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 Rolsten[3] 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.

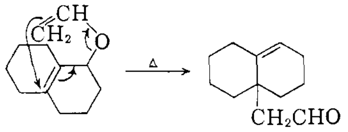
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN
LAWRENCE F. DAHL
DALE L. WAMPLER

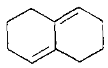
RECEIVED APRIL 6, 1959

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.*





I II III

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 allylacetaldehydes.

The vinyl ether I (b.p. 52–53° (0.08 mm.); found: C, 80.88; H, 10.38) was prepared from $\Delta^{9,10}$-octalol-1 by the transetherification procedure of Watanabe and Conlon[2] 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-octalylacetaldehyde (II), b.p. 60–61° (0.08 mm.), assayed by the 2,4-dinitrophenylhydrazone, m.p. 118–121° (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[3] *cis*-9-decalylacetic acid, m.p. 114–115°, which was further identified by degradation[3] to *cis*-9-decalincarboxylic acid, m.p. 121–122°.[3,4] Only minor amounts of dienic elimination material, *e.g.*, III,[5] could be detected in the rearrangement product II.

Similarly, the vinyl ether of 4-cholesten-3β-ol was obtained in 54% yield; m.p. 56–57°, $[\alpha]^{25}D$ +11° ($CHCl_3$) (Found: C, 84.61; H, 11.90). This on rearrangement in decalin at 195–200° for 4 hr. gave directly an 83% yield of Δ^3-5β-cholestenylacetaldehyde, m.p. 66–69°, $[\alpha]^{25}D$ +85° ($CHCl_3$) (Found: C, 84.55; H, 11.71). Catalytic reduction converted the latter to 5β-cholestanylacetaldehyde (m.p. 58–61°, $[\alpha]^{25}D$ +42° ($CHCl_3$); found: C, 84.10; H, 12.16), which was further transformed (via ethylene thioacetal formation and desulfurization with Raney nickel) into 5β-ethylcholestane, m.p. 67–69°, $[\alpha]^{25}D$ +18° ($CHCl_3$) (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 cyclohexenylacetaldehydes in 95 and 93% yields, respectively. Oxidation of these products with silver oxide, and iodolactonization[6] 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.

---

[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.

[5] W. Hückel and U. Wörffel, *Ber.*, **89**, 2098 (1956).

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

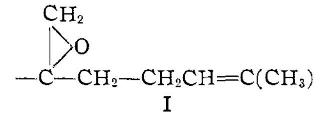
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS
ALBERT W. BURGSTAHLER
IVAN C. NORDIN

RECEIVED APRIL 27, 1959

THE NATURE OF THE SIDE CHAIN IN FUMAGILLIN[1]

Sir:

Alcohol-I, $C_{16}H_{26}O_4$, obtained[2–5] 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.



$$-C-CH_2-CH_2CH{=}C(CH_3)_2$$

I

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).

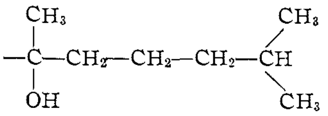
[5] J. K. Landquist, *J. Chem. Soc.*, 4237 (1956).

[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.

$H_{32}O_5$, m.p. 59.5–60.5°. The tertiary hydroxyl was eliminated by thionyl chloride–pyridine, to yield a mixture of unsaturated compounds, separated by chromatography on alumina. The major product, anhydrotetrahydroalcohol-I ab acetate A ("anhydro-A"), $C_{18}H_{30}O_4$, contained a trisubstituted double bond (813 cm.$^{-1}$) which when hydroxylated with osmium tetroxide (LAH workup of osmate ester) yielded a viscous triol, $C_{16}H_{30}O_5$. This afforded isocapraldehyde on cleavage with sodium periodate. The isomeric dehydration product, "anhydro-B," showed terminal methylene absorption (1640, 895 cm.$^{-1}$) and yielded formaldehyde (methone derivative) upon ozonization. This evidence indicates that the side chain in tetrahydroalcohol-I ab is II.



II

The possibility of rearrangement during dehydration of tetrahydroalcohol-I ab acetate was ruled out by treating anhydro-A and anhydro-B with monoperphthalic acid and reducing each epoxide with LAH; both isomeric epoxides yielded crystalline tetrahydroalcohol-I ab as the main product. The compound obtained from the epoxidation of anhydro-B (terminally unsaturated) was identical (based on rotation and infrared) with the acetate of dihydroalcohol-Ia (side chain double bond reduced), demonstrating the correctness of I for the side chain of alcohol-I.

The n.m.r. spectra of alcohol-I and some derivatives support these conclusions. Alcohol-I shows a doublet centered at 7.65 τ[9] assigned to the epoxide protons, whereas tetrahydroalcohol-I ab lacks this doublet and exhibits a new peak at 8.65 τ due to a methyl group attached to a carbon atom also bearing an oxygen atom.

Anhydro-A shows a peak at 8.30 τ characteristic of an allylic methyl group. This peak is not present in tetrahydroalcohol-I ab.

---

(9) G. Van Dyke Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(10) To whom inquiries should be addressed.

(11) Abbott Laboratories Fellow, 1957–1958.

(12) Abbott Laboratories Fellow, 1958–1959.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, N. Y.

R. M. CARMAN
D. D. CHAPMAN
N. J. MCCORKINDALE
D. S. TARBELL[10]
F. H. L. VARINO[11]
R. L. WEST[12]
D. J. WILSON

RECEIVED MAY 4, 1959

THE PROTON AFFINITY OF BENZENE

Sir:

The proton affinity of benzene long has been a matter of interest due to the importance of the $C_6H_7^+$ ion and its homologs in electrophilic aromatic substitution reactions. The $C_6H_7^+$ ion is prominent in the mass spectrum of both 1,3-cyclohexadiene and 5-methyl-1,3-cyclohexadiene; consequently the appearance potentials of $C_6H_7^+$ ion from these compounds have been determined and the proton affinity of benzene calculated from these results.

Measurements with 1,3-cyclohexadiene were made with a 180° direction focusing mass spectrometer (Consolidated Electrodynamics Corporation, Model 21-103C). The mass 84 krypton isotope was employed as a standard, equalizing the partial pressures of the gases so that the intensities of the peaks of interest (79 and 84) agreed within 10% at 70 v. electron energy. Ionizing voltage was reduced in steps and the portion of the spectrum of interest scanned after each step. Near onset the size of the steps was reduced to 0.05 v. Several years ago a single determination of Ap($C_6H_7^+$) from a sample of 5-methyl-1,3-cyclohexadiene, of unknown purity, was made employing a 90° direction focusing instrument with a sector magnet (Westinghouse Type LV), the same calibrating gas and identical methods of measurement. The 1,3-cyclohexadiene was obtained from Farchan Research Laboratory and had a purity of about 96%; this was entirely satisfactory, the maximum possible contribution from any conceivable impurity being only 0.2%.

In three replicate determinations Ap($C_6H_7^+$) from 1,3-cyclohexadiene was found to be 11.32 ± 0.05 e.v. Several measurements using such diverse calibrating gases as propane and ethylbenzene confirmed these results within 0.2–0.3 e.v. Previously we had found Ap($C_6H_7^+$) from 5-methyl 1,3-cyclohexadiene to be 10.6 e.v. The confirmation of our recent measurements by the older one is striking; assuming the neutral fragments to be H and CH_3, respectively, we obtain values for $\Delta H_f(C_6H_7^+)$ of 235 and 233 kcal./mole. The heats of formation of 1,3-cyclohexadiene and 5-methyl-1,3-cyclohexadiene were obtained by assumption of the equality of heats of hydrogenation of the cyclodiolefins and combination of the heat of hydrogenation of 1,3-cyclohexadiene[1] with heats of formation of cyclohexane and methylcyclohexane.[2]

Taking 235 kcal./mole as the most reliable value of $\Delta H_f(C_6H_7^+)$, 20 kcal./mole for $\Delta H_f(C_6H_6^+)$,[2] and 365 kcal./mole for $\Delta H_f(H^+g)$,[3] we obtain a value for the proton affinity of benzene of 150 kcal./mole.

Barker, Williams, and Hamill[4] have reported the formation of $C_6H_7^+$ by the ion molecule reaction $C_4H_6^+ + C_4H_6 \rightarrow C_6H_7^+ + C_2H_5$. Such reactions are not endothermic. Assuming zero heat of reaction and assuming $C_6H_7^+$ to be cyclic, we calculate the lower limit of the proton affinity of benzene to be 145 kcal./mole. In this same connection their observation of the formation of the ion $C_7H_9^+$, *viz.*, $C_4H_6^+ + C_4H_4 \rightarrow C_7H_9^+ + CH_3$, permits calculation of a lower limit for the proton affinity of toluene of 143 kcal./mole. Equivalently this

---

(1) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **58**, 146 (1936).

(2) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, Pittsburgh, Pa., 1953.

(3) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

(4) R. Barker, R. R. Williams, Jr., and W. H. Hamill, paper presented at meeting of A.S.T.M. Committee E-14 on Mass Spectrometry, New Orleans, Louisiana, June 2–6, 1958.