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THE ABNORMAL CLAISEN REARRANGEMENT II.

HIGH TEMPERATURE CHEMISTRY OF 1-ETHYL-2-METHYLSPIRO[2,5]OCTA-4,6-DIEN-8-ONE

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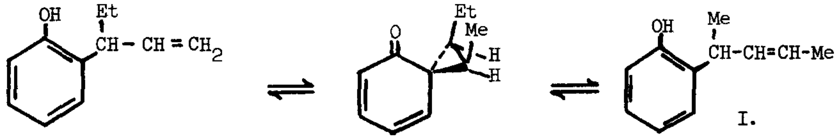
A considerable body of evidence supports the intermediacy of a 1,2-dialkylspiro[2,5]octadienone in the so-called abnormal Claisen rearrangement (1). Formation and reaction of this intermediate is formally

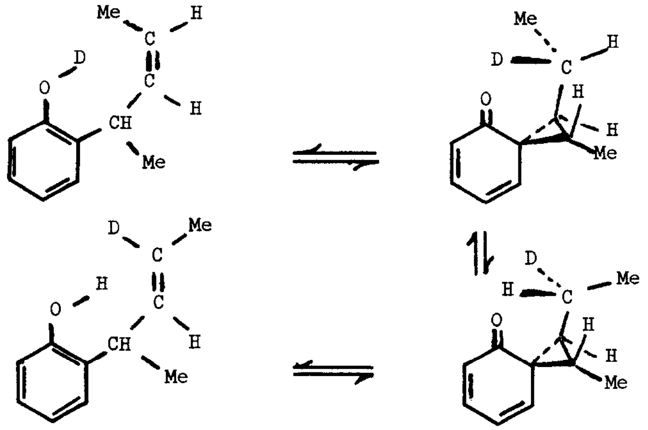


I.

analogous to the cis-1-alkyl-2-vinylcyclopropane valence isomerization (2), recently named the homodienyl-1,5 hydrogen shift (3). However, experimental evidence which would connect these two processes has been lacking. We would like to report evidence which not only permits this connection, but also provides information about the stereochemistry of the transition state.

It has been reported (4) that o-(cis-α,γ-dimethylallyl)phenol (cis-I) converts to o-(trans-α,γ-dimethylallyl)phenol (trans-I) at 165°. This extraordinarily facile cis-trans interconversion must be attributed to incursion of the abnormal Claisen rearrangement. That expectation was confirmed by heating a sample of cis-I in deuterium oxide at 205°. The resultant mixture of cis- and trans-I was separated on a 15 ft. FFAP (5) column, and the n.m.r. spectrum of trans-I showed the expected incorporation of deuterium at the gamma carbon of the allyl chain and in the alpha methyl group (1b, 1c).

Further studies of the behavior of the spirodienone intermediate were therefore carried out with this system. This is a particularly useful system since transfer of a deuteron to the gamma carbon of the allyl group gives an intermediate with four different groups on the alpha carbon of the ethyl moiety.



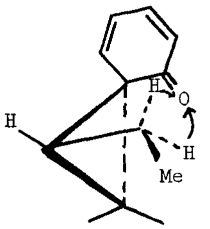
Samples of both cis- and trans-I heated at 210° produce the same equilibrium mixture of 22% cis-I and 78% trans-I. The rate of attainment of equilibrium was measured by heating cis-I in water and analyzing the product by gpc. The following data were obtained. Similar rate studies in deuterium oxide at 205° gave $k_1 = 0.27 \times 10^{-5}$ sec.$^{-1}$, thus $k_H/k_D = 2.8$. Measurement of the rate of olefinic deuterium incorporation (analysis by n.m.r. with dimethylformamide as an internal integration standard) gave $k = 0.27 \times 10^{-5}$ sec.$^{-1}$. Trans-I isolated by preparative g.p.c. after 0.7, 2.0, 3.6 and 4.8 half lives showed the presence of 1.0 olefinic proton. In all cases the γ-methyl resonance appeared as a clean singlet.

$$\text{cis-I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{trans-I}$$

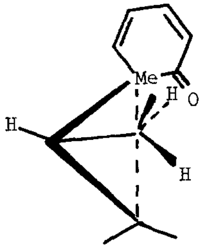
	k_1(x 10^5)	k_{-1}(x 10^5)
205°	0.76	0.21
226°	3.3	1.0
E_a	33	35
$\Delta S^{\ddagger}$	-13	-12

These data show that every cis-I molecule converted to trans-I incorporates one deuterium into the allyl side chain at the gamma carbon. Thus the proton transfer is, within the limits of the experiment, 100%

stereoselective, and completely integrated stereochemically with the conversion of the double bond to a cyclopropane ring. The result is sufficient to prove that this is truly a homodienyl-1,5 hydrogen shift. The evidence shows that there exists only a single route for the hydrogen shift. The molecule can assume a conformation (IIa) in which a proton transfer could be accomplished both from above and below the carbonyl oxygen. A transfer from both sides is specifically eliminated, though the data do not *a priori* show whether transfer occurs from above or below the oxygen. Winstein, Boikess and Glass (3) have shown theoretically that the most favorable conformation is one in which the carbon-hydrogen bond broken is nearly parallel to that cyclopropane ring bond which is also broken (IIb).

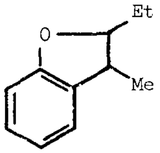


IIa

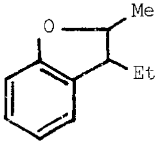


IIb

A sample of cis-I heated for 161 hrs. at 218° in water gave a mixture of four products, 49% I, 34% *A*, 12% *B* and 3% phenol (2% unidentified). *A* was identified by its spectral properties and by comparison with an authentic sample (prepared by the method of Schmid and Barner (6)) as *p*-(*trans*-α,γ-dimethylallyl)phenol. *B* showed an n.m.r. spectrum containing four groups of peaks, mult. at 6.8 ppm (4H), mult. at 4.25 ppm (1H), mult. at 2.95 ppm (1H) and a complex series of peaks between 2.0 and 0.8 ppm (8H). On the basis of this and the infrared spectrum (1228 and 774 cm.$^{-1}$) *B* was identified as a coumaran. However the multiplet at 4.25 ppm which appears as a quartet of doublets ($J \simeq 7$ and 1 cps) at 4.48 and a triplet of doublets ($J \simeq 7$ and 1 cps) at 4.03 ppm, as well as the complex between 2.0 and 0.8 ppm prove that *B* is not a single coumaran. Its spectral properties are in good accord with a gpc inseparable 1:1 mixture of IIIa and IIIb.



IIIa



IIIb

Formation of the coumaran mixture is a hitherto unobserved example of the oxocyclopropane - dihydrofuran (7) or vinylcyclopropane - cyclopentene (8) valence isomerization. The formation of both IIIa and IIIb is to be expected from such a reaction.

References

(1) a) E. N. Marvell, D. R. Anderson and J. Ong, J. Org. Chem., 27, 1109 (1962); b) A, Habich, R. Barner, R. M. Roberts and H. Schmid, Helv. Chim. Acta, 45, 1943 (1962); c) A. Habich, R. Barner, W. von Phillipsborn and H. Schmid, ibid., 48, 1297 (1965); d) R. M. Roberts and R. G. Landolt, J. Am. Chem. Soc., 87, 2281 (1965); e) R. M. Roberts, R. N. Greene, R. G. Landolt and E. W. Heyer, ibid., 87, 2282 (1965).

(2) D. S. Glass, J. Zirner and S. Winstein, Proc. Chem. Soc., 276 (1963); W. R. Roth, Ann., 671, 10 (1964); R. J. Ellis and H. M. Frey, J. Chem. Soc. 5578 (1964); W. R. Roth and J. König, Ann., 688, 28 (1965).

(3) D. S. Glass, R. S. Boikess and S. Winstein, Tetrahedron Letters, 999 (1966).

(4) E. N. Marvell, J. L. Stephenson and J. Ong, J. Am. Chem. Soc., 87, 1267 (1965).

(5) Varian Aerograph designation for their free fatty acid phase.

(6) R. Barner and H. Schmid, Helv. Chim. Acta, 43, 1393 (1960).

(7) C. L. Wilson, J. Am. Chem. Soc., 69, 3002 (1947); C. L. Wilson and D. M. A. Armitage, ibid., 81, 2437 (1959).

(8) M. C. Flowers and H. M. Frey, J. Chem. Soc., 3547 (1961); R. J. Ellis and H. M. Frey, ibid., 4188 (1964); C. S. Elliot and H. M. Frey, ibid., 345 (1965); W. von E. Doering and J. B. Lambert, Tetrahedron, 19, 1989 (1963).

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