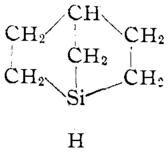
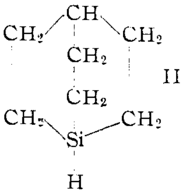
bridgehead silicon due to possible changes in bond hybridization which might invalidate general conclusions) has led to the synthesis of 1-silabicyclo-[2.2.2]octane (II) for comparison of reactivity with I.[4]


I


II

Treatment of 4-(2-hydroxyethyl)-tetrahydropyran[5] with equimolar amounts of thionyl chloride and pyridine gave 4-(2-chloroethyl)-tetrahydropyran, b.p. 71° (6 mm.); *Anal.* Calcd. for $C_7H_{13}OCl$: Cl, 23.9. Found: Cl, 23.5. The Grignard reagent prepared from 4-(2-chloroethyl)-tetrahydropyran in tetrahydrofuran was added to excess silicon tetrachloride and gave 4-(2-trichlorosilylethyl)-tetrahydropyran (III) in 63% yield, b.p. 97° (3 mm.); *Anal.* Calcd. for $C_7H_{13}SiOCl_3$: Si, 11.3; Cl, 43.1. Found: Si, 11.1; Cl, 43.1. Treatment of III with boron trichloride and then thionyl chloride gave 1,5-dichloro-3-(2-trichlorosilylethyl)-pentane (IV) in 70% yield, b.p. 130° (2.5 mm.). *Anal.* Calcd. for $C_7H_{13}SiCl_5$: Si, 9.3; Cl (attached to Si), 35.2. Found· Si, 9.2; Cl (attached to Si), 35.3. Ring-closure of IV with excess magnesium in ether gave a 30% yield of the bridgehead chloride, 1-chloro-1-silabicyclo[2.2.2]-octane (V), b.p. 59° (8 mm.). *Anal.* Calcd. for $C_7H_{13}SiCl$: Si, 17.4; Cl, 22.1. Found: Si, 17.2; Cl, 22.5. The infrared spectrum of V showed the absence of Si-H, C=C and $Si\text{-}CH_3$. Compound V is readily hydrolyzable and gives rapid quantitative reaction of the silicon–chlorine bond with 0.1 *N* alkali. Treatment of V with lithium aluminum hydride in ether at 0° gave 1-silabicyclo[2.2.2]-octane (II), b.p. 158° (733 mm.), m.p. 133° (sealed capillary), with an infrared spectrum showing the strong Si–H band at 4.7 μ and lacking maxima for C=C, $Si\text{-}CH_3$ and Si-O-Si. *Anal.* Calcd. for $C_7H_{13}SiH$: Si, 22.2; H (attached to Si), 0.80; mol. wt. (cryoscopically in benzene), 126. Found: Si, 21.9; H (attached to Si), 0.80; mol. wt. (cryoscopically in benzene), 128.

The kinetics and rate constant for II in the base-catalyzed solvolysis with hydroxide ion in 95% ethanol, $R_3SiH + OH^- + SH \rightarrow R_3SiOH + H_2 + S^-$, where SH represents solvent, have been determined. For reactions of R_3SiH with OH^- in 95% ethanol at 35° relative rates (k_2) are, for $(C_2H_5)_3SiH$ = 1; II, 10; I, 10^3; $(CH_2)_4Si(CH_3)H$, 10; $(CH_2)_5Si(CH_3)H$, 10^{-1}.

The new reactivity data offer additional support for our earlier, preliminary hypothesis.[3]

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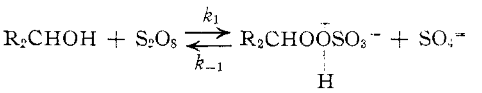
[4] A molecular model of II using accurately scaled Stuart–Briegleb atom models is easily constructed and shows only small strain at Si and complete shielding of that atom to back attack. A corresponding model of I cannot be made.

[5] D. Kohlback, E. Cekovnikov, A. Rezek and M. Piantanida, *Ann.*, **532**, 69 (1937).

PERSULFATE OXIDATION OF ISOPROPYL ALCOHOL

Sir:

In a recent paper[1] Malinowski and Levitt have proposed a mechanism for the persulfate oxidation of isopropyl alcohol which involves in the first step a reaction between isopropyl alcohol and the persulfate ion



$$R_2CHOH + S_2O_8 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R_2CHO\underset{\substack{|\\H}}{\overset{-}{O}}SO_3^- + SO_4^=$$

The intermediate is then assumed to decompose to the ketone and bisulfate ion.

This may be shown to be incorrect by our observation that induced exchange of radioactive sulfate with persulfate ion in the presence of isopropyl alcohol does not occur, whereas it is required by the above mechanism. When the reaction was carried to 25% completion in the presence of S-35 labeled sulfate, the recovered persulfate had only 10^{-4} of the activity calculated for complete exchange.

We also have observed that the addition of allyl acetate decreased the rate of disappearance of persulfate from 2.30×10^{-4} sec.$^{-1}$ (0.02 *M* isopropyl alcohol, 0.02 *M* persulfate, 0.02 *M* sulfate, *p*H 5, 60°) to the value observed in the absence of isopropyl alcohol (4×10^{-6} sec.$^{-1}$).[2] The inhibition of the oxidation of isopropyl alcohol by allyl acetate indicates that the reaction must be a chain process, that the initiation step is the first order decomposition of persulfate ion (probably to the sulfate ion-radical) and does not involve isopropyl alcohol, and that the propagation steps involve the induced decomposition of persulfate ion. The species formed in the decomposition of the persulfate ion is, in the presence of allyl acetate, consumed in initiating the polymerization of the latter. In the absence of allyl acetate, it affects the oxidation of isopropyl alcohol.

The species which initiates the oxidation of the alcohol may be either the sulfate ion-radical or the hydroxyl radical. The latter species has been shown to be involved in the decomposition of persulfate ion in water[3] and may reasonably be expected to be involved in this case also. It appears that only a reaction utilizing the hydroxyl radical can accommodate the kinetics of the reaction (first order in persulfate and independent of the alcohol concentration). Evidence for the participation of this species may be obtained from the observation that whereas the rate constant is independent of the hydroxyl ion concentration between *p*H 5–8, in more basic solution it decreases and levels off at $k = 0.2 \times 10^{-4}$ sec.$^{-1}$ between *p*H 9.5–10.5. The simplest interpretation is that the hydroxyl radical is converted to the less reactive oxygen ion-radical in the more basic solution.[4]

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[1] E. R. Malinowski and L. S. Levitt, This Journal, **80**, 5334 (1958).

[2] This technique was first used by I. M. Kolthoff, E. J. Meehan and E. M. Carr, *ibid.*, **75**, 1439 (1953), in studying the persulfate oxidation of methanol.

[3] I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

[4] E. J. Hart, S. Gordon and D. A. Hutchison, *ibid.*, **75**, 6165 (1953), have presented evidence for the hydroxyl radical having a *p*K of about 9.

A kinetic scheme which will accommodate these facts is

$$S_2O_8^{=} \xrightarrow{k_1} 2SO_4\cdot^{-}$$

$$SO_4\cdot^{-} + H_2O \xrightarrow{k_2} HO\cdot + HSO_4^{-}$$

$$HO\cdot + R_2CHOH \xrightarrow{k_3} H_2O + R_2COH$$

$$R_2\underset{\cdot}{C}OH + S_2O_8^{=} \xrightarrow{k_4} R_2C{=}O + HSO_4^{-} + SO_4\cdot^{-}$$

$$R_2COH + SO_4.^{-} \xrightarrow{k_5} R_2C{=}O + HSO_4^{-}$$

which leads to the rate law

$$v = \sqrt{\frac{2k_1k_2k_4}{k_5}}\,[S_2O_8^{=}]$$

This scheme also will accommodate the decrease in rate constant observed with rather low concentrations of alcohol or of persulfate,[1] for here other chain terminating steps become important, thus decreasing the chain length and correspondingly decreasing the rate constant.

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BOOK REVIEWS

Synthetic Methods of Organic Chemistry. Volume 12. By W. THEILHEIMER. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1958. xvi + 546 pp. 16.5 × 23.5 cm. Price, $22.25.

Dr. Theilheimer's efforts provide the preparative chemist with annual installments of what amounts to an Ariadne's thread out of the Labyrinth of current literature. The popularity of the well established series bears witness not only to its usefulness and excellence but also the increasing trend to entrust the problems created by the deluge of published scientific data to dedicated literature scientists.

The series has been fully discussed and described in previous reviews, including several by the present writer, (THIS JOURNAL, 1946, and following), and this reviewer considers his task completed by calling attention to the fact that the 1958 volume, No. 12, has appeared.

RESEARCH DEPARTMENT
CIBA PHARMACEUTICAL PRODUCTS, INC. HANS HEYMANN
SUMMIT, NEW JERSEY

Ion Exchange Resins. Second Edition. By ROBERT KUNIN, Rohm and Haas Company, Philadelphia, Pennsylvania. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1958. xiii + 466 pp. 15.5 × 23.5 cm. Price, $11.00.

In a field that is growing as rapidly as that of ion-exchange it is necessary to make periodic revisions in order that new developments can be included. The second edition of "Ion Exchange Resins" is the most complete and authoritative compilation in its field. Many developments which were treated in a cursory fashion in the first edition have been expanded to form new chapters in the present work.

The first four chapters which discuss the theory and basic principles of cation and anion exchange, as well as chapter five which describes the synthesis and tabulates the properties of the many types of commercial ion-exchange materials, are of great value to chemists and chemical engineers in general. The next nine chapters which are devoted to various applications of ion-exchange should be of special interest to the reader who wishes to become thoroughly acquainted with ion-exchange technology. Chapters fifteen, sixteen and seventeen are written primarily for the chemical engineer and are essential to a comprehensive dissertation on ion-exchange resins.

IOWA STATE COLLEGE JACK E. POWELL
AMES, IOWA

Comprehensive Inorganic Chemistry. Volume Seven. Edited by M. CANNON SNEED, Professor Emeritus of Chemistry, School of Chemistry, University of Minnesota, and ROBERT C. BRASTED, Professor of Chemistry, School of Chemistry, University of Minnesota. The Elements and Compounds of Group IVA. By HAROLD P. KLUG and ROBERT C. BRASTED. D. Van Nostrand Co., Inc., 126 Alexander Street, Princeton, N. J. 1958. ix + 302 pp. 16 × 23.5 cm. Price, $7.50.

This volume is divided into two parts. Part I (233 pp.) is devoted to the non-transitional elements of Group IV and certain of their compounds. Part II (42 pp.) is concerned with borides, carbides, silicides and related compounds.

The title of this, the seventh volume in a series of eleven, is misleading in that the treatment is not comprehensive except in the special sense set forth by the authors, *i.e.*, "comprehensive in the extensiveness of the fields covered rather than in the fullness of their treatment." Accordingly, reader reaction to this and its companion volumes will be determined largely by whether the specific topic on which information is sought was one of those selected by the authors for inclusion either briefly or in detail.

The subject matter included in Volume Seven is indeed extensive. It ranges from more or less classical descriptive and historical information of the type found in many freshman chemistry textbooks to data relating to thermodynamic properties and structural information that would be useful primarily to the research worker. Of the more purely descriptive sections, those dealing with glasses and with the allotropic forms of carbon are noteworthy.

Even though the ground rules adopted by the authors provide complete latitude with respect to inclusion or omission of specific topics, the reader nevertheless expects some internally consistent plan or viewpoint. Such is difficult to detect in the present instance. For example, only the original method for the synthesis of carbon suboxide is mentioned; a much superior procedure [*cf.* Hurd and Pilgrim, THIS JOURNAL, **55**, 757 (1933)] is not included and there is no reference to the one review paper on the chemistry of this oxide [*cf.* Ryerson and Kobe, *Chem. Revs.*, **7**, 479 (1930)]. On the other hand, silicon monoxide is discussed in more detail and all of the pertinent literature is cited. Similarly, the section on the halides of carbon makes no mention of the bromide or iodide, yet all of the halides of germanium are included at least briefly. Numerous other examples could be cited.

Part II of this volume represents an overly ambitious undertaking. Brevity and a high degree of selectivity are