

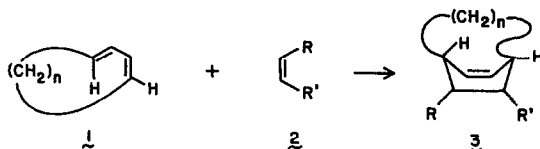
**The $2\pi + 2\pi$ Cycloaddition of an Allyl Cation to (1*Z*,3*E*)-Cycloalkadienes.
Evidence for a Stepwise Process in the Ionic Diels-Alder Reaction.**

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Abstract: Treatment of (1*Z*,3*E*)-cycloalkadienes with 2-vinyl-1,3-dioxolane under acidic conditions produced 1:1 cycloadducts in which an intermediate allyl cation added to the dienes to give trans-fused cyclobutanes as the major products.

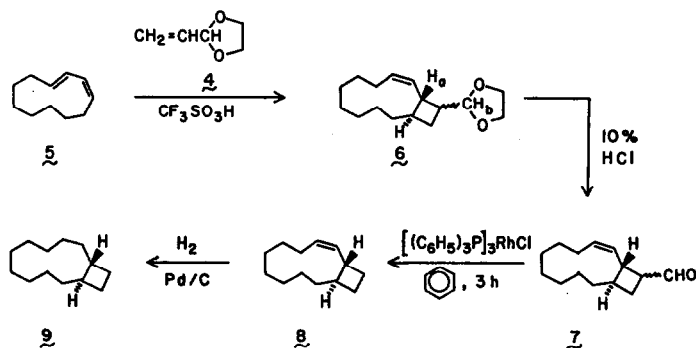
Diels-Alder addition of electron-deficient dienophiles to (1*Z*,3*E*)-cycloalkadienes has been shown by us to be a preferred method for the synthesis of bicyclic molecules with inverted bridgeheads.¹ It was found that a decrease in the ring size of the (1*Z*,3*E*)-cycloalkadiene, **1**, required a compensating increase in the reactivity of the dienophile, **2**, in order to obtain acceptable yields of **3**. For $n = 7$ and 8, maleic anhydride,



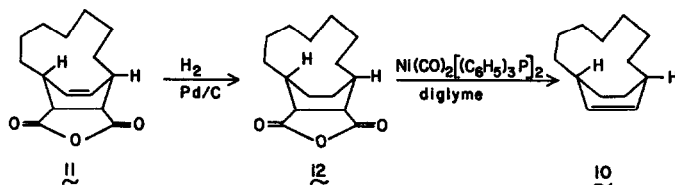
dicyanoacetylene, and hexafluoro-2-butyne were useful dienophiles.¹ However, for $n = 5$ and 6, the more reactive dienophile, *N*-phenyl-1,2,4-triazoline-3,5-dione, was required in order to obtain useful quantities of the desired inside-outside (*i,o*) bicyclic compounds.² In view of the recent findings that allyl cations are among the most powerful dienophiles in existence,³ we attempted to add an allyl cation to **1** to produce highly strained versions of **3**. We now report that the allyl cation derived from protonation of 2-vinyl-1,3-dioxolane (**4**) adds to **1** to give $2\pi + 2\pi$ cycloadducts,⁴ rather than $2\pi + 4\pi$ cycloadducts. This requires that the cycloadditions involve a stepwise process and suggests that related ionic intermediates may also be involved in the ionic Diels-Alder reaction.

Treatment of a 1:5 mixture of (1*Z*,3*E*)-cycloundecadiene (**5**) and **4** in methylene chloride with 10 mol % of triflic acid (relative to **4**) at -40 °C gave a 48% yield of **6**⁵ as a mixture of stereoisomers at the cyclobutyl carbon bearing the dioxolane moiety. In order to establish the overall skeletal structure, **6** was treated with 10% aqueous hydrochloric acid in tetrahydrofuran to give a 91% yield of **7**. Decarbonylation was achieved in 64% yield to give **8** using Wilkinson's catalyst in refluxing benzene. Analysis of **8** using ¹³C NMR spectroscopy indicated the presence of 13 different carbon resonances. The resonances for two vinyl

protons appeared at δ 5.48 [t (dd), $J = 10.6$ Hz] and 5.41 [dt (ddd), $J = 11.4$ and 4.2 Hz] in the ^1H NMR spectrum, which indicated the presence of an unsymmetrical olefin. Catalytic reduction of **8** in 95% ethanol gave a 95% yield of **9**, which had 7 carbon resonances in its ^{13}C NMR.



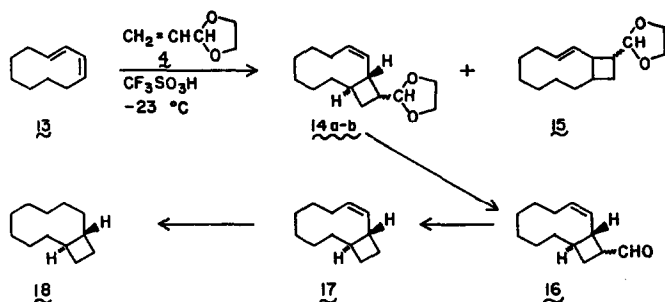
While the unsymmetrical nature of **8**, combined with the symmetrical nature of **9**, was only consistent with a $2\pi + 2\pi$ cycloaddition, it was of interest to compare **8** with the isomeric $2\pi + 4\pi$ cycloadduct, **10**. The anhydride **11**⁶ was reduced with hydrogen-palladium on carbon in 95% ethanol to give a 99% yield of **12**.



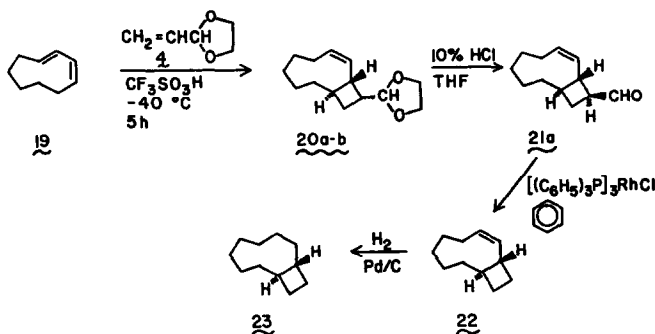
Treatment of **12** with bis(triphenylphosphine)nickel dicarbonyl⁷ in diglyme gave a 60% yield of **10**, which showed 13 different resonances in its ^{13}C NMR spectrum and two different vinyl hydrogen resonances in its ^1H NMR spectrum. Comparison of **8** and **10** showed that they had totally different structures.

The regiochemistry and the stereochemistry of the dioxolane moiety of **6**, and consequently of the aldehyde moiety of **7**, was established by a combination of ^{13}C NMR, ^1H NMR, and the use of DNOE. The major isomer of **6** was shown to have the dioxolane moiety cis to H_a via DNOE since irradiation of H_a enhanced the signal due to H_b and irradiation of H_b enhanced the signal of H_a . The stereochemistry of the ring fusion was established through comparison of the NMR spectra of **9** with those of other trans-fused cyclobutanes (*vide post*).

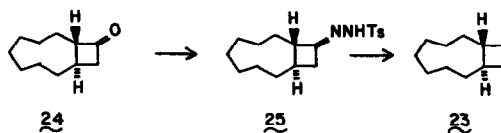
Treatment of a 1:3 mixture of (1*Z*, 3*E*)-cyclodecadiene (**13**) and **4** in methylene chloride with 16 mol % (relative to **4**) of triflic acid at -23 °C for 8 h gave 63% of **14a** and **14b** as a 75:25 mixture of stereoisomers,⁸ and 5% of **15**.^{9,10} Hydrolysis of **14** in tetrahydrofuran with 10% aqueous hydrochloric acid gave 91% of **16** (as a 75:25 mixture). Decarbonylation of **16** with Wilkinson's catalyst, as described for **7**, gave 64% of **17**. Catalytic hydrogenation of **17** over palladium on carbon gave a quantitative yield of **18**, which showed six resonances in its ^{13}C NMR spectrum.



In a procedure similar to that used for 5 and 13, a methylene chloride solution of 4 and 19 was treated with triflic acid at -40 °C to give a 51% yield of 20 as a 91:9 mixture, which was separated into its two components by MPLC. The major isomer was hydrolyzed with 10% aqueous hydrochloric acid in tetra-

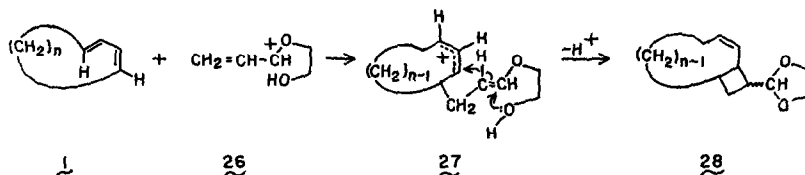


hydrofuran to give a 91% yield of 21a. Decarbonylation of a mixture of 21a-b (obtained directly from 20a-b) in the usual manner gave a 76% yield of 22, which was catalytically hydrogenated over palladium on carbon to give a quantitative yield of 23. The hydrocarbon 23 was used to establish the stereochemistry of the ring fusion. Utilizing 24, which had been reported previously in the literature,¹¹ as starting material, the



tosylhydrazone 25 was prepared in 54% yield. Reduction of 25 with catechol borane gave 23 in 28% yield. The sample of 23 prepared from 24 was identical in all respects to the sample of 23 prepared from 19. This established the stereochemistry of the ring fusion in the cycloaddition route to 23 and by spectral comparison the stereochemistry of the ring fusions for 9, 18, and all of their bicyclic precursors.

The formation of $2\pi + 2\pi$ cycloadducts in a thermal reaction would appear to require a stepwise process. Treatment of **4** with triflic acid appears to produce **26** which would be expected to react with **1** to



give the allyl cation **27** as an intermediate. Collapse of **27** with proton loss would give **28**.

Whereas Diels-Alder dienophiles, such as maleic anhydride, add to **1** to give $2\pi + 4\pi$ cycloadducts, **26** adds to give $2\pi + 2\pi$ cycloadducts by the proposed stepwise process. Allyl cations can be viewed as the *ultimate* dienophiles since there is no better electron-withdrawing group than the carbocation. The observed necessity for a stepwise process in the formation of **6**, **14**, and **20** suggests that those reactions in which allyl cations add to 1,3-dienes to give $2\pi + 4\pi$ cycloadducts may also be stepwise.³

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- The major isomer, **14a**, had the dioxolane moiety *cis* to the bridgehead hydrogen at C(1). Spectral comparison of **14a** and **14b** with the spectral properties of the two isomers of **6** confirmed the structural assignments.
- The stereochemistry of the olefinic substituents was shown to be *E* by the 15.3 Hz coupling constant observed for the two olefinic protons. Because of the minor product status of **15**, the remainder of stereochemistry was not rigorously determined.
- In addition to **14** and **15**, a third 1:1 adduct was present in *ca.* 2% yield
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