

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.

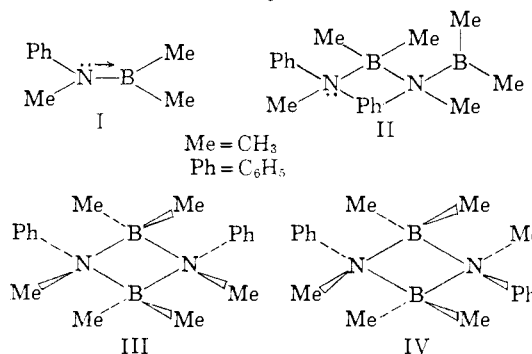
The p.m.r. spectrum at room temperature, obtained in a Varian high-resolution n.m.r. spectrometer at 60 mc., shows four distinct peaks: (1) a complex phenyl peak, (2) a single sharp N-methyl peak at 4.15 ppm. to high field of the center of the phenyl peak, (3) a sharp peak, assigned to one B-methyl, 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).

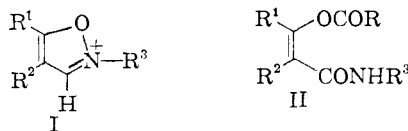
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A NEW SYNTHESIS OF PEPTIDES

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.