± 0.005 Å. With the optimal coordinates obtained from the above fitting process, the ring carbon–boron bond lengths were B(3)–C(4) = 1.606 ± 0.1 Å. and B(5)–C(4) = 1.502 ± 0.1 Å. The B–H and C–H distances were 1.250 ± 0.05 Å. and 1.090 ± 0.05 Å., 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 Lipscomb[8] 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).

JET PROPULSION LABORATORY ROBERT A. BEAUDET
CALIFORNIA INSTITUTE OF TECHNOLOGY ROBERT L. POYNTER
PASADENA, CALIFORNIA

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 study[1] 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° 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

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

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.

$$CH_3COOK + NaNH_2 \longrightarrow NaCH_2COOK + NH_3$$

$$II \longrightarrow \text{(benzoic acid)} + NaNH_2$$
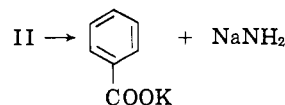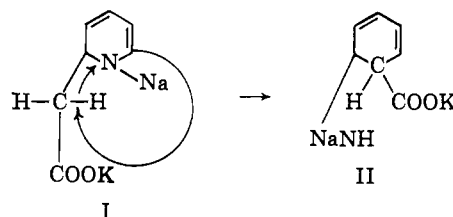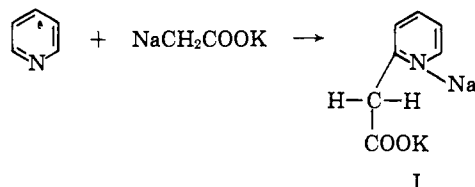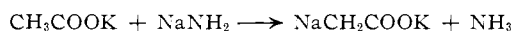
The intermediate (I) may be represented by a delocalized structure such as
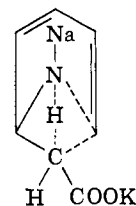
UNIVERSAL OIL PRODUCTS COMPANY LOUIS SCHMERLING
DES PLAINES, ILLINOIS W. G. TOEKELT

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 speculation[1] 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).