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An Active Catalyst for Diels-Alder Reaction of Indol with *o*-Benzoquinone

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The Diels-Alder reaction of indol with masked *o*-benzoquinone was studied. The stereo selectivity of this reaction by heterogeneous catalysis is improved. This catalyst was prepared by surface modification of nanoporous silica gel with cerium ion in aqueous ammonia. The structures of products were characterized by spectroscopic techniques.

Keywords: Silica support, Cerium, Diels-Alder reactions, *o*-Benzoquinones, Indol, Catalyst.

INTRODUCTION

The Diels-Alder reaction produced six-membered rings which are versatile building-blocks for the synthesis of numerous natural products. A simple access could be provided through these reactions to a number of poly heterocyclic quinones with antitumour activity [1,2].

Among the most easily accessible cyclohexa-2,4-dienones types, masked with *o*-benzoquinones (MOBs) can be mentioned trapped with dienophiles like indol in the Diels-Alder reaction. The adducts could be used as intermediates in a large diversity of organic materials synthesis [3-5].

Silica gel, in comparing to the other inorganic material, is an appropriate support for the heterogenization of various catalysts types, as it is affordable and accessible, with convenient adsorption properties because of their high surface area, nano porosity and providing physico-chemical stabilities during the reaction process. There are two kinds of functional groups for the silica surface including siloxane (Si-OSi) and silanol group (Si-OH). The behaviour of silanol groups on silica surface would be similar to a weak acid (pKa = 9.4). By increasing the metal charge and concentration and adding a metal ion, surface acidity was changed [6,7].

$ZnCl_2$, $AlCl_3$, $FeCl_3$, as Lewis acid catalysts can have a considerable influence on Diels-Alder reactions rate and endo selectivity. The interaction between nitrogen group of indol and the metal ions declines the dienophiles LUMO energy level and provides a more effective overlapping with diene HOMO [8,9].

In this work, considering the ion exchange approach of cerium ion(IV) in alkali conditions, different catalysis concentrations on the surface of silica gel were obtained. The Diels-Alder diastereoselective reaction of indol and masked *o*-benzoquinone were investigated. For more charge and high cerium ion concentration on the surface of silica, a high endo/exo diastereoselectivity could be observed.

EXPERIMENTAL

$Ce(SO_4)_2{\cdot}4H_2O$, indol, ammonium solution, silica (particle size 63-200 μm, kieselgel 60), di acetoxyiodo benzene (DAIB), Acetone and 2-methoxyphenols were purchased from Merck company.

Preparation of support: First of all, the ammonium solution 1 M was prepared by adding silica gel (20 g) for 5 min. To the obtained NH_4^+-SiO_2, the solution of $Ce(SO_4)_2{\cdot}4H_2O$ with various concentration [0.05, 0.06, 0.07, 0.08 M] was added in room temperature with stirring for 1 h. The ion-exchange between NH_4^+ and cerium ion occurs at this time. With 30 mL acetone, the solids were filtered and washed and then dried in oven for 2 h. For removal of none ion exchanged NH_4^+ and reducing the silanol surface, all solids were heated at 350 °C, under vacuum for 2 h. As support, until used, all obtained solids were stored in polypropylene bottle.

Diels-Alder reaction: Considering vigorous solid stirring in a stopped flask, indol solution in dry methanol (10 mmol) was added to cerium supports catalysis with various cerium concentration. A solution of 2-methoxyphenols (10 mmol) in the dry methanol was cooled to 0 °C under inert gas and diacetoxyiodo benzene (DAIB) was added as solid in one portion. The temperature of flux was controlled. For 0.5 h, the reaction mixture was stirred and cooled up to -20 °C and then with vigorous stirring, the newly prepared masked *o*-benzoquinone was added to the indol mixture. The reaction mixture was stirred at room temperature for 2-4 h. The product was afforded the chromatography (silica gel column, ethyl acetate cyclohexane [20:80, v: v]). Using GC, the reaction yield was determined. The products structures were determined considering the IR, ^{1}H and ^{13}C NMR analysis (**Scheme-I**).

m.p. 77-79 °C; FTIR (cm^{-1}): 3406, 2965, 1770, 1760, 1622, 1456, 1374, 1246, 1050, 743. ^{1}H NMR, δ ppm (500 MHz, CDCl$_3$): 6.65 (dd, $J_{3,4}$ = 10 Hz and $J_{3,5}$ = 3 Hz, 1H, H-3), 6.48 (dd, $J_{5,4}$ = 10 Hz and $J_{5,6}$ = 3 Hz, 1H, H-5), 6.4 (dd, $J_{4,5}$ = 10 Hz and $J_{4,6}$ = 3 Hz, 1H, H-4), 6.32 (dd, $J_{6,5}$ = 10 Hz and $J_{6,4}$ = 3 Hz, 1H, H-6), 6.03 (brt, $J_{11,10}$ = 12 Hz, 1H, H-11), 5.7 (d, J = 10 Hz, 1H, H-10), 3.97 (d, J = 13 Hz, 1H, H-2), 3.92 (d, J = 13 Hz, 1H, H-8), 2.7 (br s, 6H, CH$_3$O), 1.95 (brs, H-1). ^{13}C NMR (500 MHz, CDCl$_3$): 136 (CO), 129-120 (aromatic carbon signal + impurities signals), 115 (C-10), 111(C-11), 60.8 (C-2) 56.4 (C-8), 32 (C-9), 30.1 (CH$_3$O), 23 (C1), 14.5 (C-12).

RESULTS AND DISCUSSION

The obtained results of the reactions of Diels-Alder between masked *o*-benzoquinone and indol reported in the existence of different prepared supports. The reaction exhibited suitable yield, but less and poor diastereoselective reaction. As shown in Table-1, regarding the support with high cerium ion concentration on silica surface, led to the increase of yield and particularly diastereoselectivity.

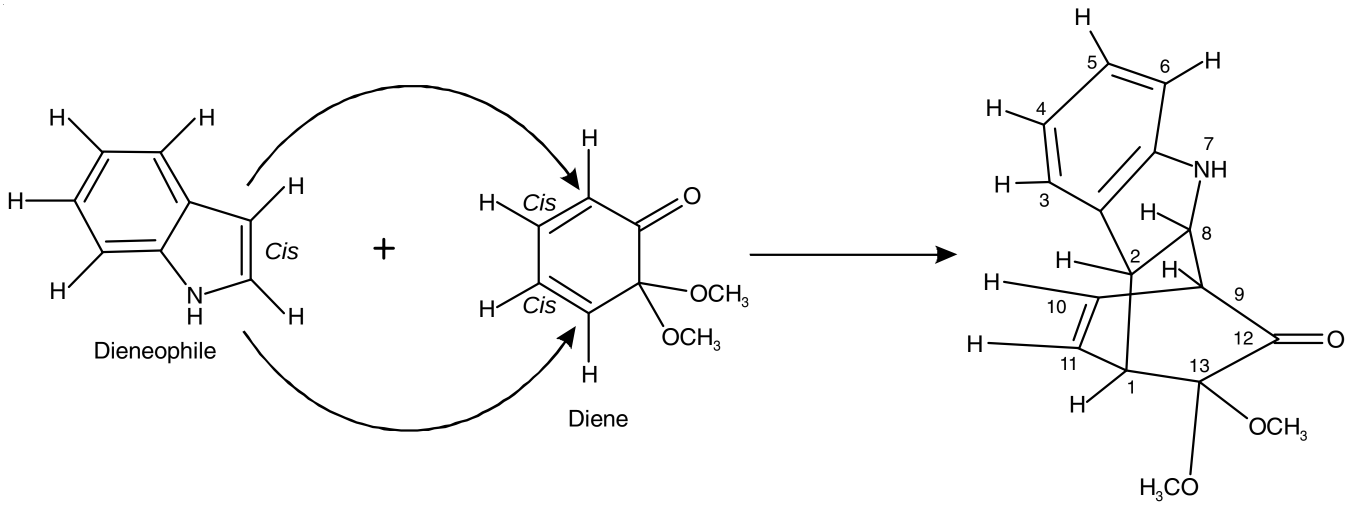
TABLE-1
DIASTEREOSELECTIVITY AND YIELD OF DIELS-ALDER REACTION OF INDOL AND MASKED *o*-BENZOQUINONE IN THE PRESENCE OF Ce(IV) LOADED ON SILICA AS SUPPORT

Concentration of Ce(IV)	mmol Ce/g	Yield (%)	Endo/exo (%)
Without catalyst	0	72	56/34
0.05	0.25	96	93/7
0.06	0.3	97	96/4
0.07	0.35	99	97/3
0.08	0.4	99	98/2

As mentioned above, by the increase of metal ion concentration on surface, the Lewis acid sites on the silica surface will be increased. The high concentration of cerium ion on the surface of silica, the diastereoselective reaction will be increased. In contrast, the yield and endo/exo diastereoselectivity are higher for Ce(IV), which may be because of its properties of relative strong acidic.

The FT-IR spectra of indol on the Ce(IV) modified silica were shown that the NH symmetry stretching frequency for indol is observed at 3406 cm^{-1}. By the loading of indol on the modified silica of Ce(IV), the wave number of the nitrogen frequency changes about 20 cm^{-1}. This NH frequency shift to low wavenumber is relevant to indol coordination with cerium ions on the surface of silica. It can be found in the literature, that this band shifted to the lower wavenumber, when Zn(II) was the metal ion [10]. Cerium(IV) is a more stronger Lewis acid in comparison with Zn(II), consequently the frequency shift of NH for cerium ion will shifts to the lower number of wave region compared to zinc ion [10]. However, the band width is relevant to hydrogen bonding with the Si-OH of silica surface. Vesselovskii and coworker suggested that within each reactant, by gathering the reacting moieties into closer proximity, the reactants adsorption on the silica particles surface may facilitate the pre-reaction complexes formation and stabilization [10,11]. A similar study has been conducted by Menger, who proposed that the functional groups rigid anchoring can stable reactants in adjacent together lower than the distance of critical bonding, consequently leading to enhancement significant rate [12]. Another study performed by Parlar and Baumann [13] proposing that only a small reactants fraction are really effectively adsorbed on the surface of silica and that the improved rates and selectivities are as a result of symmetry controlled interactions of secondary orbital between effectively adsorbed species and ones that are free to move on the surface. However, in this study, the mechanism of catalytic is suggested by the Lewis acid adsorption and coordination site of cerium ion with the indol nitrogen and perhaps the dienophiles hydrogen bonding or protonation by acidic SiOH groups on the surface of silica and then the reaction of Diels-Alder performs with facility [14-16].

As these results, the support could be recycled and reused for several times. The blank diastereoselective reaction was 55 % without support and solvent. The reaction in solvent had 56 % diastereoselectivity without support so the solvent have no influence on the diastereoselectivity improvement. To prove



Scheme-I

that before the extraction step with Soxhlet, the reaction was completed. The extraction was performed only by product filtration from the catalyst and the GC results indicated the same diastereoselectivity. Thus, the reaction was completed before the extraction step.

Conclusion

The cerium ion on the surface of silica catalysts was prepared by ion exchange method which has been proved for high diastereoselective Diels-Alder reaction of indol and dienophiles found to be efficient heterogeneous catalysts. The diastereoselective reaction highly depends on the cerium ion concentration as hard Lewis acid on the surface of silica. There is a positive correlation between cerium ion concentration and charge on the surface of silica and Diels-Alder diastereoselective reaction. The characteristic FT-IR band for NH which stretches frequency showed that with cerium ions on the silica surface the indol was coordinated. The catalytic mechanism was proposed by indol adsorption and nitrogen group coordination with cerium ion on the surface of silica which would be crucial in the Diels-Alder diastereoselective reactions.

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