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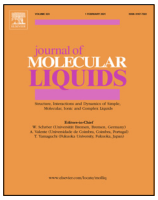

Dielectric spectroscopy and molecular dynamic simulation study of binary mixtures of benzaldehyde and methanol at 303.15 K

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ABSTRACT

The complex permittivity spectra in the frequency range of 20 Hz to 2 MHz for benzaldehyde (BZ), methanol (MeOH) and their binary mixtures at 303.15 K temperature are investigated. To understand the molecular behavior and relaxation processes under varied condition of concentrations of BZ in MeOH, various formalisms namely complex impedance and complex ac conductivity derived from complex permittivity spectra have been investigated and linked. Excess static permittivity and Kirkwood correlation factor have been used to comprehend the H-bond dynamics, and are correlated to MD Simulation. The electronic polarizability and molar volume were determined with the help of density and refractive index of the mixtures. The molecular interaction at atomistic level of several binary mixtures is examined using molecular dynamic (MD) simulation. Linkage dynamics of H-bonds, their length, and dc conductivity of the mixture solutions all contribute to a better knowledge of molecular interaction.

1. Introduction

In recent past many attempts were made to understand molecular interaction among the species of the binary mixtures of polar liquids through dielectric relaxation spectroscopy (DRS) and molecular dynamics (MD) simulation techniques [1–4]. Many researcher have used DRS in the low frequency region (few tens of hertz to several megahertz) [1–3,5–10] and MD simulation techniques [11,12], separately to study molecular interaction of polar/non-polar liquid materials as a solo or in mixture form. DRS study of such liquids and their binary mixtures gives information about different relaxation process, dielectric polarization, inter-intra molecular interaction and electrical conduction. The low frequency dielectric dispersion study of liquid provides detailed insight into the charge dynamics and electrical conduction mechanism, which are directly correlated to their dielectric polarization strength and molecular structure [9]. Frequency dependent dielectric properties of binary mixtures are useful in basic consideration of liquid structure persistence, its dynamics and in the practical application [13]. Apart from this, dielectric spectroscopy technique has great potential in understanding the H-bond interactions, dipolar alignment and hydrogen bond connectivity [4,11,12,14].

Simulation provides researchers with a novel approach to explore the microscopic behavior and structure of materials at atomistic level, which may enable the determination of compound content and the exploration of molecular mechanism of its formation [15]. Many researchers have studied the molecular mechanism using MD simulation [3,11,14–21]. MD simulation provides significant information about H-bond interactions, which is the most fundamental and important amid different types of noncovalent interactions in polar liquids. The linkage dynamics of proton or a hydrogen atom in the H-bond has increased attention due to its significant role in chemical reactions and physical properties, such as dielectricity and proton conductivity [22].

Benzaldehyde (BZ) is the simplest and industrially the most important aromatic aldehyde. It exists in nature, occurring in combined and uncombined form in many plants. The best known natural source of BZ is amygdalin, which exists in combined form as a glycoside and is present in bitter almonds [23]. It is mainly used as plasticizer and solvent, it is also used as a fragrance and flavoring in food, cosmetics etc. [24]. Benzaldehyde is highly volatile in nature, instable to air and light which is unfavorable from an application point of view. Benzaldehyde is sparkling compound in synthesis of many pharmaceutical drugs, chemical and biological reactions in which their structural stability concerns the most [25,26]. In literature, the stability of benzaldehyde against oxygen (air) is improved by complexion with β-cyclodextrin [26,27]. Methanol (MeOH), a modest toxic alcohol, is largely used as adhe-

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ORIGINAL ARTICLE

Palladium(0)-catalyzed aryne annulation: a powerful strategy for the synthesis of thio-bridged compounds

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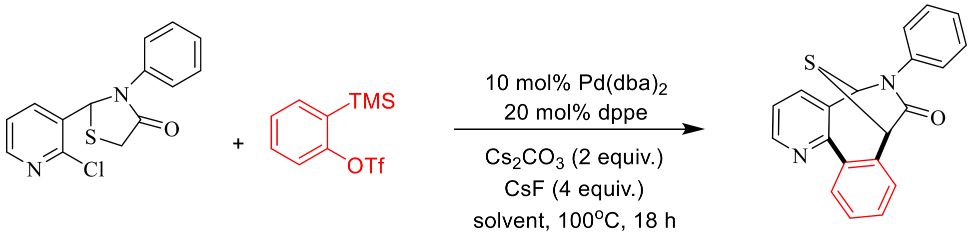
Abstract

A method for the construction of various thio-bridged compounds is developed using readily available o-(trimethylsilyl)aryl triflates as a source of aryne precursor, catalyzed by simple Pd(dba)$_2$/dppe complex. This operationally simple and modular protocol allows thio-bridged compound via C(sp^2)-C(sp^2) and C(sp^2)-C(sp^3) bond formation in promising yields with a broad substrate scope. The key part is in situ generation of an aryne from o-(trimethylsilyl)aryl triflates and their subsequent intermolecular annulation.

Graphical abstract



> Construction of relatively unexplored thio-bridged compound
> Readily available starting material
> Wide substrate scope

Keywords Thio-bridged compounds · Kobayashi precursor · Pd(0) catalyst · Aryne insertion

Introduction

The scientific community has witnessed exploitation of rigid bridge-containing compounds adorned with heteroatoms like nitrogen, oxygen, or sulfur as potentially anticipating metal binder and privileged structural building block for the synthesis of complex natural and unnatural materials [1–4]. Aza- or oxa-bridged compounds are core structures in a class of compounds with fascinating pharmacological activities. Based on bridge-containing segments, number of bioactive substances such as saliniketals A and B (ornithine decarboxylase inhibitors), (±)-Murrayazoline (antiplatelet aggregation activity), Cortistatin A (antiangiogenesis compounds), Ecteinascidin 743 (antitumor agent), Welwistatin (antimicrotubule agent), and BE-43472B (Antibiotic) were synthesized and then delivered to treat complex disease [5–10] (Fig. 1). However, the preparation of thio-bridged compound is almost an unreported work till date. Furthermore, we could not find noteworthy application of such molecules. Hence, we decided to synthesize thio-bridged compounds first, and to appraise them in terms of biological outline later.

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COMPREHENSIVE REVIEW

First-row transition metal for isocyanide-involving multicomponent reactions (IMCR)

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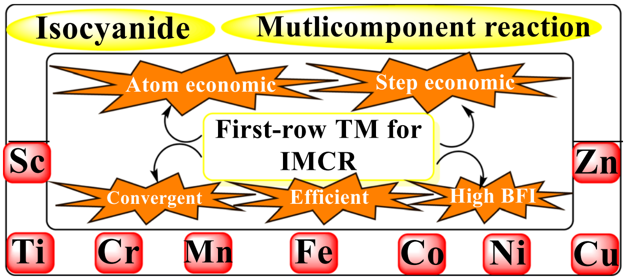
Abstract

First-row transition metal catalyzed transformations that are able to construct complex molecules from simple, readily obtainable feedstocks have become a keystone of modern synthetic organic chemistry. Particularly, the multicomponent reaction (MCR) involving carbon–carbon (C–C) as well as carbon–heteroatom (C–X) bond formation plays an essential role in many chemical conversions, and insurgencies in these reactions powerfully improve the overall synthetic efficiency. Recently, MCRs emerges rapidly because of its greener sides like eco-friendly nature, swift and straightforward execution, high atom/step economy, and construction of aimed product with lowest or no by-product, usually in quantitative yield. Curiously, the exceptional divalent carbon atoms of isocyanides make them predominantly useful components in multicomponent reactions. As a result of widespread research over the past few decades, numerous well-designed and effective procedures for the first-row TM-catalyzed MCR to afford the various entities have been reported. These aspects are summarized in this review article. A particular focus on comparative discussion of various first-row transition-metal catalyzed isocyanide-based multicomponent reactions through mechanistic details included in the review article.

Graphical abstract



Keywords First-row transition-metal catalyst · Isocyanide · Multicomponent reaction (MCR)

Introduction

Isocyanide, a linear molecule isoelectronic with carbon monoxide, display high inclination among scientific community because of the profound influences in the field of synthetic, agrochemical, medicinal, material and combinatorial chemistry [1–3]. They are isomer of the corresponding cyanides (–C≡N), so they are represented by prefix iso. Isocyanide are versatile building blocks having unique synthetic potentials like reacting with radicals, electrophiles, and nucleophiles. Moreover, isocyanides are used in oligo- and polymerizations as well as two-electron-donating ligands in organometallic chemistry [4–7]. Historically, an isocyanide (allyl isocyanide) was produced by alkylation of silver cyanide by Lieke in 1859 [8]. In view of molecular structure, the terminal carbon atom of isocyanides bearing a lone pair of

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ARTICLE

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Iron-catalyzed construction of cyanomethylated thiohydantoins by cross-dehydrogenative C(sp^3)-C(sp^3) coupling

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Abstract

The efficient and novel approach for synthesizing cyanomethylated thiohydantoin from readily obtainable acetonitrile and 1,3-dibenzyl-2-thiohydantoin through iron(II)-catalyzed cross dehydrogenative coupling (CDC) protocol is documented here. The strategy displays extensive substrate scope, and provides an effectual construction of cyanomethylated thiohydantoins in moderate to good yield. Prominently, this new methodology represents hitherto unobserved reactivity pattern for the thiohydantoin.

1 | INTRODUCTION

The construction and functionalization of azaheterocyclic compounds is an area of persistence attention due to the presence of this skeletal motif in innumerable naturally occurring products and synthetic compounds that exhibit important chemical, biological, and medicinal properties [1–7]. Particularly, thiohydantoin derivatives display a wide range of biological and pharmacological activities including antiviral, antimalarial, antimutagenic, anti-cancer, antiinflammatory, antithyroidal, and antituberculosis properties [8–13] (Figure 1). Enzalutamide is an androgenic re-ceptor antagonist and FDA recognized anticancer drug with a 2-thiohydantoin pharmacophore [14]. In this context, heterocyclic molecules incorporating thiohydantoin scaffold have received a prodigious deal of attention in the medicinal chemistry community. The development of structurally diverse thiohydantoins as privileged frameworks for the construction of molecular libraries is important in diversity-oriented synthesis. On the other hand, cyano group containing compounds are highly useful building blocks that have found extensive applications in synthetic organic chemistry owing to the fact that cyano group can be readily transformed into other functionalities such as carboxylic acid, tetrazoles, aldehyde, ketone, ester, amide, and amine [15–20].

Acetonitrile is commonly regarded as an inactive chemical reagent due to fact that the sp^3 C – H bond is comparatively weak acidic (pKa = 25 in H_2O) and is recurrently used as a solvent [21]. In last few decades, transition-metal-catalyzed cross-dehydrogenative coupling (CDC) reactions are recognized to be one of the utmost effectual approaches for the rapid synthesis of carbon–carbon and carbon-heteroatom bond [22–27]. Some of the representative pathways that have been reported for cyanomethylation in acetonitrile are preparation of cyanomethylated 3,4-dihydroquinolinones by silver-persuaded tandem radical addition/ annulation [28], palladium-catalyzed arylcyanomethylation of activated alkenes via oxidative dual C-H activation of an acetonitrile and arene [29], neutral and cationic NCOP Ni complex-catalyzed cyanomethylation of benzaldehyde through addition of it into a C – H bond of acetonitrile [30], TM-free cyanomethylation of substituted oxindoles and fluorenes with alkyl nitriles [31], palladium-catalyzed and ligand-promoted 8-aminoquinolinyl group directed regioselective cyanomethylation of aliphatic amides moiety [32], cyanomethylation of substituted tetrahydroisoquinolines in the attendance of catalytic

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RESEARCH PAPER
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Ethno-botanical dimension of Sacred Groves in Valsad District, Gujarat, India

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Key words: Sacred groves, Ethnomedicinal plants, Valsad District, *In situ* conservation

Abstract

Biodiversity conservation is a need of a day, when deforestation has reached its peak of destruction. Sacred groves (SGs) are such areas of forest which serve as tool for *in-situ* conservation by means of religious and cultural belief system of locals. Several plant species are conserved in SGs which are ecologically, economically and medicinally valuable. Study was carried out to investigate ethno-botanical significance of SGs in Valsad district. Primary data collection was done by taking interviews, using questionnaires from 'Bhagat' (traditional healer), and local tribes living around these groves. There are 480 SGs documented in Valsad district, which harbors valuable plant diversity. Among them, 48 SGs were large in size, more than 100 years old, were selected for ethno-botanical documentation. 182 species have been enumerated as valuable ethno-botanical sp. from these SGs. Plant details such as local name, scientific name, parts used for ethno medicine in various ailments like jaundice, piles, dysentery, diarrhea, fever, piles, conjunctivitis, ulcer, and kidney stone etc. were recorded. In District areas, due to high level of development, anthropogenic activities, modernization and erosion in traditional and civic values (corruption), the conservation of ethnomedicinally important species is affected largely. Existence of SGs & conservation of them has led the SGs be richer in diversity, many conserved species is available abundantly in natural conditions from SGs. Traditional knowledge from such conserved areas is needed to be preserved and should be documented in form of books or People Biodiversity Register (PBR) before SGs and/or traditional practices are destroyed.

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