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STERIC AND ELECTRONIC EFFECTS OF 1-SUBSTITUTED DIENES IN CYCLOADDITION REACTIONS WITH CYCLOHEPTATRIENONE

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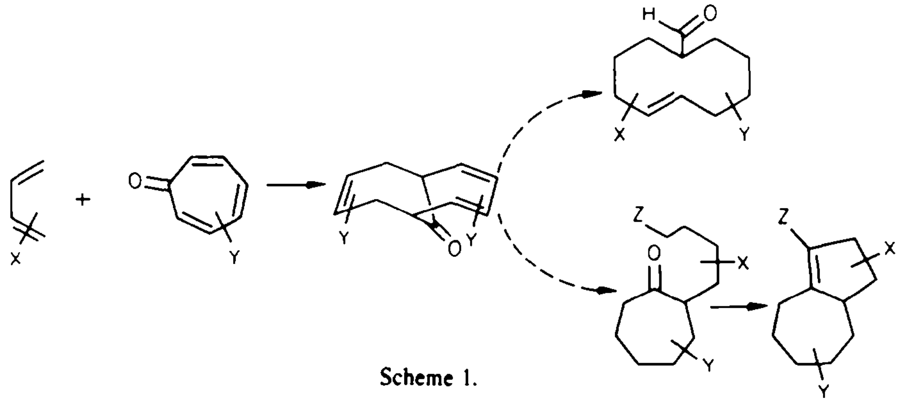
Abstract—Cycloaddition reactions of cycloheptatrienone and ten dienes were examined to define diene substituent effects in the thermal [6 + 4] cycloaddition reaction of cycloheptatrienone. The [6 + 4] adducts from dienes with greater electron density were formed more rapidly and were thermodynamically less stable than the adducts from more electron-poor dienes. This cycloaddition is subject to diene steric hinderance. Dienes with one terminal Z-substituent fail to yield [6 + 4] adducts as the major product. E-1-Acetoxybutadiene affords the thermally stable adduct (**8**) while Z-1-acetoxybutadiene provides adduct (**9**). Thermolysis of **8** and **9** afforded the Cope rearrangement products **19** and **13**, respectively.

The Diels–Alder reaction is a major method for constructing 6-membered rings. This reaction proceeds in a regio- and stereospecific fashion. Functionalized dienes and enes have been shown to undergo such cycloadditions with predictable substituent effects.[2] These effects in other cycloaddition reactions have received considerably less experimental scrutiny. The [6 + 4] cycloaddition of cycloheptatrienone (tropone) and dienes yields a bicyclo-[4.4.1]-undecan-11-one which is a rigid structure containing ten peripheral carbons. Inclusion of only one substituent on both the diene and the cycloheptatrienone portions could provide in predictable fashion a highly functionalized bicyclic structure (Scheme 1). Unfortunately, the available information about substituent effects on non-Diels–Alder cycloadditions is not even sufficient to predict the periselectivity of such reactions. As the first step in defining the role of substituents in certain [6 + 4] reactions, we wish to report on the cycloaddition reaction of cycloheptatrienone and nine 1-substituted dienes.



Scheme 1.

Cycloheptatrienone readily undergoes [6 + 4] cycloaddition with numerous dienes,[3] including cyclopentadiene,[4] cyclohexadiene,[5] cyclopentadienones,[6] pyrones,[7] isobenzofurans,[8] butadiene,[9] isoprene,[9] and piperylene.[9] Unfortunately, several other processes compete effectively with [6 + 4] addition reactions. Many of the reported [6 + 4] cycloadducts have been shown to rearrange by sigmatropic reactions or thermally by stepwise cycloreversion-readdition to form thermodynamically stable [4 + 2] products.[6] Tropone also may yield [8 + 2] adducts.[6-10] Most of these one-to-one adducts appear to be formed via the transition states predicted for concerted processes. The [4 + 2] products often appear to arise via an *endo*-transition state, and the [6 + 4], always via an *exo*-transition state.

The cyclic dienes reported to undergo cycloaddition reactions with cycloheptatrienone vary widely electronically. These dienes possess unusual cycloaddition reactivity for reasons unrelated to electron density. Although from the work of Houk[3] electron-rich dienes are expected to react rapidly with cycloheptatrienone, this has not been experimentally verified. The known adducts lack easily manipulated functional groups according to Scheme 1. We have examined the reaction of cycloheptatrienone with several 1-substituted dienes which have Diels–Alder reactivity more directly related to a standard measure of reactivity such as ionization potential. These dienes, containing a wide range of substituents, were chosen: (1) to verify diene electronic effects on tropone additions, (2) to evaluate critically diene steric effects in [6 + 4] additions, and (3) to provide a more rigorous test for the *exo*-transition state of [6 + 4] cycloadditions. The adducts obtained from acyclic dienes are less rigidly constrained than the adducts from cyclic dienes. The two or three favorable conformations from these butadiene adducts allow for all of the possible sigmatropic rearrangements occasionally observed in adducts from cyclic dienes. Information obtained from the reactions of functionalized butadienes with cycloheptatrienones might find application in other [6 + 4] cycloadditions. The obvious complementary part of this study, the examination of cycloheptatrienone substituent effects, will be reported in due course,[12] as will synthetic applications of the adducts outlined in Scheme 1.[11]

Structure of products

We have examined the reactions of ten dienes with tropone. The results are shown in Table 1. The reaction is sensitive to various conditions, especially temperature. To favor [6 + 4] addition, we have kept the reaction temperature below 200°. The crude yields ranged from 50 to 80% as determined by weight and NMR spectra. Unreacted cycloheptatrienone and diene accounted for the remainder of the material. Several of these adducts (**1–3**, **7**, **8**, **14**, and **15**) were formed to the practical exclusion of other products and were readily separated from unreacted starting materials by open column chromatography on silica gel or proved to be unstable to all purification attempts (**2** and **3**). The other adducts required high performance liquid chromatography (HPLC) for purification. Chromatography appeared to promote some decomposition since the recovery was always lower than expected.

In most instances, a preliminary evaluation of the product composition could be based upon the IR spectrum. All of the previously reported [6 + 4] adducts[3-9] have bridged carbonyls absorbing in the 1710–1720 cm^{-1} region while the [4 + 2] species[16,17] have typical enone absorptions (1670–1690 cm^{-1}). The new adducts reported in this paper exhibit similar frequencies.

The products in Table 1 exhibited appropriate mass spectra for 1 : 1 adducts. Frequently, these spectra were recorded at low ionizing voltage (7–20 eV) to maximize the intensity of the parent ion. Introduction of the compound by gas chromatographic (GC) or by direct probe techniques gave identical spectra. The mass spectra always exhibited intense peaks corresponding to the diene and to cycloheptatrienone with one of these being the base peak.

The structure of symmetrical adducts **1** and **14** followed immediately from comparison of the spectral data with those of analogous compounds.[3-9] Compounds **1** and **14** exhibited olefin and bridgehead multiplicities and shifts in the NMR spectra comparable to those reported for the butadiene[9] and cyclopentadiene 4 adducts.

Examination of molecular models suggests the conformation of these symmetric adducts (**1** and **14**) to be as drawn. The ring formed from the bridgehead and diene derived carbons is conformationally similar to a boat cycloheptene. The elongated C_1–C_6 distance prevents a costly C_7–$C_{10}\beta$ methylene hydrogen interaction. α-Substituents at C_7 or C_{10} have little effect on this conformation. Therefore the NMR spectra of these adducts are expected to be similar to that of adduct **1** or to that of the previously reported compounds.[3-9] Of course, the C-7

Table 1. Cycloaddition reactions of cycloheptatrienone

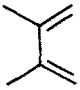
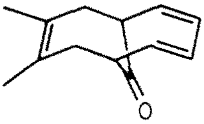
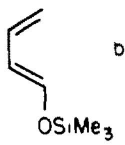
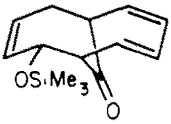
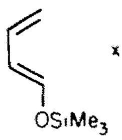
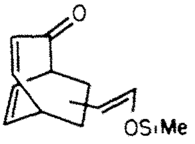
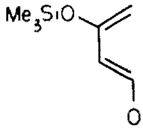
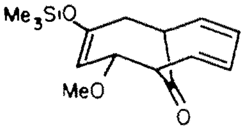
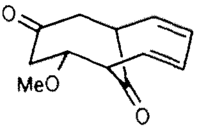
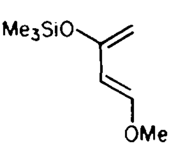
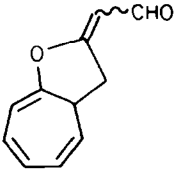
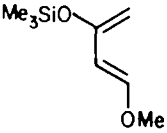
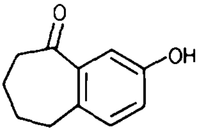
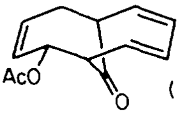
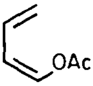
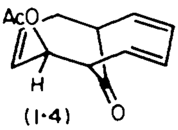
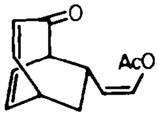
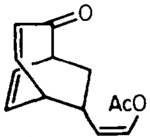
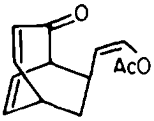
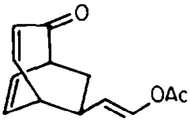
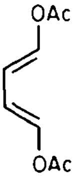
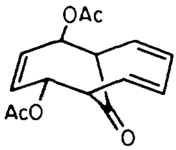
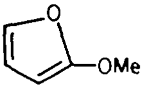
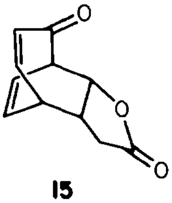
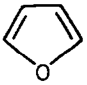
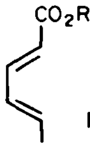
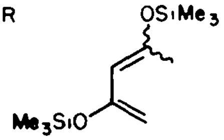
Diene	Conditions	Products (Ratios)	% Yield (%Recovered / Cycloheptatrienone)
	xylene/Δ/12 hr	 **1**	75
 	benzene/Δ/4 da	 **2** (<10% other adducts)	80
 	xylene/Δ/72 hr	 (<10% [6 + 4]) **3**	50
 	toluene/80°/96 hr	 **4** (4)  **5** (1)	40(55)

Table 1(*Contd.*)

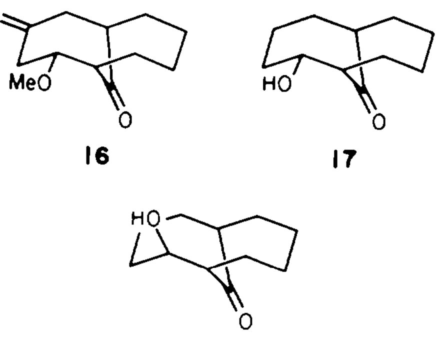
Diene	Conditions	Products (Ratios)	% Yield $\left(\frac{\%\text{Recovered}}{\text{Cycloheptatrienone}}\right)$
	toluene/Δ/15 hr	**5** (3)  **6** (4)	45(50)
	xylene/Δ/36 hr	 **7**	35(60)
	xylene/Δ/12 hr	 (< 5% others) **8**	57
	xylene/20 hr	 (1·4) **9**  (1·4) **10**  (1·8) **11**  (1) **12**  (<0·05) **13**	49
	xylene/27 hr	 **14**	25(60)
	xylene/48 hr	 **15**	14(80)
  		No reaction	

proton will have a major shift difference from adducts without heteroatom substituents while the C-6 and C-8 protons will have minor shift differences. Models indicate that a β-C_7 substituent larger than hydrogen forces a severe 1, 4 interaction with $C_{10}\beta$-proton in this boatlike array. This interaction can be relieved by forming one of the two possible twist boats in the cycloheptadienone ring. This twist boat produces a pseudo equatorial C_7 substituent, a slight distortion (*ca* 10°) of the planar diene ring and completely removes any elements of symmetry from the molecule. Therefore, the NMR spectra of [6+4] adducts with a $C_7\beta$ substituent should exhibit NMR spectra much different from the symmetric adducts.

The [6+4] nature of the 1:1 adducts **8** and **9**, established by IR and MS, was refined by NMR. The spectrum of **8** was qualitatively similar to that of **1**, of **14** and of the published data for other acyclic dienes.[3-9] The methylene protons appeared at 2.56 ppm and the bridgehead protons at 3.54 and 3.67 ppm. The methine proton adjacent to the acetoxy group came at the same shift as the olefin envelope prohibiting decoupling experiments to determine the methine-bridgehead coupling constant. The NMR spectrum of adduct **8** requires that **8** have the same conformation as **1** and **14** and therefore have an α-acetoxy group. The adduct **9** exhibited a significantly different NMR spectrum from that of **8**. Each of the methine and methylene protons resonated at a different chemical shift. Furthermore, the overall shape of the olefin envelope was different from that of **1**, **14** and **8**. Thus, [6+4] adduct **9** is only consistent with a β-acetoxy group at C_7.

Although compound **2** is clearly a [6+4] adduct contaminated with other materials (< 10%), we were unable to purify **2**. Attempted chromatography, distillation or hydrogenation of **2** resulted in complete cycloreversion to starting materials. The NMR spectrum of **2** is qualitatively similar to those of **1**, **8** and **14**. It is unlike that of **9**. Therefore, we conclude that **2** contains an α C_7 silyloxy group.

The products from 1-methoxy-3-trimethylsilyloxybutadiene and cycloheptatrienone varied greatly with temperature (Table 1). The structures are discussed in order of appearance with increasing temperature. The crude reaction mixture exhibited an NMR spectrum suggesting **4** and **5** to be present in a 4:1 ratio. The presence of **4** was clearly indicated by a triplet at 4.1 ppm (OMe methine proton) coupled by 6 Hz to an olefin doublet at 4.9 ppm. The [6+4] adduct **4** could not be purified without clean hydrolysis to **5**. To establish the stereochemistry of **4** and **5** compound **5** was correlated with **8** by the following reactions. Hydrogenation of **5** using Pd–C cleanly yielded **16** with one methine proton appearing below 3.2 ppm. The C_2 methine proton of **16** resonated at 3.8 ppm with coupling constants of 9, 8 and 3 Hz as determined by decoupling experiments. Compounds **17** and **18** were prepared from **8** and **9** respectively by olefin reduction followed by careful acetate hydrolysis.[11,13] The carbinol methine proton in **17** appeared at 4.1 ppm with coupling constants of 7, 5 and 3 Hz. Compound **18** exhibited a carbinol methine signal at 3.9 ppm with coupling constants of 11, 5 and 4 Hz. Molecular models indicate that **16**, **17** and **18** should possess comparable conformations. The similar coupling constants of **16** and **17** permit the assignment of the α-methoxy stereochemistry to **4** and **5**.



16 17 18

Scheme 2.

The [8+2] adduct **6** had a molecular weight corresponding to $C_{11}H_{10}O_2$ and IR absorptions at 2770, 1670 and 1640 cm^{-1}. NMR decoupling experiments permitted definition of a structure which includes an alkoxycycloheptatriene and an aldehyde. The presence of two aldehyde isomers was indicated by resonances at 9.72 and 10.0 ppm in a 4:1 ratio. The peak at 9.72 ppm was coupled to an olefin signal at 5.82 ppm. The smaller peak at 10.0 ppm was coupled to an olefin signal at 6.02 ppm. The presence of two olefin isomers allowed for the application of Pascal's additivity rules to assign the olefin stereochemistry.[14] These rules adequately predict the relative magnitude of shifts but do not provide accurate absolute shift data. The additivity rules predict that the olefinic proton in the compound with the aldehyde and the ether in a *Z* relationship would appear at 5.00 ppm while the *E* isomer would resonate at 5.43 ppm. We therefore assign the *Z* configuration to the major aldehyde isomer.

Compound **7** had a molecular ion corresponding to $C_{11}H_{10}O_2$ and IR absorptions at 3300, 1665 and 1600 cm^{-1}. The NMR spectrum showed one proton multiplets at 7.51, 7.13 and 7.00 ppm. Coupling constants of 2 and 8 Hz indicated that the 7.51 peak was meta to the 7.00 peak and that the 7.00 and 7.13 peaks were ortho to each other. Comparison of the NMR spectrum of **7** with the four known isomers of methoxy-1-tetralone[16] clinched the phenolic oxygen position. 7-Methoxy-1-tetralone exhibited an aromatic region with peaks at 6.99, 7.10 and 7.47 ppm with coupling constants of the same magnitude as **7**. The other methoxytetralone isomers have dramatically different NMR spectra. Further corroboration of structure **7** was obtained from the UV spectra. It exhibited peaks at 232, 261 and 328 nm (log ϵ *ca* 4–5) in ethanol which shifted to 249, 290 and 392 nm upon addition of base. These are closer to those of *m*-hydroxyacetophenone (250 and 308 nm to 266 and 349 nm upon base treatment[15]) than to that of *p*-hydroxyacetophenone (220 and 276 nm to 236 and 325 nm upon base addition[15]). The NMR and ^{13}C NMR data indicate a styrene but not an enone.

The isolation and identification of **9–13** and **15** has proven more tedious. Repetitive HPLC is required to obtain analytical samples of these compounds. The five products (**9–13**) from *Z*-1-acetoxybutadiene and cycloheptatrienone were formed in a 1.4:1.4:1.8:1:0.05 ratio in 49% yield after removal of the cycloheptatrienone (20%) and polymeric material. The [4+2] structure of the 1:1 adducts **10–13** and **15** was apparent from the IR spectra and mass spectral parent ions. Comparison of the NMR data for these new compounds with the eleven bicyclo-[3.2.2]-nona-3,6-dien-2-ones previously reported[9,10,17] shows that the NMR spectrum of the cycloheptatrienone derived portion in all instances is qualitatively similar. Therefore, compounds **10–13** and **15** are [4 + 2] adducts resulting from the cycloheptatrienone as the four electron component and the diene as the two electron component. The regio- and stereochemical assignments of **10–13** and **15** have the following basis. The eleven bicyclo-[3.2.2]-nonadienone compounds have a coupling constant of 0–2 Hz for the protons at C-1/C-8 when the C-8 proton is endo and 6–8 Hz when the C-8 proton is exo. The proton at C-5 can be unambiguously assigned by the C-4/C-5 proton coupling to the enone system. Determination of the W coupling (1–2 Hz) for the protons at C-1/C-3 permits assignment of the C-1 proton. Fortunately, neither the signals due to the C-8 protons or the C-9 protons appear to exhibit W coupling to the ring.

From molecular models we have determined the dihedral angle between the C-8 exo proton and the C-9 endo proton should be about 90°. The dihedral angle between the C-8 exo proton and the C-9 exo proton should be about 15°. The size of the coupling constant between signals due to the C-8 exo and C-9 protons can therefore be used to determine the stereochemistry of the C-9 proton. The corresponding angles for the endo proton at C-8 are about 30° for the endo proton at C-9 and about 150° for the C-9 exo proton. The coupling constant for the C-8 endo proton with either C-9 proton will be about 7 Hz.

Structures **10–12** exhibited vinyl acetate shifts of 4.6 and 7.0 ppm coupled by 6–8 Hz establishing the retention of the *Z*-enolacetate in each instance. Compound **10** shows a one proton multiplet at 2.28 ppm coupled to the C-1 proton signal by 2 Hz and a two proton multiplet at 1.58 ppm coupled to the C-5 proton signal. These shifts coincide with the shifts reported for unsubstituted C-9 protons and C-8 endo protons.[17] Compound **11** has two geminally coupled proton signals at 1.68 and 2.27 ppm (J = 14 Hz) which are assigned to the C-8 exo and endo protons, respectively. The C-8 endo proton has a coupling constant of 2 Hz with the C-1 proton while the C-8 exo proton is coupled by 6 Hz.

The proton signal at 3.42 ppm is coupled by 7 Hz to the C-8 endo proton signal and has two small coupling constants to the resonances of the C-5 proton (J = 2 Hz) and the C-8 exo proton (J = 3.5 Hz). It is therefore assigned to the C-9 endo proton. Compound **12** has been assigned the structure shown. Structure **12** has a two proton multiplet at 1.75 ppm and a one proton multiplet at 2.25 ppm assigned to the C-9 protons and the C-8 exo proton, respectively. These shifts are consistent with the assignment of structure **12**.

Compound **13**, formed in trace amounts during the cycloaddition, contained an E-enolacetate as apparent from the 13 Hz coupling constant and the shifts of the olefin signals at 5.32 and 7.18 ppm. The two geminally coupled signals at 1.59 and 2.25 ppm (J = 14 Hz) are assigned to the C-8 endo and the C-8 exo protons, respectively. The C-8 endo proton signal is also coupled to the signal at 2.65 ppm (J = 7 Hz) but not to the bridgehead C-1 proton signal (J = 0 Hz). However, the C-8 exo proton signal is coupled to the C-1 proton and to the signal at 2.65 ppm (J = 9.5 Hz). Because of this large coupling constant, the signal at 2.65 ppm is assigned to the C-9 exo proton.

Lactone **15** exhibited IR absorptions of 1789 and 1672 cm^{-1} as well as NMR resonances with bridgehead-endo coupling constants of 1 Hz and C-3a/C-8a proton shifts of 3.24 and 5.05 ppm, respectively. The proton at C-3a was coupled to the lactone protons by 5 and 11 Hz.

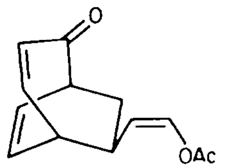
Finally, the dienes furan, 1,3-bis-trimethylsilyloxy-1-methylbutadiene and ethyl 2,4-hexadienoate gave no indication of reacting cleanly with tropone under a variety of conditions including heating at 200° (benzene/sealed tube) for several days or at room temperature for 2 months. When heated at 200°, the latter two dienes afforded several products which were not analyzed. Control experiments showed less than 10% of these products involved cycloheptatrienone and that this small percentage contained at least three components.

Discussion of cycloaddition

Three important conclusions can be drawn from the experiments outlined herein. First, all of the [6 + 4] adducts are formed via an *exo* transition state. Two of these distinct adducts are formed from dienes differing only in stereochemistry. Secondly, the rate of the [6 + 4] addition reaction is dependent upon the electron-density of the diene. The resulting adducts are also less stable thermodynamically than adducts arising from electron-poor dienes. Finally, the [6 + 4]-addition is subject to steric effects of the dienes.

Adduct stereochemistry

The previous [6 + 4] reactions of cycloheptatrienone and cyclic dienes have all occurred via the *exo* transition state[3–9] predicted for a concerted process by Woodward and Hoffmann.[18] To confirm this transition state with dienes which could isomerize if an intermediate were present, we have studied the reactions of the isomeric dienes *E*-1-acetoxy-1,3-butadiene[19] and *Z*-1-acetoxy-1,3-butadiene.[20] The *E*-diene cleanly gave adduct **8** in 57% yield. The *Z*-diene provided a stereoisomeric [6 + 4] adduct **9** in 15% yield accompanied by equivalent amounts of three [4 + 2] products (**10–12**). All of the major species derived from either diene retained the configuration of the diene. The [6 + 4] products **8** and **9** are consistent with formation via an *exo*-transition state. A trace [4 + 2] product (**13**) formed in 0.5% from the *Z*-diene exhibited vinyl acetate isomerization. To determine if **10–12** were primary products or if they had arisen from **9**, we pyrolyzed **9**. At 150° for 1–5 days **9** was cleanly converted into **13** without any trace of **8**, **10–12**, cycloheptatrienone or either diene being detected at any time during the reaction. Compound **8** was stable to these conditions. However, pyrolysis of **8** at 200° for 8 days gave **19** in 35% yield accompanied by less than 3% of at least two other [4 + 2] adducts and polymeric material. The spectral data of **19** is similar to that of **13** except that **19** clearly has a *Z*-enolacetate. The olefin protons at 4.77 and 7.03 ppm are coupled by 6 Hz. Both of the rearrangement products **13** and **19** have the regiochemistry and olefin stereochemistry predicted for the boat transition state of the Cope rearrangement of **9** and **8** respectively. A C_6–C_7 bond homolysis or heterolysis followed by recyclization is not consistent with the specific olefin geometries obtained. The [6 + 4] products from cycloheptatriene[6,21] or from N-carboalkyloxyazepines[22] have been shown to rearrange without regeneration of starting materials.



19

E-1-Trimethylsilyloxy-1,3-butadiene and E-1-methoxy-3-trimethylsilyloxy-1,3-butadiene are electron-rich dienes. The reactions of these dienes with the electron-deficient cycloheptatrienone could involve stabilized zwitterionic intermediates. The resulting [6 + 4] products 2 and 4 exhibit only the stereochemistry expected from the concerted *exo* transition state.

The formation of isomerically pure adducts 2, 4, 8 and 9 from dienes of known configuration illustrates the stereoselectivity of the [6 + 4] reaction. This cycloaddition exhibits greater stereocontrol than the [4 + 2] reaction.[23]

Electronic effects of the diene

Complementary electron density of the reacting partners is usually considered to be the primary control element in a concerted cycloaddition. In [4 + 2] reactions with two species of comparable electron density, the rate of cycloaddition is slowed, and the stereo- and regiochemical selectivity is diminished. Frontier orbital arguments have been particularly effective in rationalizing these observations.[23–25] Certain compounds undergo facile cycloaddition reactions for other reasons. For instance, the geometry of the starting material may be ideal for orbital overlap. Perhaps any cycloadduct contains less strain than the starting material. An array of electronically diverse, yet cycloaddition-reactive cyclic dienes had yielded [6 + 4] adducts with cycloheptatrienone. These reactions did not permit distinction between two possibilities. Cycloheptatrienone might possess unusual cycloaddition reactivity for some unspecified reason. Or, more likely, the reactions of cycloheptatrienone could be correlated with the electron density of simple dienes.

To distinguish these possibilities, we have examined the reactions of cycloheptatrienone with a series of dienes having normal reactivity in [4 + 2] cycloadditions. These dienes have similar steric factors. This series, *E*-1-methoxy-3-trimethylsilyloxybutadiene, *E*-1-trimethylsilyloxybutadiene, *E*-1-acetoxybutadiene, *E,E'*-1,4-diacetoxybutadiene and ethyl 2,4-hexadienoate, lends qualitative support for this electronic argument. At low temperatures, *E*-1-methoxy-3-trimethylsilyloxybutadiene and cycloheptatrienone afforded [6 + 4] adduct (4). *E*-1-Trimethylsilyloxybutadiene also yielded an adduct (2) at a comparable rate. The hindered, electron deficient 1,4-diacetoxydiene slowly gave compound 14, while ethyl 2,4-hexadienoate failed to react under vigorous conditions. Activation energy calculations using the Arrhenius equation indicate that cycloheptatrienone possesses [6 + 4] cycloaddition reactivity comparable to that of a moderately reactive ene in a [4 + 2] reaction.

These observations fit the frontier orbital arguments. Electron releasing substituents on the diene raise the diene HOMO narrowing the HOMO–LUMO energy gap. This better transition state increases the rate and selectivity.[3,24,25] The frontier orbital theory predicts periselectivity for kinetic products. In [4 + 2] additions, these expected kinetic products are often thermodynamically unstable with respect to stereoisomeric [4 + 2] products. Clearly, we see that at least the [6 + 4] adducts of reactive dienes are not thermodynamic products. As first noted by Houk and Woodward,[6] the formation of [6 + 4] products competes with both [8 + 2] and [4 + 2] adducts. We have made similar observations with 1-trimethylsilyloxy-1,3-butadiene and 1-methoxy-3-trimethylsilyloxy-1,3-butadiene. The first diene provided [6 + 4] adducts at 80° and [4 + 2] adducts at 140° paralleling observations by others.[4,6–9] The latter diene afforded hydrolytically unstable products which have been trapped. This irreversible loss of methanol or a silyloxy group prohibited examination of the adduct interconversions. This reactive diene is the only one from which we have observed [6 + 4], [8 + 2] and [4 + 2] adducts as noted by Houk and Woodward.[6] We have, however, failed to detect any of the common [4 + 2] adducts for this diene and cycloheptatrienone. Instead we have isolated a 1 : 1 cycloadduct in which the tropone is the two electron partner. It is tempting to suggest this adduct 7 arises directly from the precursor to 6 by a sigmatropic rearrangement or by a mechanism analogous to that proposed for the 9 to 13 conversion (*vide infra*). The formation of 7 as the thermodynamic product in this series is undoubtedly due to the facile formation of an aromatic system, trapping a potentially unstable [4 + 2] adduct. The site selectivity of 7 has been reported in cycloheptatrienone[6,8b] and cycloheptatriene[7,21] additions which have been often followed by aromatization.

The [4 + 2] cycloadditions observed as primary reactions in this study yield products with the same regiochemistry predominating. That is, the major, if not exclusive, adducts are substituted at C_8 rather than C_9. This regiochemistry in cycloheptatrienone addition was first observed with cyclopentadienones[6] and subsequently with fulvenes,[8a] cyclopentadiene,[4c] and acrylonitrile.[17h] Frontier orbital theory clearly suggests this regiochemistry provides maximal overlap in the transition state.[18,24,25] As with other [4 + 2] reactions, the stereochemical predictions are less certain but we see a predominance of the expected *endo* isomer.

Steric effects of the diene

The [6 + 4] reaction is subject to steric effects. Previous reports have indicated that 2-substituted cycloheptatrienones may fail to undergo [6 + 4] addition.[8,26] Our results show this reaction is also very sensitive to diene stereochemistry. The reactions in Table 1 permit three generalizations about diene steric effects. The diene can tolerate *E*-1 and 4- substituents. *Z*-1-Dienes yield substantially more [4 + 2] adducts than [6 + 4] product. 1,1-Disubstituted dienes fail to provide [6 + 4] products. Even electron-rich, yet sterically hindered dienes, failed to react with cycloheptatrienone. The [4 + 2] cycloaddition exhibits a less pronounced steric effect since all of the dienes in Table 1 undergo Diels–Alder reactions.

For example, the reaction of 2-methoxyfuran with cycloheptatrienone yields only a [4 + 2] adduct with the regio- and stereochemistry predicted for a concerted reaction. In Diels–Alder reactions 2-alkoxyfurans behave as normal four pi electron-rich partners.[27] Our failure to detect any [6 + 4] adducts under a variety of conditions from this furan implies that the [6 + 4] adduct is exceptionally unstable and/or that the addition is sterically inhibited even with 1,1-substituted cyclic dienes.

There are reports that cycloheptatrienones and cyclopentadiene yield a [6 + 4] product in the presence of toluenesulfonic or hydrochloric acid with an apparent rate increase. This observation seems somewhat curious since tropylium ions and dienes yield only [4 + 2] products of the bicyclo[3.2.2] type.[28] We examined acid catalysis of the tropone reactions with 2,3-dimethyl-1,3-butadiene and with 1-trimethylsilyloxy-1,3-butadiene. Under a variety of conditions using boron trifluroide etherate, aluminum chloride, or methanesulfonic acid in deuteriochloroform, we have been unable to detect any cycloaddition by NMR spectroscopy. Diene polymerization occurs leaving the tropone untouched. Adducts **1** and **2** were not stable to acid but did not yield the same products as attempted acid catalysis of the addition reaction. We thus conclude acid catalysis is not a useful process in cycloheptatrienone [6 + 4] cycloadditions.

We have shown that the reaction rate of unhindered acyclic dienes with cycloheptatrienone increases proportionately with the electron density of the diene as expected.[3] The [6 + 4] addition possesses greater sensitivity to diene steric effects as compared with Diels–Alder reaction. Frequently, cycloheptatrienone fails to undergo any cycloaddition with hindered or electron-poor dienes. Finally, the *exo*-transition state of the [6 + 4] process has been demonstrated in each [6 + 4] product.

We are currently examining the cycloaddition chemistry of 3- and 4-substituted tropones and the reactions of certain bicyclo [4.4.1] undecanones.[11]

EXPERIMENTAL

General. IR spectra were recorded as thin films on a Beckman IR 18-AX spectrophotometer; bands yielding structural information are reported in reciprocal centimeters (cm^{-1}) using polystyrene calibration. UV-visible absorption spectra were recorded on a Perkin Elmer 550 spectrophotometer. NMR spectra were recorded on a Varian EM 390 390 at 35° in $CDCl_3$ and peak positions are reported in ppm from TMS internal standard using multiplet (m), quartet (q), triplet (t), doublet (d), or singlet (s). Decoupling experiments were completed on a Varian HR-220 spectrometer. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer or on a Nicolet 200 MHz multinuclear, widebore spectrometer. Low resolution mass spectra were obtained from an LKB 9000 at 70 eV or at 16–20 eV ionizing voltage. High resolution spectra were performed at the California Institute of Technology Analytical Laboratory or at the UCLA mass spectroscopy facility. Microanalysis were performed by Galbraith Laboratories.

GLPC analysis was performed on a Varian 3700 gas chromatograph with FID detector outfitted with a 6 ft × 1/4 in. glass column containing 3% SE 30 or 3% DEXIL on 100/120 Gas Chrom Q (Applied Science).

Column chromatography was executed at medium pressure (50–100 psi) on E. Merck silica gel 60, particle size 0.040–0.063 mm. LC was completed on a Waters instrument using a 4 ft by 3/8 in. column packed with Li Chrosorb SI 100 (EM reagents) of 5 μm particle size

Reagents and solvents. THF was distilled from sodium-benzophenone immediately prior to use. All aromatic solvents were purified by distillation from fresh Na discarding the first 10% of the distillate. Cycloheptatrienone was prepared in 35% yield from cycloheptatriene by the procedure of Radlick.[29] 2,3-Dimethyl-1,3-butadiene was prepared by the method of Allen and Bell;[30] *E*-1-trimethylsilyloxy-1,3-butadiene and 1-methoxy-3-trimethylsilyloxy-1,3-butadiene, by the method of Danishefsky and Kitahara;[31] and 1,3-bistrimethylsilyloxy-1-methyl-1,3-butadiene, by the method of Ibuka *et al.*[32] *E*-1-Acetoxy-1,3-butadiene was prepared by the procedure of Hagemeyer and Hull;[19] other preparations of this diene gave stereochemically impure samples.[11] *Z*-1-Acetoxy-1,3-butadiene was prepared by the Rautenstrauch method.[20] These isomeric dienes were shown to be stereochemically pure by NMR and GC. The commercial dienes, *E,E*-1,4-diacetoxybutadiene (Fluka), 2-methoxyfuran (Aldrich), furan (Aldrich), and ethyl sorbate (Aldrich) were used as received after determining purity to be > 99% by chromatograph and spectral techniques. All other solvents were purchased from Mallinckrodt Chemical and used as received.

All reactions were magnetically stirred under N_2.

8,9-*Dimethylbicyclo* [4.4.1] *undeca*-2,4,8-*trien*-11-*one* (1).[34,35]

A soln of 0.30 g (2.8 mmol) cycloheptatrienone and 0.51 g (6.2 mmol) 2,3-dimethyl-1,3-butadiene in 10 ml xylene was heated at reflux for 12 hr. The solvent was removed under vacuum and the residue filtered through 10 g silica gel (hexane-EtOAc, 3 : 1) to yield 0.39 g (75%) of oily **1**; IR 3020, 2820, 2730, 1710, 1610, 1450, 1375, 1070, 875, 785, 720 and 700 cm^{-1}; NMR ($CDCl_3$) δ 1.70 (s, 6 H), 2.45 (d, 4 H, J = 6 Hz, H_7 and H_{10}), 3.45 (m, 2 H, H_1 and H_6), 5.47 (m, 2 H, H_2 and H_5) and 5.80 (m, 2 H, H_3 and H_4); HRMS, observed *m/z* 188.1201 $C_{13}H_{16}O$ requires: 188.1201.

7α-(*Trimethylsilyloxy*)*bicyclo* [4.4.1] *undeca*-2,4,8-*trien*-11-*one* (2)

A soln of 0.53 g (5 mmol) cycloheptatrienone and 0.71 g (5 mmol) *E*-1-trimethylsilyloxy-1,3-butadiene in 10 ml benzene was heated at reflux for 96 hr. The solvent was evaporated. Attempts to purify the residue by distillation or chromatography yielded substantial decomposition to cycloheptatrienone and crotonaldehyde. Likewise, hydrogenation afforded numerous products in addition to starting materials. The crude product isolated in about 80% yield after prolonged exposure to high vacuum was consistent with **2**: IR 3020, 2720, 1705, 1600, 1590, 1250, 1200, 1080, 900 and 850 cm^{-1}; NMR ($CDCl_3$) δ 0.30 (s, 9H), 2.20–3.00 (m, 2 H, H_{10}), 3.40–3.80 (m, 2H, H_1 and H_6), 4.87 (d, 1 H, J = 7 Hz, H_7) and 5.50–6.30 (m, 6 H, olefin protons).

8- *and* 9-β-*Trimethylsilyloxyvinylbicyclo* [3.2.2] *nona*-3,6-*dien*-2-*one* (3).

A soln of 1.06 g (10 mmol) cycloheptatrienone and 3.08 g (20 mmol) *E*-1-trimethylsilyloxy-1,3-butadiene in 10 ml xylene was heated at reflux for 72 hr. About 50% of the cycloheptatrienone had reacted as determined by GC. The xylene was removed to leave 1.34 g (54%) of oily adducts. Again, attempted purification led to decomposition. The major product was **3**: IR 3022, 2970, 1677 (br, intense), 1259, 1175 and 1125 cm^{-1}; NMR ($CDCl_3$) δ 0.2 (s, 9H), 1.5–2.8 (m, 3 H, H_8 and H_9), 3.0–3.5 (m, 2 H, H_1 and H_5), 4.6 (dd, 1 H, H_{10}), 5.6 (m, 1 H, H_3), 6.0–6.5 (m, 2 H, H_6 and H_7), 7.0 (m, 2 H, H_4 and H_{11}). The crude product also contained small amounts of **2** (< 10%).

7α-*Methoxy*-9-(*trimethylsilyloxy*)*bicyclo* [4.4.1] *undeca*-2,4,8-*trien*-11-*one* (4) *and* 7α-(*Methoxy*)*bicyclo* [4.4.1] *undeca*-2,4-*dien*-9,11-*dione* (5)

A soln of 0.145 g (1.4 mmol) cycloheptatrienone and 0.27 g (1.4 mmol) *E*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene with a 10% impurity of 4-methoxy-3-buten-2-one in 10 ml toluene was heated at 80° for 96 hr. After the solvent was removed, NMR of the crude mixture showed **4** and **5** present in a 4 : 1 ratio. Filtration trough silica gel with hexane-EtOAc(4 : 1) hydrolyzed **4** to **5** to yield 0.110 g (40%) of a yellow oil **5** which darkened rapidly on exposure to air: IR 3030, 2940, 1715, 1700, 1600, 1100 and 700 cm^{-1}; NMR ($CDCl_3$) δ 2.60 (dd, 1 H, J = 5, 15 Hz, H_5), 2.90 (dd, 1 H, J = 4, 15 Hz, H_5), 2.90 (d, 2 H, J = 2 Hz, H_3), 3.38 (s, 3 H), 3.56 (m, 1 H, H_6), 3.70 (m, 1 H, H_2), 3.96 (m, 1 H, H_1) 5.54 (m, 1 H, H_7), 5.69 (m, 1 H, H_{10}) and 6.08 (m, 2 H, H_8 and H_9): HRMS, observed *m/z* 174.0678, $C_{11}H_{10}O_2(M^+-CH_4O)$ requires: 174.0681.

[3A - (*E*)] - (3,3*a* -)*dihydro* - 2*H* - *cyclohept*[*b*]*furan* - 2 - *ylidine*)*acetaldehyde* (6) *and* (5)

A soln of 0.090 g (0.9 mmol) cycloheptatrienone and 0.200 g (1.0 mmol) *E*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene with a 10% impurity of 4-methoxy-3-buten - 2-one in 10 ml toluene was heated at reflux for 15 hr. The solvent was removed and the resulting dark oil was filtered through silica gel (hexane-EtOAc, 4 : 1) yielding 0.073 g (45%) of a mixture of **5** and **6**. Separation was achieved by thick layer chromatography on silica gel (hexane-EtOAc, 4 : 1) providing purified samples of **5** and **6**. Aldehyde **6** was a mixture of two isomers in a 4 : 1 ratio and exhibited the following properties: IR 3030, 2935, 2860, 2770, 1670, 1640, 1590 and 1160–1155 cm^{-1}; major isomer: NMR ($CDCl_3$) δ 3.05 (m, 1 H), 3.37 (ddd, 1 H, J = 1, 5, 19 Hz), 3.69 (ddd, 1 H, J = 1, 11, 19 Hz), 5.06 (dd, 1 H, J = 4.9 Hz), 5.82 (br d, 1 H, J = 6 Hz), 5.96 (m, 1 H), 6.16 (m, 1 H), 6.40 (m, 2H) and 9.72 (d, 1 H, J = 6 Hz); minor isomer: NMR ($CDCl_3$); (selected signals only) δ 6.02 (br d, 1 H, J = 7 Hz) and 10.00 (d, 1 H, J = 7 Hz): HRMS, observed *m/z* 174.068e, $C_{11}H_{10}O_2$ requires: 174.0681.

6,7-*Dihydro-2-hydroxy-5H-benzocyclohepten-5-one* (7).

A soln of 0.135 g (1.3 mmol) cycloheptatrienone and 0.240 g (1.3 mmol) *E*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene with a 10% impurity of 4-methoxy-3-buten-2-one in 10 ml xylene was heated at reflux for 36 hr. Column chromatography on silica gel (hexane-EtOAc, 4 : 1) yielded 0.080 g (35%) of a yellow oil 7 which darkened on exposure to air: UV (EtOH) 232 nm (ε 10,88), 261 nm (ε 2800) and 328 nm (ε 930); UV (EtOH with added NaOH) 249 nm (ε 9600), 290 nm (ε 3600) and 392 nm (ε 1200); IR 3300, 3030, 2960, 2940, 1665, 1600, 1320, 1190, 1150 and 835 cm^{-1}; NMR ($CDCl_3$) δ 2.48 (m, 2H), 2.94 (m, 2H), 6.03 (m, 1H), 6.41 (br dg 1 H, *J* = 11.5 Hz), 7.00 (dd, 1 H J = 3. 8 Hz), 7.13 (d, 1 H, *J* = 8 Hz) and 7.51 (d, 1 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 202.7 (s), 155.1 (s), 137.3 (s), 133.8 (d), 130.7 (d), 130.3 (d), 129.3 (s) 120.1 (d), 115.9 (d), 42.0 (t) and 23.8 (t); HRMS, observed *m*/*z* 174.0690, $C_{11}H_{10}O_2$ requires: 174.0681. (Found: C, 75.69; H, 5.94. Calc. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79).

7α-(*Acetoxy*)*bicyclo* [4.4.1] *undeca*-2,4,8-*trien*-11-*one* (8).

A soln of 1.06 g (10 mmol) cycloheptatrienone and 2.00 g (18 mmol) *E*-1-acetoxy-1,3-butadiene in 25 ml xylene was heated at reflux for 12 hr. Removal of the xylene and column chromatography of the residue on silica gel (hexane-EtOAc, 4 : 1) yielded 1.24 g (57%) of 8: IR 1745, 1705 and 1225 cm^{-1}; NMR ($CDCl_3$) δ 2.07 (s, 3 H), 2.56 (m, 2 H, H_{10}), 3.54 (brq, 1 H, J = 6 Hz, H_1) 3.67 (br t, 1 H, J = 6 Hz, H_6), 5.73 (m, 5 H, H_2, H_5, H_7, H_8 and H_9), and 6.10 (m, 2 H, H_3 and H_4); ^{13}C NMR ($CDCl_3$) δ 202.9 (s), 170.2 (s), 131.6 (d), 130.6 (d), 130.0 (d), 127.6 (d), 126.2 (d), 125.3 (d), 69.6 (d), 61.2(d), 55.4(d), 29.2(t) and 21.0 (q); HRMS, observed *m*/*z* 218.094, $C_{13}H_{14}O_3$ requires: 218.0943; MS (70 eV), *m*/*z* 218 (2.5), 176 (4.9), 158 (11), 149 (11), 108 (9), 107 (100) and 91 (9).

(Found: C, 71.31; H, 6.59. Calc for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47).

Examination of the crude material by HPLC indicated two minor components in < 5% of the mixture; these are not 9–13. We have been unable to isolate these components. A soln of 0.048 g of 8 in 5 ml xylene at reflux for 20 hr afforded only 8 in 95% yield.

7β-(*Acetoxy*)*bicyclo* [4.4.1] *undeca*-2,4,8-*trien*-11-*one* (9) *and bicyclo* [3.2.2]*nona*-3,7-*dien*-2-*ones* 10, 11, 12 *and* 13.

A soln of 1.06 g (10 mmol) cycloheptatrienone and 3.00 g (27 mmol) *Z*-1-acetoxy-1,3-butadiene in 10 ml xylene was heated at reflux for 24 hr. The xylene was removed to leave adducts and cycloheptatrienone in a 3 : 1 ratio. Evaporation distillation left 1.7 g of oily adducts. Filtration through 20 g silica gel (EtOAc) provided 1.07 g (49%) of 1 : 1 adducts which were purified on HPLC, hexane-EtOAc (85 : 15), and are listed in order of elution:

Compound 9. IR 3020, 2950, 1745, 1710, 1700, 1376, 1240, 1190, 1050 and 1040 cm^{-1}; NMR ($CDCl_3$) δ 2.14 (s, 3 H), 2.31 (br d, of t, 1 H, J ~ 7, 16 Hz, H_{10}, β), 2.60 (m, 1 H, H_{10}, α), 3.54 (br g, 1 H, J ~ 7, H_1) 3.75 (br s, 1 H, H_6), 5.60 (m, 3 H, H_2, H_5 and H_7) and 5.90 (m, 4 H, H_3, H_4 H_8 and H_9); ^{13}C NMR ($CDCl_3$) δ 203.3 (s), 169.8 (s), 132.6 (d), 129.7 (d), 127.2 (d), 126.8 (d), 126.3 (d), 124.3 (d), 70.6 (d), 60.8 (d), 55.5 (d), 26.5 (t) and 21.1 (q); HRMS, observed *m*/*z* 218.0941, $C_{13}H_{14}O_3$ requires: 218.0943. (Found: C, 71.66; H, 6.53. Calc for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47).

Compound 10. IR 2950, 1760, 1685, 1680, 1670, 1640, 1380, 1375, 1215, 1100, 1045 and 730 cm^{-1}; NMR ($CDCl_3$) δ 1.58 (m, 2 H, H_9), 2.17 (s, 3 H), 2.28 (m, 1 H, H_8 *endo*), 3.31 (m, 1 H, H_5), 3.48 (m, 1 H, H_1), 4.77 (dd, 1 H, J = 6, 10 Hz, H_{10}), 5.90, (dd, 1 H, J = 2, 11 Hz, H_3), 6.06 (m, 1 H, H_7), 6.62 (m, 1 H, H_6), 6.91 (dd, 1 H, J = 9, 11 Hz, H_4) and 7.02 (dd, 1 H, J = 1, 6 Hz, H_{11}); HRMS, observed *m*/*z* 218.0930, $C_{13}H_{14}O_3$ requires: 218.0943. (Found: C, 71.32; H, 6.52. Calc. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47).

Compound 11. IR 3060, 2945, 2880, 1765, 1675, 1638, 1372, 1215, 1100 and 1040 cm^{-1}; NMR ($CDCl_3$) δ 1.68 (ddd, 1 H, J = 3.5, K, 14 Hz, H_8 *exo*), 2.17 (s, 3 H), 2.27 (dd, 1 H, J = 9.5, 14 Hz, H_8 *endo*), 3.19 (br t, 1 H, J ~ 8 Hz, H_5), 3.42 (m, 1 H, H_9), 3.50 (m, 1 H, H_1), 4.79 (dd, 1 H, J = 5, 10 Hz, H_{10}), 5.80 (dd, 1 H, J = 2, 11 Hz, H_3), 6.22 (br t, 1 H, J = 8 Hz, H_7), 6.47 (br t, 1 H, J = 8 Hz, H_6), 6.96 (d, 1 H, J = 5 Hz, H_{11}) and 7.13 (dd, 1 H, J = 9, 11 Hz, H_4); HRMS, observed *m*/*z* 218.0925, $C_{13}H_{14}O_3$ requires: 218.0943

Compound 12. IR 3040, 2955, 2880, 1765, 1670, 1668, 1638, 1390, 1372, 1210 and 1049 cm^{-1}; NMR ($CDCl_3$) δ 1.75 (m, 2 H, H_9), 2.16 (s, 3 H), 2.25 (m, 1 H, H_8 *exo*), 3.33 (m, 2 H, H_1 and H_5), 4.67 (dd, 1 H, J = 6, 10 Hz, H_{10}), 5.81 (dd, 1 H, J = 1, 11 Hz, H_3), 6.20 (t, 1 H, J = 7 Hz, H_7), 6.53 (t, 1 H, J = 7 Hz, H_6), 7.03 (dd, 1 H, J = 1, 6 Hz, H_{11}) and 7.21 (dd, 1 H, J = 9, 11 Hz, H_4).

Compound 13. Trace amounts (< 1%), not separable by HPLC from 10.

[1α,5α,9β(*E*)]-9-[2-(*Acetoxy*)*ethenyl*]*bicyclo* [3.2.2] *nona*-3,6-*dien*-2-*one* (13).

A soln of 0.074 g of 9 in 7 ml xylene was refluxed for 80 hr. The enone 13 was provided in > 90% yield with no detectable 9 remaining: IR 3040, 2945, 2885, 1762, 1672, 1640, 1373, 1220 and 1100 cm^{-1}; NMR ($CDCl_3$) δ 1.59 (dd, 1 H, J = 7, 14 Hz, H_8 *endo*), 2.12 (s, 3 H), 2.25 (m, 1 H, H_8 *exo*), 2.65 (m, 1 H, H_9 *exo*), 3.27 (m, 1 H, H_5), 3.47 (m, 1 H, H_1), 5.32 (dd, 1 H, J = 10, 13 Hz, H_{10}), 5.90 (dd, 1 H, J = 2, 11 Hz, H_3), 6.04 (t, 1 H, J = 8 Hz, H_7), 6.60 (t, 1 H, J = 8 Hz, H_6), 6.89 (dd, 1 H, J = 9, 11 Hz, H_4) and 7.18 (d, 1 H, J = 13 Hz, H_{11}); HRMS, observed *m*/*z* 218.0954, $C_{13}H_{14}O_3$ requires: 218.0943. (Found: C, 71.32; H, 6.52. Calc for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47).

2α,5α-(*Bisacetoxy*)*bicyclo* [4.4.1] *undeca*-2,4,8-*trien*-11-*one* (14).

A soln of 0.20 g (1.2 mmol) *E*,*E*-1,4-diacetoxy-1,3-butadiene and 0.16 g (1.3 mmol) cycloheptatrienone in 3 ml xylene was heated at reflux for 27 hr. Column chromatography of the mixture on silica gel yielded starting diene (hexane-EtOAc, 4 : 1) and 0.08 g (25%) of 14 (hexane-EtOAc, 1 : 1): IR 3050, 2940, 1750, 1720, 1683, 1370, 1230 and 1030 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (s, 6 H), 3.65 (t, 2 H, J = 7 Hz, H_1 and H_6), 5.60–5.90 (m, 6 H, Hz–H_{10}, H_2 and H_5) and 6.25 (m, 2 H, H_3 and H_4); HRMS, observed *m*/*z* 216.070, $C_{13}H_{12}O_3$ (M-acetic acid) requires: 216.0786.

[3*a*(3*a*α,4β,8β,8*a*α)]-3*a*,4,8,8*a*-*Tetrahydro*-4,8-*etheno*-2*H*-*cyclohepta*[*b*]*furan*-2,7(3*H*)-*dione* (15).

A soln of cycloheptatrienone (0.300 g, 2.8 mmol) and of 2-methoxyfuran (0.300 g, 3.1 mmol, 1.1 equiv) in 15 ml xylene was heated at reflux for 48 hr. Removal of solvent followed by column chromatography with EtOAc afforded 0.125 g of a mixture of 15 and cycloheptatrienone in a 1 : 1 ratio. These were separated by HPLC (EtOAc) to give 0.063 g (14%) of 15: IR 2960, 1789, 1672, 1633, 1172 and 1020 cm^{-1}; NMR ($CDCl_3$) δ 2.31 (dd, 1 H, J = 5, 19 Hz), 2.88 (dd, 1 H, J = 11, 19 Hz), 3.24 (m, 1 H, H_{3a}), 3.34 br t, 1 H, J ~ 9 Hz, H_4), 3.96 (br d, 1 H, J = 8 Hz), 5.05 (br d, 1 H, J = 8 Hz, H_{8a}), 5.81 (dd, 1 H, J = 2, 11 Hz, H_6), 6.21 (br t, 1 H, J = 8 Hz, H_9), 6.60 (br t, 1 H, J = 8 Hz, H_{10}) and 7.14 (dd, 1 H, J = 9, 11 Hz, H_5), HRMS, observed *m*/*z* 190.0641, $C_{11}H_{10}O_3$ requires: 190.0630. (Found: C, 69.27; H, 5.41. Calc for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30).

Attempted reactions of cycloheptatrienone with furan, ethyl sorbate and 1,3-*bissilyloxy*-1-*methyl*-1,3-*butadiene.*

Treatment of cycloheptatrienone with each of these dienes in xylene for 4 days yielded no detectable reaction (HPLC). Ethyl sorbate did yield numerous products including one (< 10%) which was formed only in the presence of tropone. Furthermore, cycloheptatrienone and furan failed to react at − 30° or room temperature in 2 wks or after 48 hr in refluxing benzene or toluene.

2α-(*Methoxy*)*bicyclo* [4.4.1] *undeca*-4.11-*dione* (16).

A soln of 0.045 g (0.2 mmol) of 5, 0.010 g of 10% Pd-C and 50 ml abs EtOH in a Parr bottle was treated with hydrogen at 60 psi for 4 hr. The resulting solution was filtered through a celite pad which was washed with another 20 ml EtOH. Evaporation of the EtOH left 0.036 g (80%) of 16 as a yellow oil: IR 2940, 2880, 1705, 1460 and 1100 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.3 (m, 8 H), 2.68 (m, 4 H), 2.85 (m, 1 H), 3.03 (m, 1 H), 3.35 (s, 3 H) and 3.81 (m, 1 H).

[1α,5α,9β(*Z*)]-8-[2-(*acetoxy*)*ethenyl*]*bicyclo* [3.2.2] *nona*-3,6-*dien*-2-*one* (19)

A soln of 0.026 g of 8 in 0.5 ml of d_6-benzene was heated at 195–200° for 200 hr in a sealed NMR tube. The reaction was monitored by NMR until the starting triene had completely reacted. The crude product contained **19**, < 3% of a mixture of at least two isomeric products and polymeric material. Column chromatography on silica gel (hexane-ethyl acetate, 4 : 1) yielded an analytical sample (0.009 g, 35%) of **19**: IR 3050, 2940, 2865, 1750, 1672, 1630, 1370, 1215, 1100 and 1040 cm^{-1}; NMR (CDCl$_3$) δ 1.55 (dd, 1 H, J = 7, 14 Hz, H_8 *endo*), 2.17 (s, 3 H), 2.30 (ddd, 1 H, J = 7, 10, 14 Hz, H_8 *exo*), 3.15 (m, 1 H, H_9 *exo*), 3.32 (m, 1 H, H_5), 3.48 (bt, 1 H, J ~ 7 Hz, H_1), 4.77 (dd, 1 H, J = 6, 10 Hz, H_{10}), 5.90 (dd, 1 H, J = 2, 11 Hz, H_3), 6.06 (t, 1 H, J ~ 7 Hz, H_7), 6.62 (t, 1 H, J ~ 7 Hz, H_6), 6.90 (dd, 1 H, J = 8.5, 11 Hz, H_4) and 7.03 (d, 1 H, J = 6 Hz, H_{11}).

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