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ON THE THERMAL REORGANIZATION OF 6-CARBOETHOXYBICYCLO [3. 1. 0] HEX-2-ENE

Robert A. Clark

Department of Chemistry, Clarkson College of Technology

Potsdam, New York 13676

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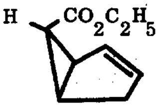
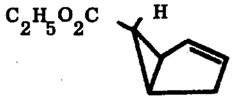
The precise mechanistic course of the thermally induced transformation of vinylcyclopropanes to cyclopentenes is not yet clearly understood (1). In simple monocyclic vinylcyclopropanes this structural reorganization is relatively free to traverse the energy surface corresponding to a fully concerted process or one in which a diradical intermediate intervenes, whichever is of lower energy. As the fully concerted process is predicted to have well-defined stereochemical requirements (2), it should be possible to virtually preclude this concerted pathway by imposing appropriate stereochemical restrictions on the reacting molecule. We report here the rearrangement of a vinylcyclopropane in which the concerted [1,3]-sigmatropic process (2) would appear to be kinetically unfavorable due to the inordinate degree of strain anticipated to be associated with the corresponding transition state. The results of stereochemical marking of this system are shown to be consistent with this expectation.

The occurrence of the structurally degenerate vinylcyclopropane rearrangement of bicyclo [3. 1. 0] hex-2-ene has been conclusively demonstrated (3). Depending upon whether the stereochemical mode of cyclopropane ring-cleavage in the bicyclo [3. 1. 0] hex-2-ene is conrotatory or disrotatory, vinylcyclopropane rearrangement by the concerted pathway requires that the product contain either a trans double bond in the five-membered ring or a *trans*-bicyclo [3. 1. 0] hex-2-ene ring fusion, respectively. The respective transition states are expected to experience a substantial fraction of this destabilization.

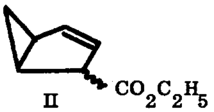
We have prepared *endo*- and *exo*-6-carboethoxybicyclo [3. 1. 0] hex-2-ene (**Ia** and **Ib**) by the published procedures (4, 5). Pyrolysis of either **Ia** or **Ib** in the vapor phase at 260° for 24 hrs. provides a mixture of 6-carboethoxybicyclo [3. 1. 0] hex-2-ene (**I**), (85%) and 4-carboethoxybicyclo [3. 1. 0] hex-2-ene (**II**), (15%) (6). A careful examination of the integrated areas in the vinyl region of the nmr spectrum (5) of the **I** recovered from the pyrolystate by preparative glpc indicates that it is, within the accuracy limitations of the nmr method, entirely (> 95%) of the exo-configuration (**Ib**) regardless of the epimeric configuration of the starting ester, i. e., **Ia** or **Ib**. That this 85: 15 mixture closely approximates the thermodynamic equilibrium mixture is indicated by the isolation of **II** from the pyrolysate and observation of the same isomer proportion upon subjecting **II** to the pyrolysis conditions. Under these conditions 3 to 5% of ethyl benzoate, formed in an irreversible side reaction, can be isolated. The proportion of this product is increased on extended or higher temperature pyrolysis.



Ia



Ib



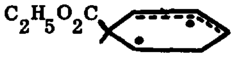
II

A consideration of the results reported here allows two definitive conclusions concerning the thermal behavior of 6-carboethoxybicyclo [3. 1. 0] hex-2-ene: (1), as anticipated the vinylcyclopropane rearrangement occurs, and (2) there is an overall loss of stereochemical integrity at C-6. Any mechanistic interpretation of the present observations thus requires not only a consideration of the vinylcyclopropane rearrangement (structural isomerization), but also the possibility of a direct <u>endo</u>-<u>exo</u> epimerization (Ia ⇄ Ib) not requiring intermediacy of II (geometric isomerization). The thermally induced geometric isomerization of suitably substituted cyclopropanes appears to be a general reaction (1). Recent theoretical considerations indicate the existence of a potential energy minimum for an extended "π-cyclopropane" of the trimethylene system, which requires that ring-closure to cyclopropane occur <u>via</u> exclusive conrotation (7). Cleavage of the C-1, C-5 bond of bicyclo [3. 1. 0] hex-2-ene <u>via</u> conrotation would appear to be kinetically unfavorable due to the introduction of what amounts to a trans double bond in a six-membered ring. Convincing kinetic evidence that the pyrolytic cleavage of alkylated cyclopropanes (8) and deuterated vinylcyclopropanes (1) occurs neither by exclusive conrotation nor disrotation has recently been presented. These results have been interpreted as convincing evidence for the existence of a diradical intermediate.

The vinylcyclopropane retrogression observed in the thermal conversion of 5-substituted bicyclo [2. 1. 1] hex-2-enes to 4- and 6-substituted bicyclo [3. 1. 0] hex-2-enes exhibits a marked preference for the stereochemical course predicted by orbital symmetry conservation (9). On the basis of the presently available results we cannot, therefore, preclude the possibility that the stereochemical randomization occurs either wholly or in part by a direct <u>endo</u>-<u>exo</u> epimerization (Ia ⇄ Ib) and that the observed vinylcyclopropane rearrangement occurs <u>via</u> two consecutive concerted steps involving the intermediacy of 5-carboethoxybicyclo [2. 1. 1] hex-2-ene (III). Orbital symmetry considerations (<u>vide supra</u>) do, however, dictate strongly against a direct concerted pathway interconnecting I and II resulting from cleavage of the C-1, C-5 bond, even though previously reported [1, 3]-sigmatropic migrations of carbon in systems where stereochemical factors appear to be comparable for the two processes demonstrate a marked preference for the concerted pathway (9, 10). The present results strongly suggest that the allylic-methine diradical (IV) is the species responsible for the observed loss of stereochemical integrity of 6-carboethoxybicyclo [3. 1. 0] hex-2-ene (I).

Experiments designed to elucidate the extent, if any, to which the 5-carboethoxybicyclo [2. 1. 1] hex-2-ene plays a role in these arrangements are in progress and will be reported in a future publication.

III



IV

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