

The cyclization described in this Communication is of interest in gaining further understanding of Ar_1 participation. Moreover, IV is quite suitable for the further construction of ring A of many natural products. The introduction of a ketone group at C_{10}^{2b} and the construction of ring A⁸ are now in progress.^{9,10}

(8) As an example of a conventional method for this purpose, see: G. Stork, H. J. E. Loewenthal and P. C. Mukharji, *ibid.*, **78**, 501 (1956).

(9) The author is grateful to Mr. John Carmody for his helpful technical assistance.

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RESTRICTED ROTATION IN AMINOBORANES

Sir:

In a recent publication concerning unsymmetrically substituted aminoboranes of the type $R_1R_2-NBR_3R_4$ the tentative suggestion was made that such compounds may exhibit *cis-trans* isomerism.¹ This hypothesis was made, in the main, on the basis of the melting points and change of melting points of mixtures of constant composition and of their molecular weights. We are now, on the basis of other observations, in a position to offer definite proof of hindered rotation about a boron-nitrogen bond, leading to *cis* and *trans* conformations.

We have investigated the proton resonance spectrum of (methylphenylamino)-dimethylborane,² $(CH_3NC_6H_5)B(CH_3)_2$, and find that, at room temperature, the two methyl groups attached to boron are non-equivalent. When the temperature is raised above 100° these two groups become magnetically equivalent as rotation about the N-B bond evidently becomes more rapid.

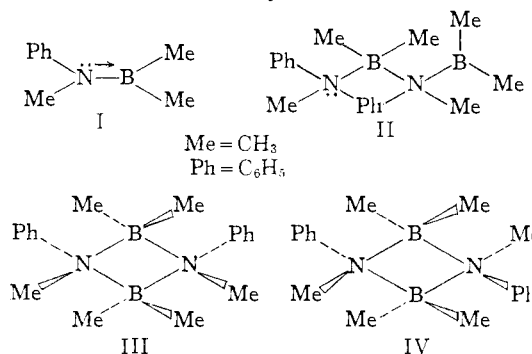
The p.m.r. spectrum at room temperature, obtained in a Varian high-resolution n.m.r. spectrometer at 60 mc., shows four distinct peaks: (1) a complex phenyl peak, (2) a single sharp N-methyl peak at 4.15 ppm. to high field of the center of the phenyl peak, (3) a sharp peak, assigned to one B-methyl, at 6.64 ppm. above the phenyl, and (4) a sharp peak, assigned to the other B-methyl, at 6.92 ppm. above phenyl. No other peaks appear.

Peaks (3) and (4) are seen to be relatively close together. As the temperature is raised, each of these peaks broadens and they move closer together, finally merging into one at about 100°; at yet higher temperatures this single peak narrows. This is the characteristic behavior when the rate of intramolecular rotation varies with temperatures.³

The molecular weight of (methylphenylamino)-dimethylborane has been determined, presumably cryoscopically in benzene for a freshly distilled sample, and indicated a monomeric species.² However, since some aminoboranes are reported to

form dimers slowly on standing^{1,2,4,5} we have considered this possibility in our case.

Therefore, the structures considered for the interpretation of the spectrum are the monomer I, the chain dimer II, and the cyclic dimers III and IV.



Structure II is ruled out because the two methyl groups attached to nitrogen would be non-equivalent, giving two bands. Structure IV would have only one kind of methyl group attached to boron. An equilibrium between two or more forms also is excluded because of the observation of only three methyl resonances. Structure III is consistent with the room-temperature spectrum, but does not afford any explanation of the change of band shape as the temperature is raised. Thus it is concluded that our sample consisted of the monomeric form, I, in the whole temperature interval.

On the basis of the temperature variation, up to 118°, of the separation and shape for the resonances associated with methyl groups attached to boron, we make a preliminary estimate of the barrier to rotation as 15 ± 3 kilocalories per mole; the lifetime of the individual molecular states is about 10^{-2} second at 100°.

(4) H. J. Becher and J. Goubeau, *Z. anorg. allgem. Chem.*, **268**, 133 (1952).

(5) E. Wiberg, A. Bolz and P. Buchheit, *ibid.*, **256**, 285 (1948).

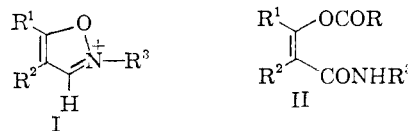
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A NEW SYNTHESIS OF PEPTIDES

Sir:

Carboxylates ($RCOO^-$) react rapidly and smoothly with 3-unsubstituted isoxazolium salts (I), under very mild conditions, to give enol esters (II).¹ We now record the application of this reaction as the carboxyl-activating step in a simple and practical new synthesis of peptides.



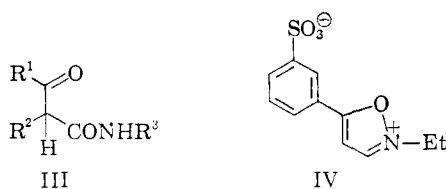
Clearly the activating reagent (I) may be varied, through specific choices for the groups R^1 , R^2 and R^3 , with a view to conferring a special degree of reactivity, or particular physical properties, on the reagent, the activated ester intermediate (II), or

(1) R. B. Woodward and R. A. Olofson, *J. Am. Chem. Soc.*, **83**, 1007 (1961).

(1) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **82**, 4223 (1960).

(2) B.p. 67° at 14.0 mm., prepared according to K. Niedenzu and J. W. Dawson, *ibid.*, **81**, 5553 (1959).

(3) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, pp. 218-224.



the by-product (III) from the reaction of the enol ester with amines. Of several isoxazolium salts so far studied by us, N-ethyl-5-phenylisoxazolium-3'-sulfonate (IV) has proved especially useful. For *activation*, a protected amino acid or peptide [exactly 1 mole], dissolved in acetonitrile or nitromethane containing triethylamine [exactly 1 mole], is added to a suspension of the zwitterion (IV) [exactly 1 mole] in the same solvent and stirred, at 0° or at room temperature, until the reagent has dissolved. For *combination*, the amino acid ester hydrochloride or peptide ester hydrochloride [exactly 1 mole], and an equivalent amount of triethylamine, are added, and the reaction mixture is stirred overnight at room temperature. For *isolation*, the solvent is removed *in vacuo*, and further simple operations appropriate to the special characteristics of the product peptide are carried out. In many cases, the residue may simply

TABLE I
SCALE: 2-4 MILLIMOLES

Peptide ^a	Yield of recrystallized peptide of given m.p., our best m.p., and best literature m.p.
A. Activation in CH ₃ CN at 0° for ca. 1 hr.	
Z.L-Phe Gly.OEt	93%, 109-110° 109.5-110.5° 109-110° ^g
Phth.Gly Gly.OEt	88%, 193.5-194.5° 193.5-194.5° 194-195° ⁱ
Z.L-Lys Gly.OEt	95%, 90.5-92.5° 91.5-93° 92-93° ^g
Z.L-Phe L-Leu.OMe	90%, 106-107° 109-109.5° ^h
Z.L-Asp Gly.OEt ^b	79%, 186-187° 186-187° 184-185° ^g
Z.Gly.L-Phe Gly.OEt ^c	90%, 116.5-117.5° 117-118° 120-120.5° ⁱ
Z.Gly.Gly L-Tyr.OMe	84%, 159.5-161.5° 159.5-161.5° ^h
Z.Gly Gly.Gly.OEt	91%, 167-168° 167-168° 167-168° ⁱ
Z.L-Met Gly.Gly.OEt	86%, 131.5-133° 132.5-133.5° 131-133° ^g
Z.L-Hypro Gly.Gly.OEt	80%, 145-146° 145-146° 144-145° ^g
B. Activation in CH ₃ NO ₂ at RT for ca. 7 min.	
Z.L-Asp Gly.OEt	80%, 185.5-187° 186-187° 184-185° ^g

Z.L-Asp L-Leu.OMe	76%, 176.5-178° 177.5-178.5° ^g
Z.L-Glu L-Val.OMe	77%, 172.5-173° 172.5-173.5° 173-175° ^g
Z.L-Glu L-Tyr.OMe	75%, 198-199° 197.5-198.5° 198-201° ^g
Z.Gly Gly.Gly.OEt ^d	90%, 167-168° ^g 167-168° 167-168° ⁱ
Z.Gly.DL-Phe Gly.OEt	89%, 132-133° 132.5-133° 132-134° ^g

^a The peptide bond was produced at the point indicated by a vertical stroke in the accompanying designations. ^b Cf. Section B of this Table. ^c This is the Anderson test [ref. 2]; in addition to the L-tripeptide, 2.2% of Z.Gly.DL-Phe.Gly.OEt was obtained. ^d Cf. Section A of this Table. ^e G. W. Anderson and R. W. Young, *J. Am. Chem. Soc.*, **74**, 5307 (1952). ^f J. C. Sheehan and J. J. Hlavka, *J. Org. Chem.*, **21**, 439 (1956). ^g J. R. Vaughan, Jr., and R. L. Osato, *J. Am. Chem. Soc.*, **74**, 676 (1952). ^h New compound. Found: C, 67.73; H, 6.92; N, 6.72. ⁱ S. S. Leach and H. Lindley, *Australian J. Chem.*, **7**, 173 (1954). ^j Ref. 2; the same laboratory reports elsewhere values varying from 116° to 120° for pure samples. ^k New compound. Found: C, 59.48; H, 5.78; N, 9.51. ^l G. W. Anderson, J. Blodinger and A. D. Welcher, *J. Am. Chem. Soc.*, **74**, 5309 (1952). ^m C. A. Dekker, S. P. Taylor, Jr., and J. S. Fruton, *J. Biol. Chem.*, **180**, 155 (1949). ⁿ N. C. Davis and E. L. Smith, *ibid.*, **200**, 373 (1953). ^o New compound. Found: C, 57.83; H, 6.84; N, 10.78. ^p E. Sondheimer and R. W. Holley, *J. Am. Chem. Soc.*, **76**, 2816 (1954). ^q Using free Gly.Gly.OEt, material of the same quality was obtained in 92% yield.

be triturated with water before recrystallization of the peptide from a suitable solvent. Alternatively the reaction mixture may be distributed between water and a suitable immiscible solvent. In all cases, the removal of the secondary product (III) is rendered especially easy by its water-solubility. A special practical merit of the method is that the peptides ordinarily are produced directly in an unusually high degree of purity; frequently a single recrystallization is sufficient to give a completely pure product. Typical results are summarized in Table I; of particular note, beyond the generally excellent yields, are (i) the very small degree of racemization, as judged by the Anderson test,² (ii) the use of hydroxyproline and tyrosine without protection of hydroxyl groups, and (iii) the very favorable results obtained with asparagine and glutamine derivatives.

N-Ethyl-5-phenylisoxazolium-3'-sulfonate (IV) [m.p. 207-208° (dec.). Found: C, 52.48; H, 4.20; N, 5.48; O, 25.18; S, 12.61] is a stable, crystalline, non-hygroscopic solid.⁸ It is prepared from 5-phenylisoxazole⁴ by treatment for 30 hours with excess pure chlorosulfonic acid at 102° [→ inseparable molecular compound, m.p. 92.6-92.8° (Found: C, 44.36; H, 2.51; N, 5.71; Cl, 14.68), containing 5-(3'-chlorosulfonylphenyl)-isoxazole and 5-(4'-

(2) Cf. G. W. Anderson and F. M. Callahan, *J. Am. Chem. Soc.*, **80**, 2902 (1958).

(3) The reagent is commercially available from Pilot Chemicals, Inc., Watertown 72, Massachusetts.

(4) L. Claisen and R. Stock, *Ber.*, **24**, 130 (1891); the preparation has been much improved in detail.

chlorosulfonylphenyl)-isoxazole in 2/1 ratio], alkylation of the resulting mixed sulfonyl chlorides in methylene chloride by triethyloxonium fluoroborate,⁵ ready separation, by crystallization from acetone/ether, of pure N-ethyl-5-(3'-chlorosulfonylphenyl)-isoxazolium fluoroborate [m.p. 161-162°. Found: C, 36.97; H, 3.22; N, 3.79; S,

(5) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

9.02], and hydrolysis of the latter by 2 *N* aqueous-alcoholic hydrochloric acid at room temperature.

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BOOK REVIEWS

Graphite and its Crystal Compounds. By A. R. UBBELOHDE, Professor of Thermodynamics, Imperial College of Science and Technology, London, and F. A. LEWIS, Lecturer in Inorganic Chemistry, Queen's University, Belfast. Oxford University Press, 417 Fifth Avenue, New York 16, N. Y. 1960. xii + 217 pp. 16 × 24 cm. Price, \$5.60.

The authors state that "this book aims to give descriptive access to current lines of research without attempting definitive treatments where these are considered to be premature." Such a statement disarms criticism since in fact no aspect of the subject can be considered to have reached definitive maturity. The book therefore provides a selective, classified and cautiously annotated bibliography, which surveys the literature to about the middle of 1959. Little effort has been made to select significant papers for especially detailed discussion or to provide theoretical background to help interpret the topics mentioned. The book is primarily designed not to provide scientific information but to provide references to sources of information.

The general level of the treatment can best be conveyed by quoting a typical paragraph.

A treatment has been proposed alternative to the tight binding theory originally introduced by Wallace (*cf.* also Yamazaki, 1957). In this approach (Slonczewski & Weiss, 1955) a detailed group theory study of the crystal is made, in order to obtain the 'topology' of the bands. In view of the large spacing between the layers the inter-layer interaction is treated by perturbation theory; this leads to a model of the energy bands which involves only a small number of parameters to be obtained by experiment. No satisfactory correlation has been found between this model and the value of the absolute magnetic susceptibility found experimentally (McClure, 1959). In application of this model to explain the results of cyclotron resonance in graphite (Nozieres, 1958) much experimental information is reviewed.

The contents are divided as follows: crystallography, physical properties, thermal properties, electron properties and band structure, crystal compounds of graphite, magnetic and electrical properties of the crystal compounds, graphite oxide, and chemical transformation of graphite to volatile products.

The treatment of the crystal compounds of graphite is exceptionally good. In general, the chemistry in this book is more adequate than the physics.

Since the book is not expensive, we can safely say that it provides good value. It may easily save many hours of time for anyone in need of a ready reference to the properties of graphite and its crystal compounds. On any particular topic, however, the original papers will need to be consulted. In order to make sure that nothing important has been missed, recourse to "Chemical Abstracts" will also be required. (This book contains about 600 references, and in 1958 alone "Chemical Abstracts" contained more than 400 references to graphite.) The system of placing the references in the text between parentheses makes the book difficult to read for any length of time.

A student wishing to obtain a good idea of the current status of this field would not be advised to turn to this book. He would do better to read some of the papers in the Proceedings of the Third Conference on Carbon, held in 1957

and published in 1959. In these papers the subject immediately becomes alive and meaningful.

The book has been beautifully printed by Vivian Ridler of the Oxford University Press. The editing has been somewhat careless, particularly in the failure to provide sufficiently descriptive captions for some of the figures, tables and illustrations. In the review copy, the paper varied in color. A slight lowering of the standards of the Oxford Press is therefore evident. In any case, one must question the value of such a monumental production for a book whose useful life can hardly be more than five years.

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Radiation Pyrometry and its Underlying Principles of Radiant Heat Transfer. By THOMAS R. HARRISON, Technical Advisor, Minneapolis-Honeywell Regulator Co., Brown Instruments Div.; formerly Director of Research, The Brown Instrument Co.; Physicist, Champion Porcelain Co.; Associate Physicist, National Bureau of Standards. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1960. xii + 234 pp. 16 × 23.5 cm. Price, \$12.00.

The title is admirably descriptive of this admirable book. The author, an authority on the technique of radiation pyrometry, states his prime purpose is to present the information needed to enable engineers to arrive at definite answers to questions arising in connection with the use of radiation pyrometers in industry. This he has done notably, but his accomplishment is much greater. To give the theoretical and practical explication of radiation pyrometers and pyrometry that he does, the author (a) presents and develops concisely and accurately the chief principles and ramifications of energy transfer by thermal radiation; (b) adopts a single, sound and acceptable terminology on the subject, which has been rather needed; (c) distinguishes clearly the multifarious concepts of spectral, total and band, and normal, angular and hemispherical, emittances, absorbances and reflectances of bodies, and their interrelationships; and (d) gives tabulated values of Planck's radiant intensity functions, in a convenient and condensed form. This compendium, although here focused on pyrometer practice, is directly applicable, and sufficient in principle, for the broader universe of radiative heat transfer problems.

The mathematics of the subject, and the equations required in pyrometer applications, are concisely and (with appendices) very completely developed. About a half of the text is devoted to particulars on different types of pyrometers and optical systems, including "light-guide" pyrometers, and the equations and factors on which their calibrations are based. Six tables give data on the emittances of materials, and optical properties of pyrometer lens and window materials; twelve tables give calibration data for particular pyrometers, and relative responses resulting with combinations of different lenses and windows; corrections for the emittance of objects sighted upon are presented in