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Computational and Synthetic Studies with Tetravinylethylenes

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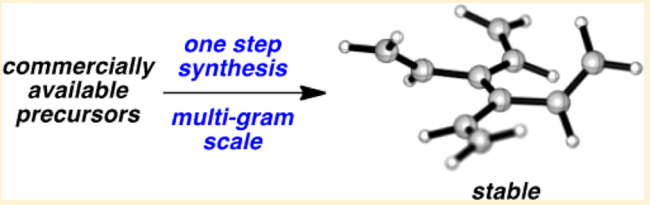
Supporting Information

ABSTRACT: Computational and experimental studies offer fresh insights into the neglected tetravinylethylene class of compounds. Both the structures and the outcomes of exploratory reactions of the parent hydrocarbon are predicted and explained in detail through high-level composite ab initio MO G4(MP2) computational studies.

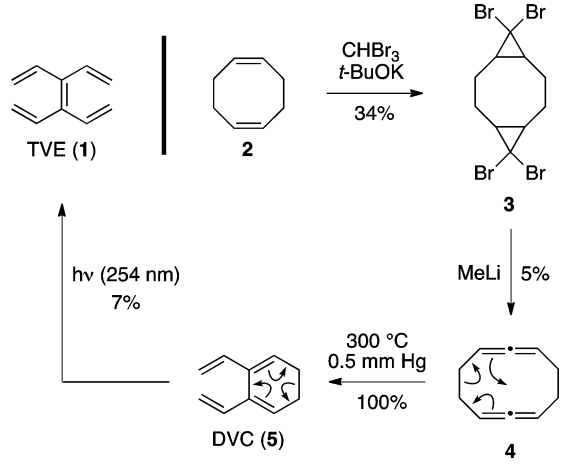


INTRODUCTION

Herein we predict and chart the physical and chemical properties of tetravinylethylene (TVE, **1**, Scheme 1) and analogues through a combined synthetic and computational approach. TVE is the smallest symmetrical oligo-olefinic structure comprising both through-conjugation (an unbranched 1,3,5-hexatriene unit) and cross-conjugation (a branched 3-alkylidene-1,4-pentadiene).

TVE was first synthesized in 1966 by Skattebøl and co-workers.[1] The synthesis commenced with the double dibromocarbene addition to cycloocta-1,5-diene (**2**) to form bis-dibromocyclopropanation product **3**. A double Doering–LaFlamme allene synthesis produced the diallene **4** in 5% yield.[2] A [3,3]-sigmatropic rearrangement, brought about by vacuum pyrolysis, gave 2,3-divinyl-1,3-cyclohexadiene (DVC, **5**) in quantitative yield. Irradiation of **5** at 254 nm resulted in the formation of **1**, by way of 6π-electrocyclic ring opening, as a mixture with precursor **5** and polymeric material. TVE (**1**) was isolated in 7% yield by gas–liquid chromatography.

Scheme 1. Skattebøl Synthesis of TVE (1)



Skattebøl's ingenious synthesis of TVE is a milestone in hydrocarbon chemistry and is the only reported synthesis of this fundamental hydrocarbon. The synthesis commences with 1,5-cyclooctadiene and generates TVE in four steps in an overall yield of 0.1%.[3]

In addition to the parent TVE, only four *substituted* tetravinylethylenes have been reported thus far (Figure 1). Dodecachloro-TVE **6** was the first to be reported in 1948,[4] octaphenyl-TVE **7** in the early 1960s,[5,6] tetracarboethoxy-TVE **8** in 1980,[7] and octamethyl-TVE **9** in 1989.[8] Only the McMurry coupling approach to octamethyl-TVE **9** can be classed as a practical synthesis.

Our computational and experimental studies with the related dendralenes[9] served as the foundation to a direct general

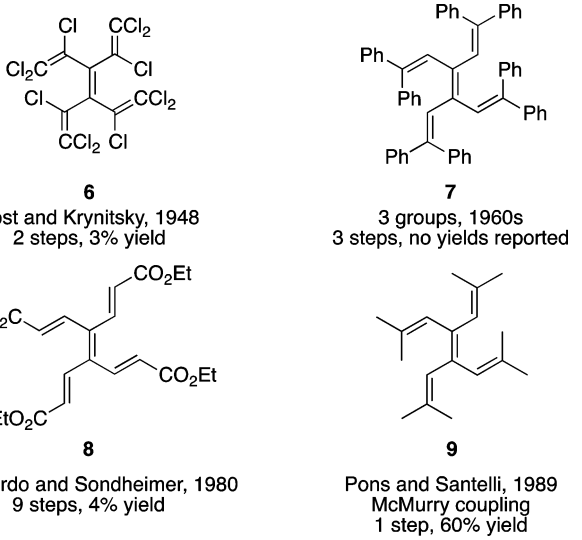


Figure 1. Only substituted tetravinylethylenes reported in the literature.

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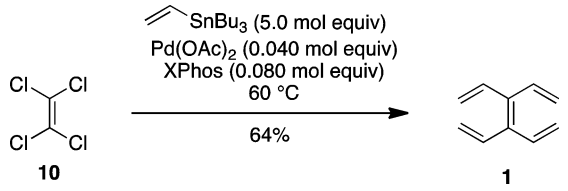
synthesis of the TVE family. Thus, we recently disclosed the first 4-fold cross-coupling reaction involving olefinic precursors and applied this method to the one-step synthesis of tetravinylethylene on a multigram scale (Scheme 2).[10] Whereas many of its close structural relatives are unstable when neat at ambient temperature, tetravinylethylene is a remarkably robust, bench-stable compound.

Scheme 2. Synthesis of TVE (1) by Four-Fold Cross-Coupling

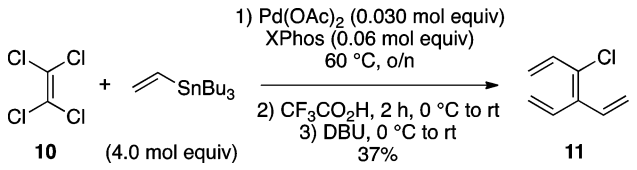


Herein we disclose the results of detailed experimental and computational investigations with TVE and related structures.

RESULTS AND DISCUSSION

Our efforts to bring about selective—instead of exhaustive—cross-couplings have met with limited success. Poor selectivity was encountered during attempts to achieve selective single and 2-fold couplings with tetrachloroethylene **10**. Gratifyingly, the 3-fold coupling product **11** can, however, be accessed (Scheme 3). A mixture of **11** and TVE **1** is isolated as the crude product; selective decomposition of **1** on exposure to trifluoroacetic acid leaves chlorotetraene **11** in pure form.

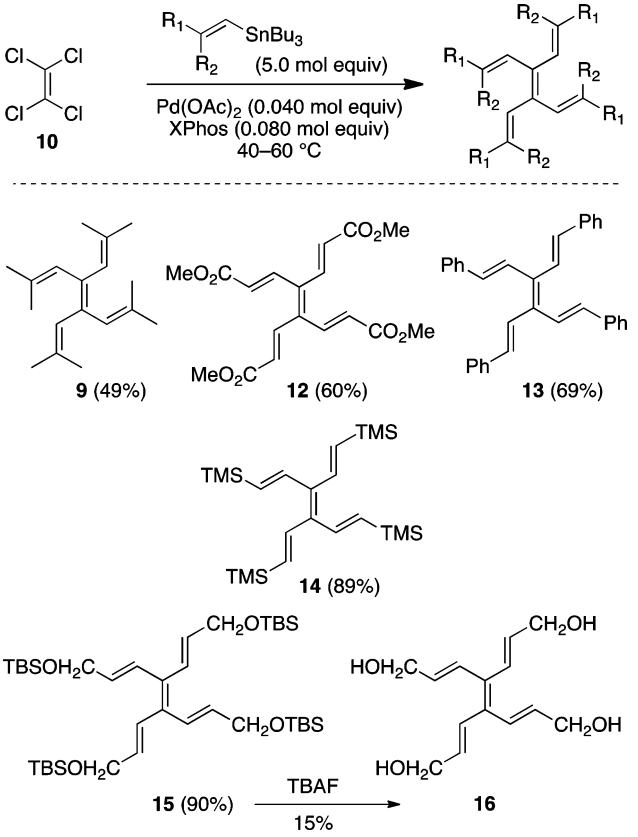
Scheme 3. Three-Fold Cross-Coupling Involving 10



In contrast to the limited success in attempts to perform *non*exhaustive couplings, the 4-fold Stille coupling depicted in Scheme 1 is one of useful scope. Thus, substituted alkenylstannanes react with tetrachloroethylene to give substituted TVEs **9**, **12**, **13**, **14**, and **15** (Scheme 4). Substitution at the α-carbon leads to more sluggish reactions, which we have thus far been unable to drive to completion without increased temperature and significant loss of material.[11] Tetrol **16** was formed by deprotection of the corresponding silyl ether.[12]

Three of these substituted TVEs, namely **13**, **14**, and **16**, gave crystals suitable for single-crystal X-ray analysis (Figure 2). None of the molecular structures from X-ray analysis showed fully planar TVE units. All three crystal structures do contain an (*E,E*)-1,3,5-hexatriene group that is *principally* in plane (dihedral angles within ca. 20°), however, presumably for conjugative stabilization reasons. Similar conformations of the TVE unit are seen in the crystal structures of tetraphenyl TVE **13** (namely ***cttt*-13**) and tetratrimethylsilyl TVE **14** (***cttt*-14**), in which one of the four 1,3-butadiene groups is *cisoid* whereas the other three are *transoid*.[13] Conversely, the crystal structure of tetrahydroxymethyl TVE **16**, ***tttt*-16**, exhibits a conformation in which all four 1,3-butadiene groups are *transoid*. Any deeper

Scheme 4. Substituted TVEs Prepared by 4-Fold Cross-Coupling



analysis of the significance of these X-ray crystal structures is undermined by the likelihood of contributions from both substituents and crystal packing forces.

We performed computational studies to identify the lowest energy conformations of the parent, *unsubstituted* TVE (**1**). Throughout this study, the accurate composite ab initio MO G4(MP2) method was used. Thus, a series of CCSD(T), MP2, and HF calculations were performed on B3LYP/6-31G(2df,p) equilibrium geometries.[14] All calculations were performed using the Gaussian 09 program[15] and refer to the gas phase, and activation parameters were generally calculated at 298.15 K. Ten conformers of TVE were located, the relative enthalpies of which spanned 45 kJ/mol, although the four most stable ones spanned only 8 kJ/mol. The geometries and relative energies of these four conformers, which differ from the conformations of the substituted TVEs seen in the X-ray crystal structures, are presented in Figure 3.

The four vinyl substituents of TVE (**1**) experience steric congestion, which results in two or more vinyl groups being twisted out of coplanarity with the central double bond, thereby attenuating conjugative stabilization. The two most stable conformers of the parent TVE (**1**) are predicted to be ***ctcta*-1** and ***ctct*-1**, both of which possess a central (*E*)-1,3,5-hexatriene spine and differ in the disposition of the remaining pair of vinyl substituents with respect to the plane of the hexatriene moiety, being on the same side of this plane in the case of ***ctcta*-1** and on opposite sides in the case of ***ctct*-1**. In ***ctcta*-1**, which possesses C_2 symmetry, these two vinyl groups are *gauche* with respect to the central double bond, each of which makes a dihedral angle of 47° with the central double bond. The magnitude of this angle is larger than the G4(MP2) value of

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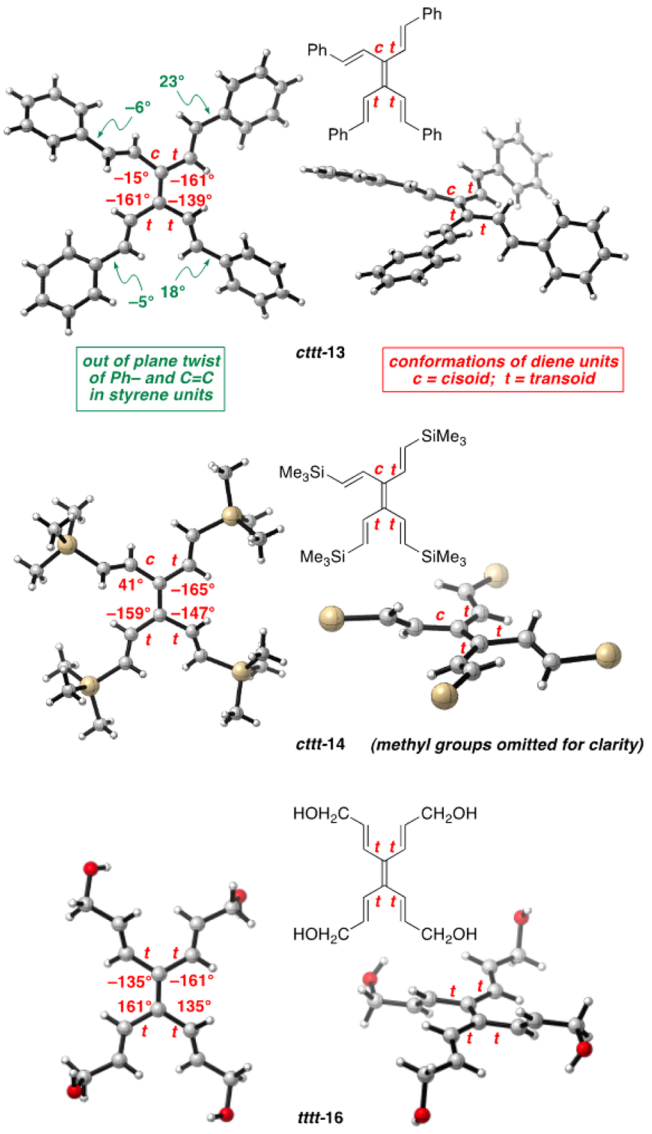

Figure 2. Molecular structures from single-crystal X-ray analyses of substituted TVEs **13** (***cttt*-13**, top), **14** (***cttt*-14**, center), and **16** (***tttt*-16**, bottom). In each case, the approximated stick representation is depicted above the molecular structures, with a plan view of the molecular structure on the left and a side view on the right.

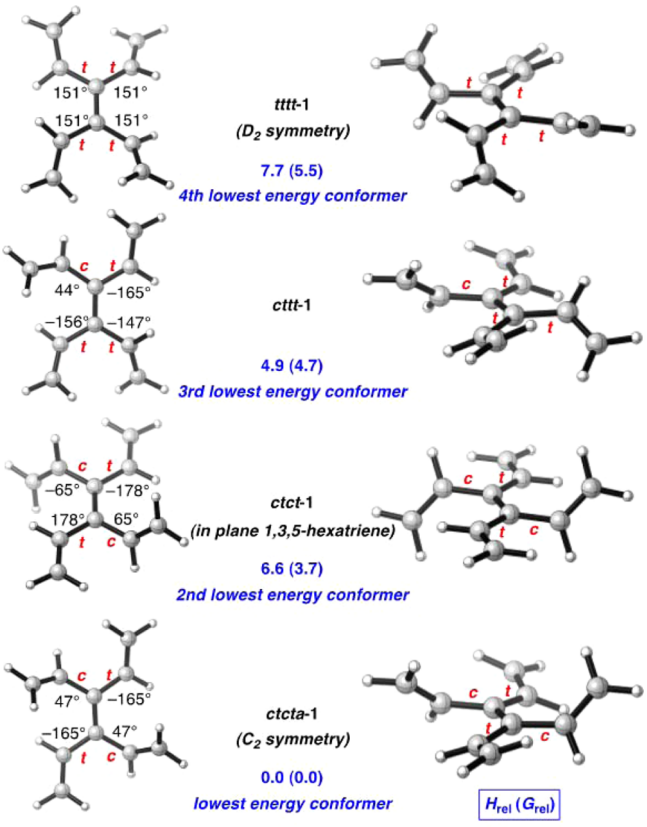

Figure 3. G4(MP2) geometries and relative enthalpies and free energies (kJ/mol) of the four most stable conformers of TVE (**1**), namely ***ctcta*-1** (bottom), ***ctct*-1**, ***cttt*-1**, and ***tttt*-1** (top).

31° calculated for *gauche* 1,3-butadiene and is the consequence of unfavorable steric interactions with the terminal vinyl groups of the hexatriene unit. Indeed, such interactions account for the finding that the hexatriene group is not planar, with the terminal vinyl groups each making a dihedral angle of −165° with the central double bond. In contrast to ***ctcta*-1**, the hexatriene unit in ***ctct*-1** is nearly planar, with the two terminal vinyl groups of the unit making dihedral angles of 178° and −178° with the central ethylene group, and this is due to the fact that the two remaining vinyl groups, which point in opposite directions from the plane of the hexatriene group, exert equal but opposite forces on the terminal vinyl groups of the hexatriene unit. Thus, in this case, adverse steric forces can only be ameliorated by increasing the dihedral angles between the 3- and 4-vinyl groups and the central double bond, relative to those predicted (47°) for ***ctcta*-1**. In fact, these dihedral angles for ***ctct*-1** are calculated to be 65° and −65°. The dihedral angle made by the four vinyl groups with respect to the central ethylene unit in ***cttt*-1** are −156°, −147°, −165°, and 44°. The least stable of these four TVE conformers is ***tttt*-1**. This conformer is predicted to possess D_2 symmetry in which each vinyl group makes a 151° dihedral angle with the central ethylene group. This structure may be obtained from the planar D_{2h} structure by performing 39° conrotatory operations on the two pairs of *vicinal*-vinyl groups.

In the laboratory, and consistent with Skattebøl's observations, TVE (**1**) undergoes 6π-electrocyclization to generate 3,4-divinyl-1,3-cyclohexadiene (DVC, **5**) under thermal and photochemical conditions (Scheme 5). In relatively high dilution solutions (10 mM), the thermal (120 °C) reaction proceeds in quantitative yield, as judged by ^{1}H NMR spectroscopy. At higher concentrations, DVC (**5**) oligomerizes, rendering the heat-promoted electrocyclization impractical. We therefore advocate photochemical promotion[16] at ambient temperature, which allows the preparation of solutions of DVC **5** of up to 0.2 M concentration.

The DVC structure **5** can be generated by linking the central olefins of [4]dendralene **18**[17] with a $-CH_2CH_2-$ tether. DVC is, therefore, a substituted [4]dendralene. The parent [4]-dendralene (**18**) is the most stable member of the unsubstituted [*n*]dendralene family, showing no sign of decomposition when stored neat at room temperature.[9,17] Despite its structural similarity, DVC (**5**) exhibits markedly different behavior, decomposing rapidly at ambient temperature when neat. We find that DVC (**5**) is best handled as a solution, and we prefer to generate the hydrocarbon in situ and use it directly.

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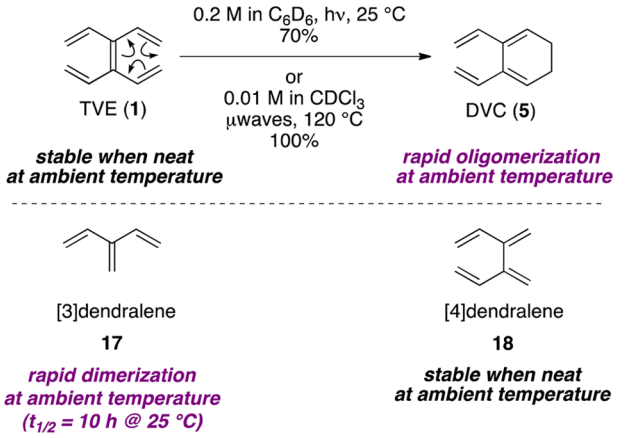
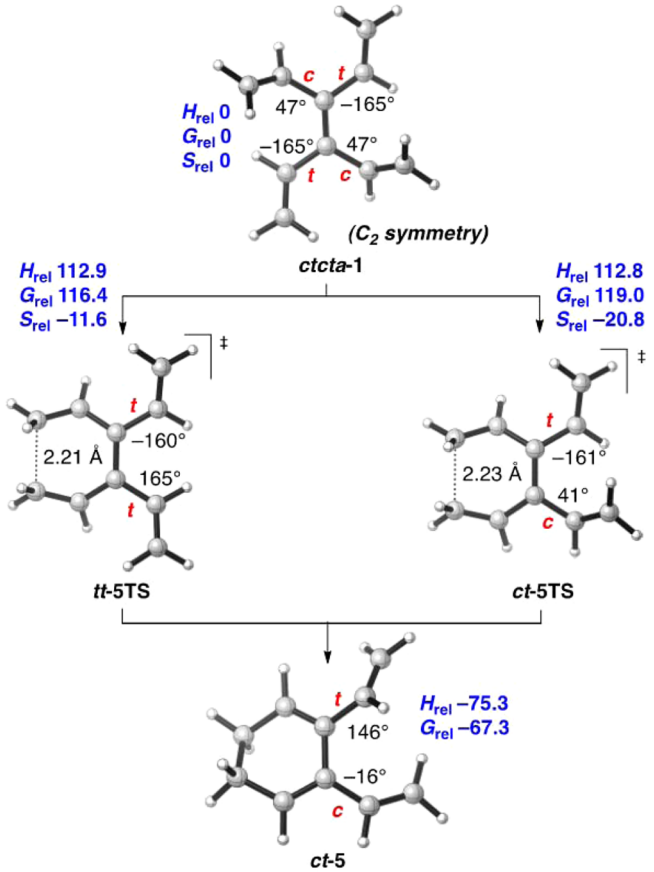
Scheme 5. Electrocyclization of TVE (1) into DVC (5) and Stability Comparisons with [3]Dendralene and [4]Dendralene



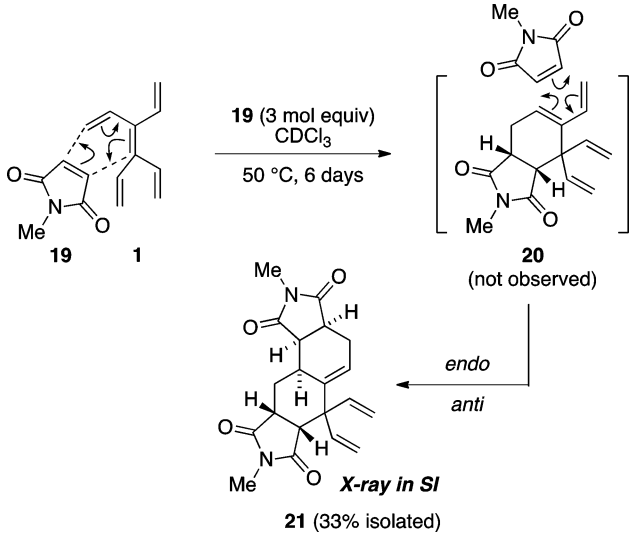
Two transition structures (TSs) for the thermal, disrotatory 6π-electrocyclic ring closure of TVE (**1**) were located, and they differ only in the conformations adopted by the pair of spectator vinyl groups (Scheme 6). Although, at 298.15 K, both TSs ***ct*-5TS** and ***tt*-5TS** are isoenthalpic, the free energy of the latter is 2.6 kJ/mol lower than that of the former TS. The activation enthalpy, $\Delta H^{\ddagger}$, and activation free energy, $\Delta G^{\ddagger}$, for the reaction are 112.9 and 116.4 kJ/mol, respectively. Using G4(MP2), we calculated $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ for the disrotatory electrocyclization of the parent (*Z*)-1,3,5-hexatriene to be 123.4 and 130.4 kJ/mol, respectively. Hence, the two spectator vinyl groups stabilize the TS for the electrocyclization of TVE by about 10 kJ/mol, compared to the parent hexatriene.

Scheme 6. G4(MP2) Geometries, Relative Enthalpies, Free Energies (kJ/mol), and Entropies [J/(mol·K)] of Reactant *ctcta*-1 (Top), Most Stable TSs *tt*-5TS and *ct*-5TS (Middle), and Product *ct*-5 (Bottom) for the Disrotatory 6π-Electrocyclic Reaction of TVE (1)



[3]Dendralene, the simplest cross-conjugated triene, is also the least stable of the parent dendralenes, undergoing Diels–Alder (DA) dimerization cleanly at ambient temperature with a half-life of around 10 h at 25 °C (Scheme 5).[18] It seems reasonable to expect that TVE (**1**), which can be thought of as two [3]dendralenes conjoined at the central alkene, would be similarly unstable. This is not the case: we routinely store TVE (**1**) neat at room temperature and witness no decomposition over several weeks. Evidently, the additional two vinyl groups serve as a strong steric impediment toward adoption of the TS for DA dimerization. Without access to this mode of decomposition, TVE is perfectly stable. [3]Dendralenes substituted at the central methylene carbon exhibit a similar enhanced stability toward DA dimerization.[19] Nevertheless, these substituted [3]dendralenes are active participants in DA reactions with electron-poor dienophiles, and TVE is no exception. As predicted computationally (vide infra), TVE reacts directly in a DA cycloaddition with *N*-methylmaleimide (NMM, **19**, Scheme 7). A reaction temperature of less than 60 °C was maintained to minimize[20] the heat-promoted TVE 6π-electrocyclization. The *single* DA adduct **20** was not isolated. In fact, no signal could be attributed to this compound upon direct analysis of ^{1}H NMR spectra of the reaction mixture. Instead, tetracycle **21**, the product of a diene-transmissive[21] double DA sequence, was formed. The stereochemistry of this compound was consistent with the second NMM dienophile docking to the convex face of single adduct **20** through the *endo*-cycloaddition mode. Evidently, the barrier toward the first DA reaction is significantly higher than that of the second. This result again highlights the difference between TVE (**1**) and [3]dendralene (**17**), the latter undergoing a much faster first cycloaddition with dienophiles such as NMM.[22]

Scheme 7. Diels–Alder Reaction between TVE (1) and NMM (19)



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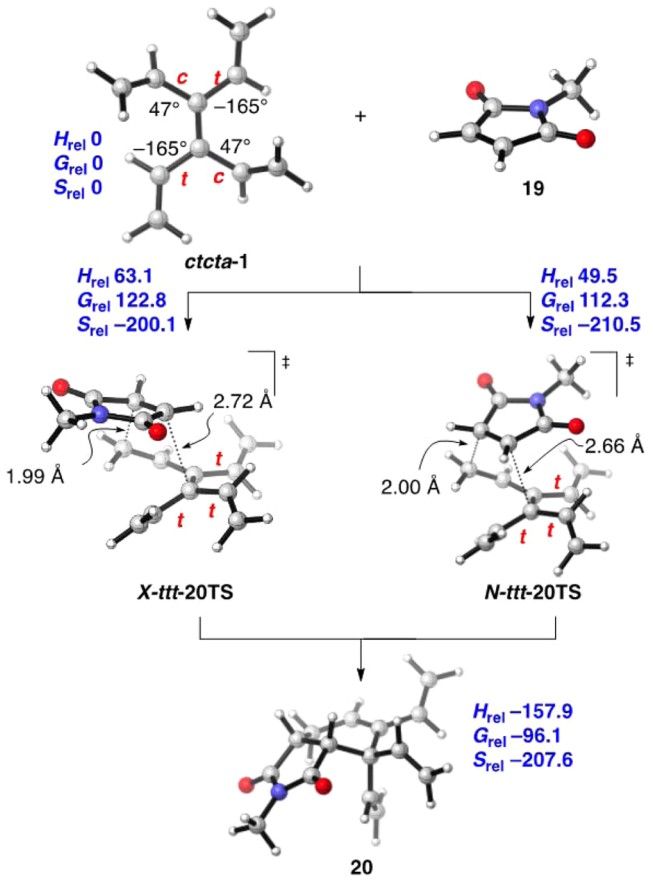
Ten TSs were located for the DA reaction between TVE and NMM (**19**). Of these, *endo*-mode TS ***N-ttt*-20TS** has the lowest energy (Scheme 8). As expected from Alder's *endo* rule,[23] this

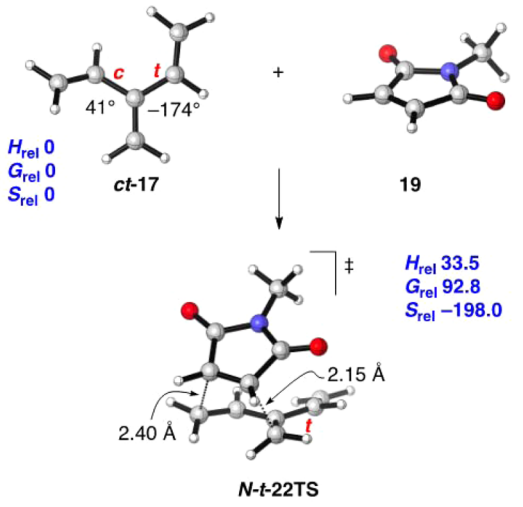
Scheme 8. G4(MP2) Geometries, Relative Enthalpies, Free Energies (kJ/mol), and Entropies [J/(mol·K)] of Reactants TVE *ctcta*-1 and NMM (19, Top), Most Stable TSs for the DA Reaction between Them *N-ttt*-20TS and *X-ttt*-20TS (Middle), and the Product DA Adduct 20 (Bottom)



endo TS is strongly favored enthalpically over the *exo* TS, ***X-ttt*-20TS**, by 13.6 kJ/mol. Both *endo* and *exo* TSs display marked bond-forming asynchronicities. The forming bonds in ***N-ttt*-20TS** are 2.003 and 2.663 Å (Δr = 0.66 Å), and those for ***X-ttt*-20TS** are 1.994 and 2.723 Å (Δr = 0.73 Å). The shorter developing bond in the TS is with the C1 carbon of TVE (**1**), as depicted in Scheme 6.

It is informative to compare the activation enthalpies and TSs geometries for the TVE−NMM DA reaction with those involving [3]dendralene (**17**) as diene (Scheme 9) on the grounds that TVE can be regarded as a disubstituted [3]dendralene (substituent = vinyl). The most stable TS for the [3]dendralene−NMM reaction, ***N-t*-22TS** (also an *endo*-mode docking of diene and dienophile), exhibits a significantly lower bond-forming asynchronicity (2.403 Å, 2.154 Å; Δr = 0.25 Å) than that seen for the TVE-NMM reaction, ***N-ttt*-20TS**. These two TSs also exhibit asynchronicity of the opposite orientation: in ***N-t*-22TS**, the shorter forming bond involves C4, whereas with ***N-ttt*-20TS**, the shorter forming bond involves C1. The short forming bond involving C4 in ***N-t*-22TS** leads to stabilization by delocalization of charge through the pentadienyl system derived from [3]dendralene.[24,25] A

Scheme 9. G4(MP2) Geometries, Relative Enthalpies, Free Energies (kJ/mol), and Entropies [J/(mol·K)] of Reactants [3]Dendralene *ct*-17 and NMM (19, Top) and Lowest Energy TS for the Diels−Alder Reaction between Them *N-t*-22TS (Bottom)



similar situation might be expected for the preferred TS for the TVE-NMM reaction. In this case, however, a steric factor appears to override this electronic effect. Specifically, a planar TVE diene component would suffer significant destabilizing steric interactions between C1 of the reacting 1,3-butadiene and its *Z*-4-vinyl substituent. In ***N-ttt*-20TS**, the *Z*-4-vinyl group is rotated away from C1 by ca. 37° (= value of the dihedral angle C2−C3−C4−C5) and also from NMM, the incoming dienophile. This twisting results in a longer developing bond to C4 in the TS. In contrast, bond formation at C1 is sterically unencumbered, thus resulting in a very short (2 Å) forming bond length. Significant closed-shell biradicaloid character should exist in such a highly asynchronous TS,[24,25] which should be further stabilized in ***N-ttt*-20TS** (and also in ***X-ttt*-20TS**) by the presence of a trivinylmethyl group in the TVE component. Steric factors also explain why the significantly larger activation enthalpy calculated for the TVE-NMM TS, ***N-ttt*-20TS** (49.5 kJ/mol), compared to that of the corresponding [3]dendralene-NMM TS, ***N-t*-22TS** (33.5 kJ/mol), is also explained by these steric effects.

As mentioned previously, two competing reactions take place upon treating TVE (**1**) with NMM (**19**), namely direct DA reaction (Schemes 7 and 8) and electrocyclization (Schemes 5 and 6). From the activation parameters given in Schemes 6 and 8, it is seen that, although the enthalpy of activation for the electrocyclic reaction is nearly 50 kJ/mol greater than that for the DA reaction, the free energy of activation for the former process is 6.4 kJ/mol *lower* than that for the latter. This arises because the activation entropy for electrocyclization is substantially larger (by a factor of 18) than that for the DA reaction. These results suggest that there exists an isokinetic temperature of about 63 °C, below which the rate constant for the DA reaction is greater than that for electrocyclization and above which, the reverse is true. Of course, the rate of the DA reaction may also be modulated by varying the concentration of NMM. It should be noted that the calculated isokinetic temperature is based on gas phase calculations and is, therefore, subject to solvent effects. In summary, the yield of DA adduct is maximized by carrying out the reaction at low temperatures

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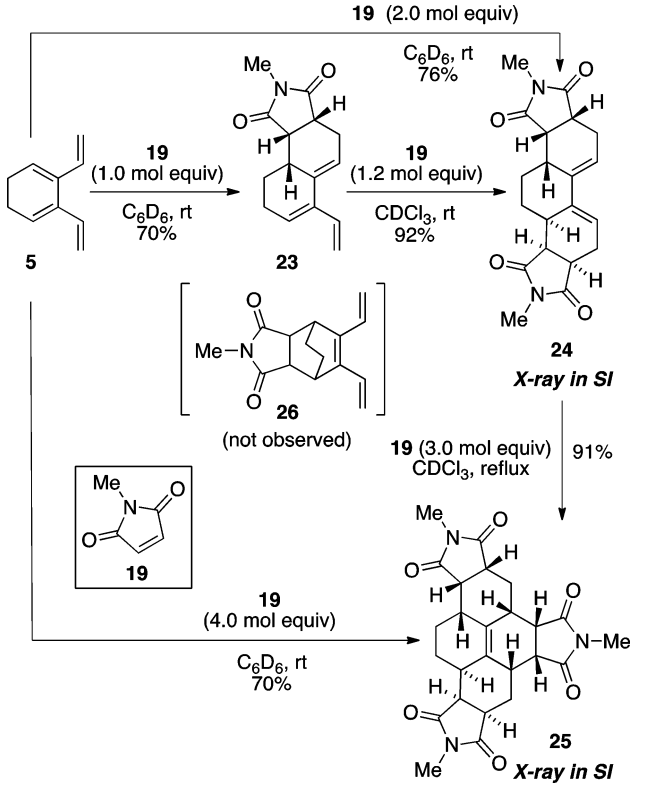
(<50 °C) and using an excess of NMM (**19**). These predictions were borne out experimentally (Scheme 7).

Without further purification, the solution from the 6π-electrocyclization of TVE (**1**, Scheme 5) was used to study the DA reactivity of DVC **5**. Using 1.0 molar equiv of NMM (**19**) led cleanly to the formation of one single DA adduct **23** (Scheme 10). The regioisomer of **23**, namely **26**, was not

Scheme 10. Diels–Alder Sequences Involving DVC (5) and NMM (19)



detected. This first cycloaddition, therefore, exhibits complete site selectivity for one of the two equivalent terminal (semicyclic) dienes over the internal 1,3-cyclohexadiene. This reaction also exhibits very high chemoselectivity in that only traces of the double NMM adduct can be detected in the reaction mixture. It is also highly stereoselective in that only the *endo*-adduct is detected.

Only the semicyclic diene site of single DA adduct **23** can adopt the *s-cis* conformation; hence, the site selectivity of the second addition is assured. In the event, exposure of single DA adduct **23** to 1 molar equiv of NMM (**19**) gave one diastereomer (by ^{1}H NMR spectroscopic analysis) of double DA adduct **24**. A single-crystal X-ray analysis of **24** confirmed *endo* selectivity for the first two cycloadditions and the *anti*-approach of NMM (**19**) in the second addition. Exposure of DVC (**5**) to 2.0 molar equiv of NMM (**19**) gave double DA adduct **24** directly.

Treatment of double DA adduct **24** with NMM (**19**) generated a single diastereoisomer of triple DA adduct **25**. This third DA reaction also proceeded through an *endo* transition state, as evidenced by single-crystal X-ray analysis of the product. The C_2-symmetrical nature of the *anti*-double adduct precludes any issue of π-diastereofacial selectivity in this third addition. Exposure of DVC (**5**) to NMM (**19**) gave the triple adduct directly. In effect, the sequence commences with TVE (**1**), which undergoes the 6π-electrocyclization and three successive DA reactions in one pot to generate one diastereomeric product carrying seven new C–C bonds and four new rings.[26]

One might be surprised by the regiochemical outcome of the first cycloaddition **5** → **23** (Scheme 10), with a conformationally flexible semicyclic diene reacting in preference to a 1,3-cyclohexadiene, which is locked in the *s-cis* conformation. A selective *single* cycloaddition to DVC (**5**) is also unexpected, since the parent [4]dendralene (**18**) undergoes a rather unselective reaction on treatment with 1 molar equiv of NMM (**19**), with *double* adducts being the major products.[17,18]

To shed light on these experimental observations, the reaction between DVC (**5**) and NMM (**19**) was investigated computationally. *Endo*- and *exo*-TSs were located for addition to both the cyclic diene site (*internal* addition), ***N*-26TS** and ***X*-26TS**, and to the semicyclic diene site (*terminal* addition), ***N*-23TS** and ***X*-23TS** (Scheme 11). Bond-forming asynchronicities in all four TSs are small, ca. 0.1 Å, with the shorter bond forming at the less substituted and, hence, less sterically congested C1 atom in the *terminal* addition mode.

Consistent with experimental findings, the *terminal* addition *endo*-TS, ***N*-23TS**, was calculated as the most stable. Both activation enthalpy and activation free energy for this addition mode ($\Delta H^{\ddagger}$ = 20.6 and $\Delta G^{\ddagger}$ = 80.3 kJ/mol) are extraordinarily small; calculated barriers for the DA addition of NMM to [3]dendralene (**17**) are significantly higher ($\Delta H^{\ddagger}$ = 33.5 and $\Delta G^{\ddagger}$ = 92.8 kJ/mol; Scheme 9). The origin of the enhanced DA reactivity of ***ct*-5** appears not to be a conformational effect in the reactants because the C1–C2–C3–C3′ dihedral angles within the reactive diene component in ***ct*-5** (Scheme 11) and ***ct*-17** (Scheme 9) are nearly identical, 39° and 41°, respectively. Neither is the enhanced reactivity due to the presence of an additional double bond in ***ct*-5** because it is connected in a cross-conjugative manner (to give a [4]dendralene analogue), and so its electronic influence should be marginal. This reasoning is supported by G4(MP2) calculations on the DA reaction between the parent [4]dendralene (**18**) and NMM (**19**, Scheme 12).

TSs for *endo* addition of NMM (**19**) to both *terminal* and *internal* dienes of the parent [4]dendralene (**18**) were calculated. Relative to the most stable conformer of [4]-dendralene, ***tct*-18**, the activation energies ($\Delta H^{\ddagger}$ = 44.2 and $\Delta G^{\ddagger}$ = 104.3 kJ/mol for *terminal* addition) are much larger than those for [3]dendralene (**17**). The preferred conformation of [4]dendralene, ***tct*-18**, comprises two essentially in plane *s-trans* 1,3-butadiene units skewed at an angle of 78° toward one other. In contrast, a *gauche* conformation of the reactive diene units exist for both [3]dendralene (**17**) and DVC ***ct*-5**. The most stable conformation of [4]dendralene, ***tct*-18**, is, therefore, not appropriate as a starting point for activation barrier comparisons. When the more satisfactory [4]dendralene conformation ***cct*-18** is employed, activation parameters ($\Delta H^{\ddagger}$ = 33.1 and $\Delta G^{\ddagger}$ = 95.0 kJ/mol) are consistent with those obtained for [3]dendralene ***ct*-17**: $\Delta H^{\ddagger}$ = 33.5 and $\Delta G^{\ddagger}$ = 92.8 kJ/mol (Scheme 8). These findings indicate that the enhanced DA reactivity (compared to [3]dendralene) of DVC ***ct*-5** is not caused by its spectator vinyl group. What is the origin of the high DA diene reactivity of DVC? Through a combination of hyperconjugative and +*I* effects, the $-CH_2CH_2-$ group in ***ct*-5** elevates DVC's HOMO. According to B3LYP/6-31G(d) calculations, the HOMO energy of ***ct*-5** is 0.7 eV higher than

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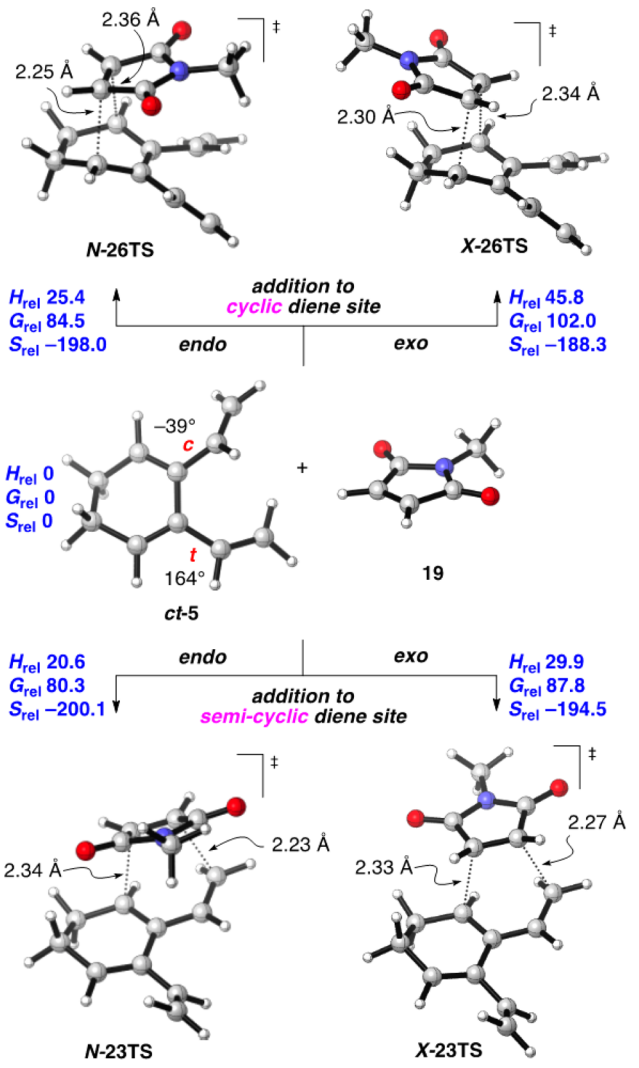
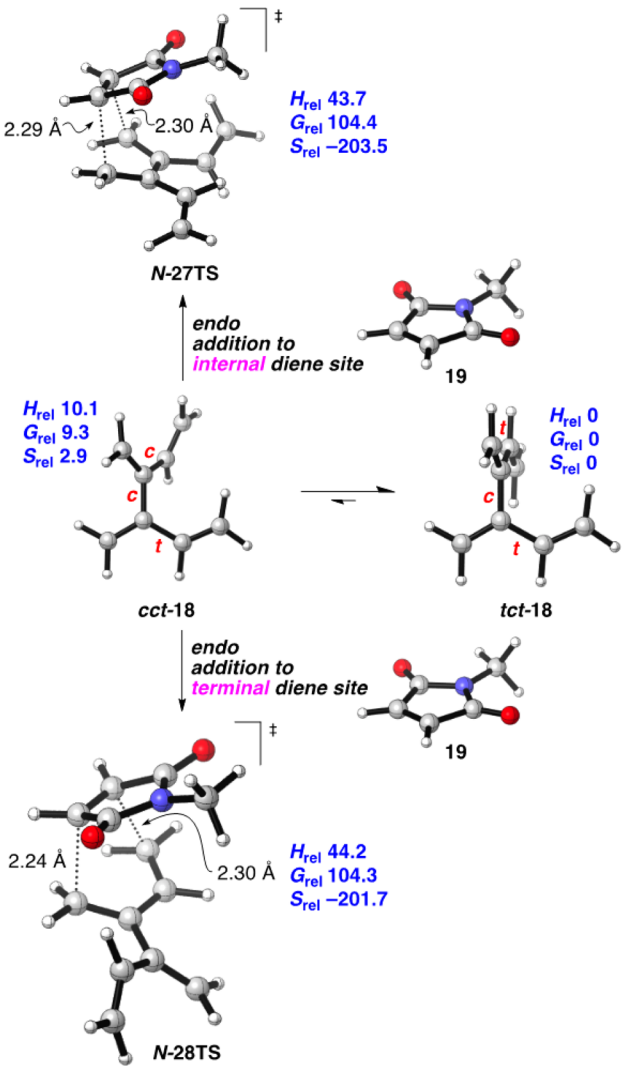
Scheme 11. G4(MP2) Geometries, Relative Enthalpies, Free Energies (kJ/mol), and Entropies [J/(mol·K)] of Reactants DVC *ct*-5 and NMM (19, Center) and Most Stable TSs for the Diels–Alder Reaction between Them: to the Cyclic Diene Site (Top) *N*-*ct*-26TS and *X*-*ct*-26TS and to the Semicyclic Diene Site (Bottom) *N*-*c*-23TS and *X*-*c*-23TS



Scheme 12. G4(MP2) Geometries, Relative Enthalpies, Free Energies (kJ/mol), and Entropies [J/(mol·K)] of Reactants [4]Dendralene *tct*-18/*cct*-18 and NMM (19, Center) and the Most Stable TSs for the Diels–Alder Reaction between Them: *N*-27TS (Internal Addition) and *N*-28TS (Terminal Addition)



those of ***ct*-17** and ***cct*-18**. This HOMO energy increase leads to a decrease in the $HOMO_{DVC}$–$LUMO_{NMM}$ energy gap, thus leading to enhanced reactivity.

In the DVC–NMM cycloaddition (Scheme 11), *endo* selectivity is predicted for both *terminal* and *internal* modes of addition, but the enthalpic preference for the *endo* mode is markedly greater, by 11 kJ/mol, at the *internal* site than the *terminal* site. This predicted stronger *endo* selectivity in the *internal* addition reaction is probably due to destabilization of the *exo*-*internal* TS, ***X*-26TS**, through steric interactions between the NMM moiety and the $-CH_2CH_2-$ group of the cyclohexadiene ring. *Terminal* addition is predicted to be preferred over *internal* addition by ca. 5 kJ/mol, presumably due to destabilizing steric interactions in the *endo*, *internal* TS, ***N*-26TS**.

Parenthetically, we note that the lack of site (i.e., *terminal vs internal*) selectivity in the DA reaction between NMM and [4]dendralene (Scheme 12) predicted by our calculations is consistent with experimental findings.[17]

That a controlled, 3-fold cycloaddition sequence involving DVC is not limited to maleimide dienophiles is demonstrated by the experimental results depicted in Scheme 13. The dienophile in this case is dimethylacetylene dicarboxylate (DMAD, **29**). Once again, the first dienophile addition occurs under milder conditions than do the subsequent ones, and the [3]dendralenic monoadduct **30** is readily isolated in pure form. The second addition in this case, unsurprisingly, proceeds with lower π-diastereofacial selectivity than with NMM (Scheme 10). Interestingly, whereas *anti*-double DA adduct **31** is isolated cleanly, *syn*-double DA adduct **32** (the putative major stereoisomer) goes on to form triple cycloadduct **33** in high selectivity.

SUMMARY AND CONCLUSIONS

In summary, the first olefin-based 4-fold cross-coupling reactions has led to a one-step synthesis of tetravinylethylenes. This study demonstrates that tetravinylethylenes are not only easily prepared employing standard laboratory equipment and

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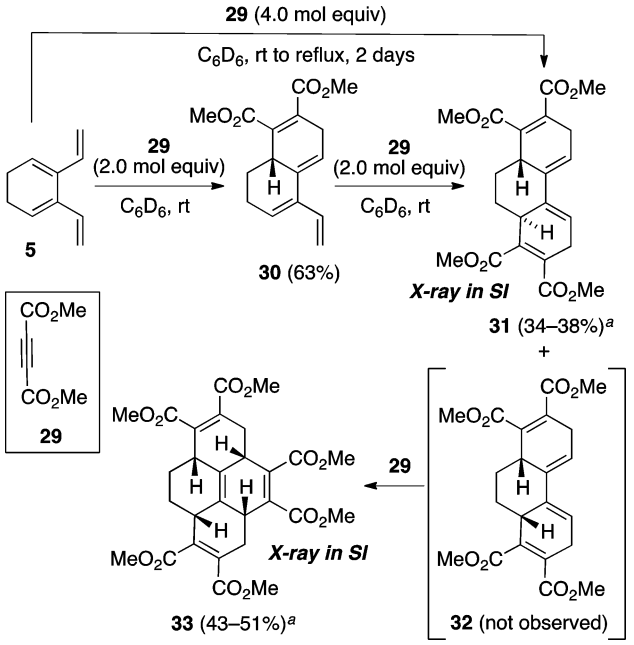
Scheme 13. Diels–Alder Sequences Involving DVC (5) and DMAD (29)



[a]For compounds **31** and **33** the lower yield was obtained through a sequence of two separate reactions, and the higher yield was obtained from a one-pot process from DVC (**5**).

methods but also require no special precautions when being manipulated. In terms of reactivity, stability, and ease of handling, TVEs are distinct from both unsubstituted [3]-dendralenes and 1,3,5-hexatrienes. Importantly, the behavior of both TVE and related structures are predictable and explainable by employing the composite ab initio MO G4(MP2) method (Scheme 14).

EXPERIMENTAL SECTION

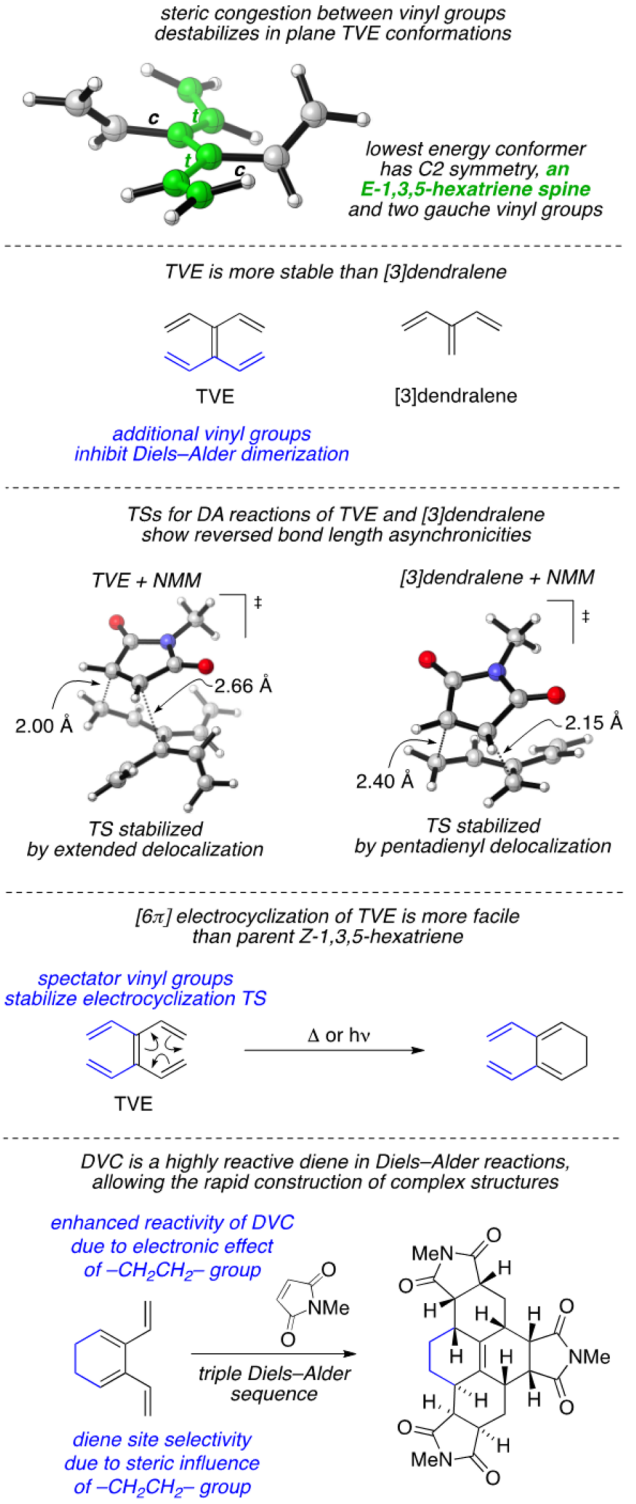
General Methods. See the Supporting Information.

Tetravinylethylene (TVE, 1). A mixture of $Pd(OAc)_2$ (133 mg, 0.567 mmol, 0.040 molar equiv) and XPhos (539 mg, 1.13 mmol, 0.080 molar equiv) in a two-neck 100 mL round-bottom flask equipped with reflux condenser was purged three times under reduced pressure and refilled with argon. Tetrachloroethylene (**10**) (2.90 mL, 28.4 mmol, 1.0 molar equiv) and vinyltributyltin (41.5 mL, 142 mmol, 5.0 molar equiv) were added. The reaction mixture was stirred and heated to 60 °C overnight. A bulb-to-trap distillation apparatus was attached to the reaction flask, and the reaction mixture was heated to 50 °C for 3 h under reduced pressure (0.47 mbar). A dry ice/acetone cooling bath was used to trap tetravinylethylene (**1**) in the distillation flask as a colorless oil (2.4 g, 64%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (dd, J = 17.3 Hz, 11.0 Hz, 4H), 5.56–5.08 (m, 8H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7 (C_q), 134.7 (CH), 119.5 (CH_2) ppm; IR (thin film) ν_{max} 3088, 2975, 2926, 2853 cm^{-1}; MS (70 eV, EI) m/z 264.2 ([2M]$^{+\bullet}$, 55), 131.1 (63) 117.1 (100);* HRMS (EI) calcd for $C_{10}H_{12}$ [M]$^{+\bullet}$ 132.0939, found 132.0938; calcd for $C_{20}H_{24}$ [2M]$^{+\bullet}$ 264.1878, found 264.1877;* UV–vis (*n*-hexane) λ_{max} = 225 nm (ε = 10700), 283.5 (ε = 14800).

*We assume that the TVE undergoes 6π-electrocyclization and the resulting DVC undergoes DA dimerization.

2,3-Divinyl-1,3-cyclohexadiene (DVC, 5) Using Microwave Heating. A solution of TVE (**1**) (13 mg, 0.10 mmol, 1.0 molar equiv) in $CDCl_3$ (10 mL) was heated at 120 °C for 2 h and gave 2,3-divinyl-1,3-cyclohexadiene (**5**) as a colorless solution in $CDCl_3$. ^{1}H NMR analysis indicated complete conversion of TVE (**1**) to 2,3-divinyl-1,3-cyclohexadiene (**5**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (dd, J = 17.4 Hz, 10.9 Hz, 1H), 6.02 (s, 1H), 5.32 (dd, J = 17.4 Hz, 1.7 Hz, 1H), 5.00 (dd, J = 10.9 Hz, 1.7 Hz, 1H), 2.13 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6 (CH), 136.1 (C_q), 125.6 (CH), 113.9 (CH_2), 22.6 (CH_2) ppm; IR (thin film) ν_{max} 3098, 3020, 2928, 2872, 2854 cm^{-1}; MS (70 eV, EI) m/z 132.2 ([M]$^{+\bullet}$, 57), 117.1 (97), 91.1 (100); MS (70 eV, EI) m/z 264.2 ([2M]$^{+\bullet}$, 63), 249.3 ([2M – CH_3], 11); HRMS (EI) calcd for $C_{10}H_{12}$ [M]$^{+\bullet}$ 132.0939, found 132.0938; calcd for $C_{20}H_{24}$ [2M]$^{+\bullet}$ 264.1878, found 264.1873; UV–vis (*n*-hexane) λ_{max} = 205 nm (ε = 14200), 229 (ε = 14500).

Scheme 14. Key Findings of this Study



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2,3-Divinyl-1,3-cyclohexadiene (DVC, 5) Using Photochemical Irradiation. A solution of TVE (**1**) (53 mg, 0.40 mmol, 1.0 molar equiv) in benzene-d_6 (2.0 mL) was degassed by bubbling N_2 for 1 min while stirring vigorously in a reaction tube (both quartz glass and Pyrex gave the same outcome). Following the degassing procedure, the reaction mixture was irradiated using a medium-pressure mercury lamp at room temperature for 2 h under N_2 while stirring. The yield can be estimated by adding durene (38 mg, 0.28 mmol, 0.70 molar equiv) as the internal standard and recording a ^{1}H NMR spectrum, which reveals 100% conversion of TVE (**1**) and a 70% yield of 2,3-divinyl-1,3-cyclohexadiene (**5**). The solution was used directly in further reactions.

Chlorotrivinylethylene (11). A mixture of $Pd(OAc)_2$ (86 mg, 0.39 mmol, 0.030 molar equiv) and XPhos (367 mg, 0.77 mmol, 0.060 molar equiv) in a two-neck 50 mL round-bottom flask equipped with reflux condenser was purged 3× under reduced pressure and refilled with argon. Tetrachloroethylene (**10**) (1.30 mL, 12.8 mmol, 1.0 molar equiv) and vinyltributyltin (15.0 mL, 51.3 mmol, 4.0 molar equiv) were added. The reaction mixture was stirred and heated to 60 °C for 20 h and cooled to 0 °C. Trifluoroacetic acid (1.96 mL, 25.6 mmol, 2.0 molar equiv) was added dropwise while maintaining the temperature of the reaction mixture below 20 °C. The reaction mixture was stirred for 2 h upon completion of addition at room temperature and cooled back to 0 °C. DBU (3.82 mL, 25.6 mmol, 2.0 molar equiv) was added dropwise while stirring the reaction mixture vigorously and maintaining the temperature below 30 °C. A bulb-to-trap distillation apparatus was attached to the reaction flask, and the reaction mixture was heated to 60 °C for 2 h under reduced pressure (1.3 mbar). A dry ice/acetone cooling bath was used to trap chlorotrivinylethylene **11** in the distillation flask as a colorless oil (668 mg, 37%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (ddd, J = 27.1 Hz, 16.9 Hz, 10.7 Hz, 2H), 6.39 (dd, J = 17.5 Hz, 11.1 Hz, 1H), 5.77 (d, J = 16.4 Hz, 1H), 5.62−5.21 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1(C_q), 134.2 (CH), 132.0 (CH), 131.8 (CH), 131.2 (C_q), 122.7 (CH_2), 120.0 (CH_2), 118.4 (CH_2) ppm; IR (thin film) ν_{max} 3092, 3058, 3021, 2978, 1833, 1784 cm^{-1}; MS (70 eV, EI) m/z 140.0 ([M]$^{+\bullet}$, 53) 105.1 (M − Cl, 100); HRMS (EI) calcd for $C_8H_9Cl^{35}$ [M]$^{+\bullet}$ 140.0393, found 140.0392; calcd for $C_8H_9Cl^{37}$ [M]$^{+\bullet}$ 142.0363, found 142.0360; UV−vis (*n*-hexane) λ_{max} = 225.5 nm (ε = 8110), 282 (ε = 25300).

2,7-Dimethyl-4,5-bis(2-methylprop-1-en-1-yl)octa-2,4,6-triene (9). A mixture of $Pd(OAc)_2$ (11 mg, 0.050 mmol, 0.10 molar equiv) and XPhos (48 mg, 0.10 mmol, 0.20 molar equiv) in a two-neck 5 mL round-bottom flask equipped with reflux condenser was purged three times under reduced pressure and refilled with dry argon. Tetrachloroethylene (**10**) (50 μL, 0.50 mmol, 1.0 molar equiv) and tributyl(2-methylprop-1-en-1-yl)stannane[27] (863 mg, 2.50 mmol, 5.0 molar equiv) were added. The reaction mixture was stirred and heated to 80 °C for 3 days. Upon cooling to room temperature, the crude mixture was subjected to flash column chromatography using silica gel eluting with petroleum ether 40−60 °C to give 2,7-dimethyl-4,5-bis(2-methylprop-1-en-1-yl)octa-2,4,6-triene (**9**) as a colorless oil (60 mg, 49%): R_f = 0.90 (100% petroleum ether 40−60 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (s, 4H), 1.78 (s, 12H), 1.57 (s, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3 (C_q), 134.1 (C_q), 126.1 (CH), 26.5 (CH_3), 19.9 (CH_3) ppm; IR (thin film) ν_{max} 2965, 2923, 2909, 2854 cm^{-1}; MS (EI) m/z 244.2 ([M]$^{+\bullet}$, 39), 229.2 ([M − CH_3]), 34), 214.1 ([M − $(CH_3)_2$], 3), 159.1 (100); HRMS (EI) calcd for $C_{18}H_{28}$ [M]$^{+\bullet}$ 244.2191, found 244.2191; UV−vis (*n*-hexane) λ_{max} = 225 nm (ε = 10900), 283.5 nm (ε = 15800).

Dimethyl (2*E*,6*E*)-4,5-Bis((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)octa-2,4,6-trienedioate (12). A mixture of $Pd(OAc)_2$ (11 mg, 0.050 mmol, 0.10 molar equiv) and XPhos (48 mg, 0.10 mmol, 0.20 molar equiv) in a two-neck 5 mL round-bottom flask equipped with reflux condenser was purged three times under reduced pressure and refilled with dry argon. Tetrachloroethylene (**10**) (50 μL, 0.50 mmol, 1.0 molar equiv) and methyl (*E*)-3-(tributylstannyl)acrylate[28] (938 mg, 2.5 mmol, 5.0 molar equiv) were added. The reaction mixture was stirred and heated to 40 °C overnight. Upon cooling to room temperature, the crude mixture was subjected to flash column chromatography using silica gel eluting with 50% EtOAc in petrol 40−60 °C to give (2*E*,6*E*)-4,5-bis((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)octa-2,4,6-trienedioate (**12**) as a colorless solid (110 mg, 60%), R_f = 0.20 (1:1 EtOAc/petroleum ether 40−60 °C). An analytical sample of dimethyl (2*E*,6*E*)-4,5-bis((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)octa-2,4,6-trienedioate (**12**) was obtained by recrystallization from CH_2Cl_2 to give colorless needles: mp 108−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 15.7 Hz, 4H), 6.09 (d, J = 15.8 Hz, 4H), 3.80 (s, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2 (C_q), 139.7 (CH), 138.5 (C_q), 127.0 (CH), 52.2 (CH_3) ppm; IR (KBr tablet) ν_{max} = 2955, 2919, 2850, 1724, 1618 cm^{-1}; MS (70 eV, EI) m/z 364.2 ([M]$^{+\bullet}$, 6), 333.1 ([M − OCH_3], 37), 273.1 ([M − $(OCH_3)_3$], 100); HRMS (EI) calcd for $C_{18}H_{20}O_8$ [M]$^{+\bullet}$: 364.1158; found 364.1158; Anal. Calcd (%) $C_{18}H_{20}O_8$: C 59.34, H 5.53; found C 59.17, H 5.88; UV−vis (acetonitrile) λ_{max} = 199 nm (ε = 23200), 256 nm ε = 23200), 329.5 (ε = 32200).

((1*E*,5*E*)-3,4-Di((*E*)-styryl)hexa-1,3,5-triene-1,6-diyl)dibenzene (13). A mixture of $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 0.040 molar equiv) and XPhos (19 mg, 0.040 mmol, 0.080 molar equiv) in a 2-neck 5 mL round-bottom flask equipped with reflux condenser was purged 3 times under reduced pressure and refilled with dry argon. Tetrachloroethylene (**10**) (50 μL, 0.50 mmol, 1.0 molar equiv) and (*E*)-tributyl(styryl)stannane[29] (983 mg, 2.5 mmol, 5.0 molar equiv) were added. The reaction mixture was stirred and heated to 60 °C overnight. The product precipitated out of the solution during the reaction and was filtered off upon cooling to room temperature. The precipitate was washed subsequently with EtOH (15 mL), EtOAc (15 mL) and Et_2O (15 mL) to give ((1*E*,5*E*)-3,4-di((*E*)-styryl)hexa-1,3,5-triene-1,6-diyl)dibenzene (**13**) as a yellow solid (150 mg, 69%). An analytical sample of ((1*E*,5*E*)-3,4-di((*E*)-styryl)hexa-1,3,5-triene-1,6-diyl)dibenzene (**13**) was obtained by recrystallization from CH_2Cl_2 to give colorless needles: mp 158−159 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.50 (d, J = 7.5 Hz, 8H), 7.42−7.20 (m, 16H), 6.82 (d, J = 16.2 Hz, 4H) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 138.0 (C_q), 137.4 (C_q), 134.7 (CH), 129.1 (CH), 128.1 (CH), 128.0 (CH), 127.0 (CH) ppm; IR (KBr tablet) ν_{max} = 3078, 3055, 3026, 2960, 2924, 2851 cm^{-1}; MS (70 eV, EI) m/z 436.2 ([M]$^{+\bullet}$, 8), 418.1 (61), 386.1 (100); HRMS (EI) calcd for $C_{34}H_{28}$ [M]$^{+\bullet}$ 436.2191, found 436.2189; UV−vis (acetonitrile) λ_{max} = 199.4 nm (ε = 79000), 273.6 nm (ε = 23400).

((1*E*,5*E*)-3,4-Bis((*E*)-2-(trimethylsilyl)vinyl)hexa-1,3,5-triene-1,6-diyl)bis(trimethylsilane) (14). A mixture of $Pd(OAc)_2$ (29 mg, 0.13 mmol, 0.040 molar equiv) and XPhos (122 mg, 0.256 mmol, 0.080 molar equiv) in a two-neck 10 mL round-bottom flask equipped with reflux condenser was purged three times under reduced pressure and refilled with dry argon. Tetrachloroethylene (**10**) (0.317 mL, 3.2 mmol, 1.0 molar equiv) and (*E*)-trimethyl(2-(tributylstannyl)vinyl)-silane[30] (6.0 g, 15.5 mmol, 5.0 molar equiv) were added. The reaction mixture was stirred and heated to 60 °C overnight. Upon cooling to room temperature, the crude mixture was subjected to flash column chromatography using silica gel eluting with *n*-pentane to give ((1*E*,5*E*)-3,4-bis((*E*)-2-(trimethylsilyl)vinyl)hexa-1,3,5-triene-1,6-diyl)bis(trimethylsilane) (**14**) as a colorless solid (1.3 g, 89%), R_f = 0.70 (100% *n*-pentane). An analytical sample of ((1*E*,5*E*)-3,4-bis((*E*)-2-(trimethylsilyl)vinyl)hexa-1,3,5-triene-1,6-diyl)bis(trimethylsilane) (**14**) was obtained by recrystallization from petroleum ether 40−60 °C to give colorless needles: mp 135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, J = 19.0 Hz, 4H), 5.95 (d, J = 19.0 Hz, 4H), 0.12 (s, 36H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5 (CH), 139.8 (C_q), 136.4 (CH), −1.0 (CH_3) ppm; IR (KBr tablet) ν_{max} = 2955, 2898, 1576 cm^{-1}; MS (70 eV, EI) m/z 420.2 ([M]$^{+\bullet}$, 20), 347.2 ([M − TMS], 27); HRMS (EI) calcd for $C_{22}H_{44}Si_4$ [M]$^{+\bullet}$ 420.2520, found 420.2520; UV−vis (acetonitrile) λ_{max} = 195 nm (ε = 15300), 246 nm (ε = 22000), 316 (ε = 25100).

(6*E*,10*E*)-8,9-Bis((*E*)-3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-1-yl)-2,2,3,3,14,14,15,15-octamethyl-4,13-dioxa-3,14-disilahexadeca-6,8,10-triene (15). A mixture of $Pd(OAc)_2$ (8.7 mg, 0.043 mmol, 0.10 molar equiv) and XPhos (41 mg, 0.086 mmol, 0.20 molar equiv) in a two-neck 5 mL round-bottom flask equipped with reflux condenser was purged 3 times under reduced pressure and refilled with dry argon. Tetrachloroethylene (**10**) (43 μL, 0.43 mmol, 1.0 molar equiv) and (*E*)-*tert*-butyldimethyl((3-(tributylstannyl)allyl)-

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oxy)silane[31] (1.19 g, 2.58 mmol, 6.0 molar equiv) were added. The reaction mixture was stirred and heated to 60 °C overnight. Upon cooling to room temperature, the crude mixture was subjected to flash column chromatography using basic alumina eluting with 10% EtOAc in petroleum ether 40−60 °C to give (6*E*,10*E*)-8,9-bis((*E*)-3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-1-yl)-2,2,3,3,14,14,15,15-octamethyl-4,13-dioxa-3,14-disilahexadeca-6,8,10-triene (**15**) as a yellow oil (275 mg, 90%): R_f = 0.50 (1:10 EtOAc/petroleum ether 40−60 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (d, J = 15.7 Hz, 4H), 5.80 (dt, J = 15.8 Hz, 5.1 Hz, 4H), 4.27 (dd, J = 5.1 Hz, 1.6 Hz, 8H), 0.92 (s, 36H), 0.08 (s, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4 (C_q), 134.0 (CH), 127.9 (CH), 64.2 (CH_2), 26.1 (CH_3), 18.6 (CH_3), −5.0 (CH_3) ppm; IR (thin film) ν_{max} 2955, 2929, 2886, 2857 cm^{-1}; MS (ESI) m/z 731.9 ([M + Na]$^{+\bullet}$, 100), 709.0 ([M]$^{+\bullet}$, 12), 577.8 ([M − OTBS], 76), 445.6 ([M − $(OTBS)_2$], 85); HRMS (ESI) calcd for $C_{38}H_{76}O_4NaSi_4$ [M]$^{+\bullet}$ 731.4719, found 731.4718; UV−vis (*n*-hexane) λ_{max} = 199 nm (ε = 23200), 256 nm (ε = 23200), 330 nm (32200).

(2*E*,6*E*)-4,5-Bis((*E*)-3-hydroxyprop-1-en-1-yl)octa-2,4,6-triene-1,8-diol (16). A mixture of **15** (54 mg, 0.077 mmol, 1.0 molar equiv) and TBAF (1.0 M solution in THF, 462 μL, 0.46 mmol, 6.0 molar equiv) in anhydrous THF (1.0 mL) was stirred for 2 h at room temperature under N_2. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography using silica gel eluting with 10% MeOH in CH_2Cl_2. Recrystallizing twice from acetone yielded pure (2*E*,6*E*)-4,5-bis((*E*)-3-hydroxyprop-1-en-1-yl)octa-2,4,6-triene-1,8-diol (**16**) as a colorless solid (3.0 mg, 15%), R_f = 0.20 (1:10, MeOH/CH_2Cl_2). An analytical sample of (2*E*,6*E*)-4,5-bis((*E*)-3-hydroxyprop-1-en-1-yl)octa-2,4,6-triene-1,8-diol (**16**) was obtained by recrystallization from MeOH/Et_2O to give colorless needles: mp 108−110 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 6.53 (d, J = 15.7 Hz, 4H), 5.88 (dt, J = 15.8 Hz, 5.6 Hz, 4H), 4.18 (dd, J = 5.6 Hz, 1.5 Hz, 8H) ppm; ^{13}C NMR (100 MHz, CD_3OD) δ 135.6 (C_q), 135.3 (CH), 129.5 (CH), 63.7 (CH_2) ppm; IR (KBr tablet) ν_{max} = 3428, 3300, 2923, 2852, 1635 cm^{-1}; MS (70 eV, EI) m/z 252.1 ([M]$^{+\bullet}$, 12), 236.2 ([M − OH], 11) 203.1 ([M − $(OH)_2$], 21), 129.1 (100); HRMS (EI) calcd for $C_{14}H_{20}O_4$ [M]$^{+\bullet}$ 252.1362, found 252.1364; UV−vis (H_2O) λ_{max} = 233.4 nm (ε = 11500), 273.6 nm (ε = 23400).

Reaction of TVE (1) with *N*-Methylmaleimide (19). A mixture of TVE (**1**) (50 mg, 0.38 mmol, 1.0 molar equiv) and *N*-methylmaleimide (**19**) (126 mg, 1.14 mmol, 3.0 molar equiv) in $CDCl_3$ (1 mL) was heated to 50 °C for 6 days in an NMR tube sealed with a Young's tap. Solvent was removed by rotary evaporation, and the residue was subjected to flash column chromatography using silica gel eluting with 20% EtOAc in petroleum ether 40−60 °C to give **21** as a colorless solid (44 mg, 33%), R_f = 0.25 (20:80, EtOAc/petroleum ether 40−60 °C); An analytical sample of **21** was obtained by recrystallization from EtOH to give colorless needles: mp 225 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (dd, J = 17.0 Hz, 10.8 Hz, 1H), 5.90−5.70 (m, 1H), 5.54 (dd, J = 17.5 Hz, 10.5 Hz, 1H), 5.44−5.17 (m, 3H), 5.01 (dd, J = 17.3 Hz, 1.4 Hz, 1H), 4.75 (d, J = 17.4 Hz, 1H), 3.53−3.21 (m, 1H), 3.15−3.03 (m, 3H), 2.99 (d, J = 10.7 Hz, 2H), 2.96 (s, 4H), 2.89 (s, 4H), 2.88−2.72 (m, 3H), 2.35−2.17 (m, 3H), 2.16−1.99 (m, 1H) ppm; ^{13}C NMR δ 179.9 (C_q), 179.4 (C_q), 177.4 (C_q), 177.1 (C_q), 141.0 (C_q), 140.6 (CH), 138.8 (CH), 124.9 (CH), 118.1 (CH_2), 117.4 (CH_2), 50.9 (C_q), 48.1 (CH), 44.2 (CH), 39.9 (CH), 39.0 (CH), 33.0 (CH), 25.1 (CH_3), 25.0 (CH_3), 24.4 (CH_2), 23.4 (CH_2) ppm; IR (KBr tablet) ν_{max} = 3082, 2932, 2882, 2831, 1772, 1684 cm^{-1}; MS (70 eV, EI) m/z 354 ([M]$^{+\bullet}$, 100), 339 ([M − CH_3], 85); HRMS (EI) calcd for $C_{20}H_{22}N_2O_4$ [M]$^{+\bullet}$ 354.1580, found 354.1582. Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.75; H, 6.50; N, 7.87.

Reaction of 2,3-Divinyl-1,3-cyclohexadiene (5) with 1.0 Molar Equiv of *N*-Methylmaleimide (19). A mixture of 2,3-divinyl-1,3-divinylcyclohexadiene (**5**) (35 mg, 0.26 mmol, 1.0 molar equiv) and *N*-methylmaleimide (**19**) (29 mg, 0.26 mmol, 1.0 molar equiv) in benzene-d_6 (2.44 mL) was stirred at room temperature for 1 h. Solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography using silica gel eluting with 20% EtOAc in petroleum ether 40−60 °C to give **23** as a colorless oil (64 mg, 70%): R_f = 0.30 (30:70 EtOAc/petroleum ether 40−60 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (dd, J = 17.3 Hz, 10.9 Hz, 1H), 5.99 (s, 1H), 5.82 (s, 1H), 5.26 (d, J = 17.5 Hz, 1H), 5.01 (d, J = 10.9 Hz, 1H), 3.19−3.06 (m, 2H) 2.89 (s, 3H), 2.82 (dd, J = 15.1 Hz, 1H), 2.62−2.48 (m, 1H), 2.35−2.13 (m, 3H), 2.11−1.88 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0 (C_q), 178.1 (C_q), 137.5 (C_q), 135.9 (C_q), 135.1 (CH), 127.8 (CH), 119.3 (CH), 115.0 (CH), 43.6 (CH), 40.9 (CH), 35.5 (CH), 24.9 (CH_3), 24.6 (CH_2), 24.5 (CH_2), 23.7 (CH_2) ppm; IR (thin film) ν_{max} 3031, 2943, 2879, 2846, 1766, 1694 cm^{-1}; MS (70 eV, EI) m/z 243.1 ([M]$^{+\bullet}$, 35), 228.1 ([M − CH_3], 2) 131.1 (100); HRMS (EI) calcd for $C_{15}H_{17}NO_2$ [M]$^{+\bullet}$ 243.1259, found 243.1260.

Reaction of 2,3-Divinyl-1,3-cyclohexadiene (5) with 2.0 Molar Equiv of *N*-Methylmaleimide (19). A mixture of 2,3-divinyl-1,3-divinylcyclohexadiene (**5**) (16 mg, 0.12 mmol, 1.0 molar equiv) and *N*-methylmaleimide (**19**) (26 mg, 0.24 mmol, 2.0 molar equiv) in benzene-d_6 (1.4 mL) was stirred at room temperature overnight. Solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography using silica gel eluting with 50% EtOAc in petroleum ether 40−60 °C to give **24** as a colorless solid (32 mg, 76%), R_f = 0.25 (50:50 EtOAc/petroleum ether 40−60 °C). An analytical sample of **24** was obtained by recrystallization from EtOH to give colorless needles: mp 188−192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (s, 2H), 3.14−3.00 (m, 4H), 2.85 (s, 6H), 2.72 (dd, J = 16.6 Hz, 7.5 Hz, 2H), 2.38 (s, 2H), 2.19−1.94 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9 (C_q), 178.1 (C_q), 138.4 (C_q), 119.5 (CH), 43.6 (CH), 40.6 (CH), 37.3 (CH), 25.1 (CH_2), 25.1 (CH_2), 24.9 (CH_3) ppm; IR (KBr tablet) ν_{max} = 2954, 1772, 1696 cm^{-1}; MS (70 eV, EI) m/z 354.1 ([M]$^{+\bullet}$, 38), 339.1 ([M − CH_3]) 200.1 (100); HRMS (EI) calcd for $C_{20}H_{22}N_2O_4$ [M]$^{+\bullet}$ 354.1580, found 354.1579. Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.78; H, 6.21; N, 8.01.

Reaction of 2,3-Divinyl-1,3-cyclohexadiene (5) with 4.0 Molar Equiv of *N*-Methylmaleimide (19). A mixture of 2,3-divinyl-1,3-divinylcyclohexadiene (**5**) (18 mg, 0.14 mmol, 1.0 molar equiv) and *N*-methylmaleimide (**19**) (60 mg, 0.54 mmol, 4.0 molar equiv) in benzene-d_6 (1.0 mL) was stirred at room temperature for 4 days. Solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel eluting with EtOAc to give **25** as a colorless solid (44 mg, 70%), R_f = 0.30 (100% EtOAc). An analytical sample of **25** was obtained by recrystallization from EtOH to give colorless needles: mp 220 °C; ^{1}H NMR (400 MHz, C_6D_6) δ = 2.95−2.85 (m, 1H), 2.81 (s, 3H), 2.75−2.60 (m, 1H), 2.66 (s, 3 H) 2.58 (s, 3H), 2.58−2.38 (m, 4H), 2.27−1.94 (m, 6H), 1.90−1.77 (m, 1H), 1.77−1.55 (m, 4H), 1.55−1.39 (m, 1H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 179.3 (C_q), 179.0 (C_q), 178.2 (C_q), 177.4 (C_q), 177.2 (C_q), 176.8 (C_q), 133.7 (C_q), 130.6 (C_q), 44.5 (CH), 43.9 (CH), 42.1 (CH), 41.4 (CH), 40.1 (CH), 37.1 (CH), 34.4 (CH), 33.0 (CH), 32.8 (CH), 32.4 (CH), 26.5 (CH_2), 25.3 (CH_3), 25.1 (CH_2), 24.6 (CH_3), 24.5 (CH_3), 23.9 (CH_2), 21.3 (CH_2) ppm; IR (KBr tablet) ν_{max} = 3060, 2937, 2875, 1771, 1694 cm^{-1}; MS (70 eV, ESI) m/z 489.4 ([M$^{+\bullet}$ + Na], 100), 466.4 ([M], 72); HRMS (ESI) calcd for $C_{25}H_{28}N_3O_6$ [M + H]$^{+\bullet}$ 466.1978, found 466.1978.

Double DA Adduct 24 from Mono DA Adduct 23. A mixture of **23** (12.6 mg, 0.0518 mmol, 1.0 molar equiv) and *N*-methylmaleimide (**19**) (7.0 mg, 0.062 mmol, 1.2 molar equiv) in $CDCl_3$ (1.0 mL) was stirred at room temperature for 2 days. Solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography using silica gel eluting with 50% EtOAc in petroleum ether 40−60 °C to give **24** as a colorless solid (17 mg, 92%). ^{1}H NMR data were consistent with those reported above.

Triple DA Adduct 25 from Double DA Adduct 24. A mixture **24** (26 mg, 0.073 mmol, 1.0 molar equiv) and *N*-methylmaleimide (**19**) (24 mg, 0.22 mmol, 3.0 molar equiv) in $CDCl_3$ (1.0 mL) was stirred at reflux overnight. Solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography using silica gel eluting with EtOAc to give **25** as a colorless solid (31 mg, 91%). ^{1}H NMR data were consistent with that reported above.

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Reaction of 2,3-Divinyl-1,3-cyclohexadiene (5) with 2.0 Molar Equiv of DMAD (29). A mixture of 2,3-divinyl-1,3-divinylcyclohexadiene (**5**) (35 mg, 0.26 mmol, 1.0 molar equiv) and DMAD (**29**) (65 μL, 0.54 mmol, 2.0 molar equiv) in benzene-d_6 (1.0 mL) were stirred at room temperature overnight. Solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel eluting with 10% EtOAc in petroleum ether 40−60 °C to give dimethyl (*S*)-5-vinyl-3,7,8,8a-tetrahydronaphthalene-1,2-dicarboxylate (**30**) as a colorless oil (46 mg, 63%): R_f = 0.50 (10:90 EtOAc/petroleum ether 40−60 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (dd, J = 17.2 Hz, 10.8 Hz, 1H), 5.85 (s, 1H), 5.71 (s, 1H), 5.36 (d, J = 17.2 Hz, 1H), 5.07 (d, J = 10.6 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.30−2.90 (m, 3H), 2.48−2.10 (m, 2H), 2.02−1.82 (m, 1H), 1.53 (dq, J = 18.0 Hz, 6.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (C_q), 167.2 (C_q), 140.8 (C_q), 136.2 (C_q), 135.8 (CH), 132.8 (C_q), 127.9 (C_q), 126.4 (CH), 117.0 (CH), 115.4 (CH_2), 52.3 (CH_3), 52.2 (CH_3), 37.1 (CH), 28.4 (CH_2), 27.7 (CH_2), 26.5 (CH_2) ppm; IR (thin film) ν_{max} 3083, 3001, 2951, 2830, 1726 cm^{-1}; MS (70 eV, EI) m/z 274.1 ([M]$^{+\bullet}$, 10), 259.1 ([M − CH_3], 1) 155.1 ([M − $(OCH_3)_2$], 100); HRMS (EI) calcd for $C_{16}H_{18}O_4$ [M]$^{+\bullet}$ 274.1205, found 274.1204; UV−vis (acetonitrile) λ_{max} = 209.5 nm (ε = 18600), 228 nm (ε = 12400).

Reaction of 2,3-Divinyl-1,3-cyclohexadiene (5) with 4.0 Molar Equiv of DMAD (29). A mixture of 2,3-divinyl-1,3-divinylcyclohexadiene (**5**) (35 mg, 0.26 mmol, 1.0 molar equiv), DMAD (**29**) (65 μL, 0.54 mmol, 2.0 molar equiv), and a crystal of BHT in benzene-d_6 (2.0 mL) were stirred at room temperature overnight. More DMAD was added (65 μL, 0.54 mmol, 2.0 molar equiv), and the reaction was heated to reflux and stirred overnight. Upon cooling to room temperature, the solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel eluting with 30% EtOAc in petroleum ether 40−60 °C. Fraction 1 contains double DA adduct **31** (42 mg, 38%); fraction 2 contains triple DA adduct **33** (60 mg, 51%).

Trimethyl (8a*S*,10a*S*)-7-((Dimethyl-λ^3-oxidanyl)carbonyl)-3,6,8a,9,10,10a-hexahydrophenanthrene-1,2,8-tricarboxylate (31). Double DA adduct **31** was isolated as a colorless solid, R_f = 0.35; 25:75 EtOAc/petroleum ether 40−60 °C. An analytical sample of double DA adduct **31** was obtained by recrystallization from ethanol to give colorless needles: mp 127−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (s, 2H), 3.78 (s, 6H), 3.74 (s, 6H), 3.28−3.00 (m, 4H), 2.91 (dd, J = 22.2 Hz, 8.3 Hz, 2H) 2.23−1.87 (m, 2H), 1.60−1.19 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3 (C_q), 167.3 (C_q), 139.7 (C_q), 137.5 (C_q), 128.2 (C_q), 116.4 (CH), 52.4 (CH_3), 52.3 (CH_3), 40.0 (CH), 31.4 (CH_2), 27.7 (CH_2) ppm; IR (KBr tablet) ν_{max} = 2996, 2951, 2847, 1722, 1648 cm^{-1}; MS (70 eV, EI) m/z 558.2 ([M]$^{+\bullet}$, 4), 527.2 ([M − OCH_3], 60), 467.1 (56); HRMS (EI) calcd for $C_{28}H_{30}O_{12}$ [M]$^{+\bullet}$ 558.1737, found 558.1728.

Hexamethyl (3a*R*,5a*S*,8a*S*,10a*R*)-3,3a,5a,6,8a,9,10,10a-Octahydropyrene-1,2,4,5,7,8-hexacarboxylate (33). Triple DA adduct **33** was isolated as a colorless solid, R_f = 0.50; 50:50 EtOAc/petroleum ether 40−60 °C. An analytical sample of triple DA adduct **33** was obtained by recrystallization from ethanol to give colorless needles: mp 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 6H), 3.78 (s, 6H), 3.72 (s, 6H), 3.40−3.12 (m, 4H), 3.07−2.85 (m, 2H), 2.30−2.06 (m, 2H), 1.91−1.71 (m, 2H), 1.59−1.46 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6 (C_q), 167.5 (C_q), 166.6 (C_q), 143.4 (C_q), 135.7 (C_q), 129.5 (C_q), 127.2 (C_q), 52.7 (CH_3), 52.4 (CH_3), 37.8 (CH), 37.0 (CH), 34.8 (CH_2), 24.7 (CH_2) ppm; IR (KBr tablet) ν_{max} = 2996, 2951, 2859, 2821, 1722, 1681, 1643 cm^{-1}; MS (70 eV, EI) m/z 416.1 ([M]$^{+\bullet}$, 7), 385.1 ([M − OCH_3], 52), 357.1 ([M − CO_2Me], 74), 230.1 (100); HRMS (EI) calcd for $C_{22}H_{24}O_8$ [M]$^{+\bullet}$ 416.1471, found 416.1474.

Double and Triple DA Adduct (31 and 33) from Mono DA Adduct (30). A mixture of mono DA adduct **30** (33 mg, 0.12 mmol, 1.0 molar equiv), DMAD (**29**) (59 μL, 0.48 mmol, 4.0 molar equiv), and 1 crystal of BHT in benzene-d_6 (1.0 mL) was stirred at reflux for 2 days. Solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel eluting with 30% EtOAc in petroleum ether 40−60 °C. Fraction 1 contains double DA adduct **31** (17 mg, 34%); fraction 2 contains triple DA adduct **33** (29 mg, 43%). ^{1}H NMR data were consistent with that reported above.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds; computational details including coordinates for all structures; cifs and anisotropic displacement ellipsoid plots for compounds ***cttt*-13**, ***cttt*-14**, ***tttt*-16**, **21**, **24**, **25**, **31**, and **33** (CCDC nos. 985422−985427, 1023991, and 1023992, respectively). 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 interest.

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