-Phenylcyclopropyl)-methanol into 1,4-Diphenyl-1,3-butadiene Catalyzed by $In(OTf)_3$ (Entry 1): Phenyl (2-phenylcyclopropyl)methanol (224 mg, 1 mmol) was sonicated in the presence of a catalytic amount (56 mg, 10 mol-%) of $In(OTf)_3$ in dichloromethane (5 mL) in an ultrasonic cleaner (Julabo, Germany) for 25 min (TLC). The reaction mixture was then diluted with diethyl ether (25 mL), washed with water and dried (Na_2SO_4). Evaporation of solvent gave a crude product, which was purified by short column chromatography over silica gel followed by recrystallization (diethyl ether/hexane, 1:2) to provide pure 1,4-diphenyl-1,3-butadiene as a white solid (196 mg, 95%); m.p. 150–151 °C (ref.[9] m.p. 152 °C) whose spectroscopic data (^1H and ^{13}C NMR) were in good agreement with the reported values.[9]

This procedure was followed for all reactions listed in Table 1. All the products except those in Entries 6, 7, 8 and 9 are known and were easily identified by comparison of their m.p., IR and NMR (^1H and ^{13}C) spectra with those reported.[9–15] The melting points, spectroscopic data (IR, ^1H and ^{13}C NMR) and elemental analysis of the compounds that have not been reported in the literature are provided below.

(*E*,*E*)-4-Phenyl-1-(4-thiomethylphenyl)-1,3-butadiene (Entry 6): White crystals; m.p. 138–140 °C. IR (KBr): $\tilde{\nu}$ = 1590, 1474, 1436 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 6.59–6.67 (m, 3 H), 6.86–6.95 (m, 3 H), 7.19–7.24 (m, 2 H), 7.30–7.36 (m, 3 H), 7.41–7.44 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.6, 126.2 (2 C), 126.5 (2 C), 126.6 (2 C), 127.4, 128.4 (2 C), 128.5, 129.1, 132.0, 132.4, 134.2, 137.2, 137.7 ppm. $C_{17}H_{16}S$ (252.37): calcd. C 80.90, H 6.39; found C 80.71, H 6.19.

(*E*,*E*)-1-(4-Allyloxyphenyl)-4-phenyl-1,3-butadiene (Entry 7): White crystals; m.p. 148–150 °C. IR (KBr): $\tilde{\nu}$ = 1600, 1590, 1506 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.55–4.57 (m, 2 H), 5.28–5.45 (m, 2 H), 6.00–6.09 (m, 1 H), 6.63 (d, J = 15 Hz, 4 H), 6.79–6.99 (m, 4 H), 7.22–7.45 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.7, 114.7, 114.9 (2 C), 117.7, 126.2 (2 C), 127.2, 127.5 (2 C), 128.6 (2 C), 129.0, 129.5, 131.6, 132.4, 133.1, 137.5, 158.2 ppm. $C_{19}H_{18}O$ (262.35): calcd. C 86.99, H 6.92; found C 86.79, H 6.72.

(*E*,*E*)-1-(3,4-Dioxomethylenephenyl)-4-phenyl-1,3-butadiene (Entry 8): White crystals; m.p. 150 °C. IR (KBr): $\tilde{\nu}$ = 1540, 1508 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.94 (s, 2 H), 6.54–6.63 (m, 2 H), 6.73–6.76 (m, 2 H), 6.77–6.87 (m, 2 H), 6.97 (s, 1 H), 7.21–7.23 (m, 1 H), 7.29–7.33 (m, 2 H), 7.40–7.23 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 101.1, 105.4, 108.4, 121.4, 126.3 (2 C), 127.4, 127.7, 128.6 (2 C), 129.3, 131.9, 132.1, 132.5, 137.5, 147.3, 148.1 ppm. $C_{17}H_{14}O$ (234.29): calcd. C 81.58, H 5.64; found C 81.40, H 5.43.

(*E*,*E*)-1-(4-Benzyloxyphenyl)-4-phenyl-1,3-butadiene (Entry 9): White crystals; m.p. 174–175 °C. IR (KBr): $\tilde{\nu}$ = 1597, 1508, 1251 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.09 (s, 2 H), 6.63 (d, J = 15.0 Hz, 2 H), 6.80–6.97 (m, 5 H), 7.34–7.43 (m, 11 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.9, 114.9 (2 C), 125.9, 126.1 (2 C), 127.1, 127.2, 127.3 (2 C), 127.5 (2 C), 127.8, 128.5 (4 C), 129.3, 130.3, 131.6, 132.2, 136.7, 137.4 ppm. $C_{23}H_{20}O$ (312.40): calcd. C 88.43, H 6.45; found C 88.28, H 6.34.

Acknowledgments

We are pleased to acknowledge financial support from CSIR, New Delhi [grant no. 01(1936)/04], for this investigation. S.B. would like to thank the CSIR for his fellowship.

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Received: January 18, 2006
Published Online: April 26, 2006

