

stants are $a = 6.65$ and 6.54 , $b = 13.95$ and 14.01 , and $c = 20.10$ and 40.36 Å. for TaI_5 and NbI_5 , respectively), an attempt was made to index the powder lines given for TaI_4 by Rolsten³ 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 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

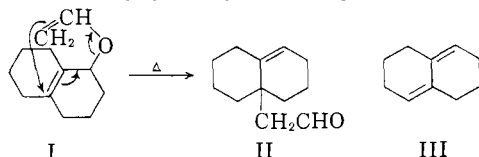
LAWRENCE F. DAHL
DALE L. WAMPLER

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,¹ we have found that, with highly purified vinyl ethers, the major course of the reaction is the desired formation of the corresponding allyl aldehydes.

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 Conlon² and purified by passage through basic alumina with petroleum ether (yield 41%). On being heated in a sealed tube at 195° for 2 hr. it furnished an 80% yield of $\Delta^4(10)$ -9-octalylaldehyde (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 known³ *cis*-9-decalylacetic acid, m.p. $114-115^\circ$, which was further identified by degradation³ to *cis*-9-decalincarboxylic acid, m.p. $121-122^\circ$.^{3,4} 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,⁵ could be detected in the rearrangement product II.

Similarly, the vinyl ether of 4-cholesten-3 β -ol was obtained in 54% yield; m.p. $56-57^\circ$, $[\alpha]^{25D} +11^\circ$ ($CHCl_3$) (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 Δ^3 -5 β -cholestenylaldehyde, m.p. $66-69^\circ$, $[\alpha]^{25D} +85^\circ$ ($CHCl_3$) (Found: C, 84.55; H, 11.71). Catalytic reduction converted the latter to 5 β -cholestanylaldehyde (m.p. $58-61^\circ$, $[\alpha]^{25D} +42^\circ$ ($CHCl_3$); found: C, 84.10; H, 12.16), which was further transformed (via ethylene thioacetal formation and desulfurization with Raney nickel) into 5 β -ethylcholestane, m.p. $67-69^\circ$, $[\alpha]^{25D} +18^\circ$ ($CHCl_3$) (Found: C, 87.17; H, 12.87).

In model experiments, the vinyl ethers of Δ^2 -cyclohexenol and 3-methyl- Δ^2 -cyclohexenol were found to give the corresponding cyclohexenylaldehydes in 95 and 93% yields, respectively. Oxidation of these products with silver oxide, and iodolactonization⁶ 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. Hüchel and U. Wörffel, *Ber.*, **89**, 2098 (1956).

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

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UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

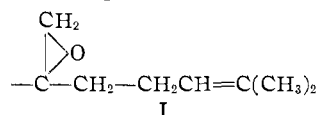
ALBERT W. BURGSTÄHLER
IVAN C. NORDIN

RECEIVED APRIL 27, 1959

THE NATURE OF THE SIDE CHAIN IN FUMAGILLIN¹

Sir:

Alcohol-I, $C_{16}H_{26}O_4$, obtained²⁻⁵ 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,³ and isocaproic acid has been isolated after oxidation of various transformation products of alcohol-I.^{4,6} Tetrahydroalcohol-I ab,⁴ in which the double bond and epoxide have been reduced,⁷ formed a crystalline monoacetate,⁸ 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.