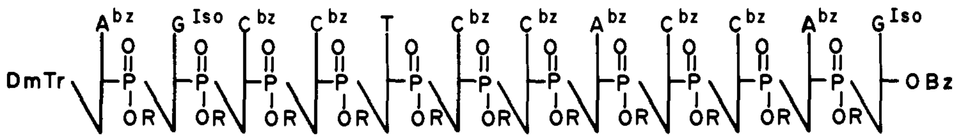

Figure 1. Abbreviated structural formula of the fully protected dodecanucleotide used in this study. Vertical lines represent the deoxyribose units. Horizontal lines represent 3′-ester linkages and slanted lines represent the 5′-ester linkages. Standard symbols are used to indicate the bases and protecting groups, R = *p*-chlorophenyl.

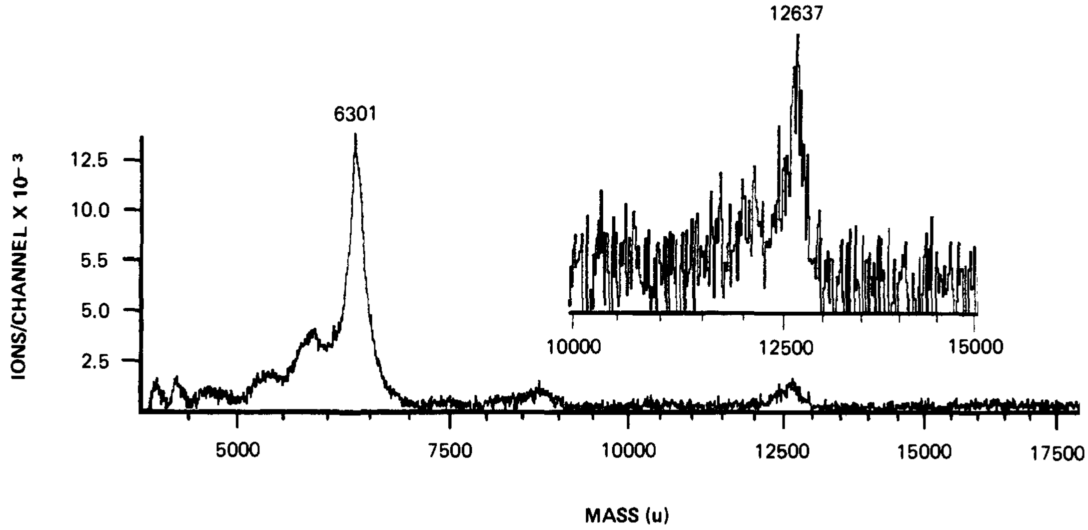

Figure 2. ^{252}Cf-PDMS positive ion spectrum of a fully protected dodecanucleotide above 4000 u. The dimer ion region is shown in more detail in the inset.

Figure 2. A peak of good intensity was observed at *m*/*z* 6301 ± 3 which is a molecular ion adduct of the form $(M + Na)^+$. This species of ions has been observed previously with the lower order oligonucleotides and the identity verified by substituting a different alkali metal ion (Cs^+) in the matrix.[3] On the basis of the known structure of this molecule, the elemental composition of this ion is $C_{279}H_{249}O_{82}N_{45}P_{11}Cl_{11}Na$ which gives an isotopically averaged mass of 6297.9 u. Within the limits of our error, the experimental result is in agreement with this value. This is the largest monomer ion that has been reported in the mass spectral literature. Negative ions were also observed at m/z 6277 ± 3 which are believed to be $M^{-\cdot}$ and/or $(M - H)^-$.

The lower order fully protected nucleotides in this series have been observed to produce oligomer ions extending to the tetramer producing ions primarily of the type $(2M + Na)^+$ and $(2M + 2Na - H)^+$, although additional species containing more sodium atoms were also present. Anticipating that this molecule might also form a dimer ion which would have a molecular weight in excess of 12 000 u, we extended the normal irradiation time a factor of 10 to obtain better statistics in the mass range above the monomer. This was made possible by a property of ^{252}Cf-PDMS, that the sample utilization is so small that repetitive scans can be made for many hours or days, if necessary, without sample degradation, in order to resolve weak ion peaks from the background by signal averaging. Figure 2 shows the spectrum obtained after an irradiation period of 13.9 h involving 100 million mass scans (or fission fragment–sample interactions). The monomer ion peak is clearly apparent at *m*/*z* 6301 but, in addition, two weak peaks at *m*/*z* 8709 ± 8 and *m*/*z* 1263 ± 10 were also observed. A statistical analysis of the region using a computerized digital filter technique[9] showed that both peaks were statistically significant. No peaks were detected above *m*/*z* 13 000 in this spectrum. In addition, no peaks above *m*/*z* 6300 were detected in the negative ion spectrum. The *m*/*z* 12 637 peak shown in the inset of Figure 2 is in the region expected for the dimer ion. The maximum in the peak intensity is five standard deviations above the background fluctuation. The measured value of *m*/*z* differs from that expected for $(2M + Na)^+$ by *m*/*z* 64 ± 10. Since no corresponding ions were observed in the negative ion spectrum, it is unlikely that these ions are from monomeric impurity species. Further, if a molecule of this mass, present in only trace levels, produced a detectable peak, it would imply that the probability for its formation is extremely high. This does not seem likely. For the *m*/*z* 12 637 species, it is therefore highly probable that multiple sodium attachment has occurred. The attachment of four Na atoms could account for the observed mass. This phenomenon has been observed in the ^{252}Cf-PDMS of large molecules, particularly when the Na content of the sample is high and several acidic hydrogens exist on the molecule.[1] Replacement of the acidic hydrogens by sodium can occur, for example, on the isobutyrlguanine residues in the molecule used in this study.[3] The ion at 8709 *m*/*z* may be a fragment of the dimer. This type of fragmentation has observed in the ^{252}Cf-PDMS of chlorophyll *a* which forms particularly stable oligomers.[4]

While we can not be definitive as to the composition of the *m*/*z* 12 637 species, it is likely that it is a dimer-adduct ion. What is remarkable is that an ion having a mass of this magnitude can be desorbed from a solid film by a nuclear fission fragment and can be detected.

Acknowledgment. We thank Professor S. A. Narang for supplying the sample of the fully protected oligonucleotide. This investigation was supported by Grant GM26096 from the National Institute of General Medical Sciences, the National Science Foundation (CHE-79-04863), and the Robert A. Welch Foundation.

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(9) Phillips, F. W.; Marlow, K. W. Naval Research Laboratory Report 3198; Naval Research Laboratory: Washington, DC, 1976.

Book Reviews

Chemical Thermodynamics. By M. L. McGlashan (University College, London). Academic Press, Inc., London and New York. 1970. XIX + 345 pp. $41.50.

The question which comes to one's mind, including this reviewer's, when seeing a freshly published book on thermodynamics is: Why do we need still another book on thermodynamics? Having read the book, I have come to the conclusion that this publication is not just another book in the field of thermodynamics. It is written by one of the foremost experts in the field, and offers a logical insight into the discipline of modern thermodynamics.

In 21 chapters, ranging from topics as basic as the first and second laws of thermodynamics to as complex as statistical thermodynamics, the author covers the subject of thermodynamics in an unusually logical, informal, and easy to follow manner. The extent of coverage of the individual topics reflects the author's own research interests. Broad coverage is given to topics such as thermometry, calorimetry, and the physical chemistry of solutions, while relatively little attention is paid to topics such as chemical equilibrium and statistical thermodynamics.

The author is well known for his clear presentation and notation. It seems therefore ironic that the reviewer's only criticism of this excellent publication is the notation. Notations such as p^{1+g}, p^{s+g} for the equilibrium pressure and $\Delta_{l}^{g}H_{m}$ for the molar enthalpy of vaporization will be difficult for some readers of the text to interpret.

The level of coverage of the material is such that the book can be used by advanced undergraduate students, graduate students, and researchers, especially those whose interest is in the physical chemistry of solutions.

Vojtech Fried, *Brooklyn College of CUNY*

Safe Handling of Chemical Carcinogens, Mutagens, Teratogens and Highly Toxic Substances. Volumes 1 and 2. By Douglas B. Walters. Ann Arbor Science, Ann Arbor, Michigan. 1980. Volume 1, xiv + 381 pp; Volume 2, xiv + 227 pp. $33.95 each.

These volumes appear at a very opportune time for all professionals who are actively engaged in chemical research. The numerous government regulations concerning chemical toxicity have resulted in an increased awareness in the chemical world of the possible physiological dangers, both present and future, inherent in the materials commonly found in the chemical workplace. Therefore, it is fortunate that this work has appeared now.

Volume 1 contains three sections: Laboratory Design, Handling, and Management; Chemical Monitoring and Medical Surveillance; and Informational Needs and Chemical Classifications. Volume 2 contains sections on Structure Activity and Toxicity Prediction; Spill Control, Degradation and Deactivation; and Disposal.

Each section is written by people currently working in the field and includes numerous references. A definite asset is the liberal use of illustrations, charts, and tables to assist the reader. Also helpful is a very complete cumulative index in each volume.

In short, this material should be mandatory reading for anyone actually engaged in chemical research using suspected (or proven) toxic reagents. Its cost is nominal and it should be well received.

Howard S. Friedman, *Organic Chemical Research Center, Ferro Corporation*

Physical and Mechanistic Organic Chemistry. By R. A. Y. Jones (University of East Anglia). Cambridge University Press, New York. 1979. 4 + 357 pp. $57.50 hardcover; $17.50 paperback.

"Physical and Mechanistic Organic Chemistry" is an excellent addition to the new group of physical organic chemistry textbooks that have been published in the last eight years. It presents a well-balanced coverage of the traditional topics introduced in an advanced organic chemistry course and is written in a clear, comprehensible style reminiscent of the earlier, classical treatments by Hine and by Gould. The length and depth of coverage are appropriate for a semester course in physical organic chemistry at the level of either an advanced undergraduate or entering graduate student.

Specific points of interest in evaluating this or any textbook include: (a) the organization of the subject material; (b) the background required of the student; and (c) the availability and value of excercises within the text. This book is divided into two parts. Part 1 introduces the student to the basic concepts of kinetics, kinetic isotope effects, acid–base theory, solvent and medium effects, linear free energy relationships, and perturbation molecular orbital theory. Each subject is briefly presented with little in-depth discussion. The reader is directed to additional texts and monographs for quantitative, theoretical, or historical development of the subject material. The second part of the text deals with organic reaction mechanisms utilizing the concepts presented in the first part. The first seven chapters of part 2 are divided among the traditional topics as defined by the Hughes–Ingold classifications of nucleophilic and electrophilic substitution reactions (S_N1, S_N2, E1, E2, etc.), electrophilic and nucleophilic additions to double bonds and to aromatic rings, carbonyl additions, and hydrolysis reactions. The final two chapters cover molecular rearrangements and pericyclic reactions. Approximately 500 citations to the original literature are sprinkled throughout the text. For these citations the author has employed Katritsky's unusual but easily adoptable format (year:journal code:page number) which, once mastered, eliminated one step in literature retrieval.

The background required of a student would include introductory college courses in organic chemistry and calculus. Very little mathematical background is demanded and there are no exercises in the text. Also, there are no chapters on free-radical or excited-state chemistry.

I found that the book's strongest areas were the discussions of the reaction mechanisms in part 2. Each topic is concisely presented in an interesting and engaging style. The final chapter on pericyclic reactions falls short, however. In this chapter, the approach is from a historical perspective starting with orbital symmetry correlations followed by the perturbation molecular orbital method. The most practical treatment of pericyclic reactions is by the aromatic–antiaromatic transition state method to which only five pages are devoted, far too short to provide the reader with a practicable knowledge of orbital symmetry. Even as a historical treatment this chapter is both inadequate and incomplete. Zimmerman's important contributions on the aromatic–antiaromatic transition state method are not included.

In judging this text against other books currently on the market, the three most directly comparable are Lowry and Richardson's "Mechanism and Theory in Organic Chemistry", Carey and Sundberg's "Advanced Organic Chemistry: Part A", and Alder, Baker, and Brown's "Mechanism in Organic Chemistry". The first two are superior in depth of coverage while the third closely parallels the Jones' text in clarity and conciseness. These three texts provide exercises at the end of each chapter, whereas Jones' does not. Despite the several limitations enumerated above "Physical and Mechanistic Organic Chemistry" should be of value primarily because it is very well written and provides an excellent introduction to reaction mechanisms.

Richard S. Givens, *University of Kansas*

Topics in Current Chemistry. Volume 88. Organic Chemistry: Syntheses and Reactivity. Edited by F. L. Boschke et al. Springer-Verlag, Berlin, Heidelberg, and New York. 1980. 170 pp. $54.90.

This volume contains four unrelated reviews: Steric Effects in Free Radical Chemistry, by C. Rüchardt (32 pages, 120 references); Silylated Synthons. Facile Organic Reagents of Great Applicability, by L. Birkofer and O. Stuhl (56 pages, 323 references); The 4a,4b-Dihydrophenanthrenes, by K. A. Muszkat (55 pages, 89 references); and Regio- and Stereo-Selectivities in Some Nucleophilic Reactions, by Nguyên Trong Anh (18 pages, 46 references). Literature coverage appears to be through early 1979. An author index for volumes 26-88 is included.

The second chapter, concerning a topic of primary interest to this reviewer, was disappointing. It is poorly written and poorly organized. It is very difficult to read, partly because the structural formulas are small, and the rather extensive schemes do not include literature references, making it necessary to hunt through the text to find a reference. Another problem is the profusion of chemical nomenclature throughout the text. Coverage is very uneven, and the reasons for the choice of topics are not obvious. Some topics, such as reactions of trimethylsilyl azide and the synthesis of silylated heterocyclic compounds, are considered in great detail. For other topics, the discussions are brief, out of date, or incomplete; for example, the discussion of hydrosilylation fails to point out that hydrosilylations of olefins frequently involve migration of the double bond, and hydrosilylations of acetylenes, even terminal acetylenes, usually give mixtures of regioisomers. The following topics are not included: reactions of allylsilanes (although vinylsilanes are considered in detail), reactions of α- and β-silyl ketones, fluoride-induced α- and β-elimination reactions, reactions of Me_3SiLi and related silylmetallic compounds, and the use of $(Me_3Si)_2NLi$ and related compounds as bases in organic synthesis.