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VINYLOGOUS DI-π-METHANE REARRANGEMENT.
THERMAL TRANSPOSITION OF BICYCLO[4.4.1]UNDECA-2,4,7,9-TETRAEN-11-OL.

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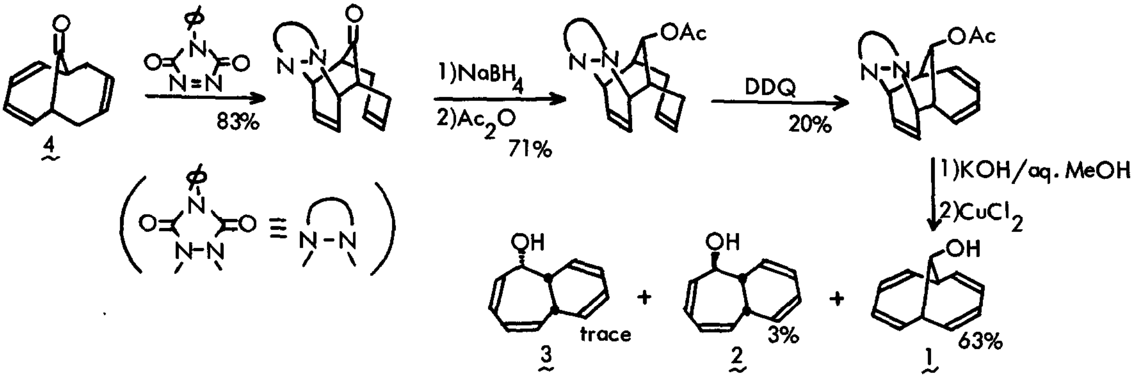
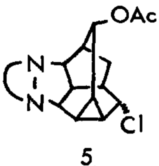
In connection with the other studies, we have synthesized the bicyclo[4.4.1]undecatetraenol **1** and observed its facile thermal rearrangement to bicyclo[5.4.0]undecatetraenols **2** and **3**. Although the rearrangement of this type has previously been interpreted as 1,5-vinyl migration, we rationalize it as concerted vinylogous di-π-methane rearrangement, which can be of fundamental importance in all similar cases.

Synthesis The alcohol **1** was derived in 6 steps starting from tropone-butadiene adduct **4** 1) as shown in Chart. The yield in each step was satisfactory except DDQ oxidation, where two other products **5** and **6** were formed in 11% and 10% yield, respectively 2). In the last step, **1** was always accompanied by minute amounts of two other alcohols **2** and **3**.



The structure of **1** was secured by its hydrogenation and the subsequent oxidation to give bicyclo[4.4.1]undecan-11-one, which was also obtained from **4**. The carbon skeleton of **2** and **3** was



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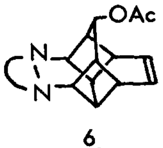

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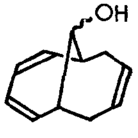
Table Spectroscopic Properties of **1**, **2** and **3**

1 m.p. 32-33°, m/e 160 (M^+), 104, 91 (b.p.), λ_{max}^{MeOH} 215 (ϵ 9110 sh), 224 (12650), 230.5 (11970), 241.5 (3500), 250 (2800), 260 nm (1970), ν^{KBr} 3325, 3000, 1610, 1030, 680 cm^{-1}, δ^{CDCl_3} 2.55 (1H, br.d, J=6, OH), 3.70 (2H, br.q, J=4.5), 4.70 (1H, m (br.t, J=4.5 on adding D_2O)), 5.35-5.97 (8H).

2 m.p. ~83°, m/e 160 (M^+), 104, 91 (b.p.), λ_{max}^{MeOH} 238 (ϵ 7710), 265 nm (2340 sh), ν^{KBr} 3300, 3025, 1610, 1305, 1045, 685 cm^{-1}, $\delta^{C_6D_6}$ 1.45 (1H, br.s, OH), 2.92 (1H, br.d, J=10), 3.10 (1H, br.d, J=10), 4.63 (1H, br.s), 5.10-6.20 (8H).

3 m.p. ~49°, m/e 160 (M^+), 104, 91 (b.p.), λ_{max}^{MeOH} 233.5 (ϵ 7540), 261 (4420 sh), 270 (3600), 282 nm (1870 sh), ν^{KBr} 3300, 3025, 1610, 1460, 1280, 1040, 680 cm^{-1}, δ^{CDCl_3} 1.96 (1H, br.s, OH), 2.88 (1H, tdd, J=9, 4, 1.5), 3.28 (1H, br.dt, J=9, 4), 4.42 (1H, dd, J=9, 3), 5.50-6.20 (8H).

established by their spectroscopic properties (Table) and their conversion to the same saturated ketone (hydrogenation and subsequent Collin's oxidation) and to benzo[b]tropone (MnO_2 oxidation)[3]. While cis-configuration of the two rings was deduced from $J_{1,7}$ (10 Hz for **2** and 9 Hz for **3**), configuration of OH was established by the result described below.



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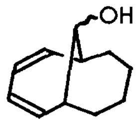

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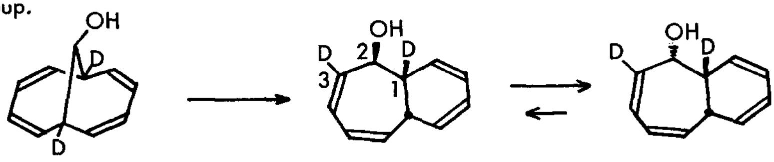
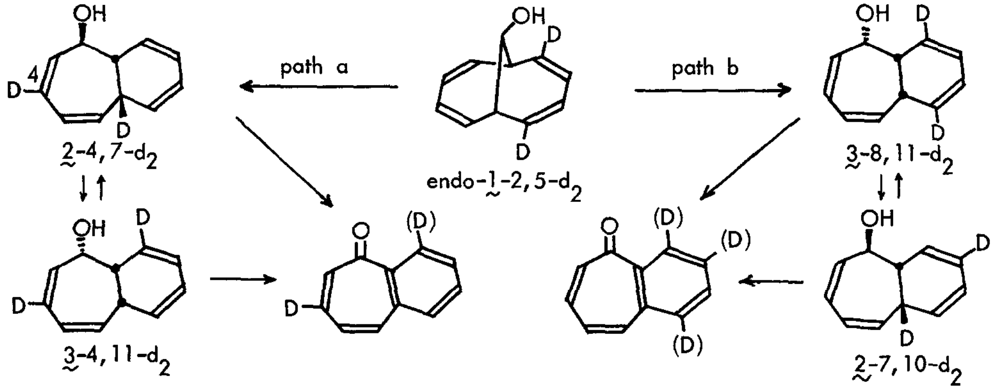
Thermal rearrangements When **1** was heated at 60° in benzene, **2** started forming first, but after 1.5 hrs **3** became predominant in the reaction mixture. This is sharp contrast to the thermal behavior of the trienol **7**[1] and the dienol **8**[4], which are stable under the same conditions. Furthermore, on heating under the same conditions, **2** and **3** reached an equilibrium in which the ratio of **2** and **3** was *ca* 1:2 (by PMR). Thus, the rearrangements **1** → **2** ⇄ **3** were revealed. In order to clarify the nature of the reaction pathways, dideuterated alcohol, **1**-1,6-d_2 (isotopic purity ~100%) was prepared[1] and its rearrangement studied. PMR spectra ($Eu(fod)_3$) of **2**-d_2 and **3**-d_2 thus obtained revealed that a deuterium atom was located at C-1 in both compounds and the other at C-3 in the latter and C-3 or C-11 in the former. MnO_2 oxidation of both deuterated products gave benzo[b]tropone-d in which 85% of the deuterium was located at C-2 and 15% at C-4[5], showing that the second deuterium atom in **2**-d_2 was also at C-3. Therefore the transformation **1** → **2**, as well as the interconversion **2** ⇄ **3** can only be rationalized by [1.5] sigmatropy of the vinyl group.



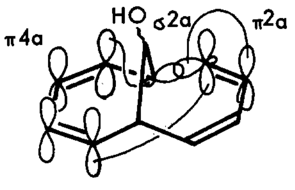
1-1,6-d_2 **2**-1,3-d_2 **3**-1,3-d_2

The rearrangement of another deuterated alcohol, endo-**1**-2,5-d_2 (isotopic purity ~96%) prepared from sulfolene-d_4 6) revealed the presence of the pathway **1**→**3** and further provided the structure assignment of **2** and **3**. If the process **1**→**3** is absent, all **3** present in the reaction mixture should be formed through **2** (path a in the following chart) and therefore one deuterium atom should be located at C-4 of **2** and **3**, and at C-3 of benzo[b]tropone, their MnO_2 oxidation product. In the process **1**→**3** (path b), on the other hand, no deuterium should be located on the 7-membered ring of the rearranged alcohols and therefore of benzo[b]tropone. Thus, the D-content in benzo[b]tropone should determine the extent of path b. The actual reaction on endo-**1**-2,5-d_2 at 50° afforded benzo[b]tropone with D-content of 63% at C-3 position (PMR). The pathway b, **1**→**3**, therefore amounts to <u>ca</u> 34% of the entire reaction. Since **2**, the kinetic product, can be formed from **1** only by the migration of the vinyl group exo to OH and deuterium labelling pattern on 7-membered ring does not change during the process **2**⇄**3**, the initial product **2** of the major pathway has to have exo orientation of the hydroxyl group.



<u>Rationalization</u> The thermal rearrangements described here are all [1.5] sigmatropic vinyl migration, which is known to proceed much faster than the alkyl migration 7). However, the present rearrangements are quite remarkable in proceeding at such a low temperature. Kinetic studies ((CCl_4:acetone=3:1)$\Delta S^{\ddagger}_{20^\circ}$=−11.9±3.5 e.u., $\Delta H^{\ddagger}_{20^\circ}$=21.3±1.0 kcal/mole, $\Delta G^{\ddagger}_{20^\circ}$=24.8±0.1 kcal/mole for **1**→**2**+**3**, $\Delta S^{\ddagger}_{20^\circ}$=−9.6±3.0 e.u., $\Delta H^{\ddagger}_{20^\circ}$= 21.7±0.9 kcal/mole, $\Delta G^{\ddagger}_{20^\circ}$=24.5±0.1 kcal/mole for **2**→**3**, small dependence of rate to solvent polarity) indicates the process to be non-ionic concerted pathways. Jones <u>et al</u>. have forwarded an explanation involving thermally-allowed interaction between the LUMO of the migrating group and the HOMO of the diene system for the racemization of 1,3-dimethyl-1-vinylindenes 7c). Although the explanation is applicable to the present cases, we propose another, perhaps better, rationalization, that is, vinylogous di-π-methane rear-

rangement[8]. As is witnessed by molecular mechanics calculations[9] and UV spectrum (Table), the carbon skeleton of **1**, for example, has a twisted conformation (C_2 symmetry) in which an end of the diene system faces to the other very closely (3.1529 Å) and appears to have π-π interaction. It should be this interaction which initiates the thermal process and the entire reaction proceeds in concerted fashion (for example, thermally allowed [4a+2a+2a] process as shown in A)[10]. The rearrangement **2** ⇄ **3** can also be rationalized in the same way (B)[10].



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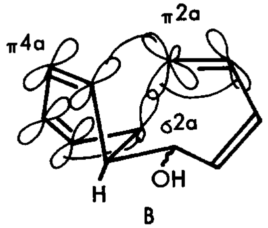

B

This rationalization can be applied to thermal rearrangements observed in cis-9,10-dihydronaphthalenes[7a] and spiro[4.4]nonatriene and -tetraene[7b]. Furthermore, facile 1,5-formyl migration[7c,11] may be called similarly as vinylogous oxa-di-π-methane rearrangement. It is noteworthy that in all these systems p-orbitals of an end of two nonconjugated π-systems direct approximately toward one another as in the present cases. The ease of the thermal rearrangement may depend on the extent of their overlap.

Reference and Notes

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1) S. Itô, H. Ohtani, S. Narita and H. Honma, Tetrahedron Letters, 2223 (1972).

2) Structure assignment of all the intermediates and detail of the reaction sequence will be discussed elsewhere.

3) A small amount of benzo[d]tropone was also obtained. This suggests a minor oxidation pathway involving the formation of benzotropylium ion as an intermediate.

4) Prepared from **4** by diimide reduction followed by $NaBH_4$ reduction.

5) A trace of benzo[d]tropone-2-d_1 was also obtained. The figures would suggest the formation of benzotropylium ion amounts roughly to 30% of the reaction.

6) J.L. Charlton and R. Agagnier, Can. J. Chem., **51**, 1852 (1973).

7) Inter al. a) E. Vogel, W. Meckel and W. Grimme, Angew. Chem., **76**, 786 (1964), Angew. Chem. Int. Ed. Engl., **3**, 643 (1964). L.A. Paquette, M.J. Carmody, J. Am. Chem. Soc., **97**, 5841, (1975). b) M.F. Semmelhack, H.N. Weller and J.S. Foos, J. Am. Chem. Soc., **99**, 292 (1977), M.F. Semmelhack, H.N. Weller and J. Clardy, J. Org. Chem., **43**, 3791 (1978). c) D.J. Field and D.W. Jones, J. Chem. Soc., Chem. Commun., 688 (1977).

8) H.E. Zimmerman, R.D. Little, J. Am. Chem. Soc., **94**, 8256 (1972), **96**, 5143 (1974).

9) Allinger type calculations, done by Dr. Y. Fukazawa to whom we are grateful.

10) The process can also be interpreted as [4a+2s+2s] or [4s+2s+2a].

11) P. Schiess and P. Fünfschilling, Tetrahedron Letters, 5191, 5195 (1972).

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