An Unusual Stereoelectronic Effect in the Rearrangement of the Diels-Alder Adducts of Cyclopropene and Furan

By RONALD W. LAROCHELLE[†] and BARRY M. TROST*

(Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706)

Summary Cyclopropene formed the exo and endo Diels-Alder adducts in a 1:1 ratio with furan; only the endoisomer readily rearranges to cycloheptadienones.

WE report an unusual stereoelectronic effect in the rearrangement of the Diels-Alder adducts of cyclopropene and furan. This Diels-Alder reaction also provides insight into the factors determining *exo* ; *endo* ratios for reactions in which cyclopropene acts as a dienophile.

In conjunction with other work, we examined the cycloaddition reactions of cyclopropene with various dienes as a method of detecting cyclopropene. Cyclopropene reacts with 2,3-dimethylbutadiene, cyclopentadiene,¹ and spiro-[4,2]hepta-2,4-diene² to generate with the last two dienes the *endo* adducts exclusively. The spiro-diene is approximately one-third as efficient a trap as cyclopentadiene. On the other hand, cyclopropene reacts with furan to yield two 1: 1 adducts in the ratio of 1:1.³

The adduct with the shorter retention time is assigned the exo-configuration (I) (see Scheme 1) on the basis of its n.m.r. spectrum. In particular, the bridgehead hydrogens $(\delta 4.55)$ show coupling only to the vinyl protons $(\delta 6.42)$ and not to the cyclopropyl methine hydrogens (δ 1.0) indicative of the latter being endo.[‡] The adduct with the longer retention time is very labile; however, its n.m.r. spectrum clearly shows it to be the corresponding endoadduct (II). The bridgehead hydrogens ($\delta 4.77$) show clear coupling to both the vinyl protons (δ 5.95) and the cyclopropyl methine hydrogens (δ 1.75) indicative of the latter having the exo-orientation (i.e., cyclopropane ring being endo). Comparison of this spectrum with that of (VI) shows them to be similar, especially with respect to the band shapes for the vinyl, bridgehead, and methine cyclopropyl hydrogens.[‡]

The kinetic formation of both the *exo* and *endo* Diels-Alder adducts with furan is in sharp contrast to the other cyclopropene cycloadducts. Such a result suggests that steric factors influence this reaction greatly. The transition state for formation of the *exo*-adduct closely resembles a boat cyclohexane. Thus, with cyclopentadiene, the flagpole 1,4-methylene interaction destabilizes the otherwise less encumbered *exo*-approach. By replacing the methylene of the diene with oxygen (*i.e.*, changing from cyclopentadiene to furan) the flagpole interaction is severely curtailed and the sterically less hindered *exo*-approach prevails. Thus, steric factors and not electronic factors best describe the orientational specificity of cyclopropene as a dienophile.

If smaller samples of the original mixture are injected into the g.l.c. column, only a peak for (I) and a new peak at longer retention times than that of (II) appear. Furthermore, injection of small samples of (II) produces only this new peak regardless of injection-port temperature or the presence of a base-washed glass liner. The mass spectrum indicates this material to be an isomer of (II). The n.m.r. spectrum shows methylene and vinyl absorptions in the ratio of 1:1. Its i.r. spectrum shows complex absorption in the carbonyl and double bond stretching regions. These i.r. absorptions are identical to those reported by Büchi and his co-workers⁴ for a mixture of (III) and (IV). That these structures represent those for this new material is further demonstrated by its catalytic hydrogenation to a single compound identical in every respect with cycloheptanone.



SCHEME 1. Diels-Alder adducts of cyclo propene

If the rearrangement is carried out to only small conversion and the i.r. spectrum taken immediately, this spectrum shows a single carbonyl band at 1680 cm^{-1} , indicative of the presence of only (III). Thus, (III) represents the initially produced product which more slowly rearranges by a 1,5-hydrogen shift to (IV).

Scheme 2 shows a possible rearrangement pathway based on two aspects of this reaction. (i) Overlap between the cyclopropyl bond and the breaking C-O bond is crucial. Thus, the *exo*-isomer (I) which cannot have effective overlap of these bonds shows no tendency to rearrange. (ii) The extent of rearrangement during g.l.c. depends only on sample size and not on injector or column temperature. The reaction appears, therefore, to be a surface phenomenon. Once the active sites on the surface are saturated, as with large samples, no further rearrangement occurs.



In Scheme 2, a proton is used to indicate an acidic site on the surface of the injector. C-O bond cleavage with

We thank Dr. Srinivasan for copies of the n.m.r. spectra of his furan-cyclopropene adducts. Whereas the n.m.r. spectrum of our *exo*-adduct was identical with that of one of his adducts, the spectrum of our *endo*-adduct differed considerably from that of his other adduct. That his second adduct is probably not the *endo* Diels-Alder adduct is suggested by the fact that the supposed bridgehead protons appear as a narrow singlet, suggesting that coupling of these protons with the *exo*-cyclopropyl methine hydrogens is approximately zero. This is inconsistent with the n.m.r. of bicyclo[2,2,1]heptene species including the other Diels-Alder adducts of cyclopropene.

[†] National Institutes of Health Predoctoral Fellow.

participation of the cyclopropyl bond generates the allylcyclopropylcarbinyl cation (VII). Hydride migration traps this cation exclusively at the homoallyl position to generate (III) ultimately. It is possible that cation (VII) closes to the protonated epoxide (VIII). Opening of (VIII) can produce either (VII) or (IX). Assuming that hydride migration would be equally easy in either cation (VII) or (IX) and that (VIII) is actually being produced, the above results suggest that an allylcyclopropylcarbinyl cation is more stable than the linearly conjugated pentadienyl cation.

The ready rearrangement also proceeds upon addition of boron trifluoride etherate to a carbon tetrachloride solution of (II). Similar experiments beginning with the exo-

adduct (I) led mainly to polymerization, although small quantities of the cycloheptadienenones could also be detected.



We thank the National Science Foundation for support of this work.

(Received, July 17th, 1970; Com. 1162.)

¹ G. L. Closs and K. D. Krantz, J. Org. Chem., 1966, **31**, 638. ² C. F. Wilcox, jun., and R. R. Craig, J. Amer. Chem. Soc., 1961, **83**, 3866.

- ³ Photolysis of furan in the gas phase has been reported to yield cyclopropene, which subsequently undergoes Diels-Alder addition to furan in its photoexcited state: see R. Strinivasan, J. Amer. Chem. Soc., 1967, 89, 4813.
 ⁴ J. Meinwald, S. L. Emerman, W. C. Yang, and G. Büchi, J. Amer. Chem. Soc., 1955, 77, 4401.