

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: Synthesis of Renewable meta-Xylylenediamine from Biomass-Derived Furfural
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201803828 Angew. Chem. 10.1002/ange.201803828

Link to VoR: http://dx.doi.org/10.1002/anie.201803828 http://dx.doi.org/10.1002/ange.201803828

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Synthesis of Renewable *meta*-xylylenediamine from Biomass-Derived Furfural

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We report the synthesis of bio-based functionalized aromatic chemicals from furfural, a building block nowadays available in large scale from low-cost biomass. The scientific strategy relies on a Diels-Alder / aromatization sequence. By controlling the rate of each step, it was possible to produce exclusively the *meta* aromatic isomer. In particular, through this route, we describe the synthesis of renewably-sourced *meta*-xylylenediamine (MXD). Transposition of this work to other furfural-derived chemicals is also discussed and reveals that functionalized bio-based aromatics (benzaldehyde, benzylamine, etc.) can be potentially produced, according to this route.

Aromatics are an important class of chemicals, in particular for the pharmaceutical, manufacture of polymers, solvents. agrochemicals, and fragrances.^[1] Aromatics are produced from fossil carbon, either by catalytic reforming of naphta or steam cracking of hydrocarbons.^[2] With the exponential growth of the world population and the resulting pressure on fossil resources, the industrial production of aromatics will face difficulties to satisfy the need of our society in a close future. The necessity to diversify our resources and the general trend of reducing our CO₂ footprint have opened opportunities to produce aromatics from biomass. Besides performance, profit, environmental and societal gains, which remain the main criteria for success, utilization of biomass for chemistry has the potential to develop chemical industries in different countries, thus creating or relocating jobs.^[3] Bio-based aromatics are typically produced by catalytic fast pyrolysis of biomass,^[4-11] bio-ethylene,[12] cyclotrimerization of depolymerization or cracking of lignin,^[13] by conversion of carbohydrates via the furanic platform,^[14] or via the bio-based pinacol platform.^[15] In many cases, these processes aim at producing benzene, toluene and xylene (BTX), which can be further used without any modification of current downstream processes and applications.

Previously, bio-based furanic derivatives such as 2-methylfuran (MF) and 2,5-dimethylfuran (DMF) have been successfully converted to BTX, through sequential Diels-Alder (DA)/aromatization reactions with ethylene over acid catalysts.^[16-27] Using the same strategy, renewable aromatics were also

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Eco-Efficient Products and Processes Laboratory, UMI 3464 CNRS/Solvay, 3966 Jin Du Road, Shanghai 201108 (CHINA) E-mail: raphael.wischert@solvay.com produced from 5-hydroxymethylfurfural (HMF) and ethylene,^[28] in particular for the synthesis of bio-based terephthalic acid. Although aromatics were produced in good yields, the lack of cost-competitive processing technologies to convert low cost sugars to MF, DMF and HMF currently hampers the industrial deployment of these routes.

Furfural is a cheap furanic derivative (1.0-1.2 \in /kg) available in large scale from biomass (>200 kT/year), making it an attractive raw material for the production of bio-based aromatics.^[29] In previous strategies, furfural was decarbonylated *in situ* to furan before the DA and aromatization reactions to yield BTX.^[30] Mainly for polymer synthesis, furfural was first converted to amines,^[31] acetals,^[32] alcohols,^[33] phenolic-type resins,^[34] amides^[35] or hydrazones,^[36] before DA reaction with alkenes. In these works, the aromatization of cycloadducts was rarely attempted.

To date, the synthesis of functionalized and industrially relevant aromatics from biomass such as benzaldehyde, benzonitrile or benzylamine derivatives, remains scarcely explored.^[15b, 28] Among them, *meta*-xylylenediamine (MXD) is an important target. MXD is widely used in the polymer industry as curing agent for epoxy resins and coatings, and in the production of polyamide, and polyurethane. Nowadays, MXD is produced at 100 kT/year scale from fossil feedstocks (isophthalic acid) and is a growing market (on average 3.45% per year), expected to reach 280 million € by 2021.^[37]

Here, we report a 100% carbon economical bio-based route to MXD from furfural and acrylonitrile, two abundant and cheap raw materials. Driving the selectivity to the *meta* aromatic isomer is an important scientific challenge, which we address in this work (Scheme 1).



Scheme 1. Pathway to *meta-xylylenediamine* (MXD) from furfural and acrylonitrile.

The direct DA reaction of furfural with acrylonitrile failed. Density functional theory calculations (DFT)^[38] at the M06-HF/cc-pVTZ level^[39] (for details and discussion see ESI) indeed confirmed that the reaction was thermodynamically unfavorable, with a substantially positive free energy of reaction ($\Delta G = +24$ kJ mol⁻¹ at 60°C) and an associated barrier of $\Delta G^{\ddagger} = 124$ kJ mol⁻¹ (Table S1, entry 1), consistent with the previously observed low reactivity of furfural in DA reactions. Attempts to use other dienophiles such as 2-pentenenitrile, acrolein, allyl alcohol or maleic anhydride also

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failed. Even in the presence of an acid catalyst or extended reaction time (up to 4 days), furfural remained unaltered, in line with calculations (Table S1, entries 2-5). The reactivity of diene and dienophile in a Diels-Alder reaction is inversely proportional to the difference in energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of diene and dienophile, respectively.^[40] Electronwithdrawing substituents stabilize the HOMO of the diene, resulting in a larger HOMO-LUMO gap and lower reactivity. In the present case, the electron-withdrawing formyl group in furfural stabilizes the HOMO by 0.5 eV, compared to furan, which is known to readily undergo DA reactions (Table S2, entries 1-2). Therefore, decreasing the electron-withdrawing character of the aldehyde group should result in a higher reactivity. Among different strategies, derivatization of furfural by acetalization^[32] with ethylene glycol (also industrially available from biomass) to 2-(furan-2-yl)-1,3-dioxolane destabilizes the HOMO by 0.6 eV (Table S2, entry 3), resulting in a thermodynamically favorable reaction with acrylonitrile ($\Delta G = -2 \text{ kJ mol}^{-1}$ at 60 °C) and an associated barrier of $\Delta G^{\ddagger} = 113 \text{ kJ mol}^{-1}$ (Table S1, entry 6). Compared to furfural, the reaction is more favorable by 26 kJ mol⁻¹ and the barrier is reduced by 11 kJ mol⁻¹. As predicted by the calculation, the reaction was successful: 51% of 2-(furan-2yl)-1,3-dioxolane was selectively converted to the corresponding DA cycloadduct (48% yield) at 60°C (Table 1, entry 1). The ortho and meta cycloadducts were produced in a 52:48 ratio, with the endo form being dominant. Time to reach equilibrium (DA vs retro-DA reaction) was 120 h, affording cycloadducts in 76% yield (Table 1, entry 2). As expected, when the temperature was increased to 100°C, conversion and yield dropped dramatically because the retro DA reaction became dominant (Table 1, entry 3). Further, the ortho to meta ratio changed to 40:60, in excellent agreement with the thermodynamic isomer ratio of 39:61 calculated by DFT (ESI).

 $\label{eq:constraint} \begin{array}{c} \mbox{Table 1. DA} & \mbox{reaction between 2-(furan-2-yl)-1,3-dioxolane and} \\ \mbox{acrylonitrile.}^{[a]} \end{array}$

	$\langle 0 \rangle$	+ 🔨 CI	D, 60° N retro	A C <u>C</u> C DA	ortho ndo / exo	0 1 + //) (end	O O O O C N neta o / exo)
Entry	<i>Т</i> (°С)	Cat.	<i>Time</i> (h)	Conv (%)	Yield (%)	ortho (%) ^[b]	meta (%) ^[c]
1	60	-	48	51	48	52	48
2	60	-	120	82	76	48	52
3	100	-	7.5	21	19	40	60
4	40	-	48	10	9	51	49
5	25	-	48	0	0	0	0
6	60	ZnCl ₂	25	78	68	53	47
7	60	Znl ₂	25	87	75	53	47

[a] 5 eq. acrylonitrile; [b] endo/exo = 7/3; [c] endo/exo = 6/4.

When the temperature was reduced to 40 °C, the yield dropped significantly and at 25 °C no conversion was observed (Table 1, entries 4-5), indicating that the activation barrier of the reaction could not be overcome, in line with calculations (Table S3 and discussion in the SI). Hence, 60 °C was selected as a compromise. Among different tested acid catalysts, only anhydrous Znl₂ and ZnCl₂ significantly decreased the time to reach the chemical equilibrium, with *ortho/meta* and *endo/exo* ratios almost identical to those obtained without catalyst (Table S4). For instance, the conversion of 2-(furan-2-yl)-1,3-dioxolane reached 78% and 87% after 25 h of reaction, in the presence of ZnCl₂ and Znl₂, respectively (Table 1, entries 6, 7). The selectivity was however slightly lower with Zn-based catalysts, due to the partial deprotection of the starting 2-(furan-2-yl)-1,3-dioxolane (~10%), water being used as a stabilizer of acrylonitrile (0.2-0.5 wt%).

Aromatization of DA cycloadducts is usually carried out in the presence of acid catalysts such as H_2SO_4 ,^[24, 41] H-Y zeolites,^[24] Hf, Zr and Sn beta zeolites,^[42] silica-supported Lewis acids,^[43] or mixed sulfonic carboxylic anhydrides in methane sulfonic acid.^[44] Unfortunately, this reaction often competes with the retro DA reaction, due to the high temperature required. In line with these reports, in the presence of H_2SO_4 , Aquivion PFSA PW65S or zeolite HY, at 100°C, both under solvent-free conditions or in dimethylsulfoxide (DMSO), no aromatization took place and only the retro-DA reaction was observed.

The presence of an acidic proton in the cycloadducts (-CH-CN group) prompted us to investigate aromatization under basic conditions, initially unsuccessful under commonly used deprotonation conditions (ESI). From the chemical shift of this acidic proton (2.75-3.30 ppm), we concluded that a superbase would be required for deprotonation. DMSO has the ability to generate such species with a pKa value of about 30-32, by solvation of counter-cations such as K⁺ or Na⁺.^[45] Pleasingly, aromatization of the DA cycloadducts (meta/ortho ratio of 1) with 20 mol% of CH₃ONa in DMSO resulted in 86% yield to aromatics after only 1 h at 30 °C, with a *meta/ortho* ratio of 1.8 (Table 2, entry 1), indicating faster reaction of the *meta* isomer. Other bases

o o c c c c c c c c c c c c c c c c c c	-0 $0mCN + 1$	CN	Base (20 mol%) 30°C DMSO	CN + CN	
ortho meta (endo / exo) (endo / exo)		neta o / exo)	ort	ho meta	
Entry	Catalyst	Time (h)	Total Yield to aromatics (%)	m <i>eta:ortho</i> ratio	
1	CH₃ONa	1	86	1.8:1	
2	<i>t</i> BuONa	1	84	1.5:1	
3	3 КОН		80	1.7:1	
4	4 NaOH		74	2.3:1	
5	5 A26		38	3.4:1	
[a] cycloadduct ortho meta ratio of 1:1					

Table 2. Deprotonation of the DA adducts obtained from 2-(furan-2-yl)-1,3-dioxolane and acrylonitrile $^{\rm [a]}$

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such as 'BuONa, KOH, and NaOH led to similar yields and ratios (Table 2, entries 2-4). To facilitate the work-up, an insoluble strongly basic anion exchange resin (Amberlyst-26, OH⁻ form) was tested. Despite being less active, aromatics were selectively produced in 38% yield in 7 h (Table 2, entry 5). In all cases, almost quantitative yields could be reached by extending the reaction time to 3 h, except for Amberlyst-26, which required 3 days. Note that, without any base, the aromatization did not proceed in DMSO. Consistent with the results presented in Table 2, the kinetic profile of the aromatization reaction revealed that the meta cycloadduct was more reactive than the ortho isomer. In particular, the aromatic ortho started to be produced only after the meta DA adduct was almost completely converted (Fig. 1). Calculations indeed support a higher acidity of the meta, compared to the ortho-CH-CN protons (by ~2 pKa units, see ESI). This difference is of strong interest since it allows the meta and the ortho aromatic isomers to be produced consecutively, but separately.



Figure. 1. Yield of ortho and meta isomers as a function of the conversion.

With this result in hands, the possibility to enrich aromatic products into the *meta* isomer was then checked (Fig. 2). At 50% conversion, the aromatization was quenched by dilution in water and the aromatic *meta* product and the unreacted *ortho* cycloadduct were both recovered by extraction with ethyl acetate. Next, these two products were heated at 120°C under vacuum to induce the quick retro-DA of the remaining *ortho* cycloadduct back to acrylonitrile and 2-(furan-2-yl)-1,3-dioxolane, leaving the *meta* aromatic unaltered. After completion of the retro-DA, distilled acrylonitrile was re-introduced into the reactor and re-submitted to DA and aromatization reactions. After these two repeated cycles, the *meta* aromatic isomer was thus produced with an overall yield of 75%. The process can be then repeated up to the nearly exclusive formation of the *meta* isomer (Fig. 2). Using the solid base Amberlyst-26 instead of CH₃ONa has the advantage





that the reaction can be easily quenched by filtration of the base, thus making product separation from DMSO unnecessary.

Deprotection of the *meta* isomer in THF in the presence of a catalytic amount of aqueous HCI afforded *meta*-cyanobenzaldehyde in quantitative yield, and ethylene glycol, which can be recycled for protection of furfural. Reductive amination of the aldehyde (80 °C, 30 bar of H₂, in the presence of Raney Co and ammonia) afforded MXD with 70% yield (results not optimized, Fig. 3).



Figure 3. Catalytic conversion of 3-(1,3-dioxolan-4-yl)benzonitrile to MXD.

Guided by DFT calculations, which predicted destabilization of the HOMO vs. furfural (Table S2, entries 3-6) and conversion to products ($\Delta G = 3$ to 9 kJ mol⁻¹, $\Delta G^{\ddagger} = 111 - 112$ kJ mol⁻¹, Table S1, entries 7-9), alternative pathways to benzonitrile derivatives were explored, starting from other furfural-derived chemicals (ethylfurfuryl ether, furfuryl alcohol, 2-methylfuran and furfuryl amine). Except from furfuryl amine, these attempts were again successful, leading to the corresponding cycloadducts in 54% to 73% yield (Table 4). Different ortho/meta ratio were obtained, because (i) the DA reaction had not reached equilibrium and (ii) slightly different electronic and steric effects. At equilibrium (after few days of reaction), the ortho/meta ratio was close to 1 in all cases. Aromatization (30°C in DMSO, 20 mol% of tBuONa) afforded the corresponding aromatics in high yield (> 80%), except for furfuryl alcohol (Table 4, entry 3). For furfuryl alcohol and ethylfurfuryl ether, the corresponding meta cycloadduct was

Table 4. Scope of the reaction.



Entry	R	Yield to cycloadduct (%)		Yield to aromatics (%) ^{[a]/[b]}		
		meta	Ortho	Total	meta ^[c]	ortho ^[c]
1	-CH ₂ OEt	18	36	66/96	88/100	62/94
2	-CH₃	13	53	53/80	29/62	72/97
3	-CH₂OH	26	47	9/32	12/42	5/21
4	$-CH_2NH_2^{(b)}$	-	-	-	-	-

[a] after 10 min; [b] after 60 min; [c] yield relative to the corresponding *ortho* or *meta* DA cycloadduct; [b] from furfuryl amine, a complex mixture of compounds was obtained due to parasite Michael addition of furfuryl amine to acrylonitrile.

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again aromatized faster than the *ortho*, suggesting that the selectivity to the *meta* aromatic can be kinetically controlled, as discussed above. Reversely, from 2-methyl furan, the *ortho* cycloadduct was more reactive (Table 4, entry 2).

In conclusion, we report here that industrially relevant aromatic chemicals, such as MXD, can be selectively synthesized from furfural and acrylonitrile through a 100% carbon-economical route. The pathway involves a Diels-Alder/aromatization sequence as a key step. Importantly, we showed that (1) the aromatization step could be catalyzed at low temperature by bases instead of acids, thus avoiding the usually observed retro-Diels-Alder reaction, and (2), by playing with the rate of the reactions, it was possible to selectively drive the reaction to the meta aromatics. One should note that, starting from furfural, all steps (protection, DA/aromatization, deprotection and hydrogenation) are highly selective and chemical intermediates can be directly engaged in the next step without purification. Furthermore, water is released as the sole by-product. Optimization of the process and DFT calculations to rationalize and predict reaction outcomes are now the topic of current investigations.

Acknowledgements

The authors are grateful to the CNRS, the University of Poitiers, the French Ministry of Research and SOLVAY for their financial support.

Keywords: Furfural • Aromatics • Diels-Alder • Amination • DFT

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Renewable meta-xylylenediamine was produce bio-base using se catalyze kinetic c step per of the m

ble <i>meta</i> -xylylenediamine was d at low temperatures from d furfural and acrylonitrile by quential Diels-Alder/base- d aromatization reactions. A ontrol of the aromatization mitted the selective formation <i>eta</i> isomer.	Base-catalyzed aromatization $\begin{array}{c} \downarrow \\ \downarrow \\ + \\ \downarrow \\ CN \end{array} \qquad $	Ivan Scodeller, Samir Mansouri, Didier Morvan, Eric Muller, Karine de Oliveira Vigier, Raphael Wischert,* and François Jérôme * Page No. – Page No. Synthesis of Renewable meta- xylylenediamine from Biomass- Derived Furfural	