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Cycloaddition Reactions of Divinylbenzenes

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The reactions of *m*- and *p*-divinylbenzene with electrophilic olefins have been explored. In reactions with tetracyanoethylene (TCNE), *m*-divinylbenzene (*m*-DVB) is markedly more reactive than *p*-divinylbenzene (*p*-DVB). The reaction of *m*-DVB with TCNE leads to 2:1 Diels–Alder adduct **1**, while the reaction of *p*-DVB with TCNE results in cyclobutane adduct **3**. With maleic anhydride and α-carbomethoxymaleic anhydride, both *m*-DVB and *p*-DVB undergo double Diels–Alder reactions. The reactions of the para and meta isomers of diisopropenylbenzene (*p*-DIB and *m*-DIB) follow the same pattern. If *p*-DIB is mixed with methyl β,β-dicyanoacrylate (DCA), the reaction pathway can be changed from the [4 + 2] to the [2 + 2] cycloaddition by adding zinc chloride to increase the electrophilicity of DCA by complexing with the cyano substituents. The different pathways and reactivities are discussed.

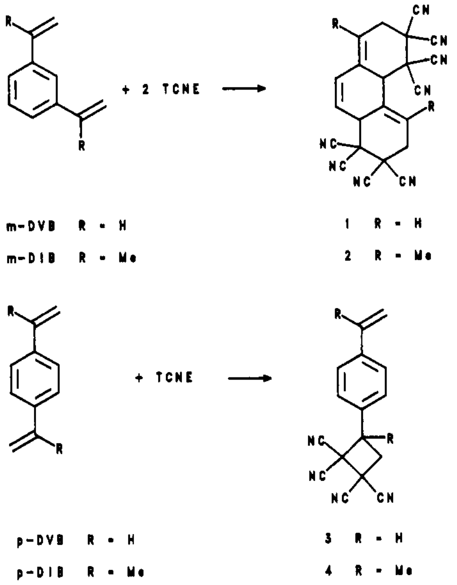
Introduction

Styrene and its derivatives have been thoroughly investigated in cycloaddition reactions. Styrene itself does not react with tetracyanoethylene (TCNE) under normal conditions, but under high pressure a [4 + 2] cycloadduct is formed that decomposes again at atmospheric pressure.[1] In contrast, *p*-methoxystyrene reacts rapidly with TCNE because it is more electron rich than styrene. In this reaction, investigated by Wiley and McKusick,[2,3] a cyclobutane adduct is formed via a zwitterionic tetramethylene intermediate. In a more detailed study of the *p*-methoxystyrene/TCNE system, using time-resolved absorption spectrometry, Nakahara and co-workers found that a reversible [4 + 2] cycloaddition first takes place.[4] Other styrenes with a donor substituent also undergo [2 + 2] cycloadditions with TCNE.[3]

As far as [4 + 2] thermal cycloadditions are concerned, Wagner–Jauregg's review quotes a few instances in which styrenes act as dienes.[5] Extreme conditions are required, and large quantities of inhibitor have to be added to the reaction mixture to prevent spontaneous copolymerizations. The reaction products are either 1:1 Diels–Alder adducts that reform the aromatic system, 2:1 bicyclic adducts (the so-called Wagner–Jauregg type adducts) obtained via two consecutive Diels–Alder reactions, or 2:1 Alder–ene adducts.

Although divinylbenzenes are very well-known to polymer chemists as cross-linking agents, these compounds have not been investigated thoroughly in cycloaddition reactions. In this work, the cycloaddition reactions of both *m*- and *p*-divinylbenzene (*m*-DVB and *p*-DVB) and *m*- and *p*-diisopropenylbenzene (*m*-DIB and *p*-DIB) with TCNE, maleic anhydride and other electrophilic olefins have been investigated. The reactions with α-carbomethoxymaleic anhydride,[6-8] an extremely reactive electrophilic olefin will also be described. In this laboratory we have previously studied the reaction of divinylbenzene with dicarbomethoxymaleic anhydride,[9] and these results will be discussed below.

Scheme I



Results

Reactions involving TCNE (Scheme I). All the cycloaddition reactions described here were run in 0.5 M acetonitrile solutions at 28 °C under argon atmosphere, unless indicated. Upon mixing TCNE with divinylbenzenes, as with other electron-rich olefins, bright colors are formed due to charge-transfer (CT) complexes. The reactions are complete when the color disappears, because this indicates that no starting material is left in the reaction mixture.

Pure *m*-DVB reacted with 2 equiv of TCNE to give the 2:1 Diels–Alder-type adduct **1** in 90% isolated yield in about 6 h. The two vinyl groups react consecutively as part of two diene systems, which results in destruction of the aromatic system. The second [4 + 2] addition could also involve the diene system that remains in the ring after the first addition; however, none of the bicyclic adduct is formed, indicating that the exocyclic addition is preferred. The same product is obtained at 80 °C. The 2:1 adduct **1** is a very stable, white crystalline product, which has been fully characterized by ^{1}H (no aromatic protons) and ^{13}C NMR, IR (no remaining aromatic or vinyl absorptions), and chemical analysis. The cycloaddition is not reversible.

Commercial DVB is roughly a 1:1:1:1 mixture of both *p*- and *m*-DVB and *p*- and *m*-ethylstyrene. The same 2:1 TCNE adduct **1** is obtained with commercial DVB, although it forms somewhat more slowly. This indicates that *m*-DVB is more reactive than *p*-DVB. The reaction is slower when diethyl ether is used as solvent because TCNE

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[1] Nakahara, M.; Uosaki, Y.; Sasaki, M.; Osugi, J. *Rev. Phys. Chem. Jpn.* 1977, *47*, 119.

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[4] Uosaki, Y.; Nakahara, M.; Osugi, J. *Int. J. Chem. Kinet.* 1982, *14*, 985.

[5] Wagner-Jauregg, Th. *Synthesis* 1980, 769.

[6] Hall, H. K., Jr.; Rhoades, J. W.; Nogues, P.; Wai, G. K. C. *Polym. Bull.* 1981, *4*, 629.

[7] Hall, H. K., Jr.; Nogues, P.; Rhoades, J. W.; Sentman, R. C.; Detar, M. *J. Org. Chem.* 1982, *47*, 1451.

[8] Evans, S. B.; Abdelkader, M.; Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.* 1989, *54*, 2848.

[9] Hall, H. K., Jr.; Sentman, R. C.; Nogues, P. *J. Org. Chem.* 1982, *47*, 3647.

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is not very soluble in ether. However, the reaction product is not soluble either, which leads to an easy workup of the reaction by simple filtration.

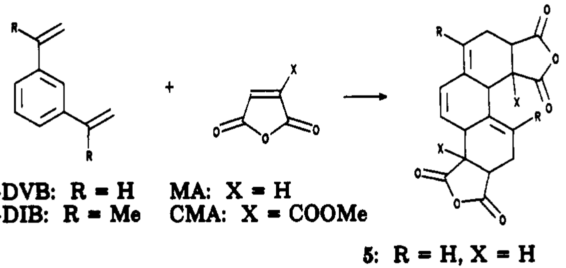
Reaction of *m*-DIB with TCNE leads to a similar 2:1 adduct **2**, but in this case the reaction is complete in about 1 h. The methyl substituent on the vinyl group increases the donor character of this diene as would be expected. Whereas the CT colors in the reactions of DVB are mostly red, the solution of TCNE and *m*-DIB is purple, indicating a stronger CT complex.

Pure *p*-DVB is much less reactive than the meta isomer, as had already been deduced from the reaction of the commerical DVB mixture. The reaction is complete after about 48 h at 28 °C or in 10 h at 80 °C; inhibitor is added to these reactions as *p*-divinylbenzene is very susceptible to spontaneous polymerizations. Remarkably, the cycloadduct in this case is the 1:1 cyclobutane adduct **3**. No [4 + 2] cycloaddition is observed; the cyclobutane **3** is formed in high yield and is also fully characterized by ^1H and ^{13}C NMR and IR spectroscopy and elemental analysis. Both the cyclobutane protons and the remaining vinyl group are easily identified in the proton NMR.

p-DIB is also less reactive than its meta isomer, but more reactive than *p*-DVB in the reaction with TCNE. Again, no [4 + 2] is observed; only [2 + 2] cycloaddition to form **4** occurs.

Reactions with Maleic Anhydride (MA) and α-Carbomethoxymaleic Anhydride (CMA). The reactions of MA and CMA[6-8] follow the same pattern with *m*-DVB and *m*-DIB as described for TCNE. Two consecutive Diels–Alder reactions take place, with both reactions involving the exocyclic double bonds. The reactions with the highly electrophilic CMA are much faster than the reactions with MA but do not proceed cleanly. Unknown side products can be noticed in the NMR spectra, and the isolated yields are low. The reactions with CMA are run in acetonitrile or ether at 28 °C and are complete within minutes in the case of *m*-DIB, while reactions with MA must be run overnight in refluxing acetonitrile.

The structures of the cycloadducts are also based on the phenanthrene skeleton. From decoupling experiments in ^1H NMR analysis, we can conclude that the COOMe substituent of CMA is "para" to the methyl group of *m*-DIB. The same orientation of the CMA moiety is obtained in its reaction with *m*-DVB.

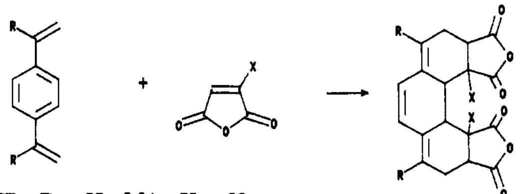


m-DVB: R = H MA: X = H
m-DIB: R = Me CMA: X = COOMe

5: R = H, X = H
6: R = Me, X = H
7: R = H, X = COOMe
8: R = Me, X = COOMe

In contrast to their reactions with TCNE, *p*-DVB and *p*-DIB undergo Diels–Alder reactions with MA and CMA. Two Japanese patents previously mentioned the reaction of *p*-DVB with MA, but no details were given.[10,11] As in the meta cases, two consecutive [4 + 2] cycloadditions take place involving the exocyclic double bonds. No [2 + 2] adducts are detected. With CMA the reactions proceed very rapidly. The reaction of *p*-DIB with CMA in ether is exothermic at 28 °C and is complete after just 2 min as witnessed by the fading of the bright yellow CT color. The reactions with MA proceed very slowly and with low yields. After overnight reflux in acetonitrile, the yield is less than 10%. Longer reaction times result in adventitious polymerization of the divinylbenzene. In the reaction products of these cycloadditions, the COOMe substituent of CMA again is "para" to the methyl substituent, based on the NMR spectra.

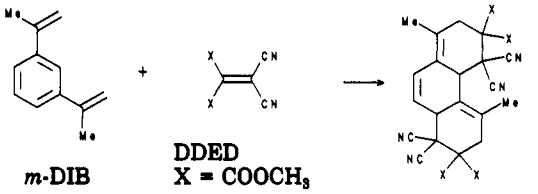
On the basis of the results of this study, the structure for the adduct of divinylbenzene and dicarbomethoxymaleic anhydride proposed in a previous study[9] has to be corrected. We erroneously wrote the double Diels–Alder adduct of dicarbomethoxymaleic anhydride with *p*-divinylbenzene as the reaction product, but this study clearly shows that in the commercial divinylbenzene mixture the meta isomer of divinylbenzene is more reactive than the para isomer. Therefore, a structure analogous to **7** has to be proposed.



p-DVB: R = H MA: X = H
p-DIB: R = Me CMA: X = COOMe

9: R = H, X = H
10: R = Me, X = H
11: R = H, X = COOMe
12: R = Me, X = COOMe

Reactions with Other Electron-Poor Olefins. Neither *m*-DVB or *p*-DVB reacts with dienophiles such as dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate (DDED), methyl cyanofumarate, or β,β-dicyanovinyl chloride at room temperature in ether or acetonitrile. However, for DDED with *m*-DIB the 2:1 adduct **13** can be obtained after longer reaction times in low yield; some polymer is also formed in these reactions.



m-DIB

DDED
X = $COOCH_3$

13

Reaction of *p*-DIB with methyl β,β-dicyanoacrylate (DCA) in acetonitrile leads to the double Diels–Alder adduct **14** in 10% yield. However, addition of zinc chloride to the reaction mixture results in the formation of cyclobutane adduct **15**.

Discussion

The most remarkable aspects of the reactions of these divinylbenzenes with dienophiles are the diversity of the products and the range of reactivities.

Both *m*-divinylbenzene and *m*-diisopropylbenzene react with strong dienophiles to form double Diels–Alder adducts with complete destruction of the aromatic system. With TCNE the reactions proceed at room temperature very cleanly in high yield. With the more reactive CMA, unknown side reactions interfere and the isolated yield is low. With MA, the reaction temperature has to be raised

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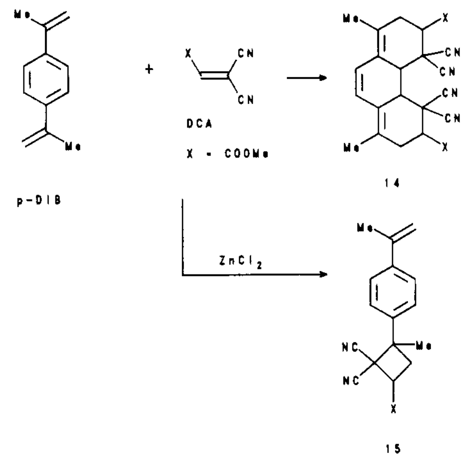
[10] Nippon Zeon Co., Jpn. Kokai Tokkyo Koho, JP 60 23,383, 1985; *Chem. Abstr.* **1985**, *103*, 37468 e.

[11] New Japan Chemical Co., Jpn. Kokai Tokkyo Koho, JP 60 32,792, 1985; *Chem. Abstr.* **1985**, *103*, 87766 w.



in keeping with its lower electrophilicity.

With *p*-divinylbenzene and *p*-diisopropenylbenzene, the reaction products vary from 2:1 [4 + 2] cycloadducts to the [2 + 2] cyclobutane adducts. The highly reactive and electrophilic CMA forms [4 + 2] cycloadducts with both *p*-DVB and *p*-DIB. MA behaves similarly, but again lower reaction rates and yields are observed. Maleic anhydride and its derivatives usually do not add thermally in [2 + 2] fashion[12] because this would lead to a highly strained cyclobutane ring fused to the five-membered ring of the anhydride. In contrast, with TCNE the cyclobutane adducts are formed. This does not exclude that the [4 + 2] adduct could be formed first in a reversible reaction as has been observed previously for *p*-methoxystyrene and TCNE.[4] An alternative mechanism involves ring-opening of a Diels–Alder adduct to a zwitterionic intermediate and formation of a cyclobutane adduct, which has been proposed by Bartlett in the reaction isodicyclopentadiene and TCNE.[13] In this study no evidence for such a mechanism has been found.

With less electrophilic olefins such as DDED (dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate) and dimethyl cyanofumarate, no reaction occurred with either *p*-DVB or *m*-DVB. A low yield of 2:1 [4 + 2] adduct was obtained from the reaction of the most reactive diene *m*-DIB with DDED. With DCA (methyl β,β-dicyanoacrylate), the double Diels–Alder adduct of *p*-DIB could be obtained in low yield after 5 days at room temperature. Addition of the Lewis acid $ZnCl_2$ to the reaction of *p*-DIB with DCA results in formation of the cyclobutane adduct. Zinc chloride forms a complex with the cyano substituents of DCA, making the olefin more electrophilic as has been shown in polymerization studies of acrylonitrile with vinyl acetate in the presence of $ZnCl_2$.[14] The more electrophilic ethylenes such as TCNE and DCA/$ZnCl_2$ complex react with *p*-DIB in [2 + 2] fashion.

The reactions of TCNE with the different isomers of divinylbenzene and diisopropylbenzene are the most surprising: with the meta isomers the [4 + 2] cycloadducts are obtained, while the para isomers are much less reactive and yield [2 + 2] cycloadducts. The most obvious difference between the divinylbenzene isomers is that in the para isomer the two vinyl groups are in conjugation and influence each other, while in the meta isomer the two vinyl groups should be totally independent of each other. Therefore, we would expect that the reactivity of the two vinyl groups in *m*-DVB to be about the same as for styrene, which is quite contrary to the results.

Table I. Calculated Ionization Potentials and 1,4-Bislocalization Energies for the Dienes

	IP[a] (eV)	β^b
m-DVB	8.86	3.29
p-DVB	8.65	3.43
m-DIB	8.76	
p-DIB	8.77	
diphenylethylene		3.26
styrene		3.51
stilbene		3.84

[a] As calculated by AMPAC. [b] Reference 16.

In cycloadditions, the reactivity of the diene generally increases with decreasing ionization potentials. To our knowledge no data on the ionization potential or photoelectronic spectra of the divinylbenzenes are available in the literature. From AM1 approximations using the AMPAC computer program,[15] we found that there is no big difference in the calculated ionization potentials for these divinylbenzenes as shown in Table I.

The AM1 calculations also reveal that the HOMO's of both *p*-DVB and *m*-DVB have a C_2 symmetry, which makes their [4 + 2] cycloadditions symmetry-allowed because TCNE also possesses C_2 symmetry.

In order to compare the stability of adducts, the 1,4-bislocalization energies β can be calculated from Dewar's perturbation molecular orbital theory.[16] These β-values for *m*-DVB and *p*-DVB are also included in Table I. If the value of β is below 3.6, reaction normally takes place. Stilbene (β = 3.84), for example, is nonreactive toward TCNE, while 1,1-diphenylethylene (β = 3.26) readily undergoes [4 + 2] cycloaddition.[17] For both divinylbenzenes, a value below 3.6 is obtained and the value for the meta is indeed smaller, which is consistent with its higher reactivity. However, this does not explain the different reaction paths.

In conclusion, we can state that for powerful electrophilic olefins, [2 + 2] cycloadducts are formed for the *p*-divinyl- and *p*-diisopropenylbenzene, while with weaker electrophiles the [4 + 2] cycloadditions occur. Sophisticated time-resolved techniques would be necessary to determine if the [4 + 2] adducts are formed first too in the reactions yielding cyclobutane adducts, as has been shown previously for *p*-methoxystyrene and TCNE.[4] The meta isomers of divinyl- and diisopropylbenzene always react in [4 + 2] fashion. Maleic anhydride and its carbomethoxy derivative as dienophile always undergo the [4 + 2] cycloaddition.

Experimental Section

General Methods. Melting points are corrected. NMR data were obtained at 250 MHz. Whenever possible, the coupling constants were determined by homonuclear decoupling. Elemental analyses were performed by Desert Analytics, Tucson, AZ. For reaction products for which no satisfactory elemental analysis could be obtained, NMR spectra are submitted as supplementary material.

Reagents. *m*-Diisopropenylbenzene and the divinylbenzene mixture were obtained from Aldrich and used without purification. *m*-Divinylbenzene, *p*-divinylbenzene, and *p*-diisopropenylbenzene were prepared via a Wittig reaction, as described by Nuyken et al. for *p*-divinylbenzene[18] (detailed experimental data in sup-

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(13) Bartlett, P. D.; Wu, C. *J. Org. Chem.* **1984**, *49*, 1880.

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(16) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975.

(17) Uosaki, Y.; Nakahara, M.; Osugi, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2569.

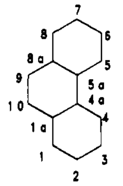
(18) Nuyken, O.; Siebzehnruebl, F. *Makromol. Chem.* **1988**, *189*, 5410.

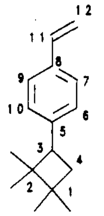
plementary material). The products were not distilled, owing to excessive loss by adventitious polymerization, but were easily purified by elution through a short silica gel column (5 cm) using hexanes as eluent. The purity of the reagents was established by NMR spectroscopy.

α-Carbomethoxymaleic anhydride,[8] methyl β,β-dicyanoacrylate,[19] dimethyl dicyanofumarate,[20] and β,β-dicyanovinyl chloride[21] were prepared according to literature procedures. TCNE (Aldrich) was purified as described previously.[22]

General Procedure for Cycloaddition Reactions. *m*-DVB (1.5 mmol, 195 mg) was dissolved in 4 mL of dry acetonitrile in a septum-capped flask under Ar. TCNE (3 mmol, 384 mg) was added, and the red color of the CT complex was observed. The mixture was stirred at rt (28 °C) under Ar, and the red color faded after 6 h. A copious white precipitate was formed, ether was added, and the solid was filtered and washed with ether. The product can be recrystallized from acetonitrile or toluene.

For the cycloadducts that are based on the phenanthrene skeleton, the carbons and hydrogens in the NMR spectra are numbered accordingly.[23] For the cyclobutane adducts, the carbons and hydrogens are numbered as shown:





1,1,2,2,5,5,6,6-Octacyano-1,1a,2,3,5a,5,6,7-octahydrophenanthrene (1, *m*-DVB and TCNE). Yield: 350 mg, (60%). Mp > 235 °C dec. ^{1}H NMR (DMS-d_6): δ 6.99 (m, H_{10}, 1 H), 6.84 (m, H_4, 1 H), 6.35 (2m, H_8 and H_9, 2 H), 4.56 (br s, H_{5a}, 1 H), 4.16 (m, H_{1a}, 1 H), 4.18–4.06 (m, H_{3ax}, 1 H), 4.01–3.91 (m, H_{7ax}, 1 H), 3.5 (m, H_{3eq} and H_{7eq}, 2 H). ^{13}C NMR (DMSO-d_6): δ 133.0, 128.8, 123.6, 122.6 (C_4, C_8, C_9, C_{10}), 129.5, 126.1 (C_{4a}, C_{8a}), 112.5, 112.3, 111.2, 110.0 (CN), 47.0, 45.5, 41.0, 39.0 (C_1, C_2, C_5, C_6), 43.8, 41.5 (C_{1a}, C_{5a}), 33.9, 33.4 (C_3, C_7). IR (KBr): 3085, 2990, 2921, 2255, 1430 (s), 1321 (w), 1249, 1124, 881, 796, 761 cm^{-1}. Raman (λ = 5145 Å, laser power 130 mV, slits 600 mn): 609, 670, 801, 1059, 1218, 1255 (CH_2 twist), 1430 (CH_2 scissors), 1624, 1669, 2257 (CN), 2927 (CH_2 ν_{as}), 2965 (CH_3 ν_{as}), 3076 (ν_{CH} olefin). Anal. Calcd for $C_{22}H_{10}H_8$: C, 68.38; H, 2.61, N, 29.00. Found: C, 68.13; H, 2.49; N, 28.71.

1,1,2,2,5,5,6,6-Octacyano-1,1a,2,3,5a,5,6,7-octahydro-4,8-dimethylphenanthrene (2, *m*-DIB and TCNE). Yield: 87%. Mp > 240 °C dec. ^{1}H NMR (acetone-d_6): δ 7.19 (dd, H_{10}, J_{9-10} = 10 Hz, J_{10-1a} = 3 Hz, 1 H), 6.32 (d, H_9, 1 H), 4.77 (s, H_{5a}, 1 H), 4.24 (s, H_{1a}, 1 H), 3.96 and 3.55 (2d each, H_3 and H_7, J = 18 Hz, 2 H), 2.24 and 2.13 (2 s, Me, 6 H). IR (KBr): 2944, 2251, 1649, 1444, 1368, 1131, 796 cm^{-1}. Anal. Calcd for $C_{24}H_{14}N_8$: C, 69.55; H, 3.41; N, 27.04. Found: C, 69.56; N, 3.63; N, 27.50.

1,1,2,2-Tetracyano-3-(*p*-vinylphenyl)cyclobutane (3, *p*-DVB and TCNE). Yield: 84%. Mp 172 °C. ^{1}H NMR (acetone-d_6): δ 7.6 (m, aromatic H, 4 H), 6.82 (dd, H_{11}, 1 H), 5.92 (dd, $H_{12trans}$, 1 H), 5.34 (dd, H_{12cis}, $^3J_{trans}$ = 17.6 Hz, $^3J_{cis}$ = 10.9 Hz, $^2J_{gem}$ = 0.6 Hz, 1 H), 5.09 (dd, H_3, 1 H), 3.92 and 3.66 (2 dd, H_4 and $H_{4'}$, ^3J = 8.9 Hz, 12.1 Hz, $^2J_{gem}$ = 12.9 Hz, 2 H). ^{13}C NMR: δ 206.3, 139.9, 136.8, 128.9, 127, 115.9 (aromatic), 112.8, 112.2, 112.1, 110.5 (CN), 47.7 (C_3), 45.5 (C_2), 36.1 (C_4), 34.8 (C_1). IR (KBr): 3054, 2257, 2219, 1630, 1512, 1410, 1146, 988, 918, 844 cm^{-1}. Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.70. Found: C, 74.08; H, 3.64, N, 21.34.

1,1,2,2-Tetracyano-3-methyl-3-(*p*-isopropenylphenyl)cyclobutane (4, *p*-DIB and TCNE): Yield: 25%. Mp 183–184 °C. ^{1}H NMR (acetone-d_6): δ 7.66 (H_6, H_{10}, *A*B, J = 8.6 Hz, 2 H), 7.42 (H_7, H_9, A*B*, 2 H), 5.52 (q, H_{12cis}, ^3J = 0.7 Hz, 1 H), 5.19 (q, $H_{12trans}$, ^3J = 1.4 Hz, 1 H), 4.09 (H_4, *A*B, J = 13.8 Hz, 1 H), 3.61 (H_4, A*B*, 1 H), 2.20 (m, Me on C_{11}, 3 H), 2.10 (s, Me on C_3, 3 H). IR (KBr): 2980, 1624, 1518, 1436, 1262, 893, 839, 823 cm^{-1}. Anal. Calcd for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.61; H, 4.87; N, 19.54.

1,1a,2,3,5a,5,6,7-Octahydrophenanthrene-1,2,5,6-tetracarboxylic Acid Dianhydride (5, *m*-DVB and MA). Reflux 14 h in acetonitrile. Yield: 16%. Mp > 300 °C dec. ^{1}H NMR (DMSO-d_6): δ 6.16 (dd, H_{10}, J = 10, 2 Hz, 1 H), 6.08 (m, H_4, 1 H), 5.75 (m, H_8 and H_9, 2 H), 3.7 (m, H_1 and H_5, 2 H), 3.5 (m, H_2 and H_6, 2 H), 3.25 (br s, H_{5a}, 1 H), 3.1 (br s, H_{1a}, 1 H), 2.7–2.1 (2 br m, CH_2 at C_3 and C_7, 4 H). IR (KBr): 2979, 1838, 1767 (s), 1250, 1178, 1082, 1031, 954, 939 cm^{-1}.

1,1a,2,3,5a,5,6,7-Octahydro-4,8-dimethylphenanthrene-1,2,5,6-tetracarboxylic Acid Dianhydride (6, *m*-DIB and MA). Reflux 18 h in acetonitrile. Yield: 40%. Mp 250–261 °C. ^{1}H NMR (acetone-d_6): δ 6.57 (dd, H_{10}, J = 10.4, 2.5 Hz, 1 H), 5.83 (dd, H_9, J = 10.4, 3.3 Hz, 1 H), 3.65–3.9 (m, H_1, H_2, H_5, H_6, 4 H), 3.55 and 3.38 (2 br s, H_{1a}, H_{5a}, 2 H), 2.5–2.8 (m, CH_2 at C_3 and C_7, 4 H), 1.93, 1.87 (2 s, Me on C_4 and C_8, 6 H). IR: 2963, 1838, 1774 (s), 1255, 1237, 1177, 1160, 1098, 938, 928 cm^{-1}.

1,5-Dicarbomethoxy-1,1a,2,3,5a,5,6,7-octahydrophenanthrene-1,2,5,6-tetracarboxylic Acid Dianhydride (7, *m*-DVB and CMA). Stir in ether for 2 days. Recrystallize from toluene at −50 °C. Adduct 7 is obtained in low yield, but NMR indicates the presence of a nonidentified impurity. Mp 91–111 °C. ^{1}H NMR (acetone-d_6): δ 6.38 (dd, H_{10}, J = 10, 2 Hz, 1 H), 6.10 (m, H_4 and H_8, 2 H), 5.82 (m, H_9, 1 H), 4.01 (2 dd, H_2 and H_6, 2 H), 3.90 (2s, Me ester, 6 H), 3.80 (m, H_{1a} and H_{5a}, 2 H), 2.4–3.0 (m, CH_2 at C_3 and C_7, 4 H).

1,5-Dicarbomethoxy-1,1a,2,3,5a,5,6,7-octahydro-4,8-dimethylphenanthrene-1,2,5,6-tetracarboxylic Acid Dianhydride (8, *m*-DIB and CMA). Yield: 45%. Mp 212 °C. ^{1}H NMR (acetone-d_6): δ 6.52 (dd, H_{10}, J = 10.5, 2 Hz, 1 H), 5.74 (dd, H_9, J = 10.5 Hz, 3.2 Hz, 1 H), 4.11 and 4.05 (2 dd, H_2 and H_6, 2 H), 4.00 (br s, H_{1a} and H_{5a}, 2 H), 2.6–2.9 (m, CH_2 at C_3 and C_7, 4 H), 1.88 (s, Me, 3 H), 1.76 (d, J = 2.4 Hz, Me, 3 H). IR (KBr): 2960, 1850, 1783(s), 1430, 1265, 1098 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_{10}$: C, 61.27; H, 4.72. Found: C, 61.46; H, 4.76.

2,3,4,4a,5a,5,6,7-Octahydrophenanthrene-3,4,5,6-tetracarboxylic Acid Dianhydride (9, *p*-DVB and MA): Reflux 14 h in acetonitrile. Yield: 7%. Mp 273–276 °C. ^{1}H NMR (acetone-d_6): δ 6.12 (s, H_9 and H_{10}, 2 H), 5.95 (m, H_1 and H_8, 2 H), 3.98 (dd, H_4 and H_5, J = 9.0, 5.5 Hz, 2 H), 3.73 (m, H_3 and H_6, 2 H), 3.59 (m, H_{4a} and H_{5a}, 2 H), 2.72 (ddd, CH_2 and C_2 and C_7, J = 16, 8, 1.5 Hz, 4 H). IR (KBr): 2956, 1847, 1768 (s), 1240, 936 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_6$: C, 66.26; H, 4.32. Found: C, 66.23; H, 4.07.

2,3,4,4a,5a,5,6,7-Octahydro-1,8-dimethylphenanthrene-3,4,5,6-tetracarboxylic Acid Dianhydride (10, *p*-DIB and MA): Reflux 18 h in acetonitrile. Yield: 51%. Mp 265–270 °C. ^{1}H NMR (acetone-d_6): δ 6.40 (s, H_9 and H_{10}, 2 H), 3.90 (dd, H_4 and H_5, J = 9.4, 5.0 Hz, 2 H), 3.73 (m, H_3 and H_6, 2 H), 3.53 (br s, H_{4a} and H_{5a}, 2 H), 2.60 (m, CH_2 at C_2 and C_7, 4 H), 1.90 (s, Me at C_1 and C_8, 6 H). IR (KBr): 1840, 1778 (s), 1239, 1193, 1103, 997, 933 cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.59; H, 5.15.

4,5-Dicarbomethoxy-2,3,4,4a,5a,5,6,7-octahydrophenanthrene-3,4,5,6-tetracarboxylic Acid Dianhydride (11, *p*-DVB and CMA). Yield: 55%. Mp > 300 °C dec. ^{1}H NMR (acetone-d_6): δ 6.15 (m, H_1, H_8, H_9, H_{10}, 4 H), 4.06 (dd, H_3 and H_6, J = 6.2, 2.0 Hz, 2 H), 3.87 (s, Me ester, 6 H), 3.66 (m, H_{4a} and H_{5a}, 2 H), 2.92 (ddd, CH_2, J = 15.3, 7.5, 2.0 Hz, 2 H), 2.59 (dt, CH_2, J = 15.3, 5.3 Hz, 2 H). IR (KBr): 1852, 1787 (s), 1736, 1433, 1261, 1098, 969 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_{10}$: C, 59.55; H, 4.12. Found: C, 59.56; H, 4.10.

4,5-Dicarbomethoxy-2,3,4,4a,5a,5,6,7-octahydro-1,8-dimethylphenanthrene-3,4,5,6-tetracarboxylic Acid Dianhydride (12, *p*-DIB and CMA). Exothermic reaction if run in ether, complete within 2 min. Yield: 73%. Mp 264 °C dec. ^{1}H NMR (acetone-d_6): δ 6.34 (s, H_9 and H_{10}, 2 H), 4.03 (dd, H_3 and H_6, J = 4.7, 3.0 Hz, 2 H), 3.85 (s, Me esters, 6 H), 3.60 (br d, H_{4a} and H_{5a}, 2 H), 2.7 (m, CH_2 at C_2 and C_7, 4 H), 1.93 (s, Me at C_1 and C_8, 6 H). IR (KBr): 2961, 1849, 1786 (s), 1736 (s), 1427,

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1265, 1098, 961 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_{10}$: C, 61.27, H, 4.72. Found: C, 61.59; H, 4.65.

Tetramethyl 1,1,5,5-Tetracyano-1,1a,2,3,5a,5,6,7-octahydro-4,8-dimethylphenanthrene-2,2,6,6-tetracarboxylate (13, *m*-DIB and DDED). Cycloaddition run in acetonitrile for 3 days. Adventitious polymerization occurred, leading to very low yield (<5%). Mp 182 °C. ^1H NMR ($CDCl_3$): δ 6.80 (dd, H_{10}, $J_{10,9}$ = 10 Hz, $J_{10,1a}$ = 3 Hz, 1 H), 6.10 (d, H_9, 1 H), 4.19 (s, H_{5a}, 1 H), 3.94 (H_{1a}, 1 H), 3.93, 3.91, 3.90 (3 s, Me esters, 12 H), 3.20 and 2.85 (2d each, CH_2 at C_3 and C_7, 4 H), 2.06 (d, 3 H), 1.98 (s, 3 H). IR (KBr): 2958, 1742 (s), 1435, 1380, 1266, 1217, 1112 cm^{-1}. Anal. Calcd for $C_{28}H_{26}N_4O_8$: C, 61.53; H, 4.80. Found: C, 61.55; H, 5.16.

Dimethyl 4,4,5,5-Tetracyano-2,3,4,4a,5a,5,6,7-octahydro-1,8-dimethylphenanthrene-3,6-dicarboxylate (14, *p*-DIB and DCA). Cycloaddition run in acetonitrile at 28 °C for 5 days. Filter off precipitated adduct 14. Yield: 10%. Mp >250 °C. ^1H NMR (acetone-d_6): δ 6.55 (s, H_9 and H_{10}, 2 H), 3.85 (s, Me ester, 6 H), 3.78 (dd, H_3 and H_6, J = 9.6, 7.8 Hz, 2 H), 3.53 (br s, H_{4a} and H_{5a}, 2 H), 2.73 (br d, CH_2 at C_2 and C_7, 4 H), 1.97 (s, Me at C_1 and C_8, 6 H). IR (KBr): 2960, 1740 (s), 1435, 1264, 1110 cm^{-1}. Anal. Calcd for $C_{24}H_{22}N_4O_4$: C, 66.96; H, 5.15; N, 13.02. Found: C, 66.98; H, 5.06; N, 13.08.

Methyl 2,2-Dicyano-3-methyl-3-(*p*-isopropenylphenyl)-cyclobutane-1-carboxylate (15, *p*-DIB and CDA). $ZnCl_2$ (0.67 g, 5 mmol) was placed under Ar in a round-bottomed flask and was dried by heating with a Bunsen burner until it melted. DCA (0.77 g, 5 mmol), dry $CHCl_3$ (30mL), and 5 mL of anhydrous ether were added, and the mixture was stirred at rt for 15 min. *p*-DIB (0.85 g, 5 mmol) was added, and a yellow CT complex could be observed. The mixture was stirred overnight at rt and extracted with water to remove $ZnCl_2$. Attempted recrystallizations failed. The cyclobutane adduct could be purified by running it very fast through a short silica gel column (15 cm), using $CHCl_3$ as eluent. After evaporation of the solvent, a sticky solid is obtained. NMR shows the presence of two isomers in a 60:40 ratio. The NMR data for the major isomer are listed, with the data for the minor isomer, if different, (between brackets). ^1H NMR ($CDCl_3$): δ 7.52 (H_6, H_{10}, *A*B, J = 8.2 Hz, 2 H), 7.16 (H_7, H_9, A*B*, 2 H) [7.55, 7.27 (AB, J = 8.3 Hz) 2 H], 5.4 (m, H_{12}, 1 H), 5.13 (m, H_{12}, 1 H), 3.85 (s, Me ester, 3 H) [3.89], 3.84 (dd, H_1, J = 8.9, 11.1 Hz, 1 H) [3.63 (dd)], 3.18 (dd, H_4, J = 11.1, 11.7 Hz, 1 H), 2.43 (dd, H_4, 1 H) [2.73 (dd)], 1.80 (s, Me on C_3, 3 H) [1.78 (s)] ppm.

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Supplementary Material Available: Experimental procedures for *p*-divinylbenzene, *p*-diisopropenylbenzene, and *m*-divinylbenzene and ^1H NMR spectra for **5–7** and **15** (5 pages). Ordering information is given on any current masthead page.

Solvent Effects on Manganese(III)-Based Oxidative Free-Radical Cyclizations: Ethanol and Acetic Acid

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Ethanol complements the typical solvent, acetic acid, for Mn(III)-based oxidative free-radical cyclizations. Cyclization of enol ether **1c** to give gibberellic acid intermediate **6c** is successful in ethanol, but not in acetic acid. Ethanol acts as a reducing agent for primary radicals, converting **13** and **33** to alkanes **17** and **32**. Acetylenes can be used as substrates since the vinyl radicals **24** and **25** are reduced by ethanol to alkenes **26–28**. The 1-hydroxyethyl radical obtained from ethanol is oxidized to acetaldehyde by Mn(III). The effect of solvent on the oxidative cyclization of unsaturated β-keto esters **35** and **48** was examined. A higher percentage of 5-exo product is obtained in ethanol. The primary cyclopentanemethyl radicals **40** and **53** are oxidized mainly to alkenes **43** and **57** in ethanol and mainly to the alcohols **42** and **55** and lactones **41** and **58** in acetic acid.

Introduction

Free-radical cyclizations of alkenes provide a valuable method for the synthesis of cyclic compounds.[1] We have recently developed an efficient oxidative free-radical cyclization using $Mn(OAc)_3$[2] to oxidize a β-keto ester, 1,3-diketone, or 1,3-diester to an enol radical that undergoes efficient cyclization to a double bond.[3] The reaction is terminated by oxidation of the radical to an alkene with $Cu(OAc)_2$. Mono, tandem, and triple cyclizations can be carried out in high yield. Tandem oxidative cyclization of acetoacetate **1a** provides 86% of bicyclo[3.2.1]octanone **6a**. Acetic acid has been the solvent of choice of these reactions and earlier studies involving intermolecular addition reactions of radicals generated by $Mn(OAc)_3$, since acetic acid dissolves both organic compounds and Mn(O-

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