

in several representative saturated compounds have been found to be of sign opposite to the large vicinal couplings,<sup>5</sup> it seems very likely that the former are negative and the latter positive, as Karplus suggested.<sup>1</sup>

An apparent exception to these generalizations is found in the spectra of substituted ethylene oxides, in which the geminal and both vicinal coupling constants have been reported to be of the same sign.<sup>6</sup> Furthermore, an analysis of the spectrum of epichlorohydrin appears to show that the coupling constants among the ring protons are of the same sign as the large geminal coupling constant in the chloromethyl group,<sup>7</sup> although the vicinal couplings to that group are of opposite sign. If the spectral analyses were correct and the geminal coupling constant in the chloromethyl group is normal, both the geminal and the vicinal coupling constants in the epoxide ring would be negative. This apparent anomaly was investigated by a double resonance experiment on ethylene oxide, in which the vicinal coupling constants<sup>8</sup> are about the same as in epichlorohydrin.<sup>7</sup> We found that the CH coupling constant and the sum of the vicinal HH coupling constants are of the same sign, presumably positive. It seems likely, therefore, that the analysis of the epichlorohydrin spectrum was in error.<sup>9</sup>

The authors wish to thank Nuclear Magnetic Resonance Specialties for making double resonance equipment available for this work, Mrs. Jane Ratka for some of the samples, and Mr. Charles B. Krabek for measurements on some of the spectra.

(5) R. R. Fraser, R. U. Lemieux and J. D. Stevens, *J. Am. Chem. Soc.*, **83**, 3901 (1961); F. Kaplan and J. D. Roberts, *ibid.*, **83**, 4666 (1961); K. A. McLauchlan, J. I. Musher, K. G. R. Pachler and R. Freeman, *Mol. Phys.*, in press.

(6) H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959); C. A. Reilly and J. D. Swalen, *ibid.*, **32**, 1378 (1960); **34**, 980 (1961).

(7) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **35**, 1522 (1961).

(8) N. Sheppard and J. J. Turner, *Proc. Royal Soc.*, **A252**, 506 (1959).

(9) It has been found recently that a calculation assuming opposite signs for the  $-CH_2Cl$  and ring geminal coupling constants gives a better fit to the observed spectrum: C. A. Reilly and J. D. Swalen, private communication.

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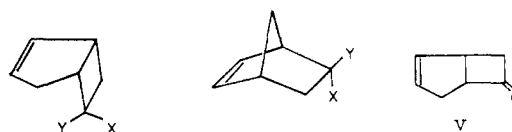
THE INTRAMOLECULAR THERMAL  
REARRANGEMENT OF THE BICYCLO[3.2.0]-  
HEPTENYL TO THE BICYCLO[2.2.1]HEPTENYL  
SYSTEM

Sir:

We wish to report the stereospecific thermal isomerization of *syn-cis*-bicyclo[3.2.0]hept-2-enyl-6-acetate (I) to *exo-5*-norbornenyl-2-acetate (III), an example of a new type of intramolecular rearrangement.<sup>1,2</sup>

(1) For a previous attempt to observe a reaction of this type, see C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1962).

(2) For formal analogs, which however have not been shown to be



I, X=H; Y=OAc  
II, X=OAc; Y=H

III, X=H; Y=OAc  
IV, X=OAc; Y=H

Reduction of the ketene-cyclopentadiene adduct<sup>3-6</sup> V with sodium borohydride<sup>7</sup> gives a mixture of alcohols I (Y = OH) (75%) and II (X = OH) (25%), whereas sodium-ethanol reduction of V gives 30% I (Y = OH) and 70% II (X = OH). Stereochemical equilibration<sup>8</sup> (fluorenone, aluminum *t*-butoxide-benzene) of the mixture of alcohols from the hydride reduction gives a I (Y = OH):II (X = OH) ratio of 45:55. Hydrogenation<sup>9</sup> of either the 75:25 or 30:70 mixture above and then stereochemical equilibration gives a dihydro-I (Y = OH):dihydro-II (X = OH) ratio of 48:52. The stereochemical assignments are based on the assumptions that hydride reduction occurs from the less hindered side<sup>10</sup> and that sodium reduction produces the more stable epimer.

Acetylation of the 75:25 mixture above and then preparative vapor chromatographic separation (3.7 m.  $\times$  2.2 cm. tri- $\beta$ -cyanoethoxypropane (TCEP)-on-firebrick column at 120° and 1100 ml./min. helium flow) gives pure I,<sup>9</sup>  $n_D^{20}$  1.4697, and pure II,<sup>9</sup>  $n_D^{20}$  1.4652.

Heating a 0.6 M solution of I in decalin at 300° causes conversion to II, III, IV, vinyl acetate, and cyclopentadiene. Identification of the products is achieved by analytical vapor chromatography (46-m. capillary column at 120°, with TCEP as the stationary phase) of the reaction mixtures as such as well as after lithium aluminum hydride reduction to a mixture containing the four unsaturated alcohols (I-IV, OAc = OH) and subsequent hydrogenation to a mixture containing the four saturated alcohols (dihydro I-IV, OAc = OH). Under the same conditions of pyrolysis, II gives qualitatively the same mixture of products, but the reaction is slower and the proportions of products are different from those obtained from I.

Although cyclopentadiene and vinyl acetate do combine to give III and IV under these conditions, the major if not the entire path for the I $\rightarrow$ III conversion in the early stages of the reaction does not involve fragmentation and Diels-Alder recombination of these addends: The III:IV (*exo*:*endo*) ratio from I is 9.4 after 60 minutes of pyroly-

intramolecular, see (a) J. J. Drysdale, U.S. Patent 2,861,095; (C.A. **53**, 9102 (1959)); (b) J. J. Drysdale, U.S. Patent 2,819,320; (C.A. **54**, 11118 (1960)).

(3) B. T. Brooks and G. Wilbert, *J. Am. Chem. Soc.*, **63**, 870 (1941).

(4) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

(5) For further discussion of the structure of V, see J. D. Roberts and W. F. Gorham, *ibid.*, **74**, 2278 (1952).

(6) In a modification of the reported<sup>3,4</sup> conditions, we have prepared V by keeping a mixture of the reactants at room temperature rather than at 100°. The reaction seems to be exothermic, and in one run carried out *without solvent*, a serious explosion occurred.

(7) For a report of this reduction using lithium aluminum hydride, see H. L. Dryden and B. E. Fargot, *J. Am. Chem. Soc.*, **77**, 5633 (1955).

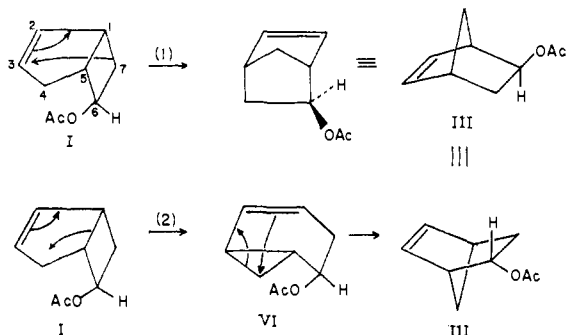
(8) W. von E. Doering and T. Aschner, *ibid.*, **71**, 838 (1949).

(9) The material obtained had the correct elementary analysis.

(10) For a reasonably close analogy, see O. L. Chapman, D. J. Pasto, G. W. Borden and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

sis (5% conversion), the shortest reaction time that allows an accurate estimate of the *exo:endo* ratio, whereas the kinetically determined product ratio from the Diels-Alder addition of cyclopentadiene and vinyl acetate in decalin at 300° is 0.43. These relationships are set out in Fig. 1. There is therefore a path for the I→III reaction that is intramolecular and largely if not completely stereospecific.

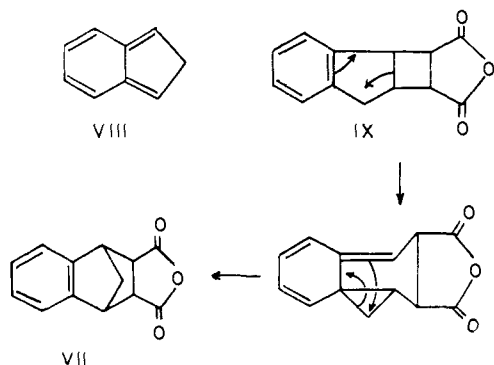
The two most likely mechanisms for the I→III conversion are: (1) cleavage at C.1-C.7, establishment of a double bond at C.1-C.2, and re-cyclization by connection of C.7 and C.3; (2) formation of a vinylcyclopropane (VI) from a cyclopentene,



followed by conversion of the latter to a different cyclopentene (III). The steps of both mechanisms can also be formulated with diradical intermediates, the concertedness of the electron shifts being presently indeterminate.

Although in simple cases the cyclopentene → vinylcyclopropane reaction is doubtless strongly endothermic and consequently is not expected to occur except at very high temperatures, this restriction is less severe in the I→VI reaction of mechanism (2), much of the price of three-membered ring formation being paid by four-membered ring opening. Several examples analogous to the second step (VI → III) of mechanism (2) are known.<sup>11</sup>

Mechanism (2) may provide an alternative explanation for the reported<sup>12</sup> formation, at ele-



(11) (a) E. Vogel, R. Palm and K. H. Ott, unpublished work, cited by E. Vogel, *Angew. Chem.*, **72**, 4 (1960); (b) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007, 4897 (1960); (c) W. von E. Doering and W. R. Roth, unpublished work, cited by W. von E. Doering, M. R. Wilcott, III, and M. Jones, Jr., *ibid.*, **84**, 1224 (1962); (d) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961).

(12) K. Alder, F. Pascher and H. Vagt, *Ber.*, **75**, 1501 (1942); K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

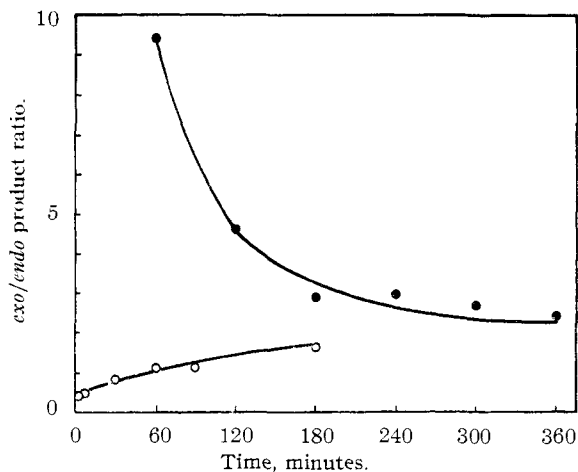


Fig. 1.—Ratio of products III/IV as a function of time and starting material in decalin solution at 300°. Solid circles show products from I; open circles show products from cyclopentadiene and vinyl acetate.

vated temperature, of the adduct VII from indene and maleic anhydride, which is believed<sup>12</sup> to involve the unknown hydrocarbon isoindene VIII as an intermediate. It is conceivable, however, that the reaction takes the course shown here, in which preliminary formation of the cycloaddition product IX, a formal benzo analog of I, is followed by rearrangement according to mechanism (2). We are investigating this possibility.

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#### A NEW AND CONVENIENT ROUTE TO THE AMINE-BORANES

Sir:

The reaction of amine-boranes with olefins to produce trialkylboranes has been reported.<sup>1,2,3</sup> This method of producing trialkylboranes has many advantages over other methods as a route to this important class of compounds. Several other important reactions of amine-boranes also have been reported. Among these are the reaction with sodium hydride to produce sodium borohydride<sup>4</sup> and the reactions with primary and secondary amines to produce borazines and borazenes, respectively. Until now amine-boranes have been prepared either by the reaction of diborane with

(1) R. Köster, *Angew. Chem.*, **69**, 684 (1957).

(2) M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

(3) E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

(4) R. Köster, *Angew. Chem.*, **69**, 94 (1957).