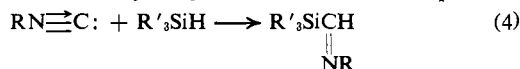


sidered to be α,α additions of amine, alcohol, and thiol to the carbon atom of isocyanide.

The present communication describes the reaction of isocyanide with trialkylsilane by a copper compound catalyst in which the isocyanide carbon atom is inserted between silicon and hydrogen of the silane compound.

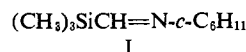


The product of formimidoylsilane is the adduct of $\equiv\text{SiH}$ to isocyanide, and the reaction may be regarded as a novel hydrosilation, which is interestingly compared to the hydrosilation of olefins with group VIII metal complex catalysts.^{3,4}

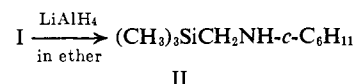
Under nitrogen atmosphere, a mixture of 12 ml (100 mmoles) of cyclohexyl isocyanide, 13.5 ml (120 mmoles) of trimethylsilane, 0.52 g (2 mmoles) of copper(II) acetylacetonate, and 10 ml of benzene (reaction solvent) was heated at 100° for 5 hr in a sealed tube. As the temperature was raised, the catalyst was gradually dissolved in the reaction mixture to form a homogeneous system at 100°. After the reaction, the mixture was distilled to isolate N-cyclohexylformimidoyltrimethylsilane (I), bp 118–120° (40 mm). *Anal.* Calcd for $\text{C}_{10}\text{H}_{21}\text{NSi}$: C, 65.50; H, 11.54; N, 7.64. Found: C, 65.19; H, 11.89; N, 7.62. The yield of I based on cyclohexyl isocyanide was 86%. The new silicon compound (I) is a colorless liquid and stable under dry nitrogen atmosphere, but vulnerable to moisture.

(3) (a) J. L. Speier, L. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957); (b) J. L. Speier and J. C. Saam, *ibid.*, **80**, 4104 (1958); (c) *ibid.*, **83**, 1351 (1961); (d) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964).

(4) A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 16 (1965).



The structure of I was convincingly confirmed by infrared, ultraviolet, and nmr spectra as well as by the reduction product. The infrared spectrum of I (neat) was consistent with the assigned structure, showing $-\text{Si}(\text{CH}_3)_3$ at 1246 and 842 cm^{-1} and $>\text{C}=\text{N}-$ at 1601 cm^{-1} . The ultraviolet spectrum of I in cyclohexane had an absorption of λ_{max} 285 μm (ϵ 70), which is assigned to the $n \rightarrow \pi^*$ transition of the $>\text{C}=\text{N}-$ group. The nmr spectrum in CDCl_3 showed a singlet at τ 1.67 (1 H, $-\text{CH}=\text{N}-$), two broad signals centered at τ 7.2 (1 H, $=\text{NCH}<$) and 8.5 (10 H, $-(\text{CH}_2)_5-$ of the cyclohexane ring), and a singlet at τ 9.87 (9 H, $-\text{Si}(\text{CH}_3)_3$). Further evidence supporting structure I was obtained in the treatment of I with lithium aluminum hydride in ether at room temperature, which afforded N-(trimethylsilylmethyl)cyclohexylamine (II), bp 208–210° (lit.⁵ bp 211°), n^{25}_{D} 1.4520 (lit.⁵ n^{25}_{D} 1.4519). The structure



of II was further confirmed by infrared and nmr spectra. Similar results were obtained with cupric chloride as catalyst.

The catalytic activity of copper compounds in reaction 4 seems quite specific. In the absence of copper catalyst both trimethylsilane and isocyanide were recovered unchanged from the heat-treated reaction mixture. Further, no reaction was observed in the presence of chloroplatinic acid, which is known to be an efficient catalyst of hydrosilation of olefins,³ as catalyst.

Reactions of various silane compounds with isocyanide by copper catalyst and mechanistic studies are now being carried out.

(5) J. E. Noll, J. L. Speier, and B. F. Daubert, *ibid.*, **73**, 3867 (1951).

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Additions and Corrections

The Crystal Structure of Azulene-1,3-dipropionic Acid [*J. Am. Chem. Soc.*, **88**, 4794 (1966)]. By HERMAN L. AMMON and M. SUNDARALINGAM. Department of Biological Structure, University of Washington, Seattle, Washington.

The fifth sentence of the first paragraph (beginning on line 13 of column 1, page 4794) should be changed to read as follows: The precision of the structure analysis was not seriously affected because an allowance was made for the disorder during the refinement; it was estimated⁷ that failure to consider the alternate orientation would have produced bond length differences no greater than 0.014 Å from those reported for the corrected structure.

In Table V, the length of the C(4)–C(10) bond in the azulene-*sym*-trinitrobenzene complex is not 1.382 as reported, but 1.392. This change affects footnote a

to Table V. In the second sentence (" $T = 12.68 \dots$ "), the value 12.68 should be replaced with 14.64 and 0.32 should be replaced with 0.21.

The Determination of the Concentration of Hydrolytic Enzyme Solutions: α -Chymotrypsin, Trypsin, Papain, Elastase, Subtilisin, and Acetylcholinesterase [*J. Am. Chem. Soc.*, **88**, 5890 (1966)]. By MYRON L. BENDER, MARIA LUISA BEGUÉ-CANTÓN, ROBERT L. BLAKELEY, LEWIS J. BRUBACHER, JOSEPH FEDER, CLAUDE R. GUNTER, FERENC J. KÉZDY, JOHN V. KILLHEFFER, JR., THOMAS H. MARSHALL, CHARLES G. MILLER, ROGER W. ROESKE, and JAMES K. STOOPS. Division of Biochemistry of the Department of Chemistry, Northwestern University, Evanston Illinois, and the Department of Biochemistry, Indiana University, School of Medicine, Indianapolis, Indiana.

On page 5893, column 2, paragraph 3, and on page 5898, column 2, the paragraph headed Second-Order Kinetics, the conditions for second-order kinetics are incorrectly stated. The correct statement for the conditions is the following: $k_2 \gg k_3$ and $K_m(\text{app}) < [S]_0 \cong [E]_0 < K_s$.

The Degenerate 9-Homocubyl Cation [*J. Am. Chem. Soc.*, **89**, 698 (1967)]. By PAUL VON R. SCHLEYER and JON J. HARPER, Department of Chemistry, Princeton University, Princeton, New Jersey 08540, and GEORGE L. DUNN, VINCENT J. DIPASQUO, and J. R. E. HOOVER, Research and Development Division, Smith Kline and French Laboratories, Philadelphia, Pennsylvania 19101.

On page 699, column 1, lines 12–16, the reported rate constants were incorrectly transcribed. The

correct values should be: 100.0° , $(3.38 \pm 0.09) \times 10^{-6} \text{ sec}^{-1}$; 125.0° , $(4.75 \pm 0.03) \times 10^{-5} \text{ sec}^{-1}$; and calculated at 25° , $8.53 \times 10^{-11} \text{ sec}^{-1}$. These corrections do not change the analysis of the rates reported in this paper.

The Microwave Spectrum and Dipole Moment of Pyrazole [*J. Am. Chem. Soc.*, **89**, 1312 (1967)]. By WILLIAM H. KIRCHHOFF. National Bureau of Standards, Washington D. C.

Equation 3 should read

$$W_n^{(4)} = \sum_t' \frac{1}{W_n^{(0)} - W_t^{(0)}} \left| \sum_m' \frac{V_{nm}V_{mt}}{W_n^{(0)} - W_m^{(0)}} \right|^2 - W_n^{(2)} \sum_m' \frac{|V_{nm}|^2}{W_n^{(0)} - W_m^{(0)2}} \quad (3)$$

Book Reviews

Procedures in Nucleic Acid Research. Edited by G. L. CANTONI and DAVID R. DAVIES, National Institutes of Health. Harper and Row, 49 East 33D St., New York, N. Y. 1966. xvi + 667 pp. $16.5 \times 24 \text{ cm}$. \$25.00.

The rapidly proliferating field of nucleic acid research has reached the point where enzymes are used as analytical reagents and polynucleotide materials are becoming more and more defined in terms of structure and/or chemical behavior. While still a long way from achieving authoritative or widely agreed standards of purity, the products, preparations, and related techniques of leading investigators can and do serve this function on an interim basis. One entering the field, or having need for only a part of its accumulated know-how, or only tangentially concerned with the lore that lies behind any given preparation would be hard put to decide which of the variety of procedures published for achieving a given product he should follow, or where he might find even one. Probably he would ask some more knowledgeable colleague for advice, to select for him not only which method but which exponent of that method seems the most advantageous. In the absence of a cookbook, one asks the nearest good cook.

Here we have, with no derogation intended, a cookbook. It brings together in one place and in a didactic, useful form a large number (62) of preparative methods for many of the enzymes and polynucleotides or nucleic acids most in demand since their discoveries and first descriptions in the research literature. To the potential user, the stature of the editors in the general field of nucleic acid research gives assurance that they would do well in selecting the individual contributors and in editing their efforts, and that the contributors are those from whose papers he would, in the absence of this compendium, dig out the desired information.

The first element of selection by the editors must perforce be in the choice of substances to be covered. In this volume, apparently and of necessity to be the first of a series, there are two broad sections: Enzymes of Nucleic Acid Metabolism; and Isolation, Preparation and Characterization of Natural and Synthetic Nucleic Acids. In the first part are three groups of endonucleases (specific and nonspecific ribonucleases, and deoxyribonucleases), phosphodiesterases (exonucleases), and phosphomonoesterases, followed by synthesizing enzymes (polymerases) and enzymes affecting transfer RNA (synthetases, etc.). The second part has multiple entries for the preparation of rRNA, tRNA, viral RNA's and "synthetic RNA's" (enzymically synthesized polynucleotides), as well as for the DNA's of bacteria and viruses. Nucleohistone and the synthetic polydeoxyribonucleotides round out the second part. Obviously omitted, for good reason, are methods for preparing substances that are presently either poorly defined or not standardizable (e.g., messenger RNA of bacteria or mammals).

Although one does not expect to find intellectual stimulation in a practical compendium of this sort, the authors have, in general, so well documented their instructions and explanations as to lend the book some value in this direction also. However, just as a good

cookbook is found in the kitchen rather than in the study, so is the proper place of "Procedures in Nucleic Acid Research" close to or on the laboratory workbench, or in the library that serves a laboratory concerned with nucleic acids or the enzymes that affect them.

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Fundamentals of Carbanion Chemistry. By DONALD J. CRAM, Department of Chemistry, University of California, Los Angeles, Calif. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. viii + 289 pp. $16 \times 23.5 \text{ cm}$. \$9.50.

Timeliness is, or should be, one of the most important criteria for writing a book. "Fundamentals of Carbanion Chemistry" meets this criteria admirably. Any number of books dealing with reactive intermediates such as carbonium ions, carbenes, and free radicals are currently accessible but, until the present work, none was available on the subject of carbanions. It is therefore pleasing that the first book on this subject, although undoubtedly not the last, has been written by Professor Donald J. Cram who himself has been a major contributor to the understanding of this area of chemistry.

The author makes no attempt to be exhaustive in the review of the literature, but instead he has judiciously selected that part of the literature which best lends itself to demonstrate the fundamental principles of the subject. This is best exemplified by the first chapter in which he lays the foundation for introducing the subject. This chapter, which deals with the thermodynamic and kinetic acidities of carbon acids, is a gem. It is a critical evaluation of the methods available for determining carbon acidities, and the author then sets out to correlate the work of McEwan, Streitwieser, Applequist, and Dessy into an amalgamated pK_a scale (MSAD) which although qualitative is very useful. He continues with an excellent discussion of the effects of medium and structure (Chapter II) on carbon acidity. The next three chapters deal with subjects with which the author has been most directly involved, the stereochemistry of carbanion and electrophilic substitution reactions. The book is concluded with a chapter on molecular rearrangements.

The monograph is written in an interesting style which makes for pleasant and exciting reading. One may find that he is not always in agreement with the author's conclusions, but perhaps this is what Cram intended since he comments in his preface "the development of a field feeds on the challenge presented by speculation." He also states that the purpose of this monograph was to stimulate interest in carbanion chemistry, and this reviewer feels that this work will certainly succeed to this end. This book is a must on every organic chemist's shelf.

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