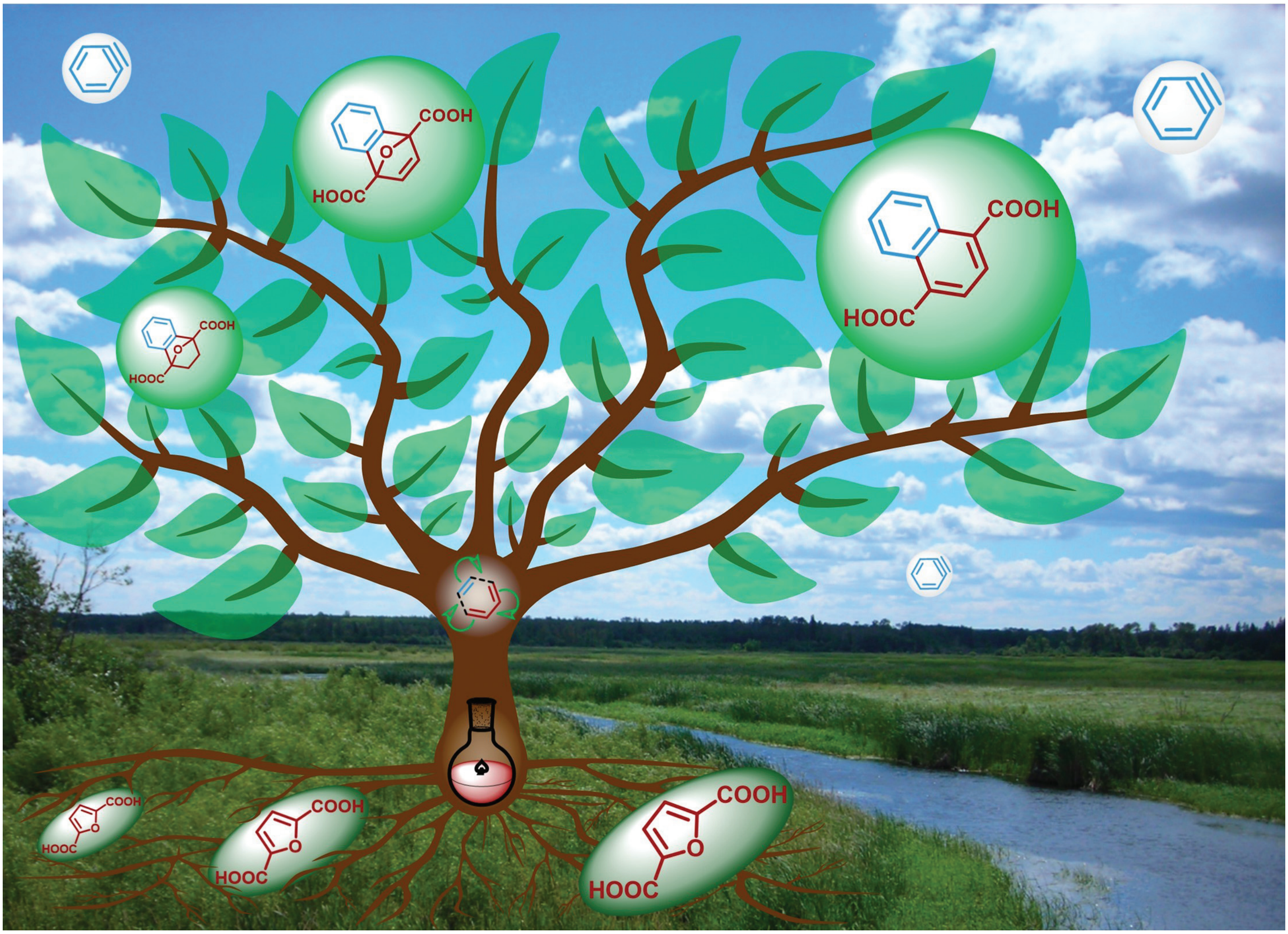
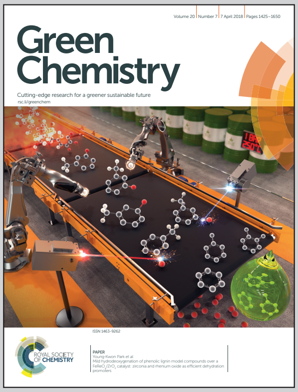


Showcasing Research from the Center for Sustainable Materials Science (CSMS), North Dakota State University, USA.

Valorization of 2,5-furandicarboxylic acid. Diels–Alder reactions with benzyne

Just as a tree combines materials from the atmosphere and soil to generate new growth, so do researchers in the chemical sciences. The leaves from yesteryear (2,5-furandicarboxylic acid, FDCA) have fallen and been incorporated into the soil which nourishes this year's leaves (value-added products from FDCA). A cycloaddition strategy has been developed which combines benzyne with biomass-derived furans to afford novel bicyclic adducts with great potential for further modification. In a new twist of the *cradle to cradle* approach, this technology takes advantage of the unique properties contained within furanic products from cellulose-biorefinery which are unknown in their petroleum cousins: potential for cycloaddition.

As featured in:



Volume 20 | Number 7 | 7 April 2018 | Pages 1425–1650

Green Chemistry

Cutting-edge research for a greener sustainable future
rsc.li/greenchem

ISSN 1463-9262

ROYAL SOCIETY OF CHEMISTRY

PAPER
Young-Kwon Park *et al.*
Mild hydrodeoxygenation of phenolic lignin model compounds over a $FeReO_x/ZrO_2$ catalyst: zirconia and rhenium oxide as efficient dehydration promoters

See Mukund P. Sibi *et al.*, *Green Chem.*, 2018, **20**, 1448.

ROYAL SOCIETY
OF **CHEMISTRY**

rsc.li/greenchem

Registered charity number: 207890

Green Chemistry

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2018, **20**, 1448

Received 28th January 2018,
Accepted 20th February 2018

DOI: 10.1039/c8gc00308d

rsc.li/greenchem

Valorization of 2,5-furandicarboxylic acid. Diels–Alder reactions with benzyne†

Eric M. Serum, [a] Sermadurai Selvakumar, [b] Nicolas Zimmermann[c] and Mukund P. Sibi *[a]

Biomass-derived 2,5-furandicarboxylic acid was valorized by conversion to 1,4-naphthalenedicarboxylic acid *via* benzyne-cycloaddition and reductive aromatization in 66% overall yield (four steps). Two novel bicyclic intermediates were isolated in 80% and 98% yield. These advances diversify the potential end uses of renewable terephalic acid analogs and other furanics available from cellulose biorefinery.

Introduction

Investigation of nonedible biomass as a sustainable alternative to petroleum continues to expand as a field of research. This expansion requires the development of biorefinery technologies along with the diversification and concomitant valorization of platform chemicals. Often, investigators choose a petroleum commodity chemical and attempt to create a sustainable alternative either through production of a facsimile or an analogous structure readily obtained from biorefinery products.

One petroleum commodity targeted for replacement by both methods is terephthalic acid **1**.[1] This has been accomplished by renewable routes[2,3] to **1** and by substitution of **1** with renewable analogs (Fig. 1).[4] The introduction of furanics derived from hemicellulose and cellulose has resulted in their use as dienes[5] in Diels–Alder strategies for renewable **1**.[6–11]

Biomass-derived 5-(hydroxymethyl)furfural **2** along with derivatives—bisacrylic acid **3** and diacid **4**[12]—have potential for redox-efficient transformation into benzenoids *via* cycloaddition followed by aromatization (Scheme 1). However, the electronic demands of the Diels–Alder reaction have led to an impasse which has been met mainly by redox-inefficient use of alkyl-substituted furans and in some cases by use of alkoxyfuranoates prepared *via* partial oxidation of **2**;[8,9] no direct synthesis of **1** has been reported from **4** or its esters.

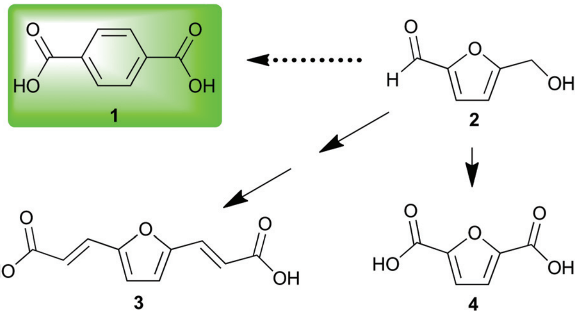


Fig. 1 Terephthalic acid and furanic analogs derived from cellulose.

Established Diels–Alder protocols involve reaction between derivatives of **2** and pressurized ethylene gas[8,9,13] or acrolein.[6] A promising approach to **1** under investigation is the thermal rearrangement of phthalic anhydride, which has been prepared from the adducts of furan and maleic anhydride by dehydroaromatization.[7,10,11] The 7-oxanorbornene intermediates must be protected from retro-Diels–Alder reaction by immediate dehydration to afford renewable *p*-xylene[13–15] or another drop-in replacement[8,9] for industrial precursors of **1**.

Having noted the difficulty in obtaining **1** or its ester **7** from biomass-derived furanics by a redox-efficient strategy (Scheme 1), we inferred that the enhanced reactivity[16] of benzyne as a dienophile may succeed where the preparation of adduct **6** from ethylene or acetylene would fail. This opportunity to synthesize a naphthalene analog of **1** directly from **4** as well as provide access to novel [2.2.1] oxygen-bridged bicycles (Scheme 1) serves to expand the structural motifs which can be realized from bio-sourced platform chemicals.

This novel valorization strategy relies upon the Diels–Alder reaction between benzyne and electron-deficient furans such as dimethyl 2,5-furandicarboxylate **5**. Whereas typical [2.2.1]

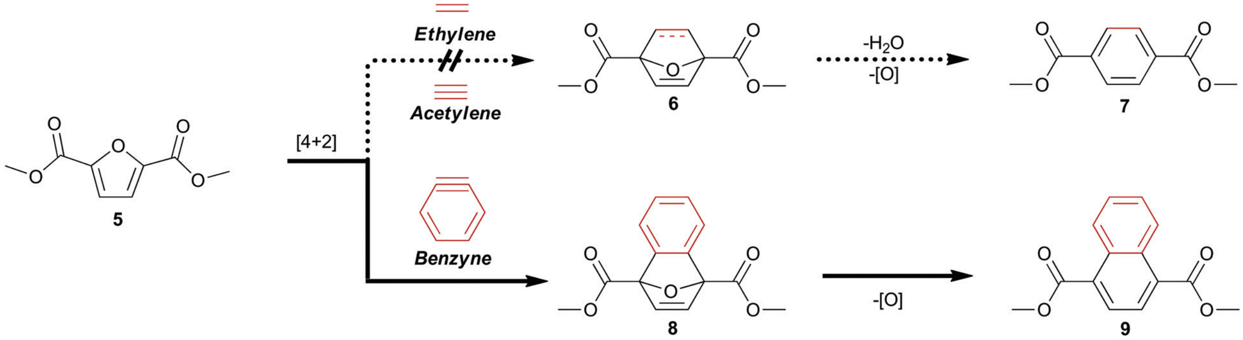
---

[a] *Department of Chemistry and Biochemistry, North Dakota State University, Dept. 2735, PO Box 6050, Fargo, North Dakota 58108, USA. E-mail: mukund.sibi@ndsu.edu*

[b] *Department of Chemistry, Central University of Haryana, Jant-Pali, Mahendergarh-123031, India*

[c] *Sigma Informatique, 8 rue Newton, CS 84533-44245 La Chapelle sur Erdre Cedex, France*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8gc00308d



Scheme 1 Diels–Alder strategy for direct access to cellulose-derived dimethyl terephthalate **7** and dimethyl 1,4-naphthalenedicarboxylate **9**.

bicyclic intermediates thusly obtained are unstable, the high energy of benzyne precludes the facile retro-Diels–Alder reaction of adducts such as diester **8** in contrast to traditional adducts such as **6** (Scheme 1).

Diacid substituted norbornenes have been used to prepare amorphous-unsaturated polyester resins which afforded degradable elastomeric thermosets upon treatment with radical initiators.[17] The low solids content observed could be remedied by using Diels–Alder adducts such as 7-oxabenzonorbornadienes due to enhanced ring strain.[18] Oxabenzonorbornadienes have also been utilized as substrates in ring opening polymerization.[19] The sensitivity of those polymers to oxidation has been addressed by blocking the allylic/benzylic bridgeheads with alkyl substitutions;[20] presumably carboxy substitutions would also be quite effective while affording additional opportunity for network connectivity. The rich chemistry of 7-oxabenzonorbornadienes led to their use in developing novel polymers as aryne surrogates in the preparation of (*o*-arylenes).[21]

While 2,6-naphthalene dicarboxylic acid is considered a high performance alternative to **1**,[22] comparable polyesters derived from 1,4-naphthalene dicarboxylic acid **10** (Fig. 2) have been classified as amorphous.[23] The drastic difference in these two naphthalenedicarboxylic acids is likely due to *peri* interactions which cause the carboxy moieties to exist in non-coplanar conformations.[24] This unique attribute has been used to create integral plasticization of insoluble ridged rod polymers by creating kinks.[25] This has the effect of improving their solubility and processability;[26] notably, **10** was used to prepare an electrochromic polyamide with good solubility and great potential for use in optoelectronics applications.[27]

Diacid **10** appears prominently in hybrid organic/inorganic materials such as coordination polymers with diverse applications including chemo sensation of nitro-explosives[28] and light-triggered release of adsorbed molecules.[29] Often, **10** serves as a spacer in metal organic frameworks (MOFs) and allows for the tuning of structural properties.[30–32] Metal–organic gels (MOGs) are important for their application in catalysis,[33] gas adsorption, and as chemical sensors. Notably, **10** was used in a MOG to assiduously remove arsenic from aqueous solution; the π–π stacking of the naphthyl ring was credited as driving nanosheet genesis.[34]

Benzyne reactions with electron-rich furans have been reported in the literature[20,35–42] as have their conversion to naphthalenes by various routes. In contrast, there are only a few examples of reactions between benzyne and heavily oxidized furans.[43,44] In this work we detail for the first time the Diels–Alder reaction of **5** with benzyne and selective conversion of the adduct to either 1,4-naphthalenedicarboxylic acid **10** (Fig. 2) or its dimethyl ester **9**. Diacid **12** was also prepared by application of this strategy while diacid **11** could not be accessed due to side reactions between benzyne and the multiply olefinated oxabenzonorbornadiene.

Results and discussion

Furan-diesters (**5**, **13**, and **14**) with potential for aromatic upgrading to benzenoids were compared with the xylene precursor **15** as targets for conversion to naphthalenes (Fig. 3). The focus of this work was direct access to value added products from furandicarboxylic acids such as **4**. However, the extreme reactivity of benzyne makes side reaction with acids[45,46] problematic. We therefore required protection of those moieties. Diesters provided an excellent alternative owing to their extensive use in polytransesterification reac-

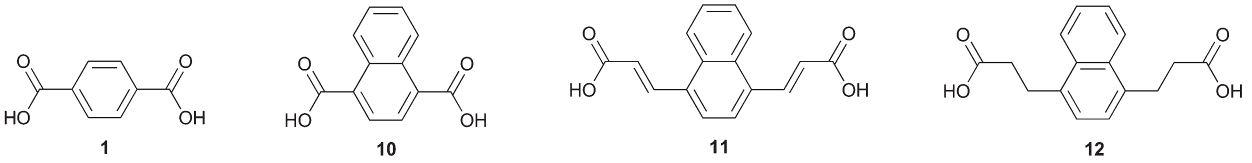


Fig. 2 Terephthalic acid and cellulose-derivable naphthalenedicarboxylic acids.

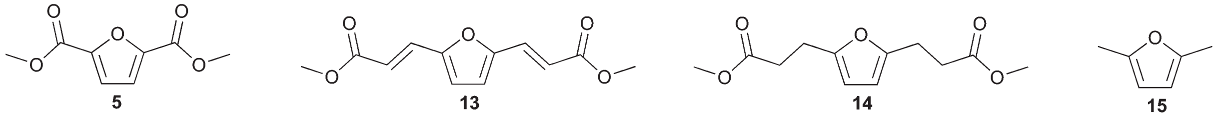


Fig. 3 Cellulose-derived furan-dienes.

tions. Diesters are also known for the ease of their purification as compared to corresponding diacids.

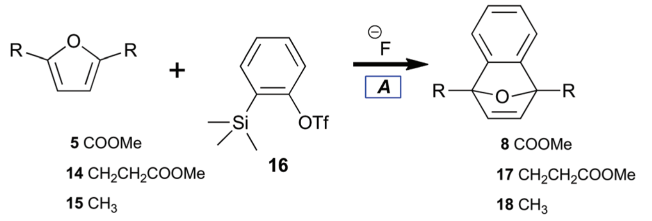
Diester **5** was prepared by esterification of crude diacid **4** with methanol; pure **5** was isolated by solid-phase extraction and recrystallization in 93% yield. Diacrylate **13** was prepared from hydroxyaldehyde **2** in three steps with an overall yield of 78%. Dipropionate **14** was prepared by selective reduction of **13** in 93% yield. Furan **15** was commercially available. Complete details of the furan syntheses with discussion of the atom economy[47] calculated for each step have been compiled in the ESI.† While atom economy is among the most preliminary of metrics,[48] it provides optimal information to guide the initial stage of process development and scale-up.

Benzyne-Diels–Alder reaction

Benzyne can been generated from various synthetic intermediates.[49] One of the most useful involves trimethylsilylphenyl-2-triflate[50,51] **16**, which undergoes fluoride-induced desilylation followed by elimination of triflate to form benzyne.[52] The desilylation protocol tightly controls solution concentrations of benzyne independent of temperature.

A preliminary investigation into the feasibility of trapping benzyne with diester **5** (electron deficient) as compared with diester **14** (electron rich) was performed (Table 1); the results indicated the relative benzyne trapping ability of dienes (**5**, **14**, and **15**) to afford 7-oxabenzonorbornadienes (**8**, **17**, and **18**). While diene **5** required refluxing in acetonitrile to achieve a reasonable conversion (Table 1, entry 1), efficient trapping by alkyl-substituted furans at room temperature was observed. No difference between the sterically more hindered **14** *versus* **15** was observed (Table 1, entries 2, 3). Overall, implementation of the desilylation protocol (Table 1) was easy and provided 7-oxabenzonorbornadienes in good yield while indicating a thermal barrier for reaction with diene **5**. Unfortunately, there are severe economic limitations to the implementation of such a procedure.

Table 1 Benzyne Diels–Alder cycloaddition: desilylation protocol



Entry	Substrate	Product	20 °C Yield[a] (%)	70 °C Yield[a] (%)
1	**5**	**8**	38	84
2	**14**	**17**	97	—
3	**15**	**18**	97	—

A Diene (1 equiv.) was dissolved in MeCN (0.04 M) and CsF (2.2 equiv.) was added to form a suspension. Benzyne precursor **16** (1.3 equiv.) was dissolved in an equal volume of MeCN and added continuously over 16 h at the specified temperature. [a] Isolated yield.

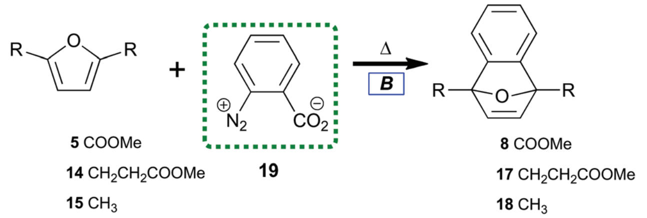
To contrast the desilylation protocol with the cheapest alternative, we examined the original method for benzyne preparation in non-basic media.[53] When first introduced, the thermolysis of benzenediazonium-2-carboxylate **19** (Table 2) provided significant advantages over the organometallic protocols prevalent in the 1960s. The study of diazotized anthranilic acids‡ greatly increased the types of benzyne which could be prepared under neutral conditions. Despite initial excitement for this protocol, recent interest in **19** as a benzyne precursor has lessened due to its established shock sensitivity when isolated.[54,55]

Importantly, a method of safely employing reactive intermediate **19** has been established on the analytical scale using flow chemistry.[56] The advent of flow technology and its proven ability to attenuate dangers associated with harsh reaction conditions/reactive intermediates while providing a linearly scalable platform for organic synthesis may lead to resurgence of aryne research based upon diazotization of anthranilic acids.

Prior to the invention of **16**'s desilylation,[52] procedures had been developed to manage hazards associated with handling of **19**. They were addition of an anthranilic acid solution to the reaction mixture at reflux[57] or partial isolation of the inner salt without allowing it to dry.[58] We chose to modify a partial isolation method[59] to juxtapose thermolysis of **19** with the desilylation of **16** for benzyne generation. This decision was motivated by consideration of the excess furan usually required for effective benzyne trapping when **19** is generated *in situ*.

Under our conditions, each diene trapped benzyne with general uniformity (Table 2). Tetraene **13** did not cleanly transform to 7-oxabenzonorbornadiene-1,4-bisacrylate. Only some adduct could be detected in the reaction along with residual starting material. Many new aromatic peaks along with new aliphatic signals were observed in ^{1}H NMR. This indicated that **13** was an effective diene but that overreaction between benzyne and olefins challenges the efficiency of this process. Furan-dienes (**5**, **14**, and **15**) smoothly transformed to 7-oxabenzonorbornadienes (**8**, **17**, and **18**). This indicated that 40 °C was sufficient to induce thermolysis while also overcoming the thermal barrier for trapping with electron-deficient dienes.

Table 2 Benzyne Diels–Alder cycloaddition: thermolysis protocol



Entry	Substrate	Product	Yield[a] (%)
1	**5**	**8**	80
2	**14**	**17**	82
3	**15**	**18**	85
4	**5**	**8**	91[b]

B Diene (1 equiv.) and benzyne precursor **19** (1.4 equiv.) were combined and diluted with DCM (0.17 M). The mixture was refluxed for 90 minutes to complete the thermolysis of **19**. [a] Isolated yield. [b] Diene (98 mmol), **19** (196 mmol), and DCM (0.17 M) were combined and refluxed (90 min).

Further experiments detailed in the ESI† explored the role of initial stoichiometric ratios between **19** and diene; the results showed approximately 60% of benzyne generated by our thermolysis method was trapped by the furans studied. Twofold excess of **19** led to yields above 90% of 7-oxabenzonorbornadienes **8** and **17**. Even at that super stoichiometry, some **5** was recovered (6%). The reaction of **5** was safely scaled up to 98 mmol and resulted in 91% isolated yield of **8** as a low-melting crystalline solid (Table 2, entry 4).

Notably, use of excess **19** led to a decreased yield of **18**. This result finally differentiated the dialkylfuran substrates by their steric qualities and indicated at least one degradation pathway which disproportionately predated upon sterically vulnerable 7-oxabenzonorbornadienes. Additional degradation of Diels–Alder adducts was observed when reactions were not protected from oxygen and residual nitrites; the nitrogen dioxide-catalyzed epoxidation[60] of 7-oxabenzonorbornadienes on the bench has not otherwise been reported.

Diels–Alder reactions have inherent potential for perfect atom economy by incorporation of all atoms from the diene and dienophile into an adduct. However, since benzyne must be generated *in situ* from a precursor such as **16** or **19**, there will be some discarded atoms. These two methods were compared with emphasis on assessing their respective atom economy, nature of side products, and intensity of preparation.

In this preliminary evaluation, we have calculated the atom economy for both Diels–Alder methods as applied to furan **5** since it embodies the direct-access strategy (see ESI† for details). For desilylation, an atom economy of 33% describes the synthesis of **8** as compared with 66% when the thermolysis protocol was employed. There is significantly greater efficiency potential for the thermolysis approach; when the nature of the side products is considered, nitrogen and carbon dioxide would clearly be preferable to trimethylsilyl fluoride and cesium triflate as environmental waste. Preparation of **16** from readily available starting materials is more intensive than preparation of **19**. However, the shock sensitivity of **19** requires extreme care and precautions for its safe handling. Halogenated solvents provide a superior reaction medium for the selective conversion of **19** to benzyne.[61] This additional environmental limitation to the thermolysis approach was neglected by calculation of atom economy.

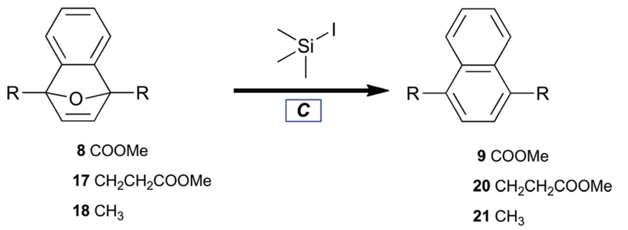
Since isolation of the shock-sensitive **19** is diametrically opposed to the principles of green chemistry, the many advantages of this otherwise benign technology are inversely proportional to **19**'s isolation. For the sake of reducing the process intensity while limiting exposure to hazards associated with **19**, we combined the partially-isolated inner salt with furans (**5**, and **14**) and allowed the thermolysis to proceed at 40 °C (Table 2). In attempts to further limit handling, the diazotization of anthranilic acid to afford **19** was kept constant. When the slurry was used without partial isolation, predictably inferior yields were observed. Commensurate yields to the partial isolation procedure were obtained by addition of the raw diazotization mixture—in small aliquots—to the refluxing furan (**14**) solution! Thus, the hazard associated with **19** can be circumvented by engineering a delivery system which only prepares small quantities of reactive intermediate immediately prior to thermolysis.

Reductive aromatization

With benzyne–Diels–Alder viability established, adducts (**8**, **17**, and **18**) were treated with trimethylsilyl iodide to afford naphthalenes (**9**, **20**, and **21**) by deoxyaromatization (Table 3).[62] Electron-deficient **8** required elevated reaction temperature to undergo deoxygenation (Table 3, entry 1), whereas alkyl-substituted 7-oxabenzonorbornadienes (**17** and **18**) readily aromatized at ambient temperature (Table 3, entries 2 and 3).

The novelty of bicycle **8** lies not only in its preparation but also in its resistance to ring opening. The stabilizing influence of electron-withdrawing groups at both bridgehead positions may be rationalized by considering the relative stabilities of

Table 3 Deoxyaromatization of 7-oxabenzonorbornadienes



Entry	Substrate	Product	20 °C yield[a] (%)	70 °C yield[a] (%)
1	**8**	**9**	0	25
2	**17**	**20**	98	—
3	**18**	**21**	92[b]	—

C 7-Oxabenzonorbornadiene (1 equiv.) was dissolved in MeCN (0.01 M); NaI (5 equiv.) and TMSCl (5 equiv.) were added. The reaction proceeded at the specified temperature for 16 h. [a] Isolated yield. [b] Conditions of the aromatization were varied: NaI (3 equiv.), TMSCl (3 equiv.), MeCN (0.15 M).

the tertiary-allylic-benzylic carbenium intermediates developed by spontaneous ring opening. The action of trimethylsilyl iodide likely entails the initial formation of a silyloxonium intermediate. Formation of that intermediate should be irreversible under these conditions due to the comparative bond strengths of Si–O *versus* Si–I.

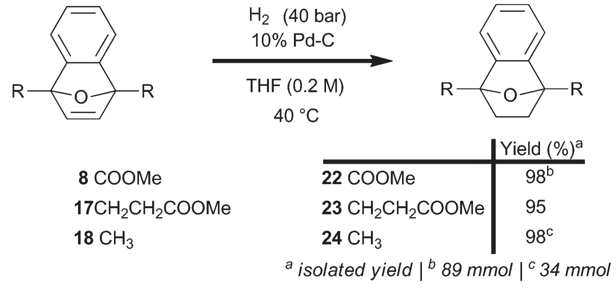
To probe the observed stability of bicycle **8**, its robust diethyl ester homolog was prepared and subjected to aggressive alkaline hydrolysis. The diester was treated with potassium hydroxide in boiling hot methanol, then neutralized with concentrated hydrochloric acid on ice. The major product was 7-oxabenzonorbornadiene-1,4-dicarboxylic acid (33% yield).

An aromatization strategy that selectively targets reduction apart from the ring-opening reaction offers potential to maximize the efficiency of the overall transformation. The olefin-reactivity of 7-oxabenzonorbornadienes (**8**, **17**, and **18**) is independent of substitution at the bridgehead, as evidenced by uniformly efficient catalytic hydrogenations using a flow system (Scheme 2); the hydrogenations also proceeded well under batch conditions and required very little Pd catalyst to convert smoothly (ESI†). Two fringe benefits were observed in the preparation of 7-oxabenzonorbornene diesters (**22** and **23**): improved processability and stability.

The diesters were crystalline solids with elevated melting points compared to 7-oxabenzonorbornadienes (**8**, and **17**), and hydrogenation blocked many degradation pathways by removing the reactive olefin. Diesters **22** and **23** were bench stable for over three months with no observable change in appearance or spectrum; liquid 7-oxabenzonorbornene **24** did slowly yellow over time.

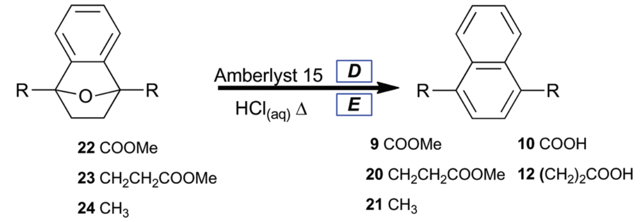
A selective method for dehydrating 7-oxabenzonorbornenes (**22**, **23** and **24**) to naphthalenes (**9**, **20**, and **21**) was sought (Table 4, Method 1). Amberlyst 15 was chosen as a reusable and highly active acid catalyst for dehydration reactions under nonaqueous conditions. Prevention of ester hydrolysis was a primary concern.

As expected, 7-oxabenzonorbornene **22** converted to dimethyl naphthalene-1,4-dicarboxylate **9** in low yield (Table 4, entry 1) under conditions which completely converted alkyl-substituted 7-oxabenzonorbornenes (**23** and **24**) to naphthalenes (**20** and **21**) in high yield (Table 4, entries 2 and 3). This comparison signifies that the enhanced stability of oxanorbornadiene **8** was conserved in oxanorbornene **22**, which implies that these novel oxygen-bridged bicycles may lead to the development of new classes of biomass-derived polymers. It also clearly shows that catalytic processes can replace stoichiometric reagents in the aromatization of furan-derived [2.2.1] oxygen-bridged bicycles, which affords significant improvement to the atom economy of the overall approach.



Scheme 2 Flow hydrogenation of 7-oxabenzonorbornadienes.

Table 4 Dehydroaromatization of 7-oxabenzonorbornadienes



Entry	Substrate	Product	Yield^a (%)
D = Method 1			
1	**22**	**9**	17
2	**23**	**20**	97
3	**24**	**21**	97
E = Method 2			
4	**22**	**10**	91
5	**23**	**12**	72
6	**24**	**21**	84

D 7-Oxabenzonorborn*e*ne (1 equiv.) was taken up in DCE (0.3 M), the solution was charged with Amberlyst 15 (15 mol%) and refluxed for 90 minutes. **E** 7-Oxabenzonorbornene (1 equiv.) was suspended in concentrated HCl (0.17 M), then heated to 100 °C for 2.2 h. ^{a} Isolated yield.

For the deoxyaromatization of **8**, an atom economy of only 16% was calculated owing to the use of a super-stoichiometric ring-opening/reducing agent. Even the combination of atom economies from catalytic hydrogenation (100%) and catalytic dehydration (93%) in the case of **8** to **22** to **9** shows more promise for development into an efficient and benign technology. Substituting toluene as the reaction solvent while increasing the reaction time to 12 h afforded diester **9** in 74% isolated yield along with diacid **10** in 15% isolated yield as a side product.

To afford naphthalenedicarboxylic acids directly, 7-oxabenzonorbornenes (**22** and **23**) were treated with concentrated hydrochloric acid at 100 °C (Table 4, Method 2). This led to the isolation of hydrolyzed naphthalenes (**10**, and **12**) with good yields by suction filtration (Table 4, entries 4, and 5). Naphthalenedicarboxylic acid **12** was isolated in lower yield under the unoptimized conditions, likely due to its greater water solubility. Naphthalene **21** was prepared from **24** and isolated by extraction (Table 4, entry 6).

Since the acid is only required catalytically, atom economy was only slightly lowered to 83% for **10** under these conditions due to the loss of methanol. Owing to the stabilizing influence of the carboxylate moieties at C1 and C4, we surmised that lowering the acid concentration could selectively hydrolyze the ester groups while leaving the strained [2.2.1] bicycle intact.

Obstinate bicycle **22** was treated with 1 M HCl at elevated temperature, and the major component of the isolate was a partial hydrolysis product with an intact oxygen-bridge: 7-oxabenzonorbornyl-1,4-dicarboxylic acid (~50%). The same conditions afforded dialkylnaphthalene **21** with complete conversion and 82% isolated yield.

Conclusions

Renewable terephthalic acid analog 2,5-furandicarboxylic acid was valorized by efficient diversification (≥80% yield) into several novel bicyclic compounds which may find use in the field of sustainable material science. Those bicycles were further valorized by conversion to naphthalene diacids (≥70%) which are currently derived solely from petroleum and which have been used extensively in the field of coordination polymers.

This is the first report describing the challenging direct conversion of dimethyl 2,5-furandicarboxylate into a cycloadduct. Two methods for generating the reactive intermediate, benzyne, were investigated. Anthranilic acid[§] was favored as a benzyne precursor to prepare 7-oxabenzonorbornadienes (**8** and **17** of Table 2) in ~80% yield, and catalytic hydrogenation afforded stable 7-oxabenzonorbornenes (**22** and **23** of Scheme 2) in >95% yield. Hydrochloric acid mediated hydrolytic-dehydration provided the most atom economical route for preparing naphthalenedicarboxylic acids (**10** and **12** of Fig. 2) from oxobridged-bicyclic diesters in good yield (91% and 72% yield respectively).

The atom economy of each step has been compared to assess the potential of a direct-access strategy for developing sustainable chemistries derived from renewable terephthalic acid analogs. Efforts to further quantify and improve the sustainability of this technology while exploring the novel chemistry of these new derivatives of cellulose biorefinery are currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the National Science Foundation (grants IIA-1330840 and IIA-1355466) for financial support. EMS thanks ND-EPSCoR for a doctoral dissertation award.

Notes and references

[‡] Anthranilic acid is predominantly prepared industrially from phthalic anhydride. Thus, benzyne prepared from **19** could be made by renewable routes in the future.

1 R. A. Sheldon, *Green Chem.*, 2014, **16**, 950–963.
2 D. I. Collias, A. M. Harris, V. Nagpal, I. W. Cottrell and M. W. Schultheis, *Ind. Biotechnol.*, 2014, **10**, 91–105.
3 J. Pang, M. Zheng, R. Sun, A. Wang, X. Wang and T. Zhang, *Green Chem.*, 2016, **18**, 342–359.
4 D. S. van Es, *J. Renewable Mater.*, 2013, **1**, 61–72.
5 E. Wenkert, P. D. R. Moeller and S. R. Piettre, *J. Am. Chem. Soc.*, 1988, **110**, 7188–7194.
6 M. Shiramizu and F. D. Toste, *Chem. – Eur. J.*, 2011, **17**, 12452–12457.
7 E. Mahmoud, D. A. Watson and R. F. Lobo, *Green Chem.*, 2014, **16**, 167–175.
8 J. J. Pacheco and M. E. Davis, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 8363–8367.
9 J. J. Pacheco, J. A. Labinger, A. L. Sessions and M. E. Davis, *ACS Catal.*, 2015, **5**, 5904–5913.
10 Y. Tachibana, S. Kimura and K.-I. Kasuya, *Sci. Rep.*, 2015, **5**, 8249.
11 S. Thiyagarajan, H. C. Genuino, M. Śliwa, J. C. van der Waal, E. de Jong, J. van Haveren, B. M. Weckhuysen, P. C. A. Bruijnincx and D. S. van Es, *ChemSusChem*, 2015, **8**, 3052–3056.
12 A. F. Sousa, C. Vilela, A. C. Fonseca, M. Matos, C. S. R. Freire, G.-J. M. Gruter, J. F. J. Coelho and A. J. D. Silvestre, *Polym. Chem.*, 2015, **6**, 5961–5983.
13 C. L. Williams, C.-C. Chang, P. Do, N. Nikbin, S. Caratzoulas, D. G. Vlachos, R. F. Lobo, W. Fan and P. J. Dauenhauer, *ACS Catal.*, 2012, **2**, 935–939.
14 Y. P. Wijaya, D. J. Suh and J. Jae, *Catal. Commun.*, 2015, **70**, 12–16.
15 C. L. Williams, K. P. Vinter, C.-C. Chang, R. Xiong, S. K. Green, S. I. Sandler, D. G. Vlachos, W. Fan and P. J. Dauenhauer, *Catal. Sci. Technol.*, 2016, **6**, 178–187.
16 N. G. Rondan, L. N. Domelsmith, K. N. Houk, A. T. Bowne and R. H. Levin, *Tetrahedron Lett.*, 1979, **20**, 3237–3240.
17 A. H. Brown and V. V. Sheares, *Macromolecules*, 2007, **40**, 4848–4853.
18 J. Howell, J. D. Goddard and W. Tam, *Tetrahedron*, 2009, **65**, 4562–4568.
19 W. P. Forrest, J. G. Weis, J. M. John, J. C. Axtell, J. H. Simpson, T. M. Swager and R. R. Schrock, *J. Am. Chem. Soc.*, 2014, **136**, 10910–10913.
20 J. M. Medina, J. H. Ko, H. D. Maynard and N. K. Garg, *Macromolecules*, 2017, **50**, 580–586.
21 S. Ito, K. Takahashi and K. Nozaki, *J. Am. Chem. Soc.*, 2014, **136**, 7547–7550.
22 A. R. Elman, *Catal. Ind.*, 2009, **1**, 184.
23 C. P. Roupakias, G. Z. Papageorgiou and G. P. Karayannidis, *J. Macromol. Sci., Pure Appl. Chem.*, 2003, **40**, 791–805.
24 V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567–641.
25 H. Al-Adwani, A. Bishara and H. Shaban, *J. Appl. Polym. Sci.*, 2003, **89**, 1808–1817.
26 H.-H. Wang and W.-P. Lin, *J. Appl. Polym. Sci.*, 1997, **65**, 1581–1593.
27 S.-H. Hsiao, G.-S. Liou, Y.-C. Kung and H.-J. Yen, *Macromolecules*, 2008, **41**, 2800–2808.

28 Z.-F. Wu, L.-K. Gong and X.-Y. Huang, *Inorg. Chem.*, 2017, **56**, 7397–7403.

29 K. Khaletskaya, J. Reboul, M. Meilikhov, M. Nakahama, S. Diring, M. Tsujimoto, S. Isoda, F. Kim, K.-I. Kamei, R. A. Fischer, S. Kitagawa and S. Furukawa, *J. Am. Chem. Soc.*, 2013, **135**, 10998–11005.

30 Y.-L. Liu, P. Liu, K.-B. Li, C.-S. Zhou and K.-F. Yue, *J. Mol. Struct.*, 2017, **1147**, 192–196.

31 T. Tsuruoka, K. Mantani, A. Miyanaga, T. Matsuyama, T. Ohhashi, Y. Takashima and K. Akamatsu, *Langmuir*, 2016, **32**, 6068–6073.

32 Y. Lou, J. Wang, Y. Tao, J. Chen, A. Mishima and M. Ohba, *Dalton Trans.*, 2014, **43**, 8508–8514.

33 M. Tian, X. Cui, M. Yuan, J. Yang, J. Ma and Z. Dong, *Green Chem.*, 2017, **19**, 1548–1554.

34 J. Sui, L. Wang, W. Zhao and J. Hao, *J. Chem. Soc., Chem. Commun.*, 2016, **52**, 6993–6996.

35 J. Haner, K. Jack, M. L. Menard, J. Howell, J. Nagireddy, M. A. Raheem and W. Tam, *Synthesis*, 2012, 2713–2722.

36 E. Carlson, J. Haner, M. McKee and W. Tam, *Org. Lett.*, 2014, **16**, 1776–1779.

37 M. McKee, J. Haner, E. Carlson and W. Tam, *Synthesis*, 2014, 1518–1524.

38 A. Tigchelaar, J. Haner, E. Carlson and W. Tam, *Synlett*, 2014, 2355–2359.

39 W. Yang, R. Luo and D. Yang, *Molecules*, 2015, **20**, 19748.

40 E. Carlson, G. Duret, N. Blanchard and W. Tam, *Synth. Commun.*, 2016, **46**, 55–62.

41 C. C. J. Loh, M. Schmid, R. Webster, A. Yen, S. K. Yazdi, P. T. Franke and M. Lautens, *Angew. Chem., Int. Ed.*, 2016, **55**, 10074–10078.

42 A. Yen, K.-L. Choo, S. K. Yazdi, P. T. Franke, R. Webster, I. Franzoni, C. C. J. Loh, A. I. Poblador-Bahamonde and M. Lautens, *Angew. Chem., Int. Ed.*, 2017, **56**, 6307–6311.

43 M. S. Newman and J. A. Cella, *J. Org. Chem.*, 1973, **38**, 3482–3484.

44 S. Sato, T. Kawada, H. Takikawa and K. Suzuki, *Synlett*, 2017, 1719–1723.

45 Z. Liu and R. C. Larock, *J. Org. Chem.*, 2006, **71**, 3198–3209.

46 M. Stiles, R. G. Miller and U. Burckhardt, *J. Am. Chem. Soc.*, 1963, **85**, 1792–1797.

47 B. M. Trost, *Science*, 1991, **254**, 1471–1477.

48 F. Roschangar, R. A. Sheldon and C. H. Senanayake, *Green Chem.*, 2015, **17**, 752–768.

49 T. Kitamura, *Aust. J. Chem.*, 2010, **63**, 987–1001.

50 S. M. Bronner and N. K. Garg, *J. Org. Chem.*, 2009, **74**, 8842–8843.

51 D. J. Atkinson, J. Sperry and M. A. Brimble, *Synthesis*, 2010, 911–913.

52 Y. Himeshima, T. Sonoda and H. Kobayashi, *Chem. Lett.*, 1983, **12**, 1211–1214.

53 M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, 1960, **82**, 3802–3802.

54 T. F. Mich, E. J. Nienhouse, T. E. Farino and J. J. Tufariello, *J. Chem. Educ.*, 1968, **45**, 272.

55 J. M. Sullivan, *J. Chem. Educ.*, 1971, **48**, 419.

56 D. L. Browne, S. Wright, B. J. Deadman, S. Dunnage, I. R. Baxendale, R. M. Turner and S. V. Ley, *Rapid Commun. Mass Spectrom.*, 2012, **26**, 1999–2010.

57 L. Friedman and F. M. Logullo, *J. Org. Chem.*, 1969, **34**, 3089–3092.

58 F. M. Logullo, A. H. Seitz and L. Friedman, *Org. Synth.*, 1968, **48**, 12.

59 L. Friedman and D. F. Lindow, *J. Am. Chem. Soc.*, 1968, **90**, 2329–2333.

60 E. Bosch and J. K. Kochi, *J. Am. Chem. Soc.*, 1996, **118**, 1319–1329.

61 C. P. Buxton, M. Fensome, H. Heaney and K. G. Mason, *Tetrahedron*, 1995, **51**, 2959–2968.

62 K. Y. Jung and M. Koreeda, *J. Org. Chem.*, 1989, **54**, 5667–5675.