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Synthesis of *p*-Xylene from Ethylene

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Ⓢ *Supporting Information*

ABSTRACT: As oil supplies dwindle, there is a growing need to develop new routes to chemical intermediates that utilize alternative feedstocks. We report here a synthesis of *para*-xylene, one of the highest volume chemicals derived from petroleum, using only ethylene as a feedstock. Ethylene is an attractive alternative feedstock, as it can be derived from renewable biomass resources or harnessed from large domestic shale gas deposits. The synthesis relies on the conversion of hexene (from trimerization of ethylene) to 2,4-hexadiene followed by a Diels−Alder reaction with ethylene to form 3,6-dimethylcyclohexene. This monoene is readily dehydrogenated to *para*-xylene uncontaminated by the *ortho* and *meta* isomers. We report here a selective synthesis of *para*-xylene, uncontaminated by the *ortho* or *meta* isomers, using ethylene as the sole feedstock.

With diminishing oil reserves, the production of commodity chemicals will increasingly rely on alternative feedstocks such as ethylene. In this regard, new routes to *para*-xylene (*para*-dimethylbenzene, PX) are of particular interest, as PX is one of the highest volume chemical intermediates derived from petroleum.[1] The primary use of PX is for the production of the dimethyl ester of terephthalic acid, which is copolymerized with ethylene glycol to produce polyethylene terephthalate (PET). The ca. 11 billion pounds of PET consumed annually in the U.S.[2] are used to manufacture a wide variety of common products including plastic bottles, polyester fibers, and films such as Mylar.

Traditionally, PX is produced by catalytic reforming of various crude oil streams, which results in a mixture of benzene, toluene, and *ortho*- (OX), *meta*- (MX), and *para*-xylene (so-called BTX). For the synthesis of PET, high purity PX is required and thus several technologies have been developed to purify and maximize PX yields.[3] The remarkably close boiling points of the xylene isomers (*ortho, meta, para*: 144.0, 139.1, 138.5 °C) make distillation an unappealing separation method. Low temperature crystallization and surface adsorption are often used, taking advantage of the difference in melting points of the three isomers (*ortho*, *meta*, *para*: −25.0, −47.4, 13.2 °C).[3a] While recent, significant progress has been made in developing new isomerization[4] and separation technologies,[5] a direct, selective route to PX from petroleum sources has yet to be developed.

Alternative approaches to xylenes from biomass feedstock have recently been reported; however these methods still rely on traditional hydrocarbon reforming technology. For example, hydrocarbons produced from plant sugars can be used to produce the normal mix of *ortho*, *meta*, and *para* isomers, requiring separation and purification as outlined above.[6] Additionally, routes to PX from 2,5-dimethylfuran (DMF), derived from carbohydrates, have also been reported.[7] Potential disadvantages of these methods include production of unwanted side products and low availability of DMF.

Here we report the synthesis of PX using ethylene as the sole feedstock. Ethylene is an attractive raw material for two reasons. First, it can be readily derived from ethanol and is therefore biorenewable. Braskem has commercialized a process using “bioethylene” derived from sugar cane, to produce 200 000 tons of polyethylene per year.[8] Second, and most significantly, the vast reserves of natural gas in the Marcellus and other shale deposits (shale gas) contain substantial fractions of ethane (up to 16%), which is readily cracked to ethylene. It is generally agreed that ethylene derived from shale gas will become a major (nonpetroleum based) source of this feedstock in the near future.[9] To that end, several petrochemical firms have announced their intention to increase U.S. ethylene production, including Shell’s proposed ethane cracker in western Pennsylvania.[9c−e]

Our strategy for implementing the synthesis of PX from ethylene is outlined in Scheme 1. Hexene can be produced via chromium-catalyzed selective trimerization of ethylene, a commercial process for preparing this monene.[10] Catalytic disproportionation of hexene via transfer dehydrogenation with another equivalent of substrate yields hexadiene and hexane. Subsequent Diels−Alder reaction of 2,4-hexadiene (2,4-HXD) with ethylene affords 3,6-dimethylcyclohexene, which, upon dehydrogenation, produces PX and hydrogen. Significantly, this synthetic route results in complete selectivity for PX, uncontaminated by the OX and MX isomers and with only minor amounts of ethylbenzene (EB). Details of the development and optimization of this process are described below.

We began our studies by exploring the conversion of 1-hexene to hexadienes. Previous work had shown catalytic transfer dehydrogenation of *n*-alkanes (C_n, $n > 5$) with iridium pincer complexes using 4 equiv of the sacrificial alkene acceptor TBE (*tert*-butylethylene) ultimately resulted in formation of cyclic aromatic products.[11] Aromatics are produced via formation of linear, conjugated trienes followed by ring closure to cyclohexadienes and further transfer dehydrogenation to the aromatic. We expected that the disproportionation of hexene (in which 1 equiv of hexene acts as the acceptor for dehydrogenation of a second equivalent of hexene) may be terminated at the diene stage prior to benzene formation. This expectation was based on the fact that olefin and diene

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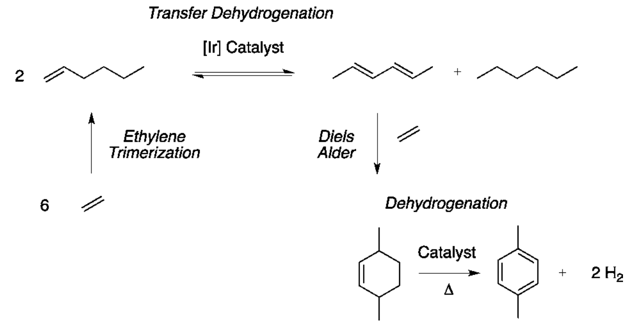
Scheme 1. Route to PX from Ethylene



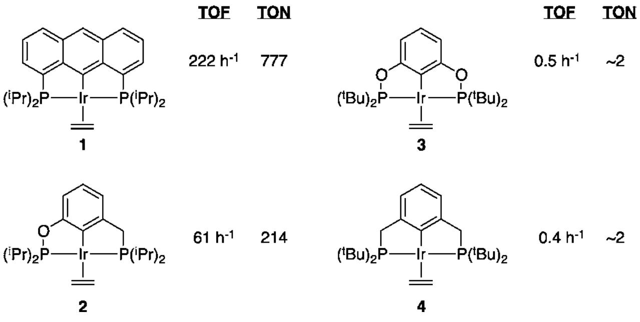


Figure 1. Catalysts screened for hexene disproportionation.

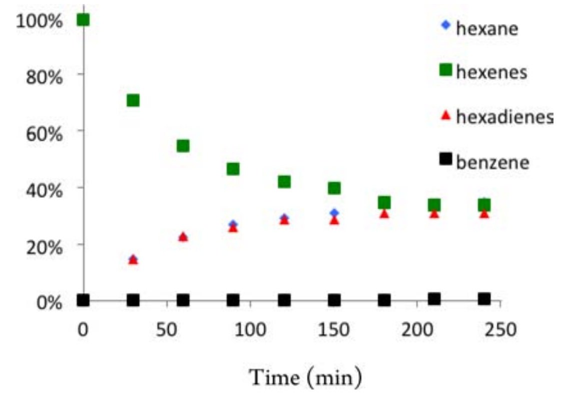


Figure 2. 1-Hexene disproportionation profile with **1**.

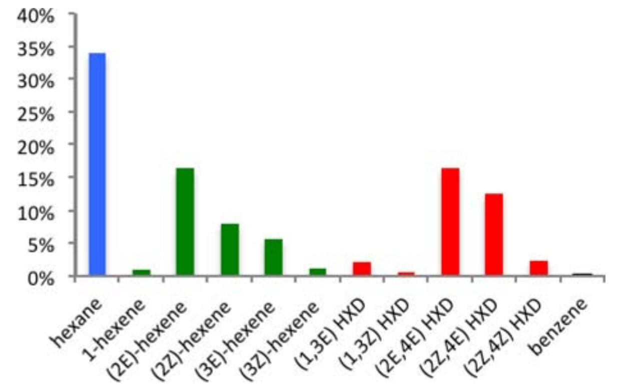
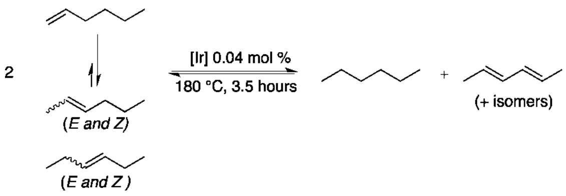


Figure 3. Product distribution at equilibrium from disproportionation of 1-hexene with **1**.

isomerizations are fast relative to dehydrogenation and thus the major diene isomers produced from hexene should be 2,4-hexadienes (2,4-HXDs). These dienes cannot undergo transfer dehydrogenation; further dehydrogenation can only occur from the thermodynamically much less favored 1,3-diene isomers.

Figure 1 shows four iridium pincer catalysts that were screened for disproportionation of 1-hexene into hexadienes and hexane. A 0.04 mol % catalyst loading was used, and the degassed hexene solution was heated in a closed, glass vessel at 180 °C for 3.5 h (eq 1).



(1)

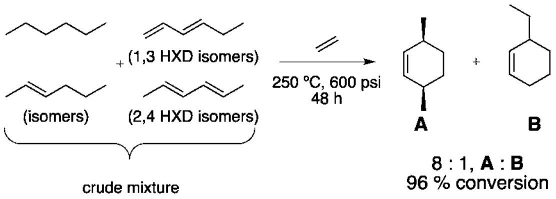
Conversions were monitored by gas chromatography. The turnover frequencies (TOFs) shown were calculated based on 30 min conversions, and the turnover numbers (TONs) were based on product formation after 3.5 h. Surprisingly, the more hindered *tert*-butyl-substituted catalysts, **3**[12] and **4**,[13] exhibited almost no activity in contrast to the remarkably high activity these complexes display in transfer dehydrogenation of cyclooctane using TBE as an acceptor.[10d,11] The less hindered isopropyl-substituted systems, **1**[11,14] and **2**,[11] showed good activities, with the anthraphos-based system, **1**, exhibiting a TOF and TON of ca. four times that of **2**.

The kinetic profile of 1-hexene disproportionation catalyzed by **1** (0.04 mol %, 180 °C) was followed by GC and is displayed in Figure 2. The iridium pincer complex, **1**, catalyzes the isomerization of hexenes and hexadienes much faster than transfer dehydrogenation under these conditions. Thus 1-hexene is rapidly converted to a thermodynamic mixture of hexenes prior to significant hydrogen transfer and the hexadienes produced appear as the thermodynamic ratio of dienes. As is evident from Figure 2, the reaction reaches equilibrium at ca. 3 h under these conditions with a $K_{eq} \approx 1$. The thermodynamic ratios of the hexene and hexadiene isomers are illustrated in Figure 3, which shows the full product distribution at equilibrium.

Next, conditions for the desired Diels–Alder reaction with ethylene were explored. Literature reports suggested that the cycloaddition reaction of pure (2*E*,4*E*)-HXD with ethylene required high temperatures and pressures (185 °C, 4300 psi) for the cycloaddition to occur. The 2*E*,4*Z* and 2*Z*,4*Z* isomers were unreactive under these conditions.[15] We were able to achieve high conversion of (2*E*,4*E*)-HXD (96%) and (1,3) HXDs (100%) in the crude reaction mixture to Diels–Alder products after 48 h at 600 psi and 250 °C. Under these conditions selective formation of the Diels–Alder adduct of the (2*E*,4*E*)-HXD isomer is observed, with minimal conversion of the (2*E*,4*Z*)- and (2*Z*,4*Z*)-HXD isomers. As shown by the results summarized in Table 1, only the concentration of the reactive dienes has changed significantly to produce **A** and **B**, illustrating the selectivity observed in this reaction. Furthermore, the GC trace for this reaction only shows one signal for isomer **A** with no other signal that could be assigned as the other stereoisomer (Figure S2).

In the final step of the synthesis of PX we sought to dehydrogenate *cis*-3,6-dimethylcyclohexene, the Diels–Alder adduct. The overall reaction shown in eq 2 involves the loss of 2 equiv of H_2 and formation of a stable aromatic structure.

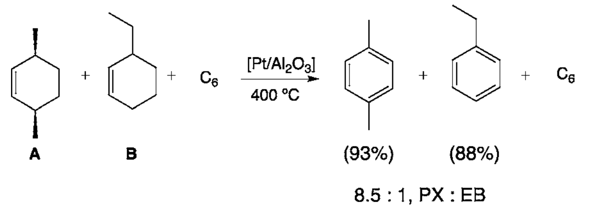
Table 1. Diels–Alder Reaction[a]

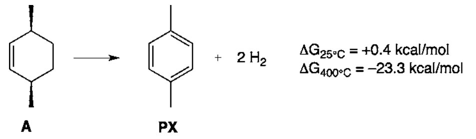


	hexane	hexenes	1,3*E*-HXD	1,3*Z*-HXD	2*E*,4*E*-HXD	2*E*,4*Z*-HXD	2*Z*,4*Z*-HXD	**A**	**B**
start	33.9	34.8	1.6	0.3	15.1	11.7	2.3	0	0
final	31.4	31.1	0	0	0.6	7.5	1.7	23.9	2.9

[a]Numbers shown are in mol % of solution.

Scheme 2. Dehydrogenation of Diels–Alder Adducts





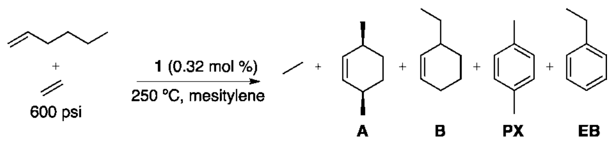
(2)

The high positive entropy offsets the positive enthalpy (ΔH = +18.4 kcal/mol) and renders the reaction highly exergonic at temperatures above 200 °C, suggesting this dehydrogenation can be accomplished "acceptorless" with a heterogeneous catalyst.[16]

Indeed, dehydrogenation of cyclohexene to benzene over heterogeneous catalysts has ample literature precedent.[17] In this study, commercial catalysts Pd/C, Pt/C, and Pt/Al_2O_3 were screened. Crude reaction mixtures of the Diels–Alder adducts were passed in the vapor phase using nitrogen as the carrier gas over a bed of these catalysts at 300–500 °C, and the product mixtures were trapped and analyzed by GC. In initial screening, all these catalysts gave good conversion (>80%) of the starting Diels–Alder adduct to PX. Upon further optimization, Pt/Al_2O_3 at 400 °C was observed to give the highest yield (93%) of PX. Ethylbenzene (EB) was also observed in high yield from this reaction (88%) with a final ratio of 8.5:1, PX/EB (Scheme 2). Importantly, EB is another valuable aromatic, as it is a precursor to styrene.

Thus far, a stepwise approach to PX using ethylene as the sole feedstock has been outlined. The efficiency and utility of this sequence could be improved if ethylene were to serve as the hydrogen acceptor for 1-hexene dehydrogenation and drive the conversion of hexene to higher yields of hexadienes. Heating 1-hexene at 250 °C with 600 psi of ethylene for 24 h in the presence of 0.32 mol % **1** resulted in conversion of 1-hexene into HXD (35.1% HXD, Table 2, entry 2). Significantly, the dienes produced underwent a subsequent Diels–Alder reaction with ethylene *in situ*, providing the 3,6-dimethylcyclohexene (16.9% **A**, entry 2) in one pot. This remarkable result demonstrates a significant step forward in this approach to PX. The yield of HXD (and ultimately PX) is no longer limited by the equilibrium disproportionation of 1-hexene into HXD and hexane, making this one-pot approach to 3,6-dimethylcyclohexene a more attractive route for PX synthesis from ethylene. Further heating of the reaction vessel resulted in nearly complete conversion with respect to hexenes (93% after 192 h, entry 6). Only trace amounts of hexane are observed, indicating ethylene has served as the dominant acceptor. To our knowledge this is the first example of ethylene serving as a hydrogen acceptor in alkane dehydrogenation. The selective conversion of 1-hexene to **A** and **B** also suggests that the unreactive HXDs are isomerized to reactive HXDs under these reaction conditions. Thus a high conversion to **A** and **B** is observed for the Diels–Alder reaction with minimal HXD remaining. Moreover, the Diels–Alder adducts are further dehydrogenated under these reaction conditions resulting in PX and EB (Table 2, aromatics) as well as partially

Table 2. One-Pot Diene Formation/Diels–Alder Reaction[a]



entry	time	hexane	hexenes	HXD	**A**	**B**	aromatics[b]	other[c]
1	24	0.4	42.1	35.1	16.2	4.7	1.5	
2	48	0.6	30.4	23.5	33.4	6.7	5.4	
3	72	0.5	24.6	14.9	44.6	8.3	7.1	
4	96	0.5	21.6	10.4	48.7	8.8	7.8	2.2
5	144	0.4	14.2	2.0	59.7	10.2	9.7	3.8
6	192	0.2	7.5	0.2	65.5	12.2	10.3	4.3

[a]Time in h; other numbers shown are in mol % of solution. Reaction monitored by GC and recharged with ethylene after sampling. [b]Aromatics consist of PX, EB, and trace benzene. [c]Others consist of partially dehydrogenated products from **A** and **B** which are readily converted to aromatics.

dehydrogenated **A** and **B** (other). Importantly, these partially dehydrogenated species as well as **A** and **B** can easily be dehydrogenated to aromatics via Pt-catalyzed dehydrogenation.

In summary, we have demonstrated a selective route to *para*-xylene using ethylene as the sole feedstock. The route features a transfer dehydrogenation of hexene to generate hexadienes using ethylene (or hexene itself) as the hydrogen acceptor. When ethylene is used, a subsequent Diels−Alder reaction occurs with hexadienes to yield, in one pot, 3,6-dimethylcyclohexene as the major product along with some 3-ethylcyclohexene. Thermal dehydrogenation over Pt/Al_2O_3 yields *para*-xylene and ethylbenzene.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, gas chromatographs, and complete ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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