Acknowledgment. This investigation was supported by VPI NASA Multidisciplinary Grant 47-004-006.

L. T. Taylor, W. M. Coleman
Department of Chemistry, Virginia Polytechnic Institute
Blacksburg, Virginia 24061

Received November 1, 1969

Increasing Terminal (ω) Chlorination of Fatty Acids by Adsorbing and Aligning the Reactants on Alumina

Sir:

Langmuir showed that fatty acids occupy an area of $20.5\ \text{Å}^2$ per molecule when adsorbed on air–water interfaces, independent of chain length or molecular weight.[1] The molecules are aligned with their axis perpendicular to the interface in a close-packed, rigid array. It has no doubt occurred to many chemists that such aligned molecules have their flanks protected and might be selectively attacked on the exposed terminal methyl group. The data in Tables I and II are believed to be the first that demonstrate such an effect.

Table I. Chlorination of Octanoic Acid at 25°

Conditions	% yields of monochlorooctanoic acids 2	3	4	5	6	7	8
Homogeneous (Cl_2)	1.5	9	15	15	19	24	17
5% on alumina (Cl_2)	2	4	7	11	22	29	25
3% on alumina (Cl_2)	1	3	5	8	20	30	33
Homogeneous ($C_6H_6Cl\cdot$)		3	14	24	30	26	3
3% on alumina ($C_6H_6Cl\cdot$)		4	12	21	28	30	5
Homogeneous (*t*-BuOCl)	6	7	14	17	22	28	6
3% on alumina (*t*-BuOCl)	6	8	13	14	21	30	8

Table II. Chlorination of Hexanoic and Butyric Acids

Conditions	% yields of monochloro acids 2	3	4	5	6
Hexanoic acid					
Homogeneous (Cl_2)	4	13	28	37	18
3% on alumina (Cl_2)	1	4	27	36	31
Butyric acid					
Homogeneous (Cl_2)	5	53	42		
3% on alumina (Cl_2)	1	47	52		

Several problems arose in attempting to use monomolecular films of fatty acids on air–water interfaces so that we turned to CCl_4–alumina interfaces in the hope that comparable alignment would obtain. Although the geometries of the alumina-adsorbed acids are not known, they are at least tightly adsorbed. For example, a limiting 7% of octanoic acid was not washed off by methanol.

Chlorination of carboxylic acids was the reaction chosen. Emphasis was placed on octanoic acid. This was a compromise between using carboxylic acids of short enough chain length to facilitate analysis and a long enough chain length to favor alignment. Butyric and hexanoic acids were also studied.

The yield of 8-chlorooctanoic acid is nearly doubled (17–33%) when the octanoic acid is adsorbed on alumina. Of equal importance, the sum of the yields of 7- and 8-chloro increases from 41 to 63% and the yields of 2–5-chloro drops from 40 to 17%. Similar results were obtained with hexanoic and butyric acids (Table II). As anticipated, the effect was smaller with shorter chains in which the London forces favoring rigid alignment have been reduced.

It had been hoped that larger attacking radicals such as the $C_6H_6Cl\cdot$ complex[2] or *t*-BuO· from *t*-BuOCl[3] would have difficulty interpenetrating between the alkane chains and thereby favor terminal chlorination. Any such effect was overshadowed by their high selectivity for secondary over primary hydrogen so that little terminal chlorination took place (Table I).

The general procedure was to reflux RCOOH for 5 hr with a suspension of alumina in CCl_4. It was critical to use neutral alumina[4] as the chlorination failed to proceed when basic aluminas were tried. An equimolar amount of Cl_2 was added and the suspension irradiated with a sun lamp while stirring.

The alumina was separated by filtration and refluxed with acetic acid for 2 days to desorb the products. Thionyl chloride was added to convert both acetic and chloro acids to their acid chlorides. Acetyl chloride was removed by distillation and the remaining acid chlorides converted to methyl esters by addition of methanol. The methyl esters were distilled before analysis.

Analysis by gc was achieved on a Barber-Coleman 5000 instrument using a flame ionization detector, a 6-ft 0.25-in. U column, and a packing of polyethyleneglycol succinate[5] on 100–120 mesh Chromasorb[5] A. Even the methyl 2–8-chlorooctanoates were resolved except for partial overlap of the bands of the 6- and 7-chloro acids. The latter were analyzed using a du Pont 310 curve resolver.

The three methyl chlorobutyrates were identified by observing direct superposition of gc bands with those of authentic samples. Methyl 8-chlorooctanoate was similarly identified. The authentic sample was prepared from cyclooctanone by a procedure identical with that used to prepare methyl 7-chloroheptanoate from cycloheptanone.[6] Strong support for the identification of methyl 8-chlorooctanoate was the observation that its yield dropped sharply in homogeneous chlorination when selective reagents, $C_5H_6Cl\cdot$ and *t*-BuOCl (Table I), were used.

Methyl 8-chlorooctanoate had the longest retention time as expected. The other chlorooctanoates as well as the chlorohexanoates were provisionally identified on the basis that increasing separation of the chloro and ester groups would lead to increased retention times as was found in the chlorobutyrates.

The products were >90% desorbed by the acetic acid treatment. However, to ensure that the results were not an artifact of selective desorption, a mixture of chlorooctanoic acids from homogeneous chlorination was added to the alumina (5% chloro acid) and de-

---

(1) J. T. Davies and E. K. Rideal, "Interfacial Phenomena," 2nd ed, Academic Press, New York, N. Y., 1963, Chapter 5.

(2) G. A. Russell, A. Ito, and D. G. Hendry, *J. Amer. Chem. Soc.*, **85**, 2976 (1963); G. A. Russell, *ibid.*, **80**, 4987, 4997, 5002 (1958); **79**, 2977 (1957).

(3) C. Walling and V. Kurkov, *ibid.*, **89**, 4895 (1967); C. Walling and M. J. Mintz, *ibid.*, **89**, 1515 (1967), and earlier papers.

(4) Fisher Scientific Co. alumina, neutral, Brockman activity I, pH 7.28.

(5) Applied Science Laboratories, State College, Pa.

(6) R. Robinson and L. M. Smith, *J. Chem. Soc.*, 371 (1937).

sorbed. No significant change in isomer ratios was observed.

Reducing the moles of Cl_2 from 1 to 0.25 did not significantly alter the ratios of monochlorooctanoic acids.

It is known that stearic acids form aligned monolayers in certain cell walls and membranes. It is also known that stearic acid and other fatty acids are characteristically oxidized at the terminal (ω) position. It is conceivable that such alignment is a factor in achieving terminal oxidation.

N. C. Deno, Richard Fishbein, Craig Pierson
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

Received November 6, 1969

Book Reviews

Elements of Advanced Quantum Theory. By J. M. ZIMAN, F.R.S., Professor of Theoretical Physics in the University of Bristol. Cambridge University Press, 32 East 57th St., New York, N. Y. 1959. xii + 269 pp. 16 × 23.5 cm. $9.50.

In a recent television news story, an illiterate denizen of Appalachia laments, "If I could only read this book (an auto repair manual), I'd be able to fix any part of any car." For a chemist possessing a moderately sophisticated background in quantum theory—the level of Dirac's book, say—Ziman likewise provides the key for understanding, or at least appreciating, recent developments in elementary particle theory, statistical mechanics, and solid-state physics. No longer need one cringe thereafter at the mention of Feynman diagram, propagator, Green function, renormalization, quasi-particle, SU(3), the Eight-Fold Way, Mandelstam representation, Kubo formula, etc., etc. Professor Ziman, an accomplished solid-state physicist, has written this book, he states, in the course of clarifying his own understanding of these advanced quantum-mechanical techniques. His effort is, in my opinion, an unqualified success. The prose style is distinguished by taste and clarity, with sensitivity to the needs of the reader. Although the development is influenced in some places by the author's specialty, it does impart an overall viewpoint of sufficient generality. The book is organized under the chapter headings (1) Bosons, (2) Fermions, (3) Perturbation Theory, (4) Green Functions, (5) Some Aspects of the Many-Body Problem, (6) Relativistic Formulations, (7) The Algebra of Symmetry. All in all, highly recommended reading.

S. M. Blinder
University of Michigan
Ann Arbor, Michigan

Organometallic Compounds of the Group IV Elements. Volume 1. The Bond to Carbon (Two Parts). Edited by ALAN G. MACDIARMID, Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1968. xv + 603 pp (Part I); xiii + 261 pp (Part II). 16 × 23.5 cm. $17.75 (both volumes same price).

The two parts of the present volume represent the first section of an ordered presentation of the chemistry of the organometallic compounds of the group IV elements. The series is structured according to the element to which the group IV atom is bound. The present volume is devoted to the group IV–carbon bond, with subsequent volumes treating the bonds with halogens, chalcogens, etc. In each volume a chapter is allocated to each of the elements, Si, Ge, Sn, and Pb. The general format of the chapters of the first volume consists of (a) methods for forming the bond under consideration, (b) reactions of that bond, and (c) physical (including spectroscopic) properties of compounds containing the bond.

The organization of the series necessitates a considerable amount of overlapping coverage among the volumes. The series editor considers such overlap desirable. In some cases this may be true, but it seems unlikely that the repetition can be always justified. There is in the present volume, for instance, an excellent 66-page critical summary of the literature on hydrosilylation of alkenes and alkynes including discussion of mechanism. Logically, the bulk of this material would have to be repeated in a chapter devoted to the Si–H bond in a future volume. Review articles in the area of organometallic chemistry have so proliferated in recent years that a contribution of the magnitude contemplated for this series would have to consist exclusively of articles of real utility in order to be justifiable. That two authors treat the same subject matter in a manner which is complementary as opposed to being merely repetitious is a great deal to expect and will certainly require some cajolery on the part of the series editor. The organization of the series does have the major advantage of bringing together in one place, and with reasonably consistent presentation, material on all four of the group IV elements. Comparisons are made relatively convenient.

There is, indeed, much in the present volume to recommend. The initial chapter by E. A. V. Ebsworth is entitled the "Physical Basis of the Chemistry of the Group IV Elements." The chapter concerns itself primarily with a critical review of evidence relating to the use of d orbitals in bonding, and it admirably cleans out a number of cobwebs surrounding this topic, which seems to pervade every discussion of the chemistry of the group IV elements.

The chapter on the silicon–carbon bond by R. W. Bott and C. Eaborn is a highly desirable up-date of a considerable amount of the material from the classic book by Eaborn which has done so much to spur research in organosilicon chemistry in the last decade. The exhaustive coverage (2414 references accompany this chapter) and the clarity of discussion of mechanism characterize this chapter as much as they did the earlier book. One can take exception with certain things, such as the presence of primary carbonium ions in mechanistic schemes, but they do not detract from a quite monumental accomplishment.

The chapters on germanium (by F. Glockling and K. A. Hooton), tin (by J. G. A. Luijten and G. J. M. van der Kerk), and lead (by L. C. Willemsens and G. J. M. van der Kerk) are much shorter than that on silicon (229 pages on all three elements compared to 431 pages on silicon alone), and are less critical reviews. This may be in large part due to the exploratory nature of most of the work which has been done to date on these elements. There exist very little data on which to base even speculations concerning mechanistic aspects of the chemistry of these elements. The chapter on lead is particularly lucidly written.

The first two chapters cover the literature reasonably comprehensively through 1967 with occasional 1968 references in the silicon chapter. There are almost no 1967 references in the last three chapters. This time lag is disturbing. There is, for instance, no mention of the excellent book on organotin chemistry by Neumann, which appeared more than a year before the present volume.

The book is very attractively done and there are few misprints (although those on p 84 of Part I are confusing to the reader). Research workers in the area of organometallic chemistry are sure to find the chapter on silicon chemistry, in particular, an invaluable aid; and general readers will find much of interest in the introductory chapter by Ebsworth.

Frank K. Cartledge
Department of Chemistry
Louisiana State University
Baton Rouge, Louisiana 70803