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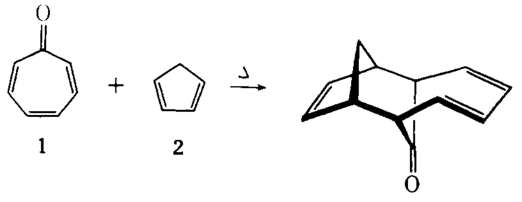
Received May 12, 1975

Effect of Pressure on the [4 + 6] Cycloaddition of Tropone to Cyclopentadiene[1]

Sir:

The pressure coefficient of the rate constant has been applied along with several other criteria to establish concertedness as one of the features characteristic of the Diels–Alder reaction.[2] Thus, it has been found in several laboratories that this reaction in general has a late transition state if the volume is used as a measure of the reaction coordinate; the activation volume is usually comparable to the overall reaction volume (−30 to −40 cm^3/mol), implying that both of the newly developing bonds must be nearly formed in the transition state. By contrast, when competition between the Diels-Alder reaction and a [2 + 2] cycloaddition occurs, the result is that the latter reaction is inhibited by the application of high pressure conditions.[3] Accordingly, it has a much less negative value of $\Delta V^\ddagger$, and this in turn is interpreted as signifying the formation of only one bond in the transition state. Potentially this technique is one of the most useful methods available for examining concertedness, since no synthesis is involved in its application (as is the case for instance in the stereochemical criterion); however, before this tool can be used on a routine basis it is of course necessary to delineate the possible pitfalls and exceptions to which it may be subject. We recently pointed out, for example, that if the intermediate has zwitterionic rather than diradical character, electrostriction may lower the volume of the transition state in the stepwise reaction to the point that it may compete favorably with a concerted reaction under pressure.[4] In this communication we present evidence that electrostriction in the *initial state* is likewise a factor that must be kept in mind in the application of high pressure to these problems.

The cycloaddition of tropone (**1**) to cyclopentadiene (**2**) to give **3** is an example of a [4 + 6] cycloaddition.[5] This type of reaction[6] has been shown by Houk to be concerted, the arguments resting primarily on the clean stereospecificity and on the fact that the products at higher temperatures rearrange to isomers expected from the stepwise reactions.[7] Thus, there is every reason to believe that the activation volume should be large and negative, comparable to that in the Diels–Alder reactions.

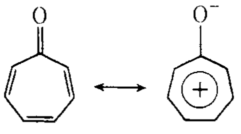

1 2 3

We have now measured this term as it applies to the reaction in *p*-dioxane at 60°. Five measurements were made for each rate constant, and this was done at six pressures ranging over 4 kbar; our value obtained at atmospheric pressure agreed exactly with that reported by Tanida.[8] The result is that $\Delta V_0^\ddagger$ equals -7.5 ± 1 cm^3/mol; clearly this value differs drastically from that characteristic of the Diels–Alder reaction.

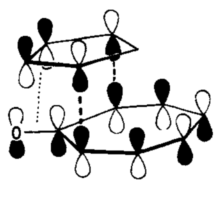
Further investigation by means of a dilatometeric experiment then revealed that the overall reaction volume is also exceptionally small: $\Delta V_0 = -4.3 \pm 1$ cm^3/mol (also in *p*-dioxane at 60°). The rate constant in this experiment again agreed with that obtained earlier at 1 atm. These data furnish a clear indication that one of the reactants must have an exceptionally low partial volume,[9] and this was verified by direct measurement. The partial volumes were evaluated[10] by means of pycnometric density determinations at several (five-six) concentrations and subsequent extrapolation to infinite dilution, by means of the expression

$$\Phi = \frac{M}{d_0} - \frac{1000}{C}\left[\frac{d - d_0}{d_0}\right]$$

The results are that the partial molar volumes of **1**, **2**, and **3** in *p*-dioxane at 60° are 85.6, 97.2, and 177.2 cm^3/mol, respectively, with a precision of about 0.5 cm^3/mol. On that basis, ΔV_0 equals $177.2 - (97.2 + 85.6) = -5.6$ cm^3/mol, in agreement with the dilatometric value. These data clearly show that the partial volume of tropone is responsible for the exceptionally low values of ΔV_0 and $\Delta V_0^\ddagger$; thus, on the basis of parachor listings[11] the molar volume of **1** is predicted to be some 20 cm^3/mol larger than that actually found. It is reasonable to attribute this small volume to the polar nature of **1**. There are several other observations testifying to the importance of **1a**; thus, Doering,[12] Dauben,[13] and Nozoe[14] have attributed the low value of $\nu_{C=O}$ (1652 cm^{-1}), the high boiling point (105° at 10 Torr), the high dipole moment (4.17 D), the complete miscibility with water, and other anomalous properties of tropone to it.


1 1a

One notable feature of these results is that the transition state is somewhat smaller than the final state. This has also been observed in those Diels-Alder reactions in which secondary orbital interactions are possible.[2b] In previous discussions it has been emphasized[6,7] that the secondary interactions between the diene and triene moieties are repulsive. In the present instance at least, an attractive interaction between the LUMO of the diene and the carbonyl portion of the tropone HOMO is apparently at least partially responsible for the exo stereochemistry.



In conclusion, we wish to emphasize that the observation of a small, negative activation volume for a cycloaddition is not enough to rule out a concerted reaction; it is also necessary to verify that unusual loss of polarity of the two molecules participating is not responsible.

Acknowledgment. This work has been generously supported by the National Science Foundation. We thank Professor K. N. Houk for comments.

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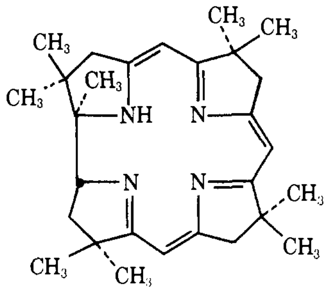
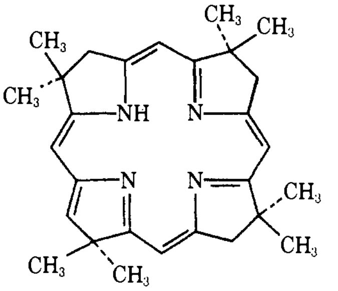
Received May 12, 1975

The Total Synthesis of Nickel(II) Octamethylcorphin

Sir:

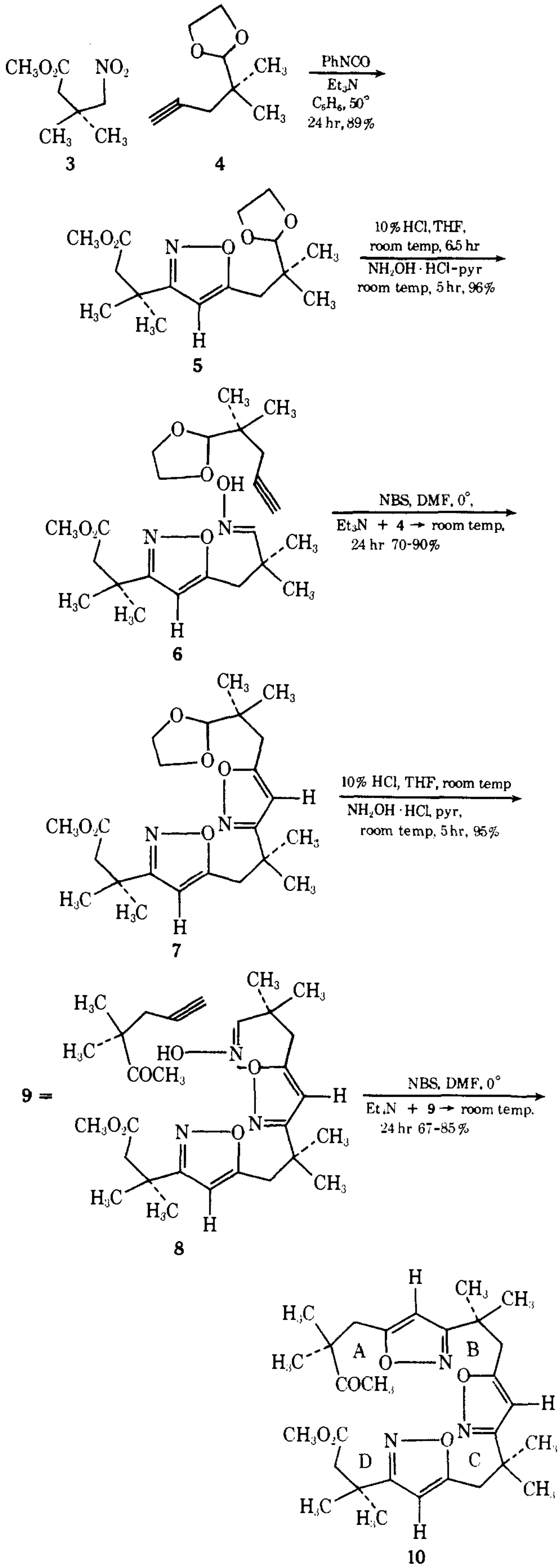


1



2

Scheme I



At the very heart of any project whose ultimate goal is the synthesis of vitamin B-12 must lie a concept for the construction of the macrocyclic ligand. In consonance with this fact we have initiated a fundamentally different approach to the synthesis of corrins and related ligands.[1] The method utilizes isoxazole nuclei as latent synthons for the crucial ring-bridging vinylogous amidine chromophores found in octamethylcorrin (**1**) or octamethylcorphin (**2**).[2,3] In principle, all of the structural features of these two substances can be incorporated into an appropriately substituted trisisoxazole (**10**) which, in turn, can be assembled from carefully selected nitrile oxides and terminal acetylenes. Thus, cycloaddition of the nitrile oxide generated[1,5] from nitroester **3** and acetylenic acetal[6] **4** gave monoisoxazole **5** (Scheme I).[7] Mild acid hydrolysis of the acetal function and treatment of the resultant aldehyde with $NH_2OH \cdot HCl$-pyr pro-