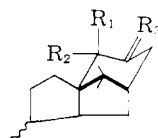


TABLE I

Secondary alcohols	Abundance <sup>a</sup> of ion M	(M-18)
Borneol	0.17	1.47
Isoborneol	0.14	2.41
<i>exo-cis</i> -Bicyclo[3.3.0]octan-2-ol <sup>b</sup>	1.44	3.53
<i>endo-cis</i> -Bicyclo[3.3.0]octan-2-ol <sup>b</sup>	0.36	4.02
Epiandrosterone	4.58	0.53
Androsterone	3.53	0.66
<i>cis-cis</i> -2-Decalol <sup>c</sup>	0.08	8.22
<i>cis-trans</i> -2-Decalol <sup>c</sup>	0.02	10.62
Tertiary alcohols		
Patchouli alcohol (I) <sup>d</sup>	3.46	0.70
Epipatchouli alcohol (II) <sup>d</sup>	0.045	4.52
Oxo-patchouli alcohol (III) <sup>d</sup>	1.55	0.51
Oxo-epipatchouli alcohol (IV) <sup>d</sup>	0.2	0.15
Epimaaliol <sup>e</sup>	0.48	2.74
Maaliol <sup>f</sup>	0.09	3.03
Secondary acetates		
Borneol acetate	0.31	5.08
Isoborneol acetate	0.04	5.94
Epiandrosterone acetate	1.07	4.56
Androsterone acetate	0.29	5.98

<sup>a</sup> % of total ion yield. Spectra taken with a CEC 21-103C mass spectrometer; inlet temp. 140°. <sup>b</sup> A. C. Cope, M. Brown and H. E. Petree, *THIS JOURNAL*, **80**, 2852 (1958). <sup>c</sup> W. G. Dauben and E. Hoerger, *ibid.*, **73**, 1504 (1951). <sup>d</sup> G. Büchi, R. E. Erickson and N. Wakabayashi, to be published. <sup>e</sup> G. Büchi, M. Schach v. Wittenau and D. M. White, *ibid.*, **81**, 1968 (1959).



- I, R<sub>1</sub> = OH, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = H<sub>2</sub>  
 II, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = OH, R<sub>1</sub> = H<sub>2</sub>  
 III, R<sub>1</sub> = OH, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = O  
 IV, R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = OH, R<sub>3</sub> = O

Thus, if the molecular models of epimeric alcohols show an appreciable<sup>1</sup> difference in their steric requirements, the mass spectra should allow the assignment of their stereochemistry.

We are indebted to Professors G. Büchi, A. C. Cope and W. G. Dauben for generous gifts of samples and to the National Science Foundation for financial support (Grant G 5051).

(1) For example, *exo*- and *endo*-norborneol gave inconclusive results.

DEPARTMENT OF CHEMISTRY K. BIEMANN  
 MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
 CAMBRIDGE 39, MASSACHUSETTS J. SEIBL

RECEIVED APRIL 1, 1959

# NIOBUM TETRAIODIDE: ITS STRUCTURE AND NATURE OF BONDING<sup>1</sup>

Sir:

Since the preparation of NbI<sub>4</sub> by Corbett and Seabaugh<sup>2</sup> there has been some question as to whether the tetravalent oxidation state of niobium exists in the solid state. One normally would expect NbI<sub>4</sub> to possess one unpaired electron and

(1) Presented in part before the Division of Physical Chemistry, American Chemical Society Meeting, April 5-10, 1959.

(2) J. Corbett and P. Seabaugh, *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).

hence be paramagnetic if the niobium were indeed tetravalent. Recently Rolsten<sup>3</sup> reported the presumably isomorphous TaI<sub>4</sub> to be diamagnetic. Rolsten speculated that the unpaired electron must be paired by the formation of a dimer, or else TaI<sub>4</sub> may exist in the solid state as Ta<sup>+3</sup>Ta<sup>+3</sup>I<sub>8</sub>. We wish to report the preliminary results of the structural determination of NbI<sub>4</sub> by X-ray diffraction and strong evidence of metal-metal interaction which will readily explain its diamagnetism as well as that of TaI<sub>4</sub>.

Single crystals of NbI<sub>4</sub> were generously furnished to us by Corbett and Seabaugh. Since the compound is extremely sensitive to water and oxygen the crystals were isolated in glass capillaries which were first evacuated and then hermetically sealed. Three dimensional X-ray data were taken with both Weissenberg and precession cameras utilizing MoK $\alpha$  radiation. The crystals are orthorhombic with space group Cmc2<sub>1</sub> and lattice constants  $a = 7.67$  Å,  $b = 13.28$  Å, and  $c = 13.93$  Å. There are eight NbI<sub>4</sub> species per unit cell.

Patterson and Fourier projections of the three principal zones gave the essential features of the structure. A least squares refinement of the observed reflections resulted in values of  $R = \Sigma |F_o| - F_c| / \Sigma |F_o| < 0.14$  for each zone.

The structure consists of infinite chains parallel to the "a" axis formed by NbI<sub>6</sub> octahedra sharing two opposite edges. The niobium atoms are shifted from the centers of the octahedra of iodine atoms, which are 3.83 Å apart, toward each other in pairs such that the distance between the paired niobium atoms is 3.2 Å. The only reasonable explanation for this shift involves a metal-metal interaction in which the unpaired electrons are coupled by exchange forming a weak metal-metal bond. It should be noted that NbI<sub>4</sub> was first reported to be paramagnetic; in view of our structural results a redetermination of the magnetic moment by Corbett and Seabaugh<sup>4</sup> revealed NbI<sub>4</sub> to be diamagnetic at room temperature. This compound represents the first known structure of its configuration which possesses metal-metal interactions.

A qualitative interpretation of the nature of bonding about each niobium atom can be given in terms of simple molecular orbital theory based on octahedral symmetry. The d<sub>22</sub> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub> metal orbitals plus the one 5s and three 5p metal orbitals interact with the corresponding symmetry orbitals of the iodides to give bonding  $\sigma$ -type molecular orbitals. The unshared electron for each niobium can be placed in the d<sub>xy</sub> orbital; the metal-metal bond for two paired niobiums is thus accomplished by the overlap of these two neighboring orbitals which are directed toward each other (*i.e.*, the  $x$  and  $y$  axes are along the shared iodide directions). The unoccupied d<sub>xz</sub> and d<sub>yz</sub> orbitals of each niobium no doubt are utilized in  $\pi$ -bonding with the filled  $\pi$ -type symmetry orbitals of the iodides.

Since the diamagnetism of TaI<sub>4</sub> can be explained easily by a similar structure, and especially since X-ray data on TaI<sub>5</sub><sup>3</sup> indicate its structure to be directly related to that of NbI<sub>5</sub><sup>5</sup> (*i.e.*, the lattice con-

(3) R. Rolsten, *THIS JOURNAL*, **80**, 2952 (1958).

(4) J. Corbett and P. Seabaugh, private communication.

(5) L. Dahl and N. Nelson, to be published.

stants are  $a = 6.65$  and  $6.54$ ,  $b = 13.95$  and  $14.01$ , and  $c = 20.10$  and  $40.36$  Å. for  $\text{TaI}_5$  and  $\text{NbI}_5$ , respectively), an attempt was made to index the powder lines given for  $\text{TaI}_4$  by Rolsten<sup>3</sup> assuming isomorphism of the two compounds. Structure factors and "d" spacings were calculated for all the possible reflections, and we were able to correlate most of the "d" values listed for  $\text{TaI}_4$ . We feel that the structures of the two compounds are similar at least with regard to the local configuration about the metal atoms.

We are indebted to the Numerical Analysis Laboratory of the University of Wisconsin for the use of their IBM 650 computer. We also wish to acknowledge the use of the facilities of the Ames Laboratory of the U. S. Atomic Energy Commission.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON 6, WISCONSIN

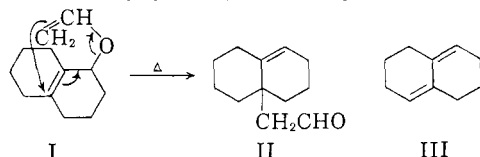
LAWRENCE F. DAHL  
DALE L. WAMPLER

RECEIVED APRIL 6, 1959

#### STEREOSPECIFIC INTRODUCTION OF ANGULAR SUBSTITUENTS BY THE CLAISEN REARRANGEMENT

Sir:

By virtue of its intramolecular character, the Claisen rearrangement of vinyl allyl ethers appeared to us to offer the possibility of being a potentially useful method for the stereospecific introduction of an angular group into suitably constituted fused polycyclic systems, *e.g.*



Although elimination is reported to be a strongly competing side reaction in the related rearrangement of phenyl ethers of substituted allyl alcohols,<sup>1</sup> we have found that, with highly purified vinyl ethers, the major course of the reaction is the desired formation of the corresponding allylacetals.

The vinyl ether I (b.p.  $52-53^\circ$  (0.08 mm.); found: C, 80.88; H, 10.38) was prepared from  $\Delta^9,10$ -octalol-1 by the transesterification procedure of Watanabe and Conlon<sup>2</sup> and purified by passage through basic alumina with petroleum ether (yield 41%). On being heated in a sealed tube at  $195^\circ$  for 2 hr. it furnished an 80% yield of  $\Delta^4(10)$ -9-octylaldehyde (II), b.p.  $60-61^\circ$  (0.08 mm.), assayed by the 2,4-dinitrophenylhydrazone, m.p.  $118-121^\circ$  (Found: C, 60.88; H, 6.43; N, 15.63). Hydrogenation of II on palladium-charcoal, and then oxidation of the resulting saturated aldehyde, afforded the known<sup>3</sup> *cis*-9-decalylacetic acid, m.p.  $114-115^\circ$ , which was further identified by degradation<sup>3</sup> to *cis*-9-decalincarboxylic acid, m.p.  $121-122^\circ$ .<sup>3,4</sup> Only minor amounts of dienic elimination

(1) See D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 14-15.

(2) W. H. Watanabe and L. E. Conlon, *THIS JOURNAL*, **79**, 2828 (1957).

(3) R. D. Haworth and A. F. Turner, *J. Chem. Soc.*, 1240 (1958).

(4) W. G. Dauben and J. B. Rogan, *THIS JOURNAL*, **79**, 5002 (1957). We are deeply grateful to Professor Dauben for a comparison sample of this acid.

material, *e.g.*, III,<sup>5</sup> could be detected in the rearrangement product II.

Similarly, the vinyl ether of 4-cholesten-3 $\beta$ -ol was obtained in 54% yield; m.p.  $56-57^\circ$ ,  $[\alpha]^{25}_D +11^\circ$  ( $\text{CHCl}_3$ ) (Found: C, 84.61; H, 11.90). This on rearrangement in decalin at  $195-200^\circ$  for 4 hr. gave directly an 83% yield of  $\Delta^3$ -5 $\beta$ -cholestenylacetaldehyde, m.p.  $66-69^\circ$ ,  $[\alpha]^{25}_D +85^\circ$  ( $\text{CHCl}_3$ ) (Found: C, 84.55; H, 11.71). Catalytic reduction converted the latter to 5 $\beta$ -cholestanylacetaldehyde (m.p.  $58-61^\circ$ ,  $[\alpha]^{25}_D +42^\circ$  ( $\text{CHCl}_3$ ); found: C, 84.10; H, 12.16), which was further transformed (via ethylene thioacetal formation and desulfurization with Raney nickel) into 5 $\beta$ -ethylcholethane, m.p.  $67-69^\circ$ ,  $[\alpha]^{25}_D +18^\circ$  ( $\text{CHCl}_3$ ) (Found: C, 87.17; H, 12.87).

In model experiments, the vinyl ethers of  $\Delta^2$ -cyclohexenol and 3-methyl- $\Delta^2$ -cyclohexenol were found to give the corresponding cyclohexenylacetaldehydes in 95 and 93% yields, respectively. Oxidation of these products with silver oxide, and iodolactonization<sup>6</sup> of the resulting unsaturated acids, demonstrated the assigned structures.

Further extensions of this work are in progress. The award of a Frederick Gardner Cottrell Grant from Research Corporation supporting the initial phases of this study and a current grant from the General Research Fund of the University of Kansas are gratefully acknowledged.

(5) W. Hückel and U. Wörfel, *Ber.*, **89**, 2098 (1956).

(6) E. E. van Tamelen and M. Shamma, *THIS JOURNAL*, **76**, 2315 (1954).

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF KANSAS  
LAWRENCE, KANSAS

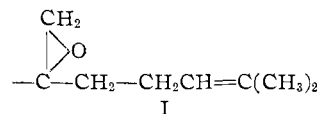
ALBERT W. BURGSTAHLER  
IVAN C. NORDIN

RECEIVED APRIL 27, 1959

#### THE NATURE OF THE SIDE CHAIN IN FUMAGILLIN<sup>1</sup>

Sir:

Alcohol-I,  $\text{C}_{16}\text{H}_{26}\text{O}_4$ , obtained<sup>2-5</sup> from the antibiotic fumagillin by hydrolysis, is now shown to contain the side chain I by chemical transformations and by n.m.r. spectral considerations.



Previous work has established the presence of the isopropylidene group,<sup>3</sup> and isocaproic acid has been isolated after oxidation of various transformation products of alcohol-I.<sup>4,6</sup> Tetrahydroalcohol-I ab,<sup>4</sup> in which the double bond and epoxide have been reduced,<sup>7</sup> formed a crystalline monoacetate,<sup>8</sup>  $\text{C}_{18}$ -

(1) Aided by a grant from the National Institutes of Health.

(2) J. R. Schenck, M. P. Hargie, D. S. Tarbell and P. Hoffman, *THIS JOURNAL*, **75**, 2274 (1953).

(3) J. R. Schenck, M. P. Hargie and A. Isarasena, *ibid.*, **77**, 5606 (1955).

(4) D. S. Tarbell, P. Hoffman, H. R. Al-Kazimi, G. A. Page, J. M. Ross, H. R. Vogt and B. Wargotz, *ibid.*, **77**, 5610 (1955).

(5) J. K. Landquist, *J. Chem. Soc.*, 4237 (1956).

(6) D. D. Chapman and D. S. Tarbell, *THIS JOURNAL*, **80**, 3679 (1958).

(7) J. M. Ross, D. S. Tarbell, W. E. Lovett and A. D. Cross, *ibid.*, **78**, 4675 (1956).

(8) Microanalyses and infrared absorption on new compounds were in agreement with the empirical formulas and structures.