Table I. Complexes Prepared

	Calcd			Found			Electrical	%
Complex	C	H	N	C	H	N	resistivity[7]	yield
5	39.88,	1.74,	7.44	39.72,	2.06,	7.35	0.6	2
				40.14,	1.98,	7.65	2	27
7	45.88,	2.75,	7.64	45.30,	2.82,	7.64	2	40
8	44.92,	2.33,	9.88	44.95,	2.49,	10.27	0.8	70
9	51.19,	3.68,	8.53	50.86,	3.78,	8.42	2	20

Acknowledgments. Dr. J. L. Gillson is thanked for his measurements of electrical resistivity.

References and Notes

(1) (a) J. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); (b) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1976).

(2) (a) For a review see G. A. Thomas, et al., *Phys. Rev. B*, **13**, 5105 (1974); (b) M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, *ibid.*, **13**, 5111 (1976).

(3) R. C. Wheland, *J. Am. Chem. Soc.*, **98**, 3926 (1976).

(4) W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).

(5) R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98**, 3917 (1976).

(6) W. R. Hertler, *J. Org. Chem.*, **41**, 1412 (1976).

(7) Resistivity in Ω cm for 2 probe, room-temperature compactions, between hardened steel pistons with sputtered gold surfaces, at a pressure of 5 kbars.

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Received August 12, 1976

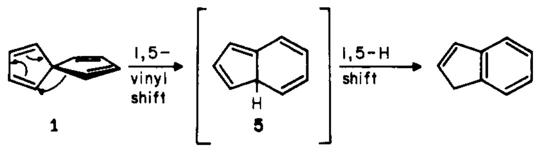
Thermal Rearrangements of Spiro[4.4]nonapolyenes. Unusually Rapid 1,5-Vinyl Migration

Sir:

Spiro[4.4]nonatetraene (**1**) is a relatively unstrained hydrocarbon and of some theoretical interest,[1] yet it eluded synthesis until recently.[2] Well-precedented elimination pathways involving moderate temperatures (>150 °C) failed uniformly.[3,4] This suggestion of unexpected instability in **1** and recent interest in thermal rearrangements of unsaturated spirocycles[5] prompted us to probe the thermochemistry of **1** and the less unsaturated analogues **2**, **3**, and **4**. These spirocycles undergo 1,5-carbon migrations when heated, producing unsaturated derivatives of the bicyclo[4.3.0]nonane skeleton. Here we report preliminary results which demonstrate the remarkably high reactivity of **1** and **2** compared to **3** and **4**.

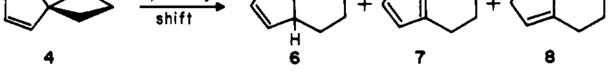
The rearrangements of **1–4** were best followed in a static gas phase reactor monitoring the disappearance of spirocycle using gas chromatography (GC).[6] In certain cases, the rearrangements have beenmonitored by increase in (product) absorption in the UV spectra, both in solution and in the gas phase, and by the disappearance of spirocycle in solution using ^{1}H NMR spectroscopy. The GC technique provided superior data which have been used to derive activation parameters as displayed in Table I.[7] The rearrangement products were isolated by gas phase flow pyrolysis over heated glass helices at ca. 0.1–1 Torr and contact times ca. 10–60 s, with collection of the product at −78 °C.

In the flow pyrolysis apparatus, **1** rearranged to indene at 260 °C (eq 1); no additional products were observed at lower temperature (partial conversion). Isoindene **5**, an unknown compound which is presumed to be important in the formation of indene, has not been detected. Repeated scanning of the UV spectrum during pyrolysis demonstrated the presence of isobestic points at 220 and 258 nm; intermediate **5**, if present, remains at very low concentration. Reaction in solution occurred four–fivefold faster than in the gas phase (Table I, entries 1 and 4), but the polarity of the solvent and the presence of sulfuric acid (entry 3, acid:spirocycle = 10:1) had little effect on the rate.



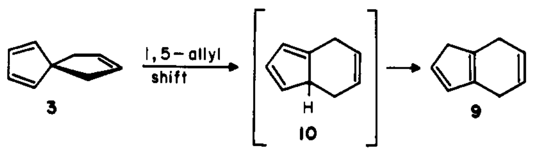
(1)

Spiro[4.4]nona-1,3-diene (**4**)[8] is stable indefinitely at 25 °C, but is converted to a mixture of **6**, **7**, and **8** upon heating (eq 2), with an activation barrier previously measured in a "micro flow reactor" by Kloosterzeil[5b] (Table, entry 9). Using GC monitoring, in a static gas phase system, we find rates and activation parameters in good agreement with Kloosterzeil's data (Table I, entry 10).



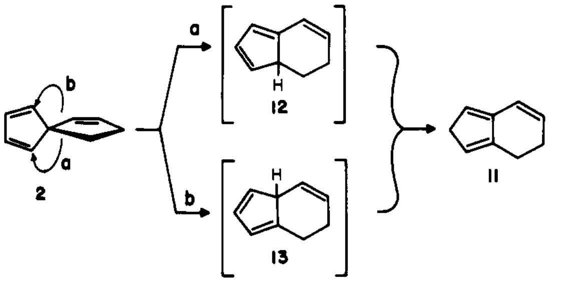
(2)

Spiro[4.4]nona-1,3,7-triene (**3**)[2,3b] rearranges during flow pyrolysis (370 °C/0.05 Torr) to a single product, isoindane **9**, presumably via the hydrogen-shift isomer, **10** (eq 3).[9] At higher reaction temperatures, indane begins to appear and is the only product in flow pyrolysis at 450 °C. Only small changes in UV absorption occur during the reaction, so kinetic data were obtained by GC monitoring (entry 8, Table I).



(3)

Spiro[4.4]nona-1,3,6-triene (**2**), previously an unknown compound, was prepared from spiro[4.4]nona-1,6-diene[10] by allylic bromination (*N*-bromosuccinimide) followed by dehydrohalogenation (potassium *tert*-butoxide/tetraglyme) under conditions (0.2 Torr) where **2** distilled as it formed at 25 °C.[11] The UV and PES spectra of **2** are perturbed compared to those of **3** and **4**, showing the effects of spiroconjugation, as in **1**.[12] The chemical reactivity of **2** is also more similar to **1** than to **3** or **4**. Flow pyrolysis at 305 °C/2.0 Torr caused rearrangement of **2** to a single product, isoindane **11**.[13] Presumably, the rearrangement occurs through a 1,5-alkyl shift (to give **12**, path a, eq 4) or a 1,5-vinyl shift (to give **13**, path b, eq 4), followed by 1,5-hydrogen shift to produce **11**. No intermediates have been detected. No data are available to suggest which path, a or b, is operating. The disappearance of **2** was monitored by GC; smooh first-order kinetics were observed but no products were detected (Table I, entry 6).



(4)

Table I. Rearrangements of Spiro[4.4]nonapolyenes

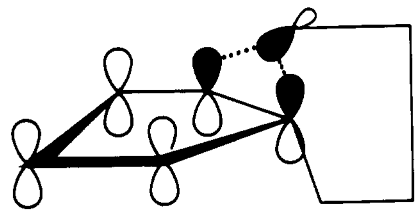
Entry	Spirocycle	Conditions	Relative rate at 78 °C	E_a (kcal/mol)	Log *A*
1	**1**	UV, 249 nm, isooctane	266 000	26.0 ± 0.4[b]	12.6 ± 0.3
2	**1**	UV, 249 nm, ethanol	296 000	26.4 ± 0.4[c]	12.9 ± 0.2
3	**1**	UV, 249 nm, ethanol (0.005 M sulfuric acid)	319 500		
4	**1**	UV, 242 nm, gas phase	83 400		
5	**1**	GC, gas phase	87 500	27.1 ± 0.8[d]	12.8 ± 0.5
6	**2**	GC, gas phase	7 150	27.4 ± 0.8[e]	11.9 ± 0.5
7	**2**	^{1}H NMR, isooctane	31 000		
8	**3**	GC, gas phase	5.0[a]	33.6 ± 0.6[f]	12.6 ± 0.3
9	**4**	[gas phase][g]	1.4[a]	35.6	13.3
10	**4**	GC, gas phase	1.0[a]	36.0 ± 1.4[h]	13.4 ± 0.7

[a] The relative rates for **3** and **4** are extrapolated to 78 °C from activation parameters obtained at 130–180 °C. [b] Over 58–73 °C. [c] Over 53–67 °C. [d] Over 54– 77 °C. [e] Over 71–105 °C. [f] Over 132–176 °C. [g] From ref 5b. [h] Over 146–187 °C.

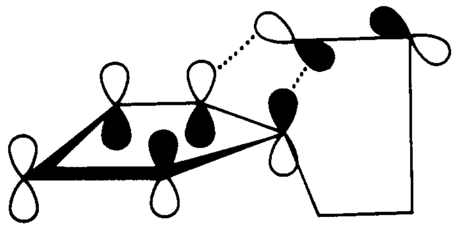
Monitoring the disappearance of **2** (0.01 M) by ^{1}H NMR showed first-order kinetics; no monomeric products were observed (Table I, entry 7). Monitoring the rearrangement of **2** in isooctane solution (following the increase in absorption at 256 nm) led to a rate constant consistent with the ^{1}H NMR data.

The thermal rearrangements of **4** and related spiro[4.*n*] alka-1,3-dienes have been interpreted as concerted suprafacial 1,5-sigmatropic shifts, followed by 1,5-hydrogen shifts to the more stable isomer.[14] For spirocycles **1–3**, this interpretation can accommodate the products observed by assuming rate-determining 1,5-carbon shifts followed by much faster 1,5-hydrogen shifts. A study of deuterium labeled **1** and **2** is underway to provide evidence concerning the rate-determining step.

The low activation barriers for **1** and **2** compared to **3** and **4** are not easily accommodated by a simple 1,5-sigmatropic shift mechanism. Parallel with the suggestions of Miller and Boyer concerning accelerated 1,5-phenyl shifts in 1-phenylindene,[15] we favor a transition state which implicates the π-system at the migrating carbon for **1** and **2**. The transition state picture (I) for a simple sigmatropic shift of a carbon unit attached to a cyclopentadiene ring is appropriate for reactions of **3** and **4**, but may be modified in the cases of **1** and **2** due to interaction of a p orbital on the migrating carbon (LUMO of an olefin or 1,3-diene unit) with the cyclopentadienyl π-system (HOMO). This HOMO-LUMO interaction (II) would stabilize the transition states, leading to the low barriers to rearrangement for **1** and **2** compared with **3** and **4**.



I, Orbital interaction during 1,5-alkyl shift



(5)

II, Secondary π-orbital interaction during 1,5-vinyl shift

Work is in progress to further define the mechanism of rearrangement of the spirocycles, through deuterium labeling studies and characterization of the transient intermediates.[16]

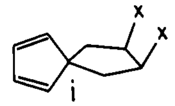
References and Notes

(1) As an example of spiroconjugation, cf. (a) H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89,** 5215 (1967); (b) R. Hoffmann, A. Imamura, and G. Zeiss, *ibid.*, **89,** 5219 (1967); (c) A. Tajiri and T. Nakajima, *Tetrahedron,* **27,** 6089 (1971); (d) M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93,** 6193 (1972). As a candidate for planar tetracoordinate carbon, cf. R. Hoffmann, R. W. Alder, and C. F. Wilcox, Jr., *ibid.,* **92,** 4992 (1971).

(2) M. F. Semmelhack, J. S. Foos, and S. Katz, *J. Am. Chem. Soc.,* **93,** 8637 (1972).

(3) (a) D. J. Cram and B. L. Van Durren, *J. Am. Chem. Soc.*, **77,** 3576 (1955); (b) D. Schonleber, *Chem. Ber.,* **102,** 1789 (1969).

(4) Early work in the authors' laboratories revealed that pyrolytic elimination from i (X = OCS_2CH_3) and i (X = $OCOCH_3$) produced indene as the only C_9H_8 product.



i

(5) For the specific case of spiro[4.*n*]alka-1,3-dienes, see (a) J. M. E. Krekels, J. W. de Haan, and H. Kloosterzeil, *Tetrhedron Lett.,* 2751 (1970); (b) L. M. Dane, J. W. De Haan, and H. Kloosterzeil, *ibid.,* 2755 (1970); (c) V. A. Mironov, A. P. Ivanov, Ya. M. Kimelfeld, L. I. Petrovskaya, and A. A. Akhrem, *ibid.*, 3347 (1969); (d) E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.,* **31,** 768 (1966); (e) E. T. McBee, G. W. Calundann, and T. Hodgins, *ibid.*, **31,** 4260 (1966); (f) M. Jones, R. Hochman, and J. Walton, *Tetrahedron Lett.,* 2617 (1970).

(6) The reactor had a volume of ca. 100 ml; it was filled with 5–10 Torr of sample, 5–10 Torr of cyclooctane as internal standard, and about 300 Torr of argon. Portions of the mixture were removed by syringe and analyzed by gas chromatography. Peak area ratios (sample:cyclooctane) were reproducible within 1.0%. Molar response factors were shown to vary by <1% over a ten-fold concentration range. Using *n*-pentane in place of argon had no significant effect on the rates. The rate constants were determined by nonlinear least-squares fit to the first-order kinetic expression, using data over at least three reaction half-lives. Quoted uncertainties are equal to one standard deviation. A kinetic run with the reactor filled with glass wool demonstrated the absence of significant surface effects.

(7) The UV solutions are ca. 10^{-4} M in spirocycle; the integrated first-order rate expression over 75–90% reaction was used in determining the rate constants, according to: F. J. Kezdy, J. Jaz, and A. Bruylants, *Bull. Soc. Chim. Belg.*, **67,** 687 (1958). Correlation coefficients >0.999 were obtained in all reported cases.

(8) C. F. Wilcox and R. R. Craig, *J. Am. Chem. Soc.,* **83,** 3866 (1961).

(9) The thermal rearrangement of **3** was reported earlier: M. Jones, Jr., R. N. Hochman, and J. D. Walton, *Tetrahedron Lett.,* 2617 (1970).

(10) Spiro[4.4]nona-1,6-diene was prepared by a combination of established procedures from spiro[4.4]nona-1,6-dione through elimination of the bistosylhydrazone salts. Cf. (a) H. Gellach and W. Muller, *Helv. Chim. Acta,* **55,** 2277 (1972); (b) D. Christiansen, Ph.D. Thesis, UCLA 1971.

(11) This compound showed ^{1}H NMR, ^{13}C NMR, UV, IR, and mass spectral data consistent with the proposed structure. Satisfactory elemental analysis was obtained on the tetracyanoethylene adduct, mp 205–206 °C dec.

(12) C. Batich, E. Heilbronner, E. Rommel, M. F. Semmelhack, and J. S. Foos, *J. Am. Chem. Soc.,* **96,** 7662 (1974).

(13) Isoindane **11** was identified through ^{1}H NMR, IR, UV, and mass spectral data on **11** and its adduct with tetracyanoethylene, mp 156–160 °C dec.

(14) The single previous example of thermal rearrangement of a substituted spiro[4.4]nonatetraene was suggested to occur by either a concerted pathway or via a diradical intermediate.[5e]

(15) L. L. Miller and R. F. Boyer, *J. Am. Chem. Soc.*, **93**, 650 (1971).

(16) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, fr financial support of this work. We are especially grateful to Professor G. M. Loudon for his assistance in obtaining kinetic data and to Professors David Lemal and M. J. Goldstein for helpful suggestions.

(17) Recipient of a Camille and Henry Dreyfuss Teacher-Scholar Grant, 1973-1978.

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Remarkably Different Structures of Two Metalloporphyrins Containing $M_2O_3{}^{4+}$ Units

Sir:

We wish to report the molecular stereochemistry of two oxometalloporphyrins which, although they possess the same molecular formula, $[O_3M_2(TPP)_2]$,[1] (M = Mo^V, Nb^V), have remarkably different structures. Synthetic methods for the preparation of oxomolybdenum(V) porphyrins were originally reported by Fleischer[2] and subsequently by Buchler and Rohbock.[3] The latter workers also reported oxometalloporphyrin derivatives with niobium(V), tungsten(V), and rhenium(V).[3,4] Niobium(V) porphyrins have also been recently reported by Guilard et al.[5] All workers reported, inter alia, derivatives with empirical formula $O_3M_2P_2$, where P is either OEP[1] or TPP. The structure suggested for these complexes, when a structure was proposed, contains a linear five-atom grouping, O=M—O—M=O, with two terminal M=O groups and a single bridging oxygen. This structure is indeed correct for the molybdenum(V) derivative but is not correct for the niobium(V) derivative

$O_3Nb_2(TPP)_2$ and $O_3Mo_2(TPP)_2$ were prepared following procedures given by Rohbock[6] for the preparation of the analogous OEP complexes. Crystals of $O_3Nb_2(TPP)_2$ were obtained from $CHCl_3$ and $O_3Mo_2(TPP)_2$ from $CHCl_3$-xylene. Crystal data and refinement results are as follows: $Nb_2O_3N_8C_{88}H_{56}\cdot CHCl_3$, monoclinic; a = 10.765 (5), b = 24.913 (6), c = 29.332 (8) Å; and β = 112.30 (2)°; ρ_{calcd} = 1.43, ρ_{obsd} = 1.44 g/cm^3; $Z = 4$; space group Cc; R = 0.063 and R_2 = 0.073;[7] 5748 unique data ($F_o > 3\sigma(F_o)$, $2\theta < 58.7°$); $Mo_2O_3N_8C_{88}H_{56}\cdot(C_8H_{10})\cdot(4CHCl_3)$, monoclinic; a = 18.211 (2), b = 19.309 (3), c = 28.989 (3) Å; β = 115.59 (1)°; ρ_{calcd} = 1.47, ρ_{obsd} = 1.42 g/cm^3; $Z = 4$; space group $C2/c$; R = 0.057 and R_2 = 0.089; 7742 unique data ($F_o > 3\sigma(F_o)$, $2\theta < 54.9°$). Intensity data were collected on a Syntex P$\bar{1}$ diffractometer with graphite-monochromated Mo Kα radiation using ω-scanning. Tables of atomic coordinates are available; see paragraph at end of paper regarding supplementary material.

The molecular stereochemistry and bond parameters of the coordination group of the two complexes are displayed in Figures 1 and 2. Bond parameters of the core are in close agreement with those observed for other porphyrins.[8] As is clearly seen in Figure 1, the two niobium(V) porphyrin moieties are joined together by not just one bridging oxo ligand but by three. Thus, each niobium atom is seven-coordinate. Only one of the bridging oxo ligands forms a nearly symmetric bridge; the other two bridges are quite asymmetric with each niobium closely associated with a different oxygen atom of the pair of asymmetric oxo bridges.[9] The molecular stereochemistry of $O_3Mo_2(TPP)_2$ (Figure 2), however, conforms to the previously suggested structure with two terminal Mo=O groups and a single oxo bridge. Thus, each molybdenum atom is six-coordinate. The molecular stereochemistry of the tungsten(V) and rhenium(V) analogues is probably that of the molybdenum complex.[10]

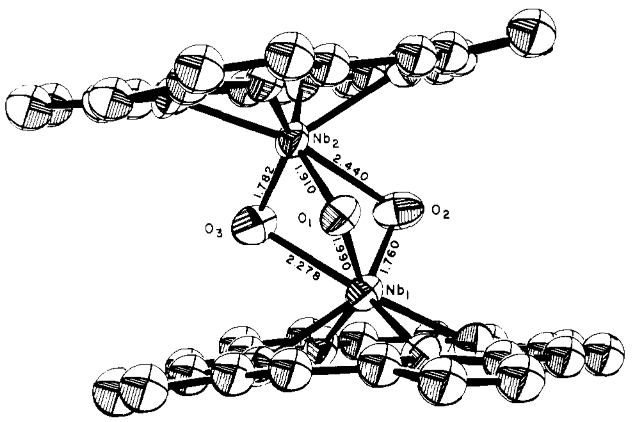

Figure 1. Model in perspective of the $O_3Nb_2(TPP)_2$ molecule. The phenyl rings of the tetraphenylporphinato ligands have been omitted for clarity. The angles at oxygen are $Nb_1O_1Nb_2$ = 94.8 (3)°, $Nb_1O_2Nb_2$ = 84.6 (3)°, and $Nb_1O_3Nb_2$ = 89.2 (3)°.

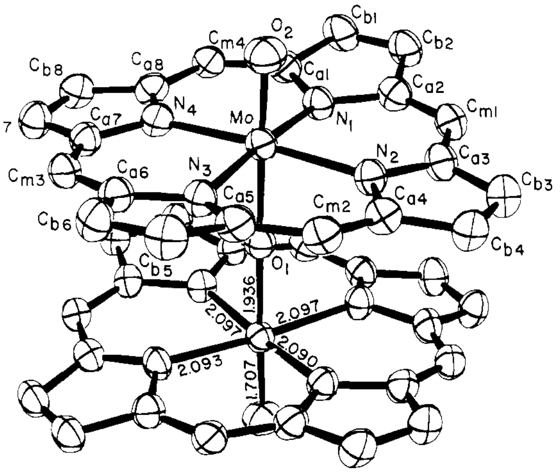

Figure 2. Model in perspective of the $O_3Mo_2(TPP)_2$ molecule. The phenyl rings of the ligand have been omitted for clarity. The crystallographically required twofold axis passes through O_1 approximately parallel to the porphyrin cores. The angles between the twofold axis and the Mo-N_4 and Mo-N_1 vectors are 15 and 75°, respectively. The Mo-O_1-Mo angle is 178.63 (6)° and O_2MoO_1 is 178.2 (2)°.

The average Nb-N distance is 2.246 (21) Å;[11] the average NNbN angle is 78.4°. Each niobium is displaced 1.01 Å out of the mean plane of the porphinato nitrogens. The distance between the two niobium(V) atoms is 2.872 (1) Å. The two porphinato planes are not quite parallel; the dihedral angle between them is 5.2°. The dihedral angles between the oxygen atom plane and porphinato cores are 3.4 and 3.1°. The two porphinato rings have a "slipped" configuration with respect to each other, the angles between the normals to the ring passing through a niobium(V) atom and the Nb-Nb vector are 18 and 21°.

The average Mo-N distance is 2.094 (3) Å and the molybdenum(V) atom is displaced 0.09 Å ot of the mean plane of the porphyrin nitrogens toward the terminal oxo ligand. The terminal Mo=O groups are trans to the Mo-O-Mo bridge, all other complexes containing a $Mo_2O_3{}^{4+}$ unit have the Mo=O terminal groups cis with respect to the Mo—O—Mo bridge.[12] The Mo—O—Mo bridge is essentially linear; the angle is 178.63 (6)°. The Mo=O (terminal) bond distance of 1.707 (3) Å and the Mo—O (bridge) bond distance of 1.936 (3) Å are slightly longer than the corresponding distances observed in the other $Mo_2O_3{}^{4+}$ binuclear complexes.[12] The slight lengthening of the two types of bonds is presumably the result