Journal of Molecular Catalysis A: Chemical 385 (2014) 26–30

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Electron-deficient naphthalene diimides as efficient planar π-acid organocatalysts for selective oxidative C–C coupling of 2,6-di-*tert*-butylphenol: A temperature effect

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ARTICLE INFO

Article history:
Received 18 November 2013
Received in revised form 7 January 2014
Accepted 14 January 2014
Available online 23 January 2014

Keywords:
Naphthalene diimides
Organocatalysis
Electron transfer catalyst and C–C coupling

ABSTRACT

An efficient planar π-acid electron transfer organocatalyst based on electron-deficient substituted naphthalene diimide has been developed for oxidative C–C coupling of 2,6-di-*tert*-butylphenol to its dimeric derivative or unexpected ring-rearranged trimeric quinone methide by controlling the reaction temperatures.

1. Introduction

The formation of carbon–carbon (C–C) bond is arguably one of the most important reactions in synthetic chemistry [1], because it allows the transformations of small, readily accessible reactants into larger, value-added products with useful physical and chemical properties. Generally, the C–C bond formation reactions, in particular the C–C coupling reactions of aromatic molecules, are kinetic unfavourable, but it can be promoted in the presence of suitable catalysts. Transition-metal based catalysts, such as Pd, Rh, Cu and Ni complexes, have already been demonstrated to be the most important class of catalysts for the C–C bond formations [2]. However, they also suffer from some intrinsic drawbacks, *e.g.* the high cost, high toxicity and air-sensitivity, which somewhat limit their scope for applications.

To overcome the aforementioned disadvantages of transition-metal based catalysts, an emerging class of catalysts based on purely organic molecules (called organocatalysts) has been successfully developed in the past decade [3]. Among the reported organocatalysts, organic π-acid catalysts are most distinctive [4]. Different from the common Lewis acid organocatalysts that generally use only single atom containing empty orbits to accept electrons from reaction substrates, such unique π-acid organocatalysts based on electron-deficient π-conjugated systems could abstract the additional electrons through a linear or planar π system, which undoubtedly increase their reaction cross sections towards the substrates. In spite of foreseeable advantages, so far only three electron-deficient π-conjugated molecules, *i.e.* tetracyanoethylene (TCNE, Fig. 1) [5], dicyanoketene acetal (DCKA) [6] and dichlorodicyanobenzoquione (DDQ) [7], have found catalytic activities for organic synthesis, wherein few examples deal with the C–C bond formation reactions [8].

Naphthalene diimides (NDIs) [9] are an attractive class of electron-deficient π-conjugated molecules since their parent core possesses a high quadrupole moment (QZZ) up to +55.5 B, which is around three times that of the explosive trinitrotoluene [10]. This makes them a strong tendency to compactly interact with and therefore possibly abstract electrons from the surrounding electron-rich atoms, groups or molecules. For example, due to a remarkable anion–π interaction with electron-rich anions, such unique class of π-acids has already been applied in the fields of anion sensors [11] and anion transports [12]. More recently, Matile and co-workers have indeed demonstrated the applications of the anion–π interactions could be extended to the catalysis field [13]. Herein, we reported a new oxidative C–C coupling of 2,6-di-*tert*-butylphenol (**2**, Scheme 1) by molecular oxygen in present of electron-deficient NDI **1** (Fig. 1), which serves as an organocatalyst through totally electron transfer but not pure anion–π interactions. The reason why NDI **1** was chosen is mainly in view of

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http://dx.doi.org/10.1016/j.molcata.2014.01.014

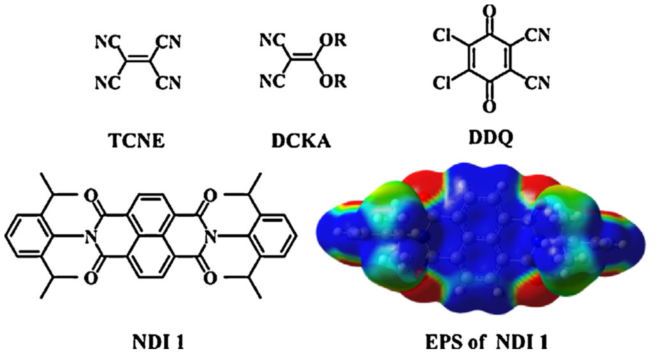


Fig. 1. Molecular structures of the available π-acid organocatalysts TCNE, DCKA, DDQ and the title compound NDI **1**, as well as its electrostatic potential surface (EPS, blue positive, red negative, ±0.01 Hartree, B3LYP/6-311G**). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

its simple structure but high solubility in most organic solvents. With regards to the reaction substrate, the phenol **2** was chosen as a proof-of-concept example since the exceptional electron donation of its anion, which is expected to offer an electron to the electron-deficient NDI **1**. Although the oxidative transformation of phenol **2** to coupling product **3** by the inorganic catalysts is very common [14], its organocatalytic reaction and particularly further ring-rearranged product quinone methide derivative **4** is first observed.

2. Experimental

2.1. Materials and measurements

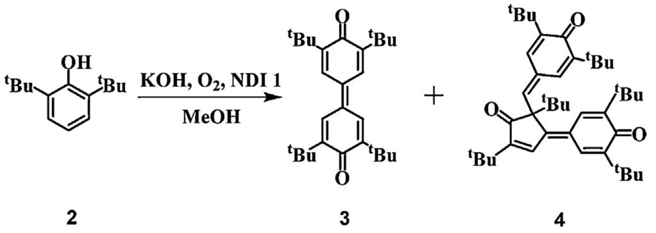
2.1.1. Materials and methods

1,4,5,8-Naphthalenetetracarboxylic (95%), 2,6-diisopropylbenzenamine (95%), 2,6-di-*tert*-butylphenol (97%), potassium hydroxide (≥99%), methanol (99.5%), dichloromethane (DCM, 99.5%) and petroleum ether (PE, 60–90 °C) were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. Column chromatography was performed using silica gel (Si60, mesh size 150 μm from Sinopharm Chemical Reagent Co., Ltd.). NMR spectra were recorded with a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. ^{1}H coupling constants *J* are given in Hertz (Hz). ESI mass spectra were recorded on a LCQ Fleet from Thermo Fisher Scientific. High-resolution mass spectra (HRMS) were acquired on the Thermo Scientific Exactive Plus Mass spectrometer equipped with an electrospray ionization (ESI) source.

2.2. Synthesis and catalytic experiments

2.2.1. Synthesis of organocatalyst NDI **1**

The synthesis of NDI **1** is similar to the procedure reported in the literature [15]. Under the argon, a mixture of naphthalene tetracarboxylic anhydrides (3 g, 11.2 mmol), imidazole (15 g, 220.1 mmol), 2,6-diisopropylaniline (10 g, 56 mmol) were added to a three-necked flask and then heated in 160 °C for 12 h. After being cooled to room temperature, the solid was poured into 1 mol L^{-1} aqueous HCl (500 mL) and extracted using dichloromethane (DCM) (100 mL) twice. The obtained organic solution was washed with aqueous $NaHCO_3$ and water twice, and further dried by anhydrous Na_2SO_4 for 2 h. Filtration and removal the organic solvents afford a gray solid, which was purified by column chromatography (SiO_2, DCM:PE = 1:1) resulting in **N**DI **1** as a white solid (2.2 g, 40%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.92 (s, 1*H*), 7.55 (t, *J* = 7.2 Hz, 2*H*), 7.40 (d, *J* = 6.9 Hz, 4*H*), 2.84–2.61 (m, 4*H*), 1.20 (d, *J* = 5.9 Hz, 24*H*); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): 162.94, 145.54, 131.60, 130.01, 130.00, 127.68, 126.92, 124.25, 29.33, 23.97. MS (ESI): calculated for $[M + H]^+$ of **3**, 587.72, found, 587.19; HRMS (ESI): calculated for $[M + H]^+$, 587.2832, found, 587.2889.



Scheme 1. Selective oxidative C–C coupling of **2** to its dimer **3** or ring-rearranged trimeric **4** in the presence of organocatalyst NDI **1**.

2.2.2. Catalytic experiments of organocatalyst NDI **1** towards oxidative C–C coupling of **2**

To a three-necked flask, a MeOH solution of NDI **1** (for entry 2, **2** is absent), starting material **2** and KOH (for entry 3, KOH is absent) was added and then reacted at 20 °C (entry 5), 40 °C (entry 1) or 90 °C (entry 6) for 24 h or 200 h (the reaction progress is monitored by thin layer chromatography). After being cooled to room temperature, the cooled mixture was poured into 1 mol L^{-1} aqueous HCl (100 mL) and extracted with DCM (50 mL) twice. The obtained organic solution was washed with a saturated solution of $NaHCO_3$ (50 mL) and water for two times, and further dried by anhydrous Na_2SO_4. Filtration and removal the organic solvents afford a brown solid, which was purified by column chromatography (SiO_2, DCM:PE = 1:1) affording compound **3** as a yellow solid (815 mg, 80%) and Compound **4** is a light yellow solid (70 mg, 5%) for entry 1, but **3** of 60 mg (*ca.* 5%) and **4** of 817 mg (85%) for entry 6. For other trials (entry 2–5), almost no oxidative products was obtained.

Compound **3**: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ = 7.73 (s, 4H), 1.38 (s, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): 186.44, 150.43, 136.13, 126.00, 36.03, 29.60. MS (ESI): calculated for $[M + H]^+$ of **3**, 409.62, found, 409.20; HRMS (ESI): calculated for $[M + H]^+$, 409.3028, found, 409.3089.

Compound **4**: ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.20 (s, 1*H*), 7.43 (d, *J* = 2.5 Hz, 1*H*), 7.02 (d, *J* = 2.5 Hz, 1*H*), 6.88 (d, *J* = 2.4 Hz, 1*H*), 6.75 (s, 1*H*), 6.27 (d, *J* = 2.3 Hz, 1*H*), 1.35 (s, 9*H*), 1.31 (s, 9*H*), 1.24 (s, 9*H*), 1.12 (s, 9*H*), 1.08 (s, 9*H*), 0.97(s, 9*H*). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): 204.51, 185.58, 185.51, 156.56, 154.19, 149.08, 148.83, 148.06, 147.51, 146.48, 143.30, 134.56, 131.88, 126.39, 126.13, 125.97, 65.01, 38.96, 35.58, 35.55, 35.52, 29.58, 29.41, 29.32, 29.26, 28.49, 27.72. MS (ESI): calculated for $[M - H]^-$ of **4**, 611.92, found, 612.25; HRMS (ESI): calculated for $[M + H]^+$, 613.4542, found, 613.4593.

3. Results and discussions

The organocatalyst NDI **1** was prepared according to the procedure reported in the literature [15], and its molecular structure was assigned by NMR spectroscopy as well as by single-crystal X-ray analysis (for details, see Supporting information). Electrostatic potential surfaces (EPS) of NDI **1** was calculated at the B3LYP/6-311G** level, which provided a visual indication of the potential reaction cross section of organocatalyst NDI **1** towards the electron-rich substrates (Fig. 1). Due to the introduction of two di-iso-propyl phenyl substituents at two imide positions perpendicularly, the positive electrostatic surface (blue) of the NDI plane was extended in a continuous way to the equatorial region of the phenyl plane, which remarkably expanded the potential reaction cross section of