

promise in detecting conformational differences. The axial and equatorial hydroxyl groups in a commercial mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl alcohols (Fig. 2) are clearly distinguished with the equatorial hydroxyl resonance at lower field, permitting quantitative analysis of the mixture. Hemiacetal and hemiketal hydroxyl protons appear as doublets and singlets, respectively, at lower field (τ 3.5–5.0) than ordinary hydroxyl protons.

The position of an alcohol hydroxyl resonance in dimethyl sulfoxide is almost independent of concentration below 25 mole % (concentration studies have been carried out on methanol, ethanol, 2-propanol, and *t*-butyl alcohol). Spectra of most medium and large molecules are run at concentrations far less than 20 mole %.

Acknowledgment.—We are grateful to Prof. W. C. Wildman for the alkaloid samples used in this study.

(3) Research Fellow of the Alfred P. Sloan Foundation.

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RECEIVED DECEMBER 26, 1963

The Structure of $C_2B_5H_7$

Sir:

Results pertinent to the structure of one of the recently synthesized carboranes, 2,4-dicarbaborane,¹ are reported. This molecule has the form of a pentagonal bipyramid with two nonadjacent carbon atoms located in the pentagonal base, as shown in Fig. 1.

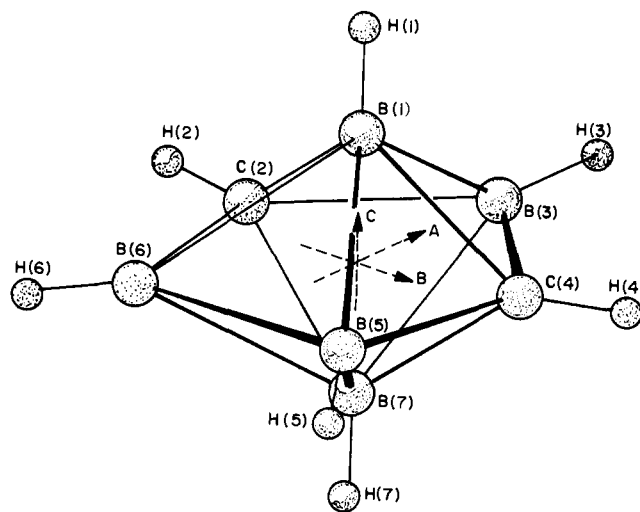


Fig. 1.—Molecular structure of 2,4-dicarbaborane, $C_2B_5H_7$. Dotted arrows show orientation of principal axes. Bond distances are given in the text.

N.m.r. and infrared measurements¹ on this molecule have shown that there are no bridge hydrogen atoms and that there are two pairs of nonequivalent boron atoms. This information does not distinguish between three different structures. Chemical arguments favor a structure in which the two carbon atoms are nonadjacent.¹

Standard microwave spectroscopic methods were used to obtain the results reported here. The five

isotopic species which were analyzed were those present in a sample with the natural ^{10}B – ^{11}B isotopic abundance. The five boron atoms have been located as accurately as this method allows,^{2,3} and good approximate positions have been determined for the two carbon atoms. Thus the basic molecular skeleton is fairly well established.

TABLE I

CENTER OF MASS COORDINATES FOR
2,4-DICARBAHEPTABORANE SKELETON

(Atom numbers correspond to labeling in Fig. 1)

Atom no.	Mass, a.m.u.	Coordinates, Å.		
		A	B	C
1	11.012789	0.1346	0	1.1541
2	12.003804	0.3275	-1.2102	0
3	11.012789	1.3879	0	0
4	12.003804	0.3275	1.2102	0
5	11.012789	-1.1204	0.8254	0
6	11.012789	-1.1204	-0.8254	0
7	11.012789	0.1346	0	-1.1541

With the rotational constants obtained from the pure rotational spectrum analysis of the five isotopic carboranes, the coordinates of the five boron atoms can be computed with respect to a standard reference molecule, which in this case was chosen as the C_2 - $^{11}B_5H_7$ molecule. The center of mass coordinates for the boron and carbon atoms are given in Table I. The position of the apical boron atom, B(1), which lies very close to the I_C axis, is poorly determined. By symmetry considerations, this atom lies in the AC plane, and may be either side of the BC plane by 0.1346 Å. From the present results one cannot distinguish between these two possibilities. If the a coordinate of this atom is positive then the B(1)–B(3) and B(1)–B(5) bond lengths are 1.704 ± 0.05 Å. and 1.894 ± 0.05 Å., respectively, whereas if the a coordinate is negative, then the corresponding bond lengths are 1.911 ± 0.005 Å. and 1.728 ± 0.005 Å. A B–B distance of 1.911 Å. is long compared to other boron compounds,^{4–7} so the shorter boron distance is more probably correct.

In contrast to the uncertainty prevalent for the apical boron atoms, the locations of the ring boron atoms are well determined. Several assumptions are necessary in order to obtain the C–B bond lengths, however. Assuming values for the B–H and C–H bond distances, and assuming that these bonds are directed outward along the bisectors of the ring angles, the C and H atom positions can be fitted to the C_2 - $^{11}B_5H_7$ observed rotational constants. Several values were assumed for the B–H distances and the carbon and hydrogen atom coordinates were refitted for each choice. The final B–H distances were chosen to reduce the difference between the calculated and observed moments of inertia to a minimum. The carbon atom position was insensitive to the B–H distance. All fitting was done such that both the carbon and hydrogen (C,H) atom positions could be varied simultaneously. The B(5)–B(6) bond distance was 1.650

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(3) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

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(5) L. E. Sutton, Ed., "Table of Interatomic Distances," The Chemical Society, London, 1958.

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(7) W. E. Strieb, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2331 (1963).

(1) T. P. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 3378 (1963); R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

$\pm 0.005 \text{ \AA}$. With the optimal coordinates obtained from the above fitting process, the ring carbon-boron bond lengths were $B(3)-C(4) = 1.606 \pm 0.1 \text{ \AA}$. and $B(5)-C(4) = 1.502 \pm 0.1 \text{ \AA}$. The B-H and C-H distances were $1.250 \pm 0.05 \text{ \AA}$. and $1.090 \pm 0.05 \text{ \AA}$., respectively.

The $B(5)-B(6)$ bond length is close to that of a pure single bond.⁴⁻⁶ The two carbon-boron bonds in the pentagonal base are close to single bond distances as found in other carbon-boron compounds,⁴⁻⁶ although one bond is a little shorter than the normal covalent single bond.

By using simple MO theory, Hoffmann and Lipscomb⁸ have predicted one of the three possible structures to be more stable than the other two. The results reported here confirm their prediction.

Acknowledgment.—The 10-mg. carborane sample used in this work was obtained on loan from Prof. T. Onak, to whom we wish to express our thanks. We also wish to thank Dr. R. E. Williams, who brought this problem to our attention. This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

(8) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

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RECEIVED JANUARY 24, 1964

Direct Conversion of Pyridine to Benzoic Acid

Sir:

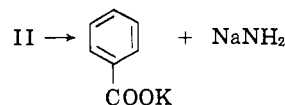
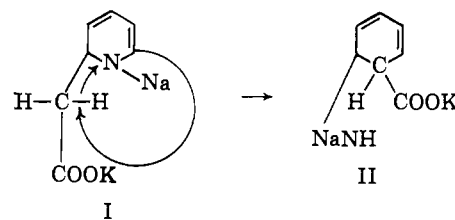
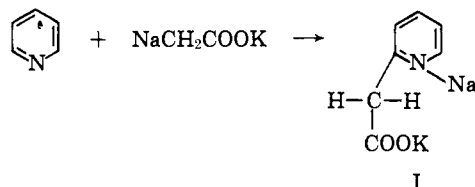
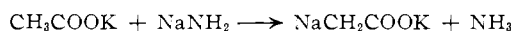
It is the purpose of this communication to describe what appears to be the first example of the direct conversion of a heterocyclic aromatic nitrogen compound to a carbocyclic aromatic compound. During a study¹ of the alkylation of salts of fatty acids with olefins in the presence of alkali metal catalysts, the use of pyridine as a diluent was investigated. Heating a mixture of 30 g. of potassium acetate, 50 g. of pyridine, and 10 g. of sodamide at $150-250^\circ$ for 4 hr. under 50 atm. initial ethylene pressure produced a dark brown mixture of liquid and solid, which was treated with cold water and then extracted with ether. The resulting aqueous solution was acidified with dilute hydrochloric acid and the liberated organic acids were taken up in ether and distilled under reduced pressure. After removal of the ether, acetic acid, and a small amount of mono- and diethylated acetic acid, there remained in the distillation flask 2 g. of amber crystalline material. Recrystallization from water yielded 1.5 g. (4% of the theoretical based on the potassium acetate) of benzoic acid, the identity of which was established by melting and mixture melting points, C and H analysis, and infrared and nuclear magnetic resonance spectroscopy. Benzoic acid was also obtained when the ethylene was replaced by nitrogen.

The relatively low yield of the benzoic acid raised the question as to whether its formation was due to interaction of pyridine and potassium acetate or to an impurity present in the reactants. That it was not due to a contaminant in the pyridine (for example, benzonitrile) was shown by infrared and gas-liquid chromatography; also, use of several different samples of pyridine always gave some benzoic acid when the

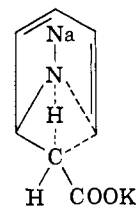
pyridine was heated with a catalyst and potassium acetate, but none when it was treated under the same conditions with other salts, such as sodium propionate. That the potassium acetate contained no potassium benzoate was proved by its acidification; furthermore, the reaction of pyridine and potassium acetate synthesized from redistilled glacial acetic acid and C.P. potassium hydroxide yielded benzoic acid.

Catalysts for the reaction included sodium, sodium hydride, potassium, and butyllithium. Yields of benzoic acid ranged from about 0.5 to 6%, depending on the catalyst and conditions.

The following sequence illustrates a possible mechanism for the formation of the potassium benzoate; the exact involvement of the catalyst is not indicated except for the initial steps.



The intermediate (I) may be represented by a delocalized structure such as



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RECEIVED JANUARY 29, 1964

Toward an Understanding of Nonclassical Carbonium Ions

Sir:

The electronic structure of the carbonium ions of norbornane (I), norbornene (II), and norbornadiene (III) has been the subject of much speculation¹ and some controversy.²

(1) For a review and references to the extensive investigations in this area, see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 111.

(2) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(1) L. Schmerling and W. G. Toekelt, *J. Am. Chem. Soc.*, **84**, 3694 (1962).