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Catalysis by ionic liquids: cyclopropyl carbinyl rearrangements catalyzed by [pmim]Br under organic solvent free conditions

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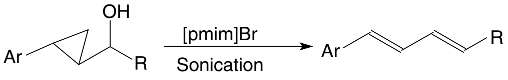
Abstract—Aryl substituted cyclopropyl carbinol derivatives undergo stereoselective rearrangements catalyzed by the ionic liquid, 1-methyl-3-pentylimidazolium bromide, under sonication, without any organic solvent, to produce the substituted conjugated all-*trans*-butadienes.

Recently, room temperature ionic liquids have been the subject of considerable interest because of their properties of non-volatility, non-flammability and recyclability, amongst others.[1] Ionic liquids have been used as solvents in chemical transformations;[1] however, the ability of ionic liquids to serve as catalysts[2] and reagents[1h,3] has not been explored to any great extent.[4,5] We demonstrate here a novel application of a neutral ionic liquid, [pmim]Br, as an efficient catalyst for the rearrangement of cyclopropyl carbinol derivatives leading to conjugated butadienes (Scheme 1).

Although cyclopropyl carbinols have been reported to undergo rearrangement to conjugated butadienes on treatment with acid[6a] or heating under reflux in DMSO for 5 h,[6b] to the best of our knowledge, there is no report of catalysis of this reaction by an ionic liquid.

The experimental procedure for this transformation is very simple.[7] The cyclopropyl carbinol is sonicated in the presence of a catalytic amount (20 mol %) of the ionic liquid, [pmim]Br. The product can be isolated by extraction with ethyl acetate.



Scheme 1.

A variety of structurally diverse aryl substituted cyclopropyl carbinol derivatives were found to undergo the rearrangement catalyzed by [pmim]Br to provide the aryl substituted all *trans*-conjugated butadienes. The results are summarized in Table 1. The trans configuration of both the double bonds was established from the couplings of the olefinic protons. All the products (except two) were crystalline solids and the observed melting points of these compounds were in good agreement with reported data. Substituents such as Cl, OMe, dioxymethylene, thiomethyl and benzyl remained unaffected under the reaction conditions. Sensitive molecules such as the furan, thiophene and pyridine derivatives (entries 12, 13 and 14) also survived the reaction.

In general, the reactions were reasonably fast (0.75–1.75 h) under sonication. The reaction can also be carried out at room temperature with stirring, where the time required for completion was found to be 3–6 h. Twenty mole percent of ionic liquid was sufficient to push the reaction forward and no other solvent was required. However, in the absence of [pmim]Br, the reaction did not proceed at all under sonication or at room temperature with stirring. The catalyst could be reused and recycled for up to five runs without any loss of activity. The products were obtained in high yields and purities after short filtration chromatography through

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Keywords: Ionic liquid; Catalysis; Rearrangement; Cyclopropyl carbinol; Butadienes.

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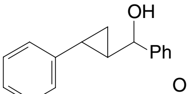
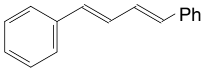
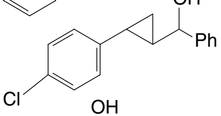
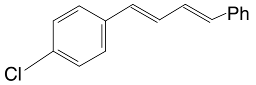
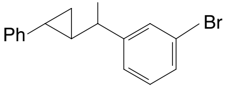
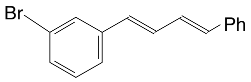
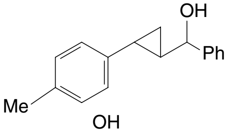
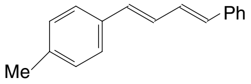
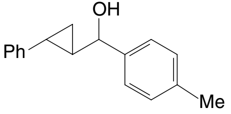
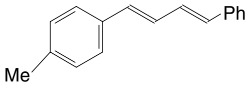
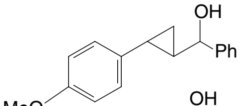
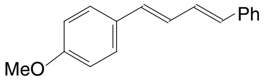
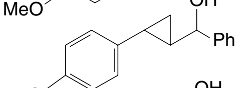
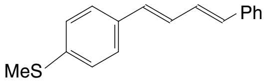
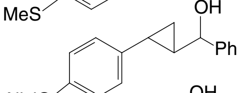
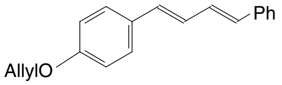
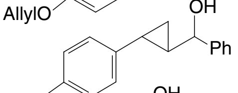
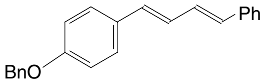
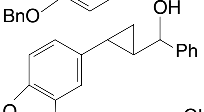
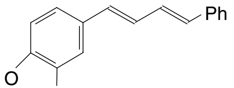
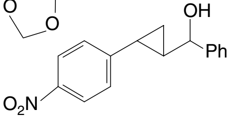
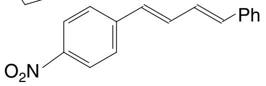
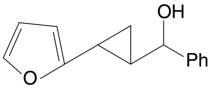
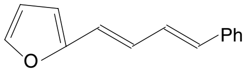
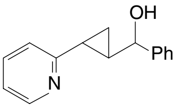
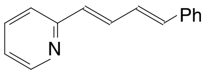
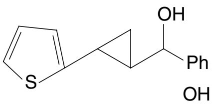
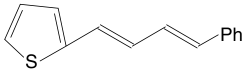
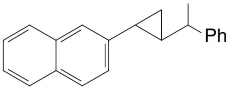
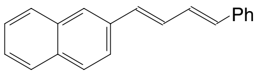
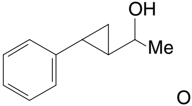
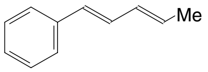
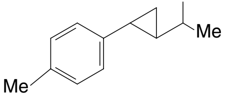
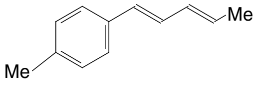
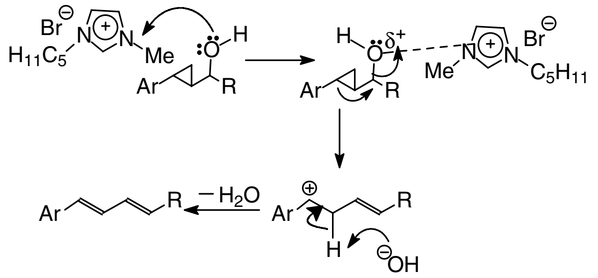
Table 1. Rearrangement of cyclopropyl carbinol derivatives catalyzed by [pmim]Br

Entry	Cyclopropyl carbinol	Time (h)	Product	Yield (%)[a]	Ref.
1		0.75		95	13
2		1.2		90	14
3		1.0		90	15
4		1.0		92	16
5		1.0		90	16
6		1.0		95	13
7		1.0		92	—
8		1.25		85	—
9		0.75		95	—
10		1.2		85	—
11		1.5		85	16
12		1.5		80	14
13		1.5		80	14
14		1.5		78	14
15		1.75		78	17
16		1.75		75	18
17		1.25		76	14

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



Scheme 2.

silica gel. No side product was isolated from any of the reactions.

Stereodefined conjugated dienes are of great importance in organic synthesis as they constitute a common structural motif in natural products[8] and serve as important synthons in Diels–Alder reactions.[9] They are also of great utility as biologically active compounds[10] and as non-linear optical materials.[11] A number of methods for the preparation of conjugated dienes are available in the literature.[6,12] Among these methods the most widely employed are those based on the cross-coupling of alkenyl metals with haloalkenes in the presence of transition metal complexes and olefin cross-metathesis reactions.

The imidazolium cation of the ionic liquid [pmim]Br may be polarizing the C–O bond of the cyclopropyl carbinol derivatives thus facilitating cleavage of the cyclopropyl moiety to produce the benzylic carbonium ion, which eventually leads to the diene (Scheme 2).

As proposed in the mechanism, the imidazolium cation of the ionic liquid may play a crucial role in directing the course of the reaction.[19] To test this hypothesis, the reaction was conducted in the presence of different imidazolium based ionic liquids such as [pmim]BF_4 and the reaction was found to proceed with equal efficiency. However, [pmim]Br, being less expensive and of neutral character was the preferred choice.

In conclusion, the present procedure using an easily accessible and inexpensive ionic liquid as 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 (75–95%) of products, considerably faster reaction time (0.75–1.75 h) and mild and neutral reaction conditions. This procedure also demonstrates the potential of a neutral ionic liquid in catalyzing a rearrangement process.

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7. *General experimental procedure for the rearrangement of cyclopropyl carbinol derivatives catalyzed by [pmim]Br. Representative procedure for 1,4-diphenyl-1,3-butadiene (entry 1).* Phenyl (2-phenylcyclopropyl)-methanol (222 mg, 1 mmol) was sonicated in the presence of a catalytic amount (47 mg, 20 mol %) of [pmim]Br (prepared by irradiation of an equivalent mixture of 1-methylimidazole and *n*-pentyl bromide (neat) in a domestic microwave oven for 2 min, then washing with a small amount of ether twice and drying under vacuum at 80 °C for 5 h) in an ultrasonic cleaner (Julabo, Germany) for 45 min (TLC). The reaction mixture was extracted with ethyl acetate (3 × 10 mL). Evaporation of the solvent left the crude product, which was purified by short column chromatography over silica gel to provide pure 1,4-diphenyl-1,3-butadiene as a white solid (196 mg, 95%), mp 150–151 °C (lit. mp 152 °C); IR(KBr) 1560, 1500, 1405 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.72 (dd, $J = 12.0$, 2.9 Hz, 2H), 7.01 (dd, $J = 12.0$, 2.9 Hz, 2H), 7.27–7.30 (m, 2H), 7.35–7.40 (m, 4H), 7.47–7.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.5 (4C), 127.6 (2C), 128.7 (4C), 129.3 (2C), 132.9 (2C), 137.4 (2C). These values are in good agreement with the literature.[10,13] This procedure was followed for the rearrangement of all the cyclopropyl carbinol derivatives listed in Table 1. All products were characterized by their IR, ^1H NMR and ^{13}C NMR spectroscopic data and by elemental analysis (for new compounds). The spectroscopic data and mp for known compounds are in good agreement with those reported.
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