decompositions lead mainly to $C_7H_6F^+$, not $C_7H_7^+$, ions. (If the latter are formed at threshold,[22] our data indicate that this reaction channel is poorly competitive at only slightly higher energies.) Formation of $C_7H_7^+$ requires **1**-F ions of higher internal energy; for these the simple cleavage loss of F giving **3** should be much more favored than the isomerization to **2**-F, so that nearly pure benzyl ions are formed from benzyl fluoride at electron energies near threshold.

Acknowledgment. We are grateful to Drs. Pierre Ausloos, B. S. Freiser, and J. C. Traeger for communication of results prior to publication, to the National Institutes of Health (GM16609) for generous financial support, and to the Army Research Office, Durham, for funds for instrument improvements.

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(25) As observed previously,[16a] the increased number of collisions per ion increased the proportion of higher energy CA fragmentations which are observed; increasing the He pressure to decrease the $C_7H_7^+$ intensity from 50% to 10% of its original value decreased $[77^+]/[74^+]$ by 17% for **3** and 35% for **4**.

(26) Ionization with 70-eV electrons should produce initial 1 ions of which ~37% will have internal energy values <2 eV above threshold.[3] Because the lowest energy ions of these will form **2**, little of the 33% **3** formed from 1 using 70-eV electrons can come from $C_7H_8^+$ with internal energy values >2 eV above threshold.

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(28) A referee has suggested the possibility that the stable $C_7H_7^+$ ions of high internal energy (>46 kcal/mol) have yet another structure, possibly ill defined, representing either **3** or **4** as limits. Although all our CA data (such as Table II) are consistent with the presence of only isomers **3** and **4**, the presence of another isomer with a similar CA spectrum cannot be ruled out. However, to be an important product in an equilibrium with **3** and **4**, or in competition with the formation of **3** or **4**, should require a comparable stability; apparently no experimental[2-7,10-13,15] or theoretical[8,9] studies to date have suggested the possibility of such a $C_7H_7^+$ isomer.

Loss of Allyl Cation Configuration in Cycloadditions to Electron-Rich Conjugated Dienes[1]

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Abstract: The cycloaddition of W-configurated 1,3-dimethyl-2-oxyallyl cations to electron-rich cyclic conjugated dienes is accompanied by configurational losses and leads to cycloadducts with α,β-configurated (equatorial, axial) methyl groups. For aromatic "dienes" such as benzene and N-alkylpyrroles, electrophilic substitution competes strongly with $[4 + 3 \rightarrow 7]$ cycloaddition which, nonetheless, can be accomplished by choice of an oxyallyl moiety with the proper blend of electrophilicity and nucleophilicity. It is suggested that formation of the seven-membered ring proceeds in two distinct stages, i.e., the stepwise pull-push mechanism involving formation of the first σ bond in an electrophilic step and the second σ bond in a nucleophilic step.

Introduction

The allyl cation route to seven-membered rings is a preparatively useful reaction which, as the increasing number of papers[3-15] shows, is meeting with general interest, not least because of the challenging synthetic and mechanistic problems which are involved. In the present paper we address ourselves mainly to a mechanistic question, i.e., the timing of bond changes on the way from reactants to products. Although the concerted $[4 + 3 \rightarrow 7]$ concept has been helpful in the past and

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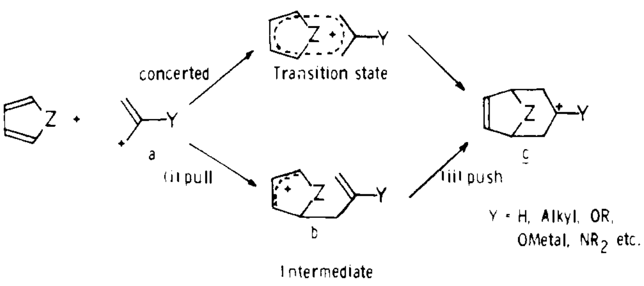
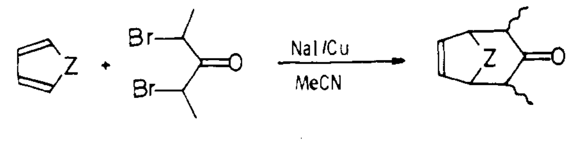
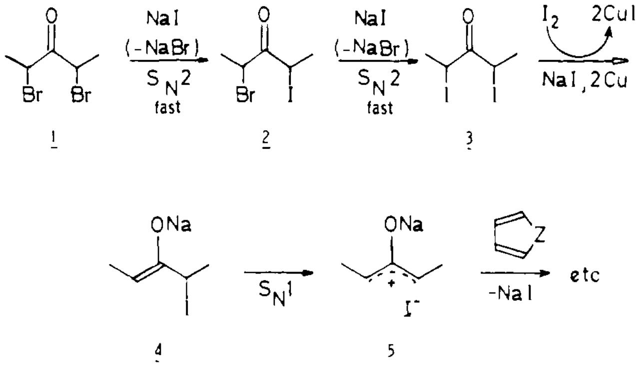
Scheme I. Concerted and Stepwise Cycloaddition of an Allyl Cation to a Cyclic Conjugated Diene



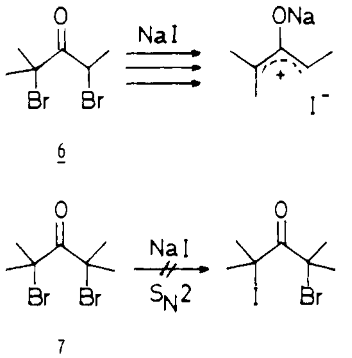
Scheme II. NaI/Cu Route to Seven-Membered Rings



Scheme III. Postulated Intermediates of the Reaction Shown in Scheme II

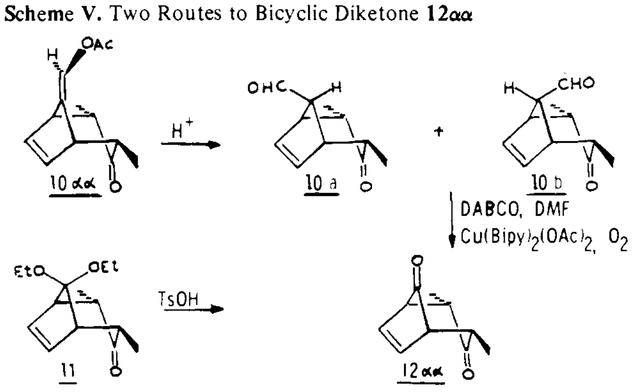


Scheme IV. Initial S_N2 Displacement of Bromide by Iodide as a Prerequisite for Sodium Oxyallyl Formation



also theoretically respectable,[16] we would like to discuss the question: Can the cyclization occur in stages (cf. Scheme I)? A useful model for study is the sodium iodide induced debromination of α,α'-dibromo ketones in the presence of copper and a conjugated diene (Scheme II). This reaction represents one of several synthetic methods for generating allyl cation equivalents which we ourselves have developed and published to date. These methods include the silver salt route, a heterocyclic route, and the combination of α,α'-dihalo ketone and zinc-copper couple[15] as well as more recent variants which are perhaps most useful from a preparative viewpoint.[1,17]

Scheme V. Two Routes to Bicyclic Diketone **12αα**



Mechanistically, we consider the reaction in Scheme II to proceed in at least four stages via a series of reactive intermediates (Scheme III). The formation of diiodo ketone **3** is fast as indicated by the sudden precipitation of NaBr which, unlike NaI, is much less soluble in acetonitrile; precipitation of NaBr is generally complete within about 30 s of mixing a homogeneous solution of α,α'-dihalo ketone with NaI in acetonitrile. In further support of Scheme III, simple diiodo ketones such as 1,3-diiodo-2-butanone and even 2,4-diiodo-3-pentanone (**3**) can be isolated, although these compounds are sensitive to light and decompose rapidly on standing.[18]

The next two stages, i.e., nucleophilic attack of iodide ion on the positively polarized iodine in **3** and finally the crucial and presumably slow S_N1 reaction (**4** → **5**) to yield sodium oxyallyl **5**, are inferred from (a) studies of various alkylated dibromo ketones, (b) comparisons with the reactivity of the corresponding zinc oxyallyl species, and (c) general mechanistic grounds. As shown in Scheme IV a ditertiary dibromo ketone such as 2,4-dibromo-2,4-dimethyl-3-pentanone (**7**) fails to react with NaI/Cu in the desired sense, but the secondary, tertiary precursor **6** does react. Thus, a positively polarized bromine as in **7** is not attacked by iodide ion, nor is an initial S_N2 displacement on **7** possible. Cyclopropanones[19] or allene oxides[12,20-22] are not involved in these reactions.[23] Finally, trapping experiments of the sodium oxyallyl species with cyclopentadiene show that the reactive allyl cation moiety is formed with complete (at least >98%) W configuration, because no α,β adduct is discernible under kinetic control, but present to the extent of 30% after equilibration (Chart I, footnote *b*).

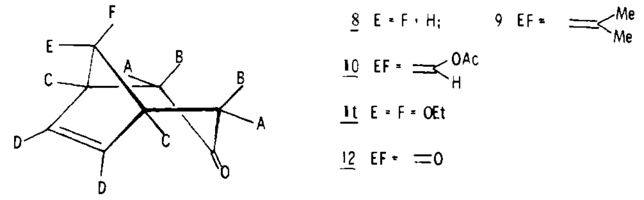
Results

Most of our experimental results are summarized in Tables I and II and in Chart I. The letters $\alpha\alpha$ stand for cis-diequatorial methyl groups, $\beta\beta$ for cis-diaxial, and $\alpha\beta$ for axial-equatorial methyl groups. Epimer ratios were determined and assigned by GLC and detailed ^{1}H NMR spectroscopy, as discussed below.

In the case of the cyclopentadiene adducts we were able to isolate the cis-diequatorial derivative **8αα** as a crystalline 1:1 $AgNO_3$ complex. Interestingly, the cis-diaxial epimer **8ββ**, although of higher energy content than **8αα**, did not react with $AgNO_3$ and remained in the mother liquor. A possible explanation is as follows. In epimer **8ββ** the two methyl groups, being syn diaxial, repel each other. On complexation with $AgNO_3$, the carbon-carbon double bond lengthens and the syn-diaxial clash of the two methyl groups increases (inverse reflex effect).[24]

Cycloaddition to 6-acetoxyfulvene gave **10αα** and **10αβ** in addition to syn aldehyde **10a** and anti aldehyde **10b**. The latter aldehydes were oxidized degradatively to the diketone **12αα**, which was obtained independently by ketal hydrolysis of **11** (Scheme V). Cycloaddition to the highly reactive 5,5-diethoxycyclopentadiene—which dimerizes readily—was accomplished in the two-phase reaction medium *n*-pentane-acetonitrile (ca. 2:1), acetonitrile being the lower, denser layer; 8,8-diethoxy-2α,4α-dimethylbicyclo[3.2.1]oct-6-en-3-one (**11**) was formed as the single isomer, and gave—after ketal hydrolysis—2α,4α-dimethylbicyclo[3.2.1]oct-6-ene-3,8-dione (**12αα**). Various attempts to induce cycloadditions of 5,5-

Table I



	8αα	8ββ	9αα	9ββ
A	[a]0.95 d (J = 7 Hz) (6 H)	2.20 q (J = 7.5 Hz) (2 H)	0.99 d (J = 7 Hz) (6 H)	2.35 q (J = 7.5 Hz) (2 H)
B	2.38 q (J = 7 Hz) of d (J = 3 Hz) (2 H)	1.16 d (J = 7.5 Hz) (6 H)	2.35 q (J = 7 Hz) of d (J = 3 Hz) (2 H)	1.07 d (J = 7.5 Hz) (6 H)
C	2.68 br s (2 H)	2.50 d (J = 5 Hz) (2 H)	3.26 br s (2 H)	3.12 br s (2 H)
D	6.03 br s (2 H)	6.07 br s (2 H)	6.04 t (J = 1.5 Hz) (2 H)	6.08 t (J = 1.5 Hz) (2 H)
E	2.10 d (J = 10.8 Hz) of t (J = 5.4 Hz) (1 H)	2.16 d (J = 10 Hz) of d (J = 5 Hz) (1 H)	1.70 s (6 H)	1.76 s (6 H)
F	1.94 d (J = 10.8 Hz) (1 H)	1.88 d (J = 10 Hz) (1 H)	1.70 s (6 H)	1.76 s (6 H)
ν_{max} (C=O), cm^{-1}	1710		1710	1705

	10αα	10αβ	11αα	12αα
A	1.00 d (J = 7 Hz) (3 H)	1.09 d (J = 7 Hz) (3 H)	0.96 (J = 7 Hz) (6 H)	1.14 d (J = 7 Hz) (6 H)
A′	1.04 d (J = 7 Hz) (3 H)	2.36 q (J = 7.5 Hz) (1 H)		
B	2.48 q (J = 7 Hz) of d (J = 3.5 Hz) (1 H)	2.48 q (J = 7 Hz) of d (J = 3 Hz) (1 H)	2.61 q (J = 7 Hz) of d (J = 3 Hz) (2 H)	2.73 q (J = 7 Hz) of d (J = 2.8 Hz) (2 H)
B′	2.51 q (J = 7 Hz) of d (J = 3.5 Hz) (1 H)	1.13 d (J = 7.5 Hz) (3 H)		
C	3.13 br s (1 H)	2.82 br s (1 H)	2.68 br s (2 H)	2.88 br s (2 H)
C′	3.49 br s (1 H)	3.34 br s (1 H)		
D	6.10 (d (J = 6 Hz) of d (J = 2 Hz) (1 H)	6.04 d (J = 6 Hz) of d (J = 2 Hz) (1 H)	6.00 t (J = 1.5 Hz) (2 H)	6.44 br s (2 H)
D′	6.19 d (J = 6 Hz) of d (J = 2 Hz) (1 H)	6.16 d (J = 6 Hz) of d (J = 2 Hz) (1 H)		
E	2.10 s (3 H) (OCH_3)	2.08 s (3 H) (OCH_3)	1.11 t (J = 7.5 Hz) (3 H) 3.42 q (J = 7.5 Hz) (2 H)	
F	6.94 s (1 H)	7.04 s (1 H)	1.21 t (J = 7.5 Hz) (3 H) 3.57 q (J = 7.5 Hz) (2 H)	
ν_{max} (C=O), cm^{-1}			1710	1770 and 1715

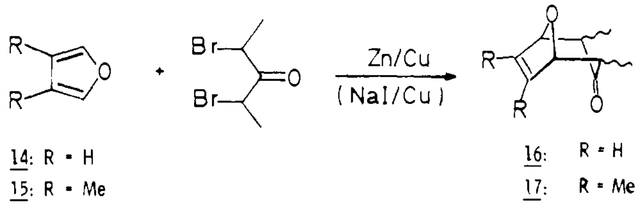
[a] Chemical shifts in parts per million downfield from Me_4Si.

dimethylcyclopentadiene and of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene to 1,3-dimethyl-2-oxyallyl cations, generated both by the zinc-copper couple and the sodium iodide/copper powder technique, failed to give even a trace of the desired products **13a** and **13b**.

Spectroscopic Identification of the Cycloadducts

It can be seen, from chemical shift values of the methyl groups in isomers of **8**, that a methyl in the β configuration is deshielded with respect to a methyl in the α configuration. This

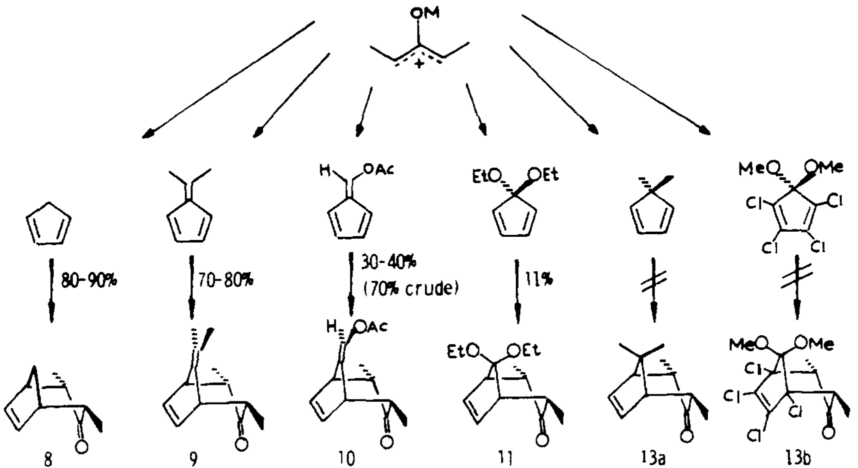
Table II. Epimer Ratios for the Reaction of 1,3-Dimethyl-2-oxyallyl with Furan and 3,4-Dimethylfuran



entry	diene (R = H or Me)	solvent	added salt	αα	αβ	ββ
1	furan[a]	MeCN		90.9	6.1	3.0
2	furan	DME		73.9	17.4	8.7
3	furan	MeCN		74.5	15.2	10.3
4	furan	DME	$Bu_4N^+ClO_4$[b]	79.0	12.9	8.1
5	furan	DME	$LiClO_4$[b]	92.1	4.3	3.6
6	equilibration[c]			59.7	36.5	3.8
7	3,4-dimethylfuran	DME		45.0[d]	21.3[d]	33.7[d]

[a] NaI/Cu procedure; entries 2, 3, 4, 5, and 7 refer to Zn/Cu procedure. [b] 0.8 M solution, equimolar with dibromo ketone. [c] Isomer ratio after equilibration with 2 M sodium methoxide in methanol. [d] Product distribution determined by ^1H NMR after use of Eu(fod)$_3$.

Chart I. Stereoisomeric Products ($\alpha\alpha$:$\alpha\beta$:$\beta\beta$)[a] from the Reaction of Metal Oxyallyls (M = Na, Zn) with Cyclic Conjugated Dienes



	8	9	10	11	13a	13b
NaI/Cu	6.4 : 0 : 1 [b]	4.6 : 0 : 1 [c]	5.2 : 1 : 0	1.0 : 0 : 0	-	-
Zn/Cu	1.7 : 0 : 1	12.2 : 1 : 10	-	-	-	-

[a] Product ratios are given in this sequence. [b] At equilibrium 8$\alpha\alpha$:8$\alpha\beta$:8$\beta\beta$ = 15:7:1. [c] At equilibrium 9$\alpha\alpha$:9$\alpha\beta$:9$\beta\beta$ = 4.7:4.9:1.

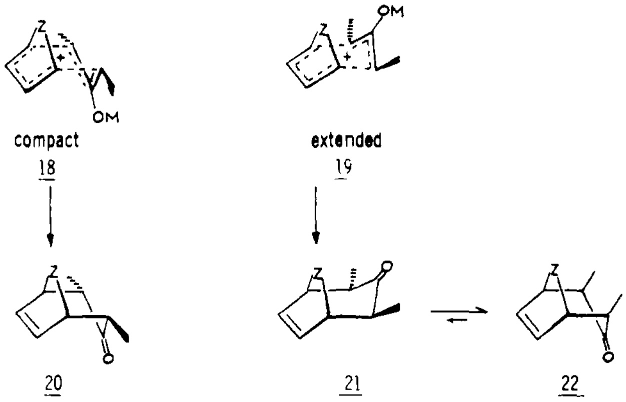
trend had been observed earlier,[24] although the ^{1}H NMR data given here for **8αα** and **8ββ** were not reported in detail, since the two compounds could not be separated at the time. The same trend can also be seen in the isomeric pairs of **9**. It will be noticed that the vicinal coupling constant J^3 between methyl protons A (in the α configuration) and the methine proton B (in the β configuration) is consistently 7 Hz. In the instance of a methyl B with β configuration and a methine proton A with α configuration, however, J^3 = 7.5 Hz in each case (previously reported for **8ββ** as 7 Hz).[24] At the same time, the methine proton B has a vicinal coupling constant J^3 = 3 Hz with the bridgehead proton C; in the case of a methine proton A (in the α configuration) this coupling is reduced to less than ca. 1 Hz, with the result that the methine proton appears as a broadened quartet.

These observations have been used to assign the stereochemistry of the minor isomer formed in the cycloaddition to 6-acetoxyfulvene. Since the methyl groups in **10** are nonequivalent, owing to the asymmetry of the C-8 grouping, distinction between methyls in α and β configurations cannot be made on the basis of chemical shift trends as previously noted and also found here. However, from the various coupling constants a distinction may be made. Thus the values observed for the minor isomer of **10** show it to be the αβ isomer, i.e., a methyl with J^3 = 7 Hz (in an α configuration) and a methyl with J^3 = 7.5 Hz (in a β configuration). Furthermore, the methine protons can be seen to have differing vicinal couplings to their adjacent bridgehead protons, i.e., a methine proton with J^3 = 3 Hz (in a β configuration) and a methine proton with $J^3 < 1$ Hz (in an α configuration). Whereas in compounds **8**, **9**, **11**, and **12** the designations αβ and βα represent a *dl* pair, in **10** this is not the case as **10αβ** and **10βα** are diastereoisomers. However, it is not possible, from the data available, to distinguish between **10αβ** and **10βα** so that the isomer is referred to as simply **10αβ**.

Discussion

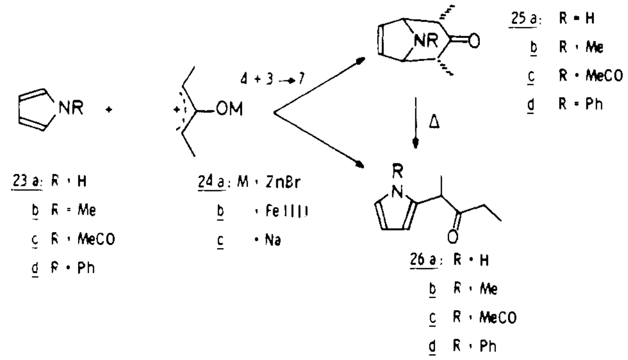
The cycloaddition of an allyl cation to conjugated diene can proceed via the compact transition state **18** and the extended alternative **19** (Scheme VI).[41] Given a W-configurated acyclic allyl cation, and an extended transition state, the initial conformation **21** containing a six-membered boat is thermodynamically unfavorable and ring flipping occurs to give the more stable conformer **22**; the ratio αα:ββ indicates the proportion of compact vs. extended attack. Earlier experiments and the results in Chart I lend support to the rule that the proportion of extended attack of the diene increases with increasing electrophilicity of the allyl cation and is higher for zinc oxyallyl than for sodium oxyallyl.[15] On the other hand, formation of an αβ adduct under kinetic control from a W allyl cation amounts to configurational loss and suggests incursion of a stepwise cycloaddition via an intermediate (cf. *b* in Scheme I), which must be sufficiently long lived to allow rotation about the newly formed σ bond(s). Thus, the likelihood of rotation will depend inter alia on the nature of atom or group Z (Scheme I). Moreover, the equilibrium $\alpha\alpha \rightleftharpoons \alpha\beta \rightleftharpoons \beta\beta$ is important in that the αβ epimer must be sufficiently stable relative to αα, if it is to have a chance of being formed at all. Among the reactions listed in Chart I the greatest loss of configuration is observed for dienes with good electron donors Z; 6-acetoxyfulvene (Z = C=CHOAc) gives **10αα**:**10αβ** = 5.2:1. In addition, the introduction of an sp^2 center into position 8 of bicyclo[3.2.1]oct-6-en-3-ones appears to destabilize epimer αα relative to αβ (compare **9αα** and **9αβ**, Chart I, footnote *c*). Presumably, flattening of the six-membered ring has now progressed to such an extent that the terms equatorial and axial are no longer very meaningful and are better replaced by α and β, respectively.

Scheme VI. Formation of **20** and of **22** by Compact and Extended Cycloaddition, Respectively

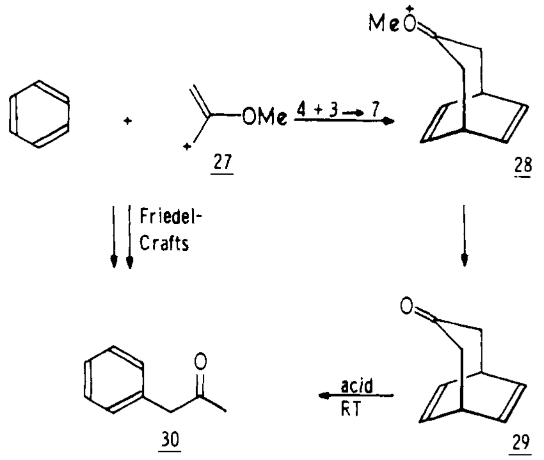


Let us now turn our attention to a series of dienes which are incorporated into cyclic 6π systems of increasing aromaticity. In the case of furan, i.e., Z = O, we find that all three epimers **14αα**, **14αβ**, and **14ββ** are formed. The amount of epimer **14αβ** fluctuates depending on the concentration of reagents and reaction conditions (Table II).

Scheme VII. Cycloaddition vs. Electrophilic Substitution with Pyrroles



Scheme VIII. Cycloaddition vs. Friedel–Crafts Reaction with Benzene

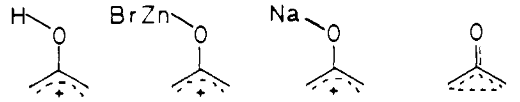


When zinc oxyallyl is the reactive intermediate, one cannot be completely certain that a W-configurated allyl cation is always formed cleanly. Unlike the NaI/Cu procedure, which basically is a homogeneous reaction, the Zn/Cu reaction is not, at least not during the initial stages when the metal dissolves to form zinc enolate. It is conceivable that some leakage into a sickle cation occurs, although the axial, equatorial adduct from cyclopentadiene, i.e., **8αβ**, can be detected neither for the Zn/Cu reaction nor for the NaI/Cu reaction.

Moreover, Table II shows that substantial leakage into the α,β epimer occurs for 3,4-dimethylfuran (entry 7). 3,4-Dimethylfuran is not excessively electron rich, but it does have two methyl groups which hinder a compact approach of the W-configurated allyl cation. As a consequence, **17αβ** (21.3%) is also accompanied by a considerable amount of cis-diaxial adduct **17ββ** (33.7%), and it seems clear that α,β epimer formation, i.e., stepwise cyclization, is favored not only by electronic, but also by steric factors, in this case the relative destabilization of **17αα**.

What happens if we turn from furan to the more aromatic pyrrole and, finally, to benzene itself? Both iron oxyallyl^{25} as well as zinc oxyallyl (**24a**) react with simple pyrroles (**23a,b**) to give the products of electrophilic substitution (**26**) only; a change to *N*-acetylpyrrole (**23c**) promotes [4 + 3 → 7] cycloadditions (Scheme VII).^{25} However, even simple pyrroles without an electron-attracting group at the nitrogen atom^{26} and also *N*-phenylpyrrole (**23d**) react to give **25a,b,d**, respectively, provided that one uses *sodium* oxyallyl (**24c**) as electrophilic intermediate. Finally, it is mechanistically significant that benzene enters into [4 + 3 → 7] cycloadditions with the proper electrophilic intermediate, in this case the parent 2-methoxyallyl cation (**27**) which has been generated by the silver salt route. Formation of cycloadduct **29** is accompanied by that of the Friedel–Crafts product **30** which arises from benzene directly and also by fragmentation of **29** (Scheme VIII). In contrast, the same 2-methoxyallyl cation **27** reacts with mesitylene (1,3,5-trimethylbenzene) to give very predominant Friedel–Crafts product, and only a trace of [4 + 3 → 7] cycloadduct.^{27}

Scheme IX. The Spectrum of Oxyallyl Intermediates



Stepwise [4 + 3 → 7] cycloadditions are visualized to proceed in two distinct stages (Scheme I): the first, electrophilic stage (i) in which the allyl cation attacks the diene with formation of one σ bond; and the second, nucleophilic stage (ii), in which the nucleophilic moiety so generated donates its electrons to form the second σ bond. It is in the second stage that a good donor Y at the central atom of the erstwhile allyl cation will be helpful. If a [4 + 3 → 7] cycloaddition is to succeed with an aromatic donor, the proper blend of electrophilicity and nucleophilicity of the oxyallyl species, i.e., the nature of the atom bonded to the oxygen atom, is important. We have previously suggested that one may envisage a spectrum of oxyallyl intermediates^{15} which ranges from the very electrophilic and poorly nucleophilic hydroxyallyl through metal oxyallyls to the free oxyallyl species itself (Scheme IX), where the electron density on oxygen increases along the series from left to right. In this context the facile acid-catalyzed breakup of bicyclo[3.2.2]nona-6,8-dien-3-one (**29**) to 1-phenyl-2-propanone (**30**) (Scheme VIII), the breakup of *N*-alkylpyrrole adducts (**25b** → **26b**) (Scheme VII), and also that of 8-oxabicyclo[3.2.1]oct-6-en-3-one^{28} are of interest. Inspection of Scheme I shows that these three fragmentations are the reverse of step (ii) for Y = O^- or OH and Z = CH=CH, NR, and O, respectively. Microscopic reversibility suggests that the *formation* of adduct c (Scheme I) also proceeds via intermediate b, i.e., stepwise. In any case, unlike the retro-Diels–Alder reaction which generates or regenerates diene and dienophile,^{29} attempted reversion of the allyl cation cyclization appears to be fundamentally different in that it does not regenerate an oxyallyl species under thermal conditions but rather stops after cleavage of *one* σ bond.

In summary, we believe that two-step [4 + 3 → 7] cycloadditions exist and can be induced by suitable diene–allyl cation pairs. The present work suggests that electronic as well as steric factors can be made to play an important role.^{30} The two-step route is not confined to the class of examples discussed in this paper. Indeed, this route has recently been suggested to account for the cycloadducts formed from the reaction of *trans*-1,3-pentadiene—an acyclic, conformationally mobile, asymmetric diene—with an unsymmetric zinc oxyallyl species.^{30b}

Experimental Section

General. Instrumentation. ^{1}H NMR spectra were recorded at either 100 MHz on a Varian HA 100 spectrometer in the sweep frequency mode or at 60 MHz on a Varian T-60 spectrometer. Chemical shifts were measured with reference to internal tetramethylsilane (Me_4Si) as standard, unless otherwise stated, and are quoted on the δ parts per million scale. IR spectra were recorded on a Perkin-Elmer 177 diffraction grating spectrometer. Absorptions are quoted in wavenumbers (cm^{-1}) using the spectrometer's internal calibration marker. GLC analysis and semimicro preparative separations were performed on a Varian 920 chromatograph. Mass spectra were obtained on an AEI-MS12 spectrometer at 70 eV, samples being introduced by direct insertion.

Reagents. Sodium iodide (reagent grade) was dried at ca. 250 °C overnight and stored in sealed bottles. Copper powder, commercially available electrolytic material, was used without purification. Woelm silica gel, reduced to activity 2 by the instructed method, was generally used in column chromatography.

Solvents. Acetonitrile (reagent grade) was stored over 4 Å molecular sieves, for at least 1 week, in sealed bottles, prior to use. Pentane, light petroleum (bp 40-60 °C), and dichloromethane were distilled from P_4O_{10}. 1,2-Dimethoxyethane and tetrahydrofuran were distilled from lithium aluminum hydride as required. Benzene was distilled and stored over sodium wire in sealed bottles.

2,4-Dimethylbicyclo[3.2.1]oct-6-en-3-one (8). Sodium Iodide Method. To a well-stirred mixture of sodium iodide (121 g, 0.8 mol), copper powder (38.5 g, 0.61 mol), and cyclopentadiene (32.15 g, 0.487 mol) in acetonitrile (350 mL) under a nitrogen atmosphere was added dropwise a solution of 2,4-dibromo-3-pentanone (49.18 g, 0.203 mol) in acetonitrile (150 mL) over a period of 30 min at room temperature. Before the addition was half complete, the temperature of the reaction mixture had risen to ca. 45 °C. After ca. 3 h the temperature began to drop. Stirring was continued for an additional 1 h and the reaction mixture was worked up by pouring directly into a mixture of concentrated aqueous NH_3 (sp gr 0.880) (1 L), distilled water (1 L), and ether (500 mL) contained in a 5-L separating funnel. The yellow copper complex was decomposed by vigorous shaking to leave a clear, deep blue aqueous layer, which was separated and extracted with several portions of ether. The combined ethereal solutions were washed with dilute ammonia solution and then with water until neutral. After washing with saturated brine the ethereal solution was dried (Na_2SO_4). Removal of the solvent at reduced pressure gave crude **8** (27.64 g, 90.7%) as a clear, red-brown oil free from organic impurities by ^{1}H NMR.

8αα was obtained as a colorless liquid by the following procedure. To the crude product (27.64 g, 0.184 mol) was added a saturated solution (20 °C) of silver nitrate (39 g, 0.23 mol) in distilled water (25 mL), while stirring by hand. The resulting thick paste was transferred to a sintered funnel and sucked dry (ca. 1 h) to give a light brown, crystalline solid (37 g), which could be recrystallized from ethanol to give sand-colored crystals, mp 140 °C dec. Anal. Calcd for $C_{10}H_{14}AgNO_4$: C, 37.52; H, 4.41; N, 4.37. Found: C, 37.83; H, 4.48; N, 4.13.

The complex was decomposed as follows. A chromatographic column was prepared of silica gel (activity 2) (110 g) in dichloromethane and the solvent head adjusted to within ca. 4 cm from the top of the silica gel. The dry silver nitrate complex (37 g) was carefully added to the top of the column and then eluted with dichloromethane in the usual way to give pure **8αα** (17.6 g, ca. 66%). Material so purified was stable to conditions of distillation, bp 96–98 °C (19 mm). The dark, viscous filtration liquor, obtained from the crude complex, was decomposed by adding water and ether, shaking, and filtering the insoluble material. The filtrate was separated, the aqueous layer was extracted with several portions of ether, and the combined ether layers were dried (Na_2SO_4). Removal of the solvent at reduced pressure gave a dark oil (9.6 g, 31%). GLC analysis (10% F.S. 1265, 12 ft × ¼ in. at 150 °C, He flow 55 mL/min) showed this to be an approximately 1:1 mixture of **8αα** and **8ββ** with retention times of 16 and 17 min, respectively. **8αα**: ^{1}H NMR (CCl_4), see Table I; IR (film) cm^{-1} 3050 (w), 2910 (s), 2850 (m), 1710 (s), 1465 (m), 1390 (m), 1365 (w), 1230 (w), 1120 (m), 1000 (m), 950 (m), 875 (w), 845 (w), 815 (w), 730 (s).

2,4-Dimethyl-8-isopropylidenebicyclo[3.2.1]oct-6-en-3-one (9). Sodium Iodide Method. To a stirred suspension of copper powder (27 g, 0.425 mol) and sodium iodide (84 g, 0.560 mol) dissolved in dry acetonitrile (300 mL), under a nitrogen atmosphere at 20 °C, was added a solution of 6,6-dimethylfulvene[31] (15 g, 0.159 mol, 11% excess) and 2,4-dibromo-3-pentanone (34.5 g, 0.142 mol) in dry acetonitrile (200 mL) over a period of 15 min. The resulting mixture was stirred at 20 °C for 24 h and then worked up as described above to afford the crude product (25.7 g) as a golden yellow liquid. ^{1}H NMR analysis indicated this to contain ca. 11% of starting 6,6-dimethylfulvene as the only observable impurity, corresponding to a yield of 85% based on recovered fulvene. A 2-g sample of the crude material was chromatographed on silica gel (activity 2) (ca. 250 g) and eluted with 10% ethyl acetate in light petroleum (bp 40-60 °C), giving pure samples of **9αα** as an oil and **9ββ** (crystals, mp 48-49 °C). ^{1}H NMR spectra (CCl_4 solvent): see Table I. IR (CCl_4) cm^{-1} **9αα**: 3060 (w), 2980 (m), 2970 (m), 2930 (m), 2870 (m), 1710 (s), 1450 (m), 1370 (m), 1340 (w), 1120 (m), 1035 (w), 985 (w) 930 (m) 690 (m). **9ββ**: 3060 (w), 2980 (m), 2970 (m), 2930 (m), 2870 (m), 1705 (s), 1450 (m) 1375 (m), 1365 (m), 1335 (w), 1255 (w), 1150 (m), 1085 (w), 1025 (s), 930 (s), 870 (w), 710 (m). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.11; H, 9.64.

The bulk of the crude material (23.7 g) was fractionated through a short column (10 × 1 cm) packed with glass helices at 0.05 mmHg. The fraction boiling steadily at 65 °C was collected and amounted to 13.50 g of a dark green liquid (50% yield). The green color was slowly discharged on standing at room temperature to give a light amber liquid, with no observable changes in the NMR spectrum. GLC analysis (10% F.S. 1265, 6 ft × ¼ in. at 150 °C, He flow 55 mL/min) showed this to be a 12.2:1:1.3 mixture of **9αα:9αβ:9ββ** with retention times of 31, 36, and 42 min, respectively. GLC analysis of the crude product, prior to distillation, showed it to be a 4.6:1 mixture of **9αα**:**9ββ** (retention times 31 and 42 min, respectively). A sample of the minor component (42 min) was collected and found to be pure **9ββ** by comparison with authentic material obtained by column chromatography.

Preparation of 9αα and 9ββ Using the Zinc-Copper Couple Technique. To a stirred suspension of acid-free zinc-copper couple[32] (60 mg, 9.2 × 10^{-4} g-atom) and fulvene (245 mg, 2.3 mmol) in dry 1,2-dimethoxyethane (0.25 mL) under nitrogen at −15 °C was added 2,4-dibromo-3-pentanone (293 mg, 1.26 mmol) in dry DME (0.25 mL). The mixture was stirred at −15 °C and a further three portions of zinc-copper couple (60 mg each) were added at 30-min intervals. The deep yellow solution was allowed to warm to room temperature. After a short delay (ca. 5 min) a highly exothermic reaction ensued. The viscous, yellow mixture was allowed to cool to ca. 25 °C and DME (0.25 mL) was added to facilitate stirring. The golden yellow color was slowly discharged over a period of ca. 15 min, and the mixture was worked up by diluting with ether and filtering the solids, which were washed with ether. The combined ether solutions were evaporated almost to dryness and the residue was taken up in ether (ca. 30 mL). After the solution was washed with saturated ammonium chloride, water, and saturated brine and dried (Na_2SO_4), the solvent was removed at reduced pressure to give a viscous, yellow oil, which was shown by GLC to be a mixture of **9αα:9αβ:9ββ** (12.2:1:10).

Equilibration of Epimers 9. Distilled **9** (50 mg, 0.26 mmol) was stirred under nitrogen in a 2 M solution of sodium methoxide in methanol (1 mL). Aliquots (ca. 5 drops) were removed at 12-h intervals, shaken with a mixture of ether (ca. 0.3 mL) and 2 N hydrochloric acid (0.2 mL), and analyzed by GLC. After 48 h the composition remained constant, being **9αα:9αβ:9ββ** = 4.7:4.9:1.

8-Acetoxymethylene-2,4-dimethylbicyclo[3.2.1]oct-6-en-3-one (10). To a stirred suspension of copper powder (16.5 g, 258 mmol) and sodium iodide (52 g, 340 mmol) in acetonitrile (200 mL) at 20 °C was added a solution of 6-acetoxyfulvene[33] (11.88 g, 87.3 mmol) and 2,4-dibromo-3-pentanone (21.25 g, 87.3 mmol) in acetonitrile (150 mL) over a period of 40 min. The resulting mixture was stirred for 18 h at 20 °C and then worked up in the usual manner to give crude **10** (13.45 g, 70%) as a clear, red-brown oil. GLC analysis (F.S. 1265 6 ft × ¼ in. at 170 °C, He flow 55 mL/min) showed this to be a mixture of anti-8-aldehyde **10b** (retention time 15.5 min, 3.2%), syn-8-aldehyde **10a** (retention time 19.7 min, 6.3%), enol acetate **10αα** (retention time 29 min, 73%), and **10αβ** (retention time 33 min, 17.4%).

Chromatography of this mixture (ca. 2 g) on silica gel (activity 2) and elution with dichloromethane gave pure enol acetate **10αα** (200 mg) in fractions 4–26; fractions 27–37 contained mixtures of **10αα** and **10αβ** together with **10a** and **10b** in varying proportions. Fractions 37–44 contained predominantly **10αβ.** The remaining crude product (ca. 11.5 g) was distilled at 0.03 mm and the fraction boiling at 95–110 °C collected (ca. 6.5 g, 33%), consisting mainly of isomeric enol acetates and a trace of **10a.** Pure **10b** (350 mg), mp 83 °C, was isolated from the crude product, obtained in an initial run on a 30-mmol scale, by chromatography on silica gel (activity 2) and elution with dichloromethane, followed by repeated recrystallization from light petroleum (bp 40–60 °C). ^{1}H NMR (CCl_4): 1.01 (d, J = 6.7 Hz, 6 H, $Me_{(2,4)}$), 2.53 (q, J = 6.7 Hz, of d, J = 2.5 Hz, 2 H, $H_{(2\beta,4\beta)}$), 2.90 (t, J = 4.5 Hz, 1 H, $H_{(8\text{-syn})}$), 3.04 (m, 2 H, $H_{(1,5)}$), 6.19 (t, J = 1.3 Hz, 2 H, $H_{(6,7)}$), 9.98 (s, 1 H, CHO). IR ($CHCl_3$) cm^{-1}: 3080 (w), 3010 (m), 2960 (m), 2930 (m), 2860 (m), 2800 (w), 2700 (m), 1715 (sh), 1705 (s), 1455 (m), 1445 (m), 1375 (s), 1340 (m), 1250 (m), 1120 (m), 1105 (m), 1025 (m), 995 (s), 975 (m), 920 (m), 900 (m), 870 (m), 700 (s). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.08; H, 7.95.

Hydrolysis of Enol Acetate 10. The enol acetate mixture (1 g, ca. 4 mmol) was refluxed in 15 mL of dioxane and 2 N sulfuric acid (1:1) for 3 h, cooled, neutralized with dilute potassium carbonate, and extracted with several portions of ether. The combined extracts were washed with water and saturated brine and dried (Na_2SO_4). Removal of the solvent at reduced pressure gave the crude product, 739 mg (91%), as a dark brown oil, which was shown by ^{1}H NMR to be a 5:1 mixture of **10a** and **10b**, respectively. Treatment of the enol acetate mixture (1 g) with acid, as described above, for 60 h gave 377 mg (47%) of crude aldehydes, with more than 95% **10a**: ^{1}H NMR 1.04 (d, J = 7 Hz, 6 H, $\mathrm{Me}_{(2,4)}$), 2.38 (q, J = 7 Hz, of d, J = 3 Hz, 2 H, $\mathrm{H}_{(2,4)}$), 2.74 (br s, 1 H, $\mathrm{H}_{(8\text{-anti})}$), 3.10 (m, 2 H, $\mathrm{H}_{(1,5)}$), 6.04 (br s, 2 H, $\mathrm{H}_{(6,7)}$), 9.54 (s, 1 H, -CHO).

Oxidative Decarbonylation of Aldehydes 10a and 10b.[34] A 1:2 mixture of **10a** and **10b** (674 mg, 3.8 mmol), cupric acetate (α,α'-bipyridyl) 1:1 complex (40 mg), and 1,4-diazabicyclo[2.2.2]octane (Dabco, 250 mg) in dry *N*,*N*-dimethylformamide (1 mL) were stirred at 45 °C while oxygen was bubbled through the solution for 3 h. The cooled mixture was poured into dilute hydrochloric acid (ca. 10 mL) and the flask rinsed with ether. The aqueous layer was separated and extracted with several portions of ether. The combined ether solutions were washed with dilute hydrochloric acid, water, and saturated brine and dried ($\mathrm{Na_2SO_4}$). Removal of the solvent at reduced pressure gave the crude product (410 mg) as a dark brown oil, which was shown to be a 1:1 mixture of syn aldehyde **10a** and diketone **12$\alpha\alpha$** by integration of the olefinic proton resonances at δ 6.04 and 6.44, respectively.

Cycloadditions to 5,5-Diethoxycyclopentadiene. 5,5-Diethoxycyclopentadiene was prepared by the bromination–dehydrobromination sequence first reported by Eaton and Hudson.[35] Contrary to another report,[36a] the use of pyridinium hydrobromide perbromide, a readily available material, was found satisfactory in the preparation of 2,5-dibromocyclopentanone diethyl ketal, which was obtained in almost quantitative yield. When washed free of acid and base, the compound could be stored neat at ca. −10 °C for several months without decomposition (cf. ref 36b). The following procedure is typical.

2,5-Dibromocyclopentanone Diethyl Ketal. To a stirred solution of cyclopentanone diethyl ketal (15.8 g, 0.1 mol) in absolute ethanol (200 mL) at 0 °C was added pyridinium hydrobromide perbromide (63.96 g, 0.2 mol). The mixture was stirred at 0 °C until the red color had been discharged and was then poured into ice-water (800 mL) and extracted with several portions of pentane. The combined extracts were washed with ice-cold water, ice-cold dilute hydrochloric acid (ca. 5% v/v), cold dilute sodium bicarbonate, and saturated brine and dried ($\mathrm{Na_2SO_4}$). Removal of the solvent at reduced pressure gave 2,5-dibromocyclopentanone diethyl ketal (29.07 g, 92%) as a clear liquid, which was stable for long periods at −10 °C (solidified), but was normally used immediately.

8,8-Diethoxy-2α,4α-dimethylbicyclo[3.2.1]oct-6-en-3-one (11). The following preparation was performed in two steps. In order to avoid delays the reaction vessel, used in the second step, was prepared before starting the first part. Thus into a 2-L, five-neck, flange-top flask, equipped with a vibromixer, water-cooled condenser, nitrogen inlet, bubbler outlet, and addition funnel, were placed sodium iodide (29.8 g, 0.2 mol), copper powder (9.48 g, 0.15 g-atom), and acetonitrile (200 mL). The addition funnel was charged with a solution of 2,4-dibromo-3-pentanone (12.1 g, 0.05 mol) in acetonitrile (20 mL).

Part 1. Preparation of a Pentane Solution of 5,5-Diethoxycyclopentadiene. (This step must be carried out swiftly.) To a vigorously stirred solution of potassium *tert*-butoxide (44.8 g, 0.4 mol) in dry dimethyl sulfoxide (200 mL) under nitrogen at 18 °C was added, rapidly, a solution of 2,5-dibromocyclopentanone diethyl ketal (29.07 g, 92 mmol) in dry dimethyl sulfoxide (20 mL) over a period of ca. 3 min. The temperature was maintained at 18–22 °C by intermittent cooling in a $\mathrm{CO_2}$-acetone bath. After completion of the addition, the dark solution was stirred at ca. 18–22 °C for 1 min and then poured into ice-water (1 L) and extracted with ice-cold pentane (4 × 125 mL). Extracts were maintained at −10 to 0 °C in an alcohol-ice bath during the workup procedure. The combined pentane solutions were washed rapidly with ice-water and dried briefly by shaking with anhydrous sodium sulfate at ca. 0 °C for 1 min.

Part 2. The pentane solution of 5,5-diethoxycyclopentadiene was filtered directly into the prepared 5-L flask (see above). The vibromixer was started and the 2,4-dibromo-3-pentanone solution added rapidly. The mixture was vigorously stirred for 18 h at 20 °C and then worked up in the usual way to give crude **11** (10.4 g) as a pale yellow syrup. This was fractionated at 0.6 mm and the portion boiling at 91–126 °C collected (3.95 g). Chromatography on silica gel (activity 2) (150 g) and elution with dichloromethane gave 1.45 g (ca. 12%) of **11** which was found to be >95% pure by NMR (see Table I). IR (film) cm^{-1}: 3000 (m), 2980 (m), 2900 (m), 1710 (s), 1460 (m), 1405 (w), 1395 (m), 1340 (m), 1290 (m), 1240 (w), 1135 (s), 1105 (m), 1075 (s), 1030 (w), 975 (m), 955 (w), 905 (w), 800 (m), 760 (m).

2α,4α-Dimethylbicyclo[3.2.1]oct-6-ene-3,8-dione (12$\alpha\alpha$). Ketal **11** (180 mg, 0.75 mmol) in dry "AnalaR" acetone (20 mL) was treated with toluenesulfonic acid monohydrate (10 mg) at room temperature for 16 h. The solvent was evaporated at reduced pressure almost to dryness and the residue diluted with ether. The resulting solution was washed with saturated sodium bicarbonate and dried ($\mathrm{Na_2SO_4}$). Removal of the solvent at reduced pressure gave crude **12$\alpha\alpha$** (110 mg, 89%), which was purified by chromatography on silica gel (activity 2) and eluting with dichloromethane to give **12$\alpha\alpha$** (90 mg, 73%). ^{1}H NMR ($\mathrm{CCl_4}$): 1.14 (d, J = 7 Hz, 6 H, $\mathrm{Me}_{(2,4)}$), 2.73 (q, J = 7 Hz, of d, J = 2.8 Hz, 2 H, $\mathrm{H}_{(2\beta,4\beta)}$), 2.88 (m, 2 H, $\mathrm{H}_{(1,5)}$), 6.44 (m, 2 H, $\mathrm{H}_{(6,7)}$). IR ($\mathrm{CHCl_3}$): cm^{-1} 3060 (w), 2970 (m), 2930 (m), 2870 (w), 1770 (s), 1715 (s), 1455 (m), 1445 (m), 1375 (m), 1170 (w), 1120 (m), 1070 (w), 1030 (w), 995 (w), 980 (w), 960 (w), 950 (m), 860 (m), 805 (m), 790 (m).

5,5-Dimethylcyclopentadiene was prepared employing the method of Kwart[37a] with that of Wilcox.[37b] As with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene all attempts to induce cycloaddition with 1,3-dimethyl-2-oxyallyl cation, generated both via zinc–copper couple and sodium iodide–copper, failed.

3,4-Dimethylfuran (15). A. Conversion of Diethyl Furan-3,4-dicarboxylate into 3,4-Bis(hydroxymethyl)furan. Diethyl furan-3,4-dicarboxylate[38] (50 g) in 50 mL of anhydrous ether was added dropwise to a mechanically stirred suspension of $\mathrm{LiAlH_4}$ (10 g) and anhydrous diethyl ether (300 mL) in a 1-L three-necked flask. The rate of addition was adjusted to maintain gentle reflux of the solvent, an efficient condenser being necessary to prevent substantial loss of the ether. The mixture was stirred for 1 h at room temperature after addition of the ester was complete. Ice water was then added dropwise until the vigorously stirred suspension had changed in color from gray to white. The solid was dissolved by cautious addition of ice-cold 30% (v/v) sulfuric acid. The ether layer was separated and kept while the aqueous layer was continuously extracted with ether for 12 h. The combined ether extracts were dried (flame-dried $\mathrm{MgSO_4}$) and the solvent was removed on a rotary evaporator to afford 21.8 g (72%) 3,4-bis(hydroxymethyl)furan as a viscous oil.

B. Preparation of 3,4-Bis(chloromethyl)furan.[39] Bis(hydroxymethyl)furan (30 g) was dissolved in 90 mL of chloroform and 50 mL of AnalaR pyridine and cooled to −5 °C. The mixture was magnetically stirred and treated dropwise with 52.5 mL of thionyl chloride in 50 mL of chloroform. When the addition was complete the resulting red suspension was poured onto ice and the organic layer separated and washed once with ice water. After drying ($\mathrm{CaCl_2}$) the solvent was removed on a rotary evaporator to afford 32 g (83%) of 3,4-bis(chloromethyl)furan.

C. 3,4-Dimethylfuran (15) by Reduction of 3,4-Bis(chloromethyl)furan. 3,4-Bis(chloromethyl)furan (32 g) in 20 mL of anhydrous ether was added dropwise to a mechanically stirred suspension of $\mathrm{LiAlH_4}$ (10 g) and anhydrous ether (250 mL) in a 1-L three-necked flask. After complete addition the mixture was refluxed for 4 h, cooled at room temperature, and treated cautiously with ice water until effervescence ceased. The organic layer was separated and dried ($\mathrm{CaCl_2}$), and the solvent was removed by distillation using a water bath at 50 °C and then the product was distilled from an oil bath at 120 °C, bp 97–99 °C, 15.2 g (80%). ^{1}H NMR ($\mathrm{CCl_4}$): 1.89 (s, 3 H), 7.00 (s, 1 H). 3,4-Dimethylfuran was stored under nitrogen at 0 °C, since rapid yellowing occurred in air.

2α,4α-Dimethyl-*N*-phenyl-8-azabicyclo[3.2.1]oct-6-en-3-one (25d). To a well-stirred suspension of sodium iodide (32.5 g, 217 mmol), *N*-phenylpyrrole[40] (7.9 g, 55 mmol), and copper powder (6.8 g, 0.10 g-atom) in 170 mL of acetonitrile, under a nitrogen atmosphere at 20 °C, was added dropwise 2,4-dibromo-3-pentanone (12.7 g, 69 mmol) over a period of 45 min. After 3.5 h the reaction mixture was cooled to 0 °C, added to 120 mL of ice-cold dichloromethane, and poured into ice water (1.2 L). The mixture was suction filtered through powdered cellulose and the residue washed with dichloromethane (20 mL). After a further extraction of the aqueous layer with dichloromethane (50 mL) the combined organic layer was freed from any remaining copper by washing with two 50-mL portions of dilute ammonia. The organic layer was washed with water (2 × 50 mL) and dried ($\mathrm{K_2CO_3}$) and the solvent was removed to give a viscous oil which was purified by preparative thin layer chromatography on alumina using benzene as eluent to give a sample of 2α,4α-dimethyl-*N*-phenyl-8-azabicyclo[3.2.1]oct-6-en-3-one (**25d**) as a waxy solid: ^{1}H NMR 1.0 (d, J = 7 Hz, 6 H), 2.59 [d (J = 4 Hz) of q (J = 7 Hz), 2 H_β), 4.46 (d, J = 4 Hz, 2 H), 6.33 (d, $J \sim$ 1.5 Hz, 2 H), 6.4–7.4 (m, 5 H); IR (Nujol) cm^{-1} 3075 (m), 3020 (w), 1710 (s), 1630 (w), 1603 (s), 1575 (m), 1503 (s), 750 (s), 695 (s). Anal. Calcd for $C_{15}H_{17}NO$: C, 79.2; H, 7.5; N, 6.24. Found: C, 77.4; H, 7.5; N, 6.0.

Acknowledgments. We thank Olgierd R. Lalko and Heidrun Vathke for experimental contributions. Our work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Science Research Council.

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The Degenerate Side Chain Approach to the Carbon Analogue of the Claisen Rearrangement. Formation of Nine-Membered Rings by a Sterically Accelerated Ene Reaction

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Abstract: The first step of the carbon Claisen rearrangement can be examined without reference to the second step through introduction of a suitably labeled ortho allyl substituent, which would be identifiably inserted into the butenyl side chain on reversal of the first step. We have prepared substrates containing the potentially degenerate side chain, labeled alternatively with deuterium and with methyl. Interchange of the side chains does not occur up to about 350 °C, so that the activation energy of the [3,3] sigmatropic step of the carbon Claisen rearrangement must be at least 32-35 kcal mol^{-1}. These results suggest that the first step, rather than the second step as previously thought, is rate determining. The effect of oxygen vs. carbon and of aliphatic vs. aromatic can then be readily understood in terms of perturbations on the frontier molecular orbitals of the starting materials. The substrates constructed with degenerate side chains produce, as the alternative reaction at 350 °C, a high-yield ene cyclization to form nine-membered rings. This unprecedented result for simple 1,8-nonadienes is attributed to a steric acceleration arising from loss of rotational degrees of freedom on placement of the ene components in ortho-related side chains on a benzene ring.

The [3,3] sigmatropic shift is found in two classic organic rearrangements, the Claisen (eq 1) and the Cope (eq 2). Both reactions involve the migration of a σ bond between the termini of two allyl groups. In the commonest form of the Claisen rearrangement, one of the allyl double bonds is part of an aromatic ring and one allyl atom is oxygen (eq 1). The reaction

0002-7863/79/1501-1793$01.00/0