give successively crystals of radioactivity 268, 226, 225, and 226 counts/(min mg).

The enzymic formation of 29,30-bisnoramyrin (**4**) from 29,30-bisnor-2,3-oxidosqualene (**3**) is remarkable for a number of reasons. The cyclization which generates ring E, presumably involving **6** → **7** → **8**, or **6** → **9** (or their covalently coordinated cation equivalents),[11] proceeds regardless of whether R is methyl or hydrogen.[12] If **7** is an intermediate (as proposed for the biosynthesis of β-amyrin[11b]) a *primary* cation or its equivalent must be involved. On the other hand, if the E ring is formed *via* process **6** → **9** (as proposed for the biosynthesis of α-amyrin[11b]), then further conversion of **9** to **4** must involve a change in at least one of the groups (H instead of CH_3) undergoing migration to generate the amyrin system enzymically.[13] It should be possible to distinguish between these interesting alternatives experimentally, and such tests are planned. The study of substrate **3** with cyclase that produces *exclusively* α- or β-amyrin is also of interest, as is the extension to other enzymic systems such as lupeol or taraxerol cyclases.

The capacity of enzymes which normally produce pentacylic triterpenes from 2,3-oxidosqualene to handle other substrates raises the question as to the limits of enzyme specificity with regard to changes in substrate structure as well as other intriguing questions and opportunities for new research.[14]

(11) (a) L. Ruzicka, A. Eschenmoser, and H. Heusser, *Experientia*, **9**, 357 (1953); (b) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955).

(12) Since both α- and β-amyrins are formed in *Pisum sativum* (the latter in larger amount), both α- and β-cyclases may be present in the soluble enzyme preparation used in the above work. Clearly either might effect the conversion of **3** to **4**, and intermediates of type **8** and **9** are equally plausible at this time.

(13) As has been pointed out previously,[10,11b] the appropriate sequence of 1,2-*cis* migrations from cations **7** or **9** leads to the correct stereochemistry of α- and β-amyrins.

(14) This work was supported by the National Science Foundation and the National Institutes of Health.

(15) Radcliffe Institute Scholar, 1966–1968.

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Structure of the $C_2H_5O^+$ Ion in the Mass Spectra of 2-Alkanols

Sir:

From deuterium labeling and energetics studies of fragmentation reaction 1 in 2-alkanols, Van Raalte and Harrison[1] suggested that the $C_2H_5O^+$ ions fragmenting

$$C_2H_5O^+ \longrightarrow H_3O^+ + C_2H_2 \qquad (1)$$

had the protonated ethylene oxide structure I rather than the expected structure II. Support for this proposal has been advanced by Shannon and McLafferty[2] who studied the metastable peaks observed at *m/e* 8.02 and 18.7 for reactions 1 and 2, respectively. They

$$C_2H_5O^+ \longrightarrow HCO^+ + CH_4 \qquad (2)$$

found the ratio of intensities *m/e* 8.02:*m/e* 18.7 to be constant for $C_2H_5O^+$ ions derived from 2-alkanols ($CH_3CH(OH)Y$), ethoxy derivatives (CH_3CH_2OY), and β-substituted ethanols ($HOCH_2CH_2Y$). On a structural basis one might expect the $C_2H_5O^+$ ions from the three classes to have structures II, III, and IV, respectively. They also observed that the metastable peak at *m/e* 18.7 was "flat-topped" in all cases, with the energy release identical within experimental error. To explain their results they proposed that the $C_2H_5O^+$ ions derived from the three classes of compounds had undergone rearrangement to a common intermediate, probably I, prior to fragmentation.

In an attempt to obtain definitive evidence concerning the structure of the $C_2H_5O^+$ ion derived from 2-alkanols we have examined the mass spectrum of 2-propanol-2-^{13}C.[3] Mass spectra were obtained at high resolution (~15,000) using an AEI MS-902 mass spectrometer. Table I records the ion current ratios for the ^{13}C-labeled ionic species and the corresponding unlabeled ion for the molecule ion, the $C_2H_5O^+$ ion, and the HCO^+ ion at 70-eV ionizing electron energy.

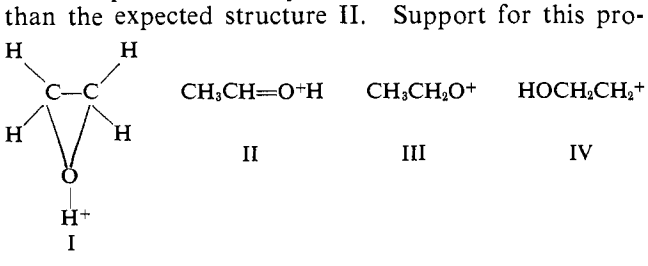
Table I. Relative Intensities at 70 eV

Ion ratio	Ratio of intensities
$^{13}CC_2H_5O^+ : C_3H_5O^+$	0.186
$^{13}CCH_5O^+ : C_2H_5O^+$	0.175
$^{13}CHO^+ : CHO^+$	0.118

The lower ^{13}C content of the $C_2H_5O^+$ is in good agreement with that expected for loss of a CH_3 group with natural ^{13}C abundance. The ^{13}C content of the CHO^+ ion was studied as a function of electron energy and found to decrease to $^{13}CHO^+ : CHO^+ = 0.108$ in the 30–20-eV region and then remain constant to 12 eV (all energies nominal values), the lowest energy at which significant intensities could be observed.[4]

The 70-eV data lead to 74% ^{13}C retention in the CHO^+ ion derived from $^{13}CCH_5O^+$, while the low-energy data lead to 68% ^{13}C retention. Neither value agrees with that predicted for the fragmentation of structure I or structure II alone. Fragmentation from the symmetrical structure I should lead to 50% ^{13}C retention, while fragmentation from structure II should lead to 100% ^{13}C retention.

In contrast to the ratio $^{13}CHO^+ : CHO^+ = 2.84$ at 70 eV for fragmentation reactions 3 and 4, the "metastable" intensities observed for fragmentations occurring in the



I

$CH_3CH{=}O^+H$ II

$CH_3CH_2O^+$ III

$HOCH_2CH_2^+$ IV

(1) D. Van Raalte and A. G. Harrison, *Can. J. Chem.*, **41**, 3118 (1963).

(2) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966).

(3) Prepared by the $LiAlH_4$ reduction of acetone-2-^{13}C with final purification by gas chromatography.

(4) The fragmentation pathway $(CH_3)_2CHOH^+ \rightarrow (CH_3)_2C{=}OH^+ + H \rightarrow C_2H_4 + CH_2OH^- \rightarrow CHO^- + H_2$ can also lead to formation of CHO^+. The CH_2OH^+ intensity in 2-propanol is quite low and by comparison with the high-resolution spectrum of *t*-butyl alcohol, which fragments by a similar mechanism, we estimate that at 70 eV only 7% of the CHO^+ ion would originate by the above mechanism. Since the ^{13}C retention in CH_2OH^+ ($^{13}CH_2OH^+ : CH_2OH^+ = 0.107$) is similar to that observed for CHO^+, this contribution does not alter the interpretation of the results. Further, the onset potential for formation of CHO^+ by the above route should be more than 2 eV higher than formation of CHO^+ through reaction 2 and therefore should make a negligible contribution at low energies.

$$^{13}CCH_5O^+ \longrightarrow {}^{13}CHO^+ + CH_4 \quad (3)$$

$$^{13}CCH_5O^+ \longrightarrow CHO^+ + {}^{13}CH_4 \quad (4)$$

first drift region[5] were found to be in the ratio m^*_3: $m^*_4 = 1.06$.[6] This ratio is not significantly different from unity and indicates that the fragmentation reaction responsible for the metastable peaks proceeds from an intermediate in which the carbons have become equivalent. In agreement with Shannon and McLafferty, we consider that the most logical structure for this intermediate is I. To explain the over-all ^{13}C retention one must postulate that CHO^+ is formed by a second fragmentation reaction which does not exhibit a metastable transition and proceeds with much higher ^{13}C retention. We propose that this route is the direct fragmentation from structure II leading to 100% ^{13}C retention. Simple calculations show that the data can be explained if at 70 eV 52% of the $C_2H_5O^+$ ions fragment from structure I and 48% from structure II, while at low energy 64% fragment from structure I and 36% from structure II.

(5) K. R. Jennings, *J. Chem. Phys.*, **43**, 4176 (1965).
(6) The metastable peaks observed for fragmentations in the second drift region also were in an appoximate 1:1 ratio; however, this ratio could not be determined accurately owing to overlap of the "flat-topped" metastables for m/e $45^+ \rightarrow 29^+$ and m/e $46^+ \rightarrow 29^-$.

It should be noted that the above conclusions refer only to those ions with sufficient internal energy to fragment by reaction 2. The appearance potentials of $C_2H_5O^+$ ions from 2-alkanols lead to $\Delta H_f(C_2H_5O^+) = 145$ kcal/mol.[7] If this is assumed to refer to structure I, the proton affinity of ethylene oxide is calculated to be ~208 kcal/mol, a value which appears much too high when compared to PA (CH_3OH) ≈ 170 kcal/mol.[8] Assumption of structure II leads to the reasonable value PA (CH_3CHO) ≈ 180 kcal/mol. We therefore suggest that the $C_2H_5O^+$ ions from 2-alkanols have structure II at the threshold and that rearrangement to the symmetrical structure occurs only for ions with internal excitation.

Acknowledgment. The authors gratefully acknowledge the financial support of the National Research Council of Canada.

(7) A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966).
(8) M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964).
(9) Holder of a Province of Ontario Graduate Fellowship, 1967–1968.

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Book Reviews

Aromatic Amine Oxides. By EIJI OCHIAI, Emeritus Professor of Pharmaceutical Chemistry, University of Tokyo (Japan). Translated by DOROTHY U. MIZOGUCHI, Chemotherapy Information Center, Cancer Institute, Tokyo, Japan. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1967. ix + 456 pp. 16.5 × 23 cm. $30.00.

The year 1940 represents the turning point in the interest and research dealing with aromatic amine oxides. In that year Linton reported an unexpectedly low dipole moment for pyridine N-oxide which suggested structural contributions from canonical forms that required electron release by the N–O oxygen. This paper immediately attracted Ochiai's attention. He recognized the potential for electrophilic substitution and other reactions and over the next two and one-half decades contributed a massive amount of research on aromatic amine oxides. Other workers entered the field in the late 1940's and subsequent years and are continuing to expand and develop the chemistry of aromatic amine oxides.

Thus it is quite fitting that Professor Ochiai should write the most extensive review in the "Aromatic Amine Oxides," a further mark of his contributions to this growing field of chemistry. The book is well organized and reflects Ochiai's mastery of the subject. After an interesting introductory chapter and a quick survey of the field, Ochiai discusses in depth the methods for the preparation of aromatic amine oxides and the various physico-chemical properties characterizing this class of compounds. The latter chapter gives extensive tables listing dipole moments, reduction potentials, dissociation constants, nmr chemical shifts, infrared frequencies, and uv absorption spectral data for numerous aromatic amine oxides and their derivatives. The discussion of chemical properties follows next and covers in considerable detail the deoxygenation of the N-oxides (Chapter V), electrophilic substitution, particularly nitration (Chapter VI), and the nucleophilic substitution reactions with organometallics, reactive halides, and acid anhydrides (Chapter VII). Chapter VIII clarifies the influence of the amine oxide function on other substituents on the heterocyclic ring located *ortho* or *para* to the N-oxide grouping. In addition this chapter contains other topics such as rearrangements which are not suitable for treatment under the other chapter headings. The concluding chapter describes the biological properties of aromatic amine oxides. Although there is some overlap of material in a few of the chapters, this does not detract in any way from the book.

The book is well documented and covers the literature thoroughly up to the beginning of 1964. Much of the early work on aromatic N-oxides was published in the Japanese language; these reports are thoroughly reviewed in this book. One interesting feature of the book is the insertion of experimental procedures at the conclusion of most sections, describing representative examples of reactions just discussed. All but two of these experimental procedures were taken from the Japanese literature or private communications, thus making available in the English language information previously difficult to obtain.

One of the problems of writing in a field of active, current interest is the rapidity with which new knowledge is reported in the literature. Thus the extensive work on the mechanistic aspects of the reaction of aromatic amine oxides with acylating agents, discovery of new oxidative reactions, information on rearrangement reactions, new reports in the growing field of photochemical processes, and other developments reported since 1964 were not available for inclusion in this book. Although this information gap exists, the book provides a solid foundation in the preparation, properties, and reactions of aromatic amine oxides. Mechanistic interpretations are presented for numerous reactions but play a secondary role in the book.

This reviewer recommends the "Aromatic Amine Oxides" to all organic chemists who have an interest in this class of compounds. The extensive factual information presented in this work will provide the base for frequent use as a reference source.

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