(*cis*-*e*-*a*-10). trans *a*-*a*:cis *a*-*e*:cis *e*-*a* = 89:6:5; MS m/e (rel intensity) 296 (2, M), 223 (1, M − 73), 207 (5, M − 73 − 16), 135 (86, M − 146 − 15, $PhSiMe_2^+$), 73 (100), 45 (17), 43 (6); IR (liquid film) 3000 (w, HC=), 2930 (s), 2880 (m), 1585 (m, C=C), 1545 (w), 1430 (w), 1395 (w), 1250 (shoulder), 1240 (s), 1180 (w), 1150 (w), 825 (s), 740 (m), 680 (m), 620 (w) cm^{-1}. Anal. Calcd for $C_{15}H_{32}Si_3$: C, 60.73; H, 10.87; Si, 28.40. Found: C, 60.72; H, 10.91; Si, 28.45.

***trans*-α,α-10**: ^{1}H NMR (270 MHz, $CDCl_3$), δ 5.80 (d, $J = 7.2$ Hz, 1 H), 5.67 (d, $J_1 = 9.6$ Hz, 1 H), 5.53 (dd, $J_1 = 9.6$ Hz, $J_2 = 6.2$ Hz, 1 H), 1.80 (d, $J = 7.2$ Hz, 1 H), 1.70 (d, $J = 6.2$ Hz, 1 H), 0.12 (s, 9 H, Me_3SiC_{dienic}), 0.09, 0.01 (2s, 9 H and 9 H, $Me_3SiC_{allylic}$).

3,6-Bis(trimethylsilyl)cyclohexa-1,4-dienes (14). A mixture of the cis and trans isomers: GC (temperature program: 40 °C for 5 min, then to 220 °C at 10 °C/min), $t_R = 20.4$ (*trans*-14) and 22.0 min (*cis*-14), trans:cis = 70:30; IR (liquid film) 1600 cm^{-1} (m, C=C). ^{1}H NMR (250 MHz, $CDCl_3$): the spectrum of the mixture was very similar to this described in;[20] the spectra of both isomers (described below) are very close: for the *trans*-14 isomer, the Me_3Si singlet is 1.5 Hz downfield, the $H_{ethylenic}$ multiplet is 2 Hz upfield and the $H_{allylic}$ multiplet is 32 Hz upfield, trans:cis = 70:30; for the assignment, it was assumed that, in the trans isomer, the $H_{allylic}$, located in the perpendicular area of the Si–C bond, is shielded by the magnetic anisotropy of this bond. Such an effect was previously observed for the trans isomer of the 1,2-bis(trimethylsilyl)ethylene in which the $H_{ethylenic}$ is 0.1 ppm shielded by the *cis*-Si–C bond.[36]

***trans*-14**: crystallized, mp = 50 °C (EtOH); ^{1}H NMR (250 MHz, $CDCl_3$), δ 0.118 (s, 18 H, Me_3Si), 2.25 (m, 2 H), 5.52 (m, AB type, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$), δ 123.43 (T), 30.67 (T), −3.57 (P); ^{29}Si NMR (39.73 MHz, $CDCl_3$) δ 1.23. Anal. Calcd for $C_{12}H_{24}Si_2$: C, 64.20; H, 10.78; Si, 25.02. Found: C, 64.18; H, 10.85; Si, 25.06.

***cis*-14**: liquid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.112 (s, 18 H, Me_3Si), 2.37 (m, 2 H), 5.52 (m, AB type, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$), δ 122.75 (T), 30.41 (T), −2.98 (P); ^{29}Si NMR (39.73 MHz, $CDCl_3$) δ −0.58.

Cyclohexa-1,4-diene was shown to be almost planar;[37] 14 does not seem strictly planar because of the AB-type spectum presented by the $H_{ethylenic}$ of both isomers, but the weak difference for the ^{13}C chemical shifts of the $C_{allylic}$ of both isomers indicates a structure not far from planarity. Moreover, the presence, in the ^{1}H NMR spectrum of both isomers, of a single signal for the 2 $H_{allylic}$ on the one hand and for the 2 $SiMe_3$ groups on the other hand, would indicate the existence of a rapid conformational isomerism at room temperature. This assumption was confirmed by their ^{13}C and ^{29}Si NMR spectra also showing a single signal for the Me_3Si groups.

1-Methyl-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene (*trans*-15): bp 96 °C (2.5 mmHg); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.07 (s, 9 H, Me_3SiC_6), 0.13 (s, 9 H, Me_3SiC_3), 1.71 (t, $J = 1.5$ Hz, 3 H), 2.19 (m, 2 H, $H_{allylic}$), 5.21 (m, 1 H, H_2), 5.54 (m, 2 H, H_4, H_5); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 132.13 (Q, C_1), 125.64 (T, C_4 or C_5), 122.29 (T, C_4 or C_5), 117.46 (T, C_2), 35.79 (T, C_3), 30.74 (T, C_6), 24.78 (P, CH_3), −1.74 (P, Me_3SiC_3), −3.35 (P, Me_3SiC_6); IR (liquid film) 1610 cm^{-1} (m, C=C). Anal. Calcd for $C_{13}H_{26}Si_2$: C, 65.46; H, 10.99; Si, 23.55. Found: C, 65.50; H, 10.91; Si, 23.65.

Acknowledgment. The authors are indebted to AFME (Agence Française pour la Maîtrise de l'Energie, Paris) and to the Conseil Régional d'Aquitaine, Bordeaux, for financial assistance.

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Synthesis and Dimerization of Two Cross-Conjugated Trienes: 3-Methylene-1,4-pentadiene and 1,2,3-Trimethylenecyclohexane[1]

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3-Methylene-1,4-pentadiene (8) and 1,2,3-trimethylenecyclohexane (10) are prepared in moderate to high yields in good purity by the flash vacuum pyrolysis of 1,5-diacetoxy-3-(acetoxymethyl)pentane (12) and 1,2,3-tris(acetoxymethyl)cyclohexane (17), respectively. Triene 8 dimerizes cleanly at a moderate rate in benzene at 95 °C to give only one major product, [4 + 2] dimer 1,4,4-trivinylcyclohexene (13). Triene 10, the conformationally restricted all cisoid analog of 8, dimerizes more rapidly in benzene at 95 °C to give only one major dimer, a [4 + 2] dimer (21). It is concluded that the dimerization proceeds by a two-step mechanism: rate-determining attack at the middle methylene group to form a resonance-stabilized diradical intermediate followed by rapid closure of the diradical to give a [4 + 2] dimer.

Introduction

2,3-Dimethylene-2,3-dihydrofuran (1), the furan-based *o*-quinodimethane (*o*-QDM), has been studied extensively by our research group during the past decade.[2–7] Much of our work has focused on the mechanism of the dimerization of 1 which occurs readily in solution at temperatures above −30 °C. Of special interest is the fact that the dimerization gives almost quantitatively the head-to-head [4 + 4] dimer 2.[2] On the basis of a secondary deuterium kinetic isotope effect study, it was concluded that the

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(1) Based on work by K.A.K. in partial fulfillment of the requirements for the M.S. degree of Iowa State University.

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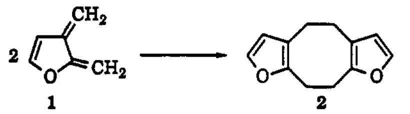
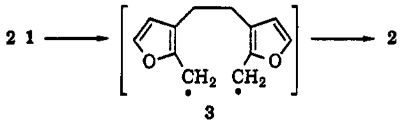


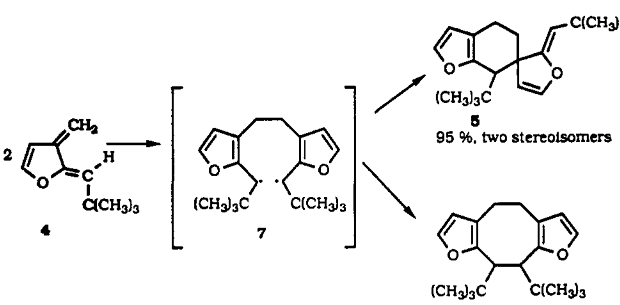
1 2

dimerization involves rate-determining formation of diradical 3, followed by rapid closure of the diradical to give the dimer.[3,7a] Additional support for this two-step mechanism was obtained from studies of the effect on the dimerization rates and products of methyl[5,7d] and *tert*-butyl[6,7b] group substitution on the 2-methylene and 3-methylene groups.



3

Although *o*-QDM 1 dimerizes to give almost exclusively the [4 + 4] dimer,[2,3] some simple derivatives of 1 give a fair amount of the [4 + 2] dimers expected from closure of the intermediate diradical[5,6,7a,b,d] and many indole-based,[8] thiophene-based,[9] and benzene-based[10] *o*-QDM's give predominantly or exclusively [4 + 2] dimers. For example, the *tert*-butyl derivative 4[6,7b] gives a high yield of two stereoisomeric [4 + 2] dimers (5) and a small amount of [4 + 4] dimer 6, dimers expected from diradical 7.

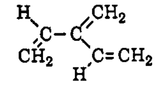


4 7 5 6

95 %, two stereoisomers

5 %, one stereoisomer

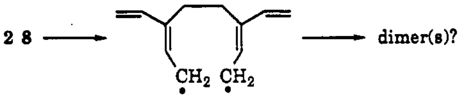
The carbon–carbon double bond system of *o*-QDM 1 corresponds to that of cross-conjugated trienes, the simplest of which is 3-methylene-1,4-pentadiene (8). While triene 8 has been the subject of numerous theoretical calculations,[11] relatively little experimental work with the molecule has been reported.[12] The preparation of 8 was first reported by Bloomquist and Verdol[13] in 1955 and also by Bailey and Economy[14] shortly thereafter. Both groups prepared 8 by pyrolysis procedures and reported that a dimer or dimers of 8 of unknown structure were formed in addition to 8 during the pyrolyses.[13,14] Both groups reported that 8 was very reactive and readily formed dimers or polymers.[13-15]



8

Recently, the structure of 8 was investigated by gas-phase electron diffraction and by vibrational, NMR, and ultraviolet spectroscopy.[16] Another recent report presents a clean route to 8 involving the conversion of 3-vinyl-2,5-dihydrothiophene 1,1-dioxide to 8 and sulfur dioxide by flash vacuum pyrolysis (FVP) at 550 °C; in this study, 8 in a pure state is shown to be an easily handled compound that can be used in Diels–Alder cycloadditions.[17]

Because of the structural relationship of 8 to 1 we felt that 8 might also undergo dimerization by a stepwise mechanism analogous to that of 1 involving diradical 9.



9

The possibility of a stepwise mechanism for the dimerization of 8 was also suggested by reports that the next lowest homologous polyene, 1,3-butadiene, might also dimerize by a nonconcerted stepwise mechanism.[18] Although there is considerable controversy about whether a diradical intermediate is actually formed in the dimerization of 1,3-butadiene,[18d,e] such an intermediate seems consistent with the formation of minor amounts of [4 + 4] and [2 + 2] dimers in addition to the major [4 + 2] product, 4-vinylcyclohexene.[18d,e] The existence of a common diradical intermediate for the production of the [4 + 2], [4 + 4], and [2 + 2] dimers is also suggested by the observation that either the [4 + 4] or the [2 + 2] dimers yield the [4 + 2] dimer when pyrolyzed.[18c]

In the case of 1,3-butadiene dimerization, the formation of a diradical seems to be energetically feasible because of the allylic resonance stabilization of the diradical.[18] Considering the additional resonance stabilization of a pentadienyl radical relative to an allyl radical[19] it would seem that formation of a diradical in the dimerization of 8 would also be energetically feasible.

In this paper we report the study of the dimerization of trienes 8 and 10. The diradical expected from 8, diradical 9, could exist in conformations that would require intramolecular rotations in the formation of [4 + 4] dimers. However, the conformations of the pentadienyl units of

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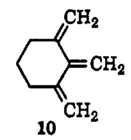
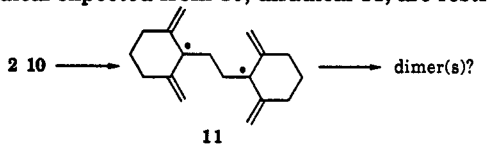


10

the diradical expected from 10, diradical 11, are restricted,

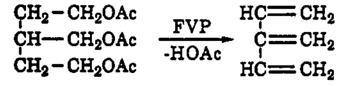


11

and thus the formation of [4 + 4] dimers would not involve intramolecular rotations of the pentadienyl units of the intermediate diradical and this should allow [4 + 4] dimer formation to compete more favorably with [4 + 2] dimer formation.

Results

1,5-Diacetoxy-3-(acetoxymethyl)pentane (12) was prepared by the method of Bailey and Economy.[14] FVP of 12 at 900 °C and 10^{-4} Torr gave as the pyrolysate collected at −196 °C a white solid. Benzene-d_6 was transferred under vacuum into the trap containing the frozen pyrolysate, and the mixture was allowed to warm to room temperature. The resulting solution was filtered slowly through a column of sodium carbonate to give an acetic acid-free solution of 8, 0.1–0.4 M. Analysis by ^1H and ^{13}C NMR spectroscopy and GC indicated that 8 was obtained in relatively high purity in >70% yield. Triene 8 was reasonably stable in

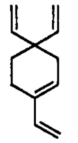


12 8 (>70%)

benzene-d_6 at room temperature; only a small amount of dimerization took place after several days.

When solutions of 8 in benzene-d_6 (0.1–0.4 M) were heated to 95 °C in sealed tubes, 8 dimerized quite cleanly (after 22 h, 90% of 8 was gone) to give predominantly one major dimer (>81% relative to other dimers produced). By GC/MS analysis it was determined that four other minor dimers were also formed, each in relative yields of 1–5%. No higher oligomers of 8 were detected.

The ^1H and ^{13}C NMR spectra of the major dimer are consistent with either structure 13 or 14. The structure



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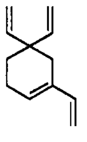
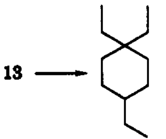


14

of the major dimer was determined by reducing it to the corresponding cyclohexane. Tetraenes 13 and 14 should give 15 and 16, respectively. Cyclohexane 15 would be



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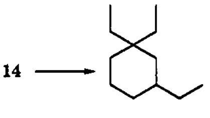
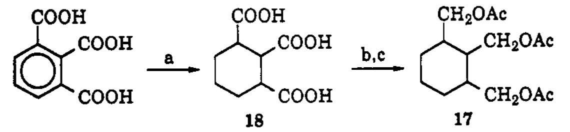


16

expected to exhibit only 10 ^{13}C NMR signals, but 16 should show 12 signals. Catalytic hydrogenation of the major dimer gave an alkane which showed 10 ^{13}C NMR signals, and therefore structure 13 is assigned to the major dimer obtained from 8.

The synthesis of 1,2,3-tri(acetoxymethyl)cyclohexane (17) is summarized in Scheme I. Hydrogenation of

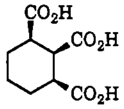
Scheme I[a]



18 17

[a] (a) H_2 (4–5 atm), Pt, HOAc, trace CF_3COOH; (b) $LiAlH_4$; (c) Ac_2O, AcOH.

1,2,3-benzenetricarboxylic acid proceeded readily at 4 atm in glacial acetic acid containing a trace of trifluoroacetic acid. No partially hydrogenated intermediate products were detected, and the production of a single major product was apparent by ^1H NMR. The structure of the major hydrogenated product is presumably that of a single stereoisomer of 1,2,3-cyclohexanetricarboxylic acid (18). Since the ^{13}C NMR spectrum of 18 showed only two signals for the carboxyl groups with approximate relative intensities of 2:1, the structure of the hydrogenation product is one of the meso isomers, 19 or 20. It should be noted



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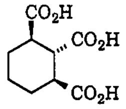
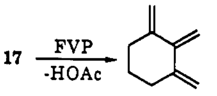


20

that hydrogenation of 1,2,3-benzenetricarboxylic acid using 5% Rh/C catalyst in water has been reported to give the cis,cis isomer (19).[20] The authors apparently assumed cis addition of H_2 to the aromatic ring.

A modification of the reductive acetylation method used to prepare triacetate 12[14] was used to convert 18 to 17. One major triacetate product was obtained as evidenced by both ^1H NMR and GC analysis of the distilled product. The structure of the product was presumably one of the meso isomers corresponding to triacid 19 or 20.

FVP of 17 at 860 °C, 10^{-4} Torr, generated triene 10 in typical yields of about 40–45% and in relatively high purity

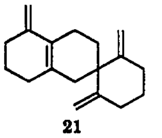


10 (40-45%)

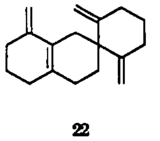
as evidenced by ^1H NMR spectrum of the material taken after removal of the acetic acid.

Triene 10 is clearly more reactive than triene 8. Triene 10 is very sensitive to molecular oxygen, and bubbling oxygen into a solution of 10 in benzene-d_6 led to the rapid decay of 10 to yield unidentified products. The apparent oxygen sensitivity of 10 is consistent with that reported for similar molecules possessing exocyclic double bonds.[7a,21]

When the dimerization of 10 was carried out in benzene-d_6 in evacuated sealed tubes at 95 °C, 10 was found to undergo dimerization quite cleanly to give only one major product as determined by GC and GC/MS analysis. The ^1H and ^{13}C NMR and mass spectra of the product are consistent with those expected for structure 21. Although regioisomer 22 cannot be excluded on the basis of these



21



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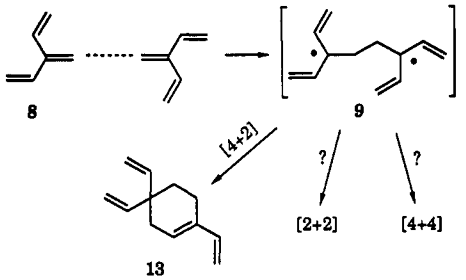
Scheme II



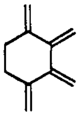
spectral data, the major dimer is assigned structure **21** on the basis of analogy to the regiochemistry of the [4 + 2] dimer obtained from the dimerization of triene **8**.

The dimerization of **10** is very rapid. After heating a ca. 0.05 M solution of **10** in benzene-d_6 in a sealed tube to 95 °C for 2.5 h, >90% of **10** had reacted. This shows that the dimerization rate constant at 95 °C in benzene-d_6 for **10** is 1–2 orders of magnitude greater than that of **8**.

Discussion

FVP of triacetate **12** is clearly an excellent source of 3-methylene-1,4-pentadiene (**8**) free of significant amounts of impurities such as dimers. The procedure results in a solution of **8** free of the byproduct acetic acid and should allow **8** to be obtained in any neutral volatile organic solvent. Triacetate **12** is readily prepared in gram quantities,[14] and moderate quantities (>100 mg) of **12** are conveniently converted to **8** in high yield by FVP.

1,2,3-Trimethylenecyclohexane (**10**) is also prepared in reasonable yield by FVP of the appropriate triacetate, **17**. The absence of significant impurities (including dimers) from the product mixtures obtained from pyrolyses of **17** indicate that FVP is also a good method for the preparation of **10**. Although the preparation of structurally related molecules such as **23**,[21a] **24**,[22] and **25**[22,23] have been reported this is the first report of triene **10**.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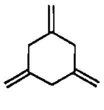
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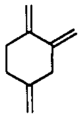
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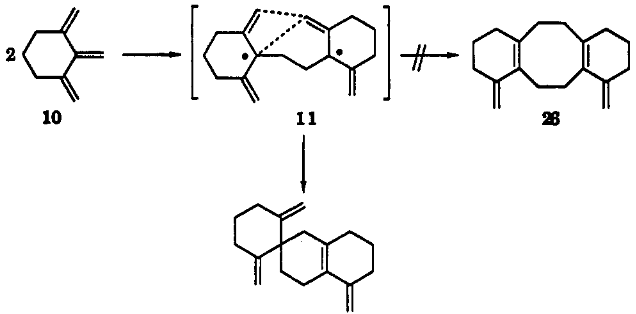
Preparation of the two cross-conjugated trienes **8** and **10** by FVP of the appropriate triacetate provides another good example of the use of FVP in the preparation of reactive olefins in reasonable quantities and high purity.[24]

Triene **8** was found to dimerize at a moderate rate in benzene solution at 95 °C to give the [4 + 2] dimer, 1,4,4-trivinylcyclohexene (**13**), as the major product (>80% of the mixture of five dimers produced).

In principle, there are four possible [4 + 2] dimers that could be obtained from the dimerization of **8**. The production of **13** as the major [4 + 2] dimer product is consistent with the stepwise diradical mechanism for the dimerization of **8** (see Scheme II) which is analogous to the mechanism for the dimerization of the furan-based *o*-QDM, **1**, discussed above. Closure of diradical **9** to form the [2 + 2] or [4 + 4] dimer accounts for two of the four minor dimers observed. The other two minor dimers may be formed by addition to the terminal rather than central double bond of one of the monomers.

Monomer **10** was found to undergo rapid dimerization in benzene solution at 95 °C to give [4 + 2] dimer **21** as the only product. Presumably this monomer undergoes dimerization initially to give a symmetrical diradical of structure **11** which closes to the observed product **21**.



Diradical **11** formed from the dimerization of **10** would not have to undergo a conformational change involving intramolecular rotations of the pentadienyl units to give either the [4 + 4] (**26**) or [4 + 2] (**21**) dimer as might be the case for diradical **9** formed from **8**. Despite this difference triene **10** gives only the [4 + 2] dimer (**21**). This suggests that for 1,2,3-trimethylenecyclohexane (**10**) factors other than the conformations of the postulated diradical intermediate (**11**) control whether a [4 + 4] or [4 + 2] dimer product is formed.

The exclusive production of a [4 + 2] dimer from **10** indicates that the barrier for closure of diradical **11** to give the 8-membered ring [4 + 4] product **26** is significantly higher than the barrier for closure to form the 6-membered ring [4 + 2] dimer **21**. This result is consistent with Doering's conclusion[18d] that other factors being equal, strain-free diradicals of cis,cis configuration are expected to close to 6-membered rather than 8-membered ring products because of the additional strain of the 8-membered (octadiene) ring as compared to the 6-membered ring. This strain is presumably felt in the transition state and thus the barriers for closure.[18d]

With *o*-QDM's the [4 + 4] dimers are thermodynamically much more stable than the [4 + 2] dimers because of the additional stability resulting from the second aromatic ring. In contrast to this situation, the [4 + 4] dimers possible from **8** or **10** would not be expected to be more stable than [4 + 2] dimers; there is no factor to offset the additional strain energy of the 8-membered ring.

Experimental Section

Methods and Materials. The pyrolysis apparatus has been previously described.[25] Gas chromatographic analyses were performed on a Hewlett-Packard Model 5840A gas chromatograph equipped with a 30-m fused silica DB-1 (J & W Scientific; 0.25-mm i.d.; 0.25-μm film thickness) capillary column and a FID detector. All GC analyses were performed using a N_2 carrier flow rate of 24.0 mL/min with injector and detector temperatures of 200 and 250 °C, respectively. Gas chromatographic/mass spectral (GC/MS) analyses were obtained at an ionzing voltage of 70 eV on a Finnigan Model 4000 quadrapole mass spectrometer equipped with a Finnigan Model 9610 GC (30-m DB-1 column) and an Incos 2300 data system. Exact mass measurements were made by

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(22) Benson, R. E.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 4247.

(23) (a) Hopf, H.; Kretschmer, O.; Ernst, L. *Chem. Ber.* **1990**, *123*, 1169. (b) Hopf, H.; Gottschild, D.; Lenk, W. *Isr. J. Chem.* **1985**, *26*, 79.

(24) (a) Wiersum, U. E. *Recl.: J. R. Neth. Chem. Soc.* **1982**, *101*, 317,365. (b) Sauer, N. N.; Angelici, R. J.; Huang, Y. C. J.; Trahanovsky, W. S. *J. Org. Chem.* **1986**, *51*, 113.

(25) (a) Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. J.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem.* **1971**, *36*, 3575. The FVP apparatus is available from Kontes Scientific Glassware, Vineland, NJ 08360. (b) For review, see: Brown, R. C. F. *Pyrolysis Methods in Organic Chemistry*; Academic: New York, 1980; Chapter 2.

GC/high-resolution mass spectrometry using a Kratos MS50 (double focusing, magnetic sector) instrument.

^{1}H NMR spectra were obtained at 300.068 MHz on a Nicolet NT-300 instrument. ^{13}C NMR spectra were obtained at either 22.5 or 75.47 MHz on either a JEOL FX-90Q or a Nicolet NT-300 instrument. Chemical shift δ values are reported relative to tetramethylsilane (Me_4Si). Me_4Si internal standard was not added to benzene-d_6 solutions. The resonance position of the residual proton resonance of benzene-d_6 was set at δ 7.15 ppm relative to Me_4Si for ^{1}H spectra. For ^{13}C spectra of benzene-d_6 solutions, the center of the benzene 1:1:1 triplet was set at 128.0 ppm relative to Me_4Si. ^{1}H NMR computer simulation was done using Nicolet NT-300 NIC-SIM software.

1,2,3-Benzenetricarboxylic acid dihydrate, benzene-d_6 (Gold Label), and platinum(IV) oxide were purchased from Aldrich Chemical Co. Palladium on carbon was obtained from Matheson, Coleman, and Bell.

1,5-Diacetoxy-3-(acetoxymethyl)pentane (12) was prepared by the procedure of Bailey and Economy.[14] The crude product was distilled (Kugelrohr Apparatus, pot temperature = 100–110 °C; ca. 0.01 mmHg) to give 2.00 g of slightly impure (as evidenced by light yellow coloration and weak extra ^{1}H NMR signals) product. The liquid was redistilled (Kugelrohr Apparatus, pot temperature = 100–110 °C; ca. 0.01 mmHg) to give 1.81 g of a clear, colorless distillate. Analysis of the material by capillary GC indicated it was >90% pure: ^{1}H NMR ($CDCl_3$) δ 4.13 (t, J = 6.7 Hz, 4 H), 4.04 (d, J = 5.4 Hz, 2 H), 2.06 (s, 3 H), 2.05 (s, 6 H), 2.00–1.86 (a 7-line pattern similar to a heptet centered at 1.94 ppm, $J \simeq 6$ Hz, 1 H), 1.78–1.64 (m, 4 H).

1,2,3-Tris(acetoxymethyl)cyclohexane (17). To a 250-mL hydrogenation bottle was added 0.25 g (1.0 mmol) of 1,2,3-benzenetricarboxylic acid (BTC) dihydrate and 30.0 mL of glacial HOAc. The solution was stirred to completely dissolve all of the acid. To the solution were added trifluoroacetic acid and 0.0640 g of platinum(IV) oxide. The bottle was placed in a Parr Model 3910 hydrogenation shaker and charged with 80 psi of H_2 gas. The reaction bottle was shaken in the Parr apparatus at room temperature. H_2 uptake (as evidence by drop in pressure) was steady for the first 5 h, after which time the pressure had dropped to 72 psi. Shaking at this pressure for an additional 2 d resulted in no significant pressure change. The bottle was removed from the shaker, and the platinum catalyst was removed by gravity filtration. The filtrate was concentrated to yield 0.18 g of a white solid. ^{1}H NMR analysis of a portion of this solid dissolved in D_2O revealed a relative ratio of starting material to 1,2,3-cyclohexanetricarboxylic acid (18) of 21:79 with no partially reduced products. The solid was redissolved in 30.0 mL of glacial HOAc containing four drops of trifluoroacetic acid. This solution was transferred to a 250-mL hydrogenation bottle, and 0.0646 g of PtO_2 was added. The hydrogenation bottle was charged to 80 psi as before. After shaking for 5 h the pressure had dropped to 76.5 psi, and no further change in pressure was observed. The Pt and HOAc were removed to leave 0.20 g of a white solid. ^{1}H NMR analysis revealed the hydrogenation was ca. 80% complete: ^{1}H NMR (D_2O, H_2O peak set at 4.65 ppm relative to Me_4Si) δ 3.58 (t, J = 3.4 Hz, 1 H), 2.56 (dt, J_d = 12.5 Hz, J_t = 3.4 Hz, 2 H), 1.80–1.65 (m, 3 H), 1.45–1.25 (m, 2 H), 1.25–1.10 (m, 1 H); ^{13}C NMR (22.5 MHz, 1:1 $CDCl_3$/DMSO-d_6) δ (multiplicity when off-resonance decoupled) 173.5 (s), 171.8 (s), 43.1 (d), 42.4 (d), 23.0 (t), 22.0 (t).

Into a dry 50-mL round-bottomed flask fitted with a soxhlet extractor was added 0.1474 g (3.89 mmol) of $LiAlH_4$. A volume of 35.0 mL of dry diethyl ether (distilled from N_2/benzophenone) was added to the flask (through a septum). Into the Soxhlet extractor (containing a plug of glass wool) was placed 0.18 g (0.83 mmol) 1,2,3-cyclohexanetricarboxylic acid (18). The ether in the reaction flask was heated to reflux through the soxhlet extractor under nitrogen with magnetic stirring to slowly dissolved the acid over a period of 3 d. The flask was fitted with a short-path still-head, and 30.0 mL of n-butyl ether was added on portions with the distillative removal of the diethyl ether. The butyl ether solution was allowed to cool to room temperature, and 0.4 mL of glacial HOAc was added dropwise to the reaction mixture to decompose excess $LiAlH_4$. The reaction solution was heated to about 100 °C and 4.0 mL of acetic anhydride was slowly added. The reaction solution was held at 110 °C, under N_2, for an additional 2 d, after which time the large clumps of solid that were initially suspended in solution had become finely dispersed. The reaction solution was allowed to cool, and the gray solid suspended in the solution was removed by filtration. Removal of the n-butyl ether by distillation at reduced pressure left 0.20 g of a yellow-brown liquid. The liquid was distilled (Kuglerohr apparatus, pot temperature $\simeq$ 110–120 °C, <0.3 mmHg) to yield 0.18 g (72%) of a clear, colorless, viscous liquid. Analysis of the material by capillary GC showed it to be about 85% pure: mass spectrum, m/e (base intensity) 257 (M–43, 0.9), 197 (17.9), 138 (13.8), 121 (14.5), 120 (100.0), 107 (18.1), 95 (16.2), 94 (16.1), 93 (13.0), 92 (13.8), 91 (11.2), 79 (15.7); ^{1}H NMR ($CDCl_3$) δ 4.11 (d, J = 5.8 Hz, 2 H), 4.10–3.90 (an 8-line AB portion of an ABX pattern with the lowest field peak overlapping the upfield peak of the 4.11 signal, 4 H), 2.30–2.20 (m, 1 H), 2.06 (s, 6 H), 2.02 (s, 3 H), 1.95–1.80 (m, 4 H), 1.65–1.55 (m, 3 H), 1.5–1.1 (m, 1 H); IR (neat film between NaCl plates) 2932 (s), 1771 (sh), 1740 (s), 1369 (m), 1234 (s), 1038 cm^{-1} (m); exact mass (CI) calcd for $C_{15}H_{25}O_6$ (MH^+) 301.16512, found 301.16455.

General Pyrolysis Procedure. The standard procedure has been described.[25] Benzene-d_6 was transferred under vacuum into the trap containing the frozen pyrolysate at the conclusion of each pyrolysis. The residual proton resonance of the benzene-d_6 was used both as a chemical shift reference and as a quantitative internal standard to determine the absolute yield of desired products. The number of moles of residual protons (between δ 7.29 and 7.04 ppm) per 1.00 mL of the benzene-d_6 was determined as follows. A volume of 1.00 mL of benzene-d_6 was added to an NMR tube. A 0.0123-g quantity of HPLC-grade MeCN was added to the tube (0.2996 mmol of MeCN; 0.8989 mmol of methyl H's). The relative integral of the δ 7.29–7.04 resonance to the MeCN methyl resonance was 0.5938:1.000. Multiplication of the number of moles of protons for the MeCN methyl resonance by the factor 0.5938 led to the result that there were 0.5338 mmol of residual protons (between δ 7.29 and 7.04) per 1.00 mL of the benzene-d_6.

2-Methylene-1,4-pentadiene (8). A quantity of 0.208 g (0.798 mmol) of 1,5-diacetoxy-3-(acetoxymethyl)pentane (12) was pyrolyzed (oven 900 °C; sample chamber 80 °C; pressure 5×10^{-4} Torr) in a normal manner. After about 80 min all of the starting triacetate was gone from the sample compartment and a white band of frozen material had been deposited in the trap. The system was isolated from the diffusion pump and reopened to the roughing pump. A volume of 5.00 mL of benzene-d_6 was transferred into the trap via a sidearm. The system was brought back up to atmospheric pressure with N_2 gas. The material in the trap was slowly allowed to warm to room temperature under a nitrogen atmosphere.

About 1.5 g of anhydrous Na_2CO_3 was placed in a pasteur pipet containing a small plug of glass wool. A small amount of benzene-d_6 was passed through the pipet to wet the Na_2CO_3. The pyrolysate solution in benzene-d_6 was slowly passed through the Na_2CO_3 to remove all of the HOAc from solution. The absolute yield of 8 was found by comparison of the integral of the residual benzene resonance at δ 7.09–7.14 ppm to the integral of the doublet of 8 at δ 5.35–5.21 ppm in the ^{1}H NMR spectrum. Using this method, the overall yield of 8 was found to be 0.603 mmol (75.6%): ^{1}H NMR (benzene-d_6, 298 K) δ 6.33 (dd, J = 17.4 Hz, J' = 10.8 Hz, 2 H), 5.30 (dd, J = 17.5 Hz, J' = 1.5 Hz, 2 H), 4.99 (s, 2 H), 4.95 (dd, J = 10.9 Hz, J' = 1.6 Hz, 2 H); ^{13}C NMR (75.47 MHz, benzene-d_6, 298 K) δ (multiplicity when off resonance decoupled) 166.14 (s, (low intensity)), 145.18 (t), 136.26 (d), 115.77 (t);[26] analysis of the solution by capillary GC revealed only one major component: mass spectrum, m/e (% base intensity) 80 (47.50), 79 (100.00), 77 (46.75), 53 (11.97), 52 (23.94), 51 (21.75), 50 (15.38).

1,2,3-Trimethylenecyclohexane (10). Because of its reactivity 10 was generated immediately before use. The method of preparation from triacetate 17 is similar to that used for generating

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(26) Our ^{1}H NMR data for 8 are very similar to the data reported[16,17] and the minor differences can be attributed to the use of different solvents: this study, C_6D_6; Almenningen et al.,[16] CD_2Cl_2; Cadogan et al.,[17] $CDCl_3$. However, for the ^{13}C NMR data, neither reference reports the 166.14 signal which we assign to the quaternary carbon, Cadogan et al.[17] does not report the 145.18 signal, and both groups of workers report a doubling of the 115.77 signal which we did not observe (possibly this occurs at lower temperatures).

3-methylene-1,4-pentadiene (8) from 12. The oven temperature was 860 °C.

At the end of the pyrolysis a volume of 2.00 mL of benzene-d_6 was slowly transferred into the trap via a sidearm. The system was brought back up to atmospheric pressure with N_2 gas. The frozen pyrolysate/benzene-d_6 was slowly allowed to warm to room temperature under a N_2 atmosphere to yield a homogeneous solution that was quite yellow in color. The yellow solution was passed through the Na_2CO_3 in a pipet soon after melting to remove all HOAc. The absolute yield of 10 was found by comparison of the residual benzene resonance at δ 7.11–7.19 ppm to the combined integral of the two singlets of 10 between δ 5.13 and 5.05 in the ^{1}H NMR spectrum. Using this method, the overall yield of 10 was found to be 0.0972 mmol (39.7%): ^{1}H NMR (benzene-d_6) δ 5.10 (s, 2 H), 5.08 (d, $J < 2$ Hz, 2 H), 4.61 (d, $J < 2$ Hz, 2 H), 2.15 (t, $J = 6.1$ Hz, 4 H), 1.45 (p, $J = 6.2$ Hz, 2 H).

Dimerization of 3-Methylene-1,4-pentadiene (8). A volume of 1.00 mL of a solution containing 0.603 mmol of 8 in 5.00 mL of benzene-d_6 (as determined by ^{1}H NMR) was added to an NMR tube. The solution was frozen by immersing the tube in liquid N_2. The tube was then evacuated to a pressure of 0.01 mmHg using a vacuum pump, and the tube was sealed under vacuum. The sealed tube was placed into an oven equilbrated at a temperature of 95 °C. The tube was withdrawn from the oven periodically, and the sample was analyzed by ^{1}H NMR. After heating at this temperature for 22 h, 90% of the monomer was gone and the production of a new product was apparent by ^{1}H NMR.

The sealed tube was opened and analysis of the solution by capillary GC revealed the presence of five major components with the following relative percentages (component, retention time, %): A, 19.18 min, 81.1%; B, 20.64 min, 6.0%; C, 20.76 min, 5.8%; D, 20.95 min, 2.7%; E, 22.06 min, 4.4%. The sample was analyzed by GC/MS.

Component A [1,4,4-trivinylcyclohexene (13)]: *m/e* (base intensity) 160 (6.54), 145 (7.08), 132 (11.17), 131 (12.22), 118 (5.78), 117 (13.81), 106 (8.89), 105 (10.26), 93 (6.15), 92 (8.13), 91 (22.23), 80 (40.27), 79 (100.00), 78 (8.17), 77 (19.13).

Component B: *m/e* (base intensity) 160 (15.73), 105 (2.15), 93 (2.01), 91 (4.25), 81 (6.32), 80 (100.00), 79 (24.00).

Component C: *m/e* (base intensity) 160 (15.44), 145 (11.57), 131 (18.84), 118 (10.89), 117 (24.43), 106 (14.15), 105 (26.71), 104 (14.53), 93 (14.48), 92 (17.65), 91 (49.01), 80 (28.76), 79 (100.00), 78 (14.78), 77 (29.86), 65 (12.84).

Component D: *m/e* (base intensity) 160 (20.56), 93 (8.52), 80 (100.00), 79 (32.39), 77 (10.81).

Component E: *m/e* (base intensity) 160 (10.84), 132 (13.69), 131 (11.37), 119 (16.65), 117 (19.60), 91 (23.15), 80 (31.87), 79 (100.00), 77 (20.54).

The ^{1}H and ^{13}C NMR spectra of this dimer mixture were recorded.

Component A [1,4,4-trivinylcyclohexene (13)]: ^{1}H NMR (benzene-d_6) δ 6.35 (dd, $J = 17.4$ Hz, $J' = 10.8$ Hz, 1 H), 5.74–5.63 (a 6-line pattern for the X portion of an ABX pattern, 2 H), 5.34 (br s, 1 H), 5.05 (br d, $J \simeq 16.8$ Hz, 1 H), 5.00–4.70 (m, contains AB portion of ABX pattern partially overlapped with a doublet for another proton the outer peak of which was at 4.89 ppm, 5 H), 2.09–2.00 (m, 4 H), 1.55–1.47 (m, 2 H); ^{1}H NMR simulation of 3-spin ABX portion of the spectrum: close fit achieved where $\nu_A = 1489$ Hz, $\nu_B = 1492$ Hz, $\nu_X = 1710$ Hz and $J_{AX} = 17.51$ Hz, $J_{BX} = 10.90$ Hz, and $J_{AB} = 1.40$ Hz; ^{13}C NMR (75.47 MHz, benzene-d_6) δ (multiplicity when off resonance decoupled) 144.31 (d), 139.94 (d), 135.76 (?), 115.68 (?), 112.69 (t), 110.17 (t), 42.19 (s), 34.75 (t), 31.68 (t), 21.62 (t).

The exact mass of component A was determined by GC/high-resolution MS: calcd for $C_{12}H_{16}$ 160.12520, found 160.12586.

Hydrogenation of Dimer Product Mixture of 8. A solution of 0.340 mmol of 3-methylene-1,4-pentadiene (8) in 2.00 mL of benzene-d_6 was prepared by pyrolysis of 1,5-diacetoxy-3-(acetoxymethyl)pentane (12). The solution was transferred to an NMR tube, and the tube was evacuated and sealed. The sealed tube was placed in an oven at 95 °C to affect dimerization of 8. The progress of the dimerization was followed by ^{1}H NMR. After approximately 12 h of heating at 95 °C >90% of 8 that was initially present in solution had reacted.

The sealed tube was opened and analysis of the solution by capillary GC revealed the presence of five major components with the following relative percentages (component, retention time, %): A, 19.02 min, 78.1%; B, 20.37 min, 8.0%; C, 20.49 min, 5.8%; D, 20.67 min, 3.6%; E, 21.73 min, 4.4%.

The GC analysis as well as the ^{1}H NMR spectrum of this dimer mixture indicated it was very similar to the dimer mixtures obtained from all other dimerizations of 8 conducted. A ^{13}C NMR spectrum of the mixture showed 10 major peaks, 6 in the olefinic region and 4 in the aliphatic region; thus only peaks for major dimer component A were observed. The chemical shift δ values for the carbon signals were identical to those of major dimer A obtained in the dimerization experiments of 8 previously described.

The total volume of the dimer solution in benzene-d_6 was added to a 10-mL round-bottomed flask followed by the addition of 0.0134 g of 10% Pd/C. The flask was fitted with a condensor, and the system was purged with H_2 gas. A balloon filled with H_2 gas was attached to the reaction flask. The benzene-d_6 solution was stirred vigorously at room temperature under H_2 with the use of a magnetic stirrer. The progress of the reduction was followed by capillary GC. After about 48 h of stirring under H_2 the hydrogenation was essentially complete. The GC trace of the solution after this reaction time indicated the presence of one major component, 1,1,4-triethylcyclohexane (15): mass spectrum, *m/e* (base intensity) 168 (0.19), 139 (38.12), 138 (25.26), 97 (33.73), 83 (100.00), 69 (48.65), 67 (10.44), 57 (30.40), 55 (68.37); ^{1}H NMR (benzene-d_6) δ 1.55–1.40 (m, 3 H), 1.29 (q, $J = 7.7$ Hz, 2 H), 1.24–1.18 (m, 2 H), 1.18 (q, $J = 7.5$ Hz, 2 H), 1.04–0.96 (m, 6 H), 0.89 (t, $J = 7.4$ Hz, 3 H), 0.78 (t, $J = 7.4$ Hz, 3 H), 0.73 (t, $J = 7.5$ Hz, 2 H); ^{13}C NMR (75.47 MHz, benzene-d_6) δ (multiplicity when off-resonance decoupled) 39.88 (d), 35.12 (t), 34.80 (s), 33.23 (t), 30.19 (t), 28.28 (t), 24.28 (t), 11.84 (q), 7.62 (this signal apparently contains two nearly superimposed carbons, two barely resolved q's were observed with off-resonance decoupling); exact mass of the major component 15, calcd for $C_{12}H_{24}$ 168.18781, found 168.18695.

Dimerization of 1,2,3-Trimethylenecyclohexane (10). A volume of 1.00 mL of a solution containing 0.0972 mmol of 10 in 2.00 mL of benzene-d_6 (as determined by ^{1}H NMR) was added to an NMR tube. The solution was frozen by immersing the tube in liquid N_2. The tube was then evacuated to a pressure of 0.01 mmHg using a vacuum pump, and the tube was sealed under vacuum. The sealed tube was placed into an oven equilibrated at 95 °C. The tube was withdrawn periodically, and the sample was analyzed by ^{1}H NMR. After heating at this temperature for 2.5 h very little 10 remained and the production of a new product was apparent by ^{1}H NMR.

The sealed tube was opened and analysis of the solution by capillary GC revealed one major component identified as spiro[(2′,6′-dimethylenecyclohexane)-1′,2-(5-methylene-1,2,3,4,5,6,7,8-octahydronaphthalene)] (21): mass spectrum, *m/e* (base intensity) 240 (64.10), 225 (29.46), 212 (35.84), 211 (32.36), 197 (29.93), 183 (17.75), 170 (24.72), 109 (24.94), 157 (15.88), 145 (63.21), 129 (19.66), 117 (24.65), 105 (71.43), 92 (47.53), 91 (100.00), 79 (41.78), 77 (36.35); ^{1}H NMR (benzene-d_6) δ 4.92 (s, 1 H), 4.78 (s, 1 H), 4.76 (s, 2 H), 4.59 (s, 2 H), 2.37–2.26 (m, 6 H), 2.16–2.06 (m, 4 H), 197–1.87 (m, 2 H), 1.73 (t, $J = 6.4$ Hz, 2 H), 1.66–1.56 (m resembling a pentet with $J = 6.3$ Hz, 4 H); ^{13}C NMR (75.47 MHz, benzene-d_6) δ 153.33, 144.66, 133.92, 114.10, 107.49, 105.36, 48.02, 46.29, 39.16, 33.28, 32.88, 32.08, 30.20, 23.80, 23.21; exact mass calcd for $C_{18}H_{24}$ 240.18781, found 240.18713.

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Registry No. 8, 13753-03-2; 10, 50325-72-9; 12, 141805-81-4; 13, 121904-50-5; 15, 141805-84-7; 17, 141805-82-5; 18, 141805-83-6; 21, 141805-85-8; 1,2,3-benzenetricarboxylic acid, 569-51-7.