± 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).

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## 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.

$$CH_3COOK + NaNH_2 \longrightarrow NaCH_2COOK + NH_3$$
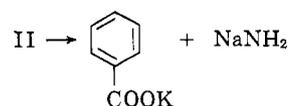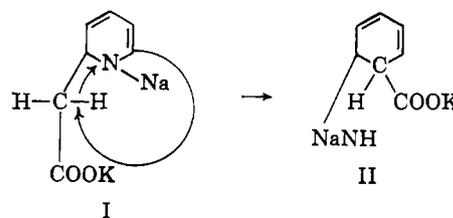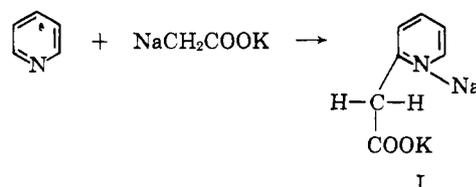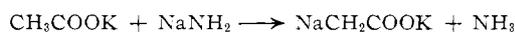
The intermediate (I) may be represented by a delocalized structure such as
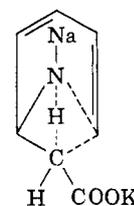
UNIVERSAL OIL PRODUCTS COMPANY   LOUIS SCHMERLING
DES PLAINES, ILLINOIS   W. G. TOEKELT

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).

I   **II**   **III**
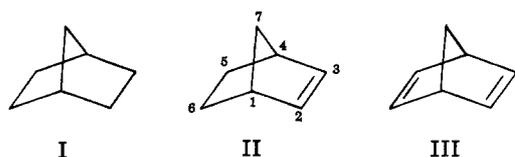
Recently an extended Hückel theory[3] has been applied to a study of important carbonium ions.[4] For the ions based on the bicyclo[2.2.1]heptane structure it was found that in each of the three epimeric pairs,[5]
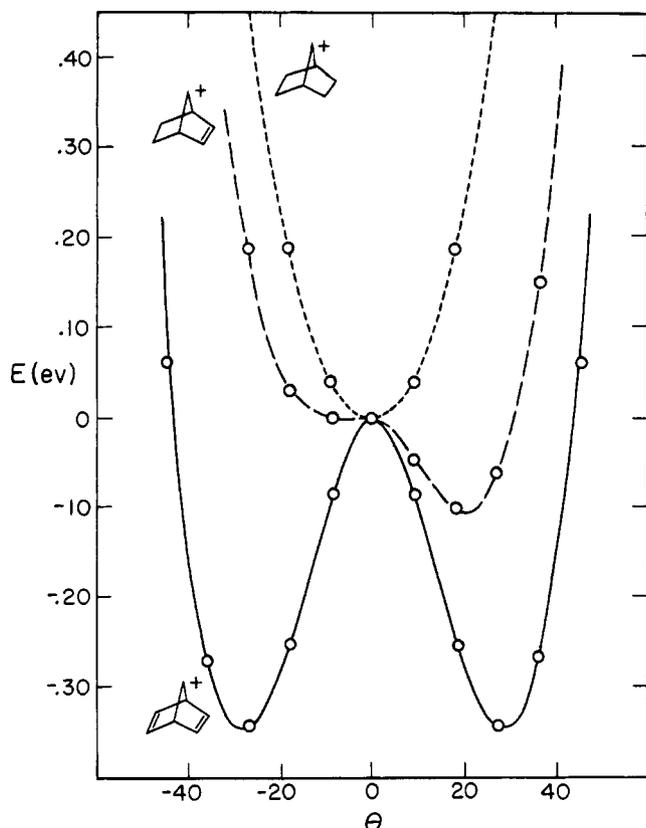

Fig. 1.—Potential energy curves for the 7-norbornyl, 7-norbornenyl, and 7-norbornadienyl cation. The zero of energy is chosen for each molecule at the symmetrical position. θ (in degrees) measures the rotation of the C1, C7, C4 plane from the symmetrical locus.

the relative stabilities of the cations were correlated with the calculated stabilities of the incipient, tetrahedral carbonium ions. However, when all the calculations were placed on the same scale, the 7-cations of II and III did not emerge as particularly stable. Stimulated further by the finding of asymmetry in 7-norbornadienyl,[6] a study of one particular distortion of the trigonal 7-cations was undertaken, in which C-7 with its hydrogen is displaced on an arc in the plane bisecting C-2, C-3 and C-5, C-6, keeping C-7, C-1 and C-7, C-4 at 1.54 Å.[7,8]

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963):

(4) R. Hoffmann, *ibid.*, in press.

(5) *exo*- and *endo*-2-norbornyl, *syn*- and *anti*-7-norbornenyl, *exo*- and *endo*-5-norbornenyl cations.

(6) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962); P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. C. Kornegay, *ibid.*, **85**, 3630 (1963).

(7) The geometry of norbornane is from the model of C. F. Wilcox, Jr. [*ibid.*, **82**, 414 (1960)]; that chosen for the unsaturated compounds is discussed in ref. 4.

(8) The method is not sufficiently reliable to permit a trustworthy comparison of the stabilities of the distorted form discussed here and one of the

Let the extent of distortion be described by an angle θ of displacement of the 1,7,4-plane from the symmetrical position, positive θ corresponding to motion toward the double bond in II. The calculated potential energy curves for the 7-cations of I, II, and III are shown in Fig. 1. The symmetrical structure is the equilibrium geometry of 7-norbornyl; 7-norbornadienyl clearly prefers an unsymmetrical molecule; for 7-norbornenyl the shallower minimum lies toward the double bond. The association of increased delocalization with stability may be appreciated by some sample charge distributions shown in Fig. 2.
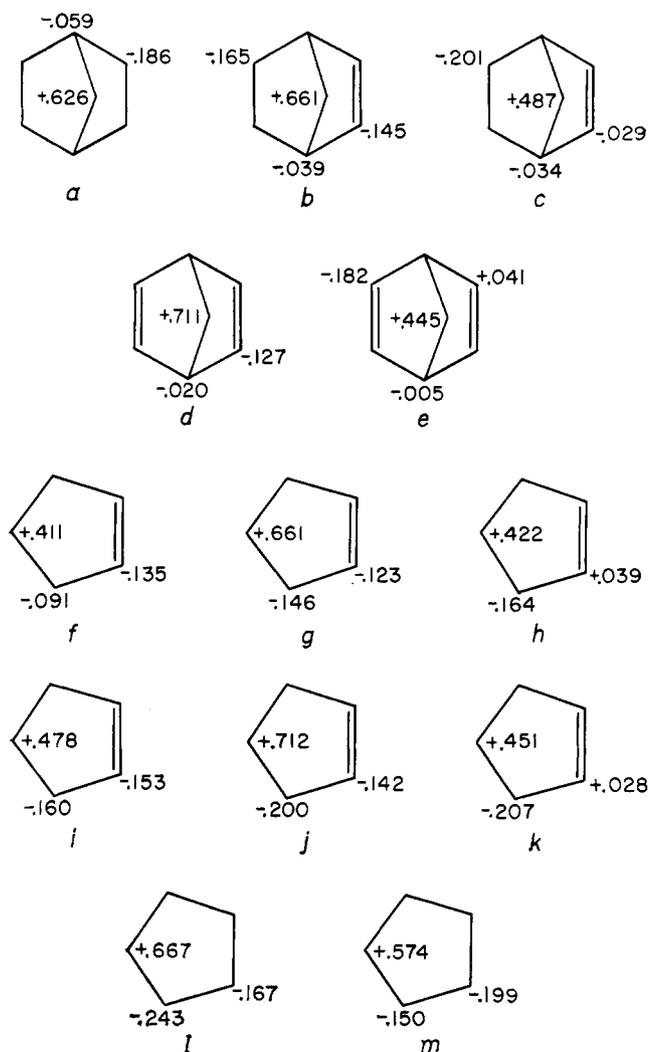

Fig. 2.—Carbon charge distributions in some cations: a, $\theta = 0°$; b, $\theta = 0°$; c, $\theta = 18.5°$; d, $\theta = 0°$; e, $\theta = 27°$; f, planar unstrained, $\theta = -54.5°$; g, unstrained, $\theta = 0°$; h, unstrained, $\theta = 27°$; i, strained, $\theta = -27°$; j, strained, $\theta = 0°$; k, strained, $\theta = 27°$; l, strained, $\theta = 0°$; m, unstrained, $\theta = 18.5°$.

To explore further the nature of these potential energy surfaces, similar distortions were examined for the 4-cations of cyclopentane (IV) and cyclopentene (V). The carbon skeleton of norbornene was retained and two modifications were studied: "strained," in which independent of the motion of C-4, the tertiary hydrogen of norbornene was used at positions 3 and 5, and another hydrogen added in the direction of a hypothetical carbon located as in norbornene; "un-

pairs of tricyclic classical ions suggested by Brown (ref. 2). Nevertheless, for 7-norbornadienyl at $\theta = 27°$, a motion of C-7 parallel to C-2, C-3 was examined and found to be destabilizing.

IV   V

strained,"[9] in which the hydrogens at 3 and 5 were placed in their natural positions, following the distortion. Figures 3 and 4 show the computed potential energy curves. Strained cyclopentyl has a minimum
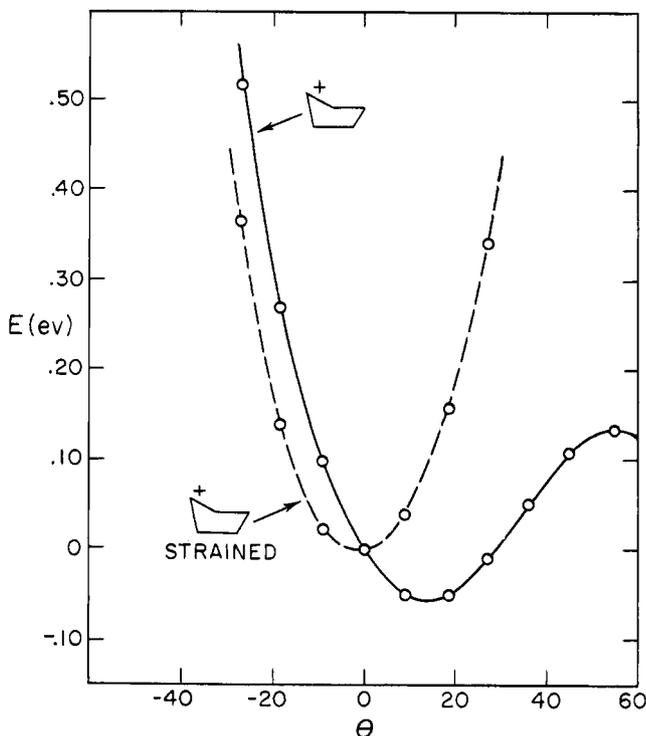

Fig. 3.—Potential energy curves for 4-cyclopentyl cation. Angle θ, measured in degrees from position in norbornane fragment, with zero of energy set at this angle for both forms. Planar molecule at $\theta = 54.5°$. On an absolute scale, the unstrained curve should be displaced down by 1.315 e.v.

very close to the norbornene fragment geometry; the unstrained form, while still preferring a puckered shape, resists less a distortion toward planarity of the carbon framework. The strained cyclopentenyl exhibits two minima, one puckered nearly 90° and stabilized by charge transfer to the double bond, the other, nearly planar, stabilized by charge transfer to the adjacent carbons and their hydrogens. Unstrained cyclopentenyl, while clearly preferring a planar molecule, still retains a second minimum. Insofar as these factors can be isolated, the favored planarity of cyclopentenyl contrasted to the slight puckering of cyclopentyl can be attributed to the absence of eclipsing hydrogen configurations in the former.

Approximate superposition of the strained cyclopentyl and cyclopentenyl curves (including an attenuation factor to account for the fact that carbons and not hydrogens are responsible for the strain) results in the energy variation exhibited for 7-norbornenyl in Fig. 1. A superposition of two strained cyclo-

(9) The "unstrained" form still retains in its carbon framework the strain imposed by the norbornane geometry, such as the small CCC angle at C$^+$

pentenyl moieties gives a reinforcement of the double minima, resulting in the deep wells of 7-norbornadienyl. A distortion in the latter molecule is thus stabilized not only by improved charge transfer to the nearer
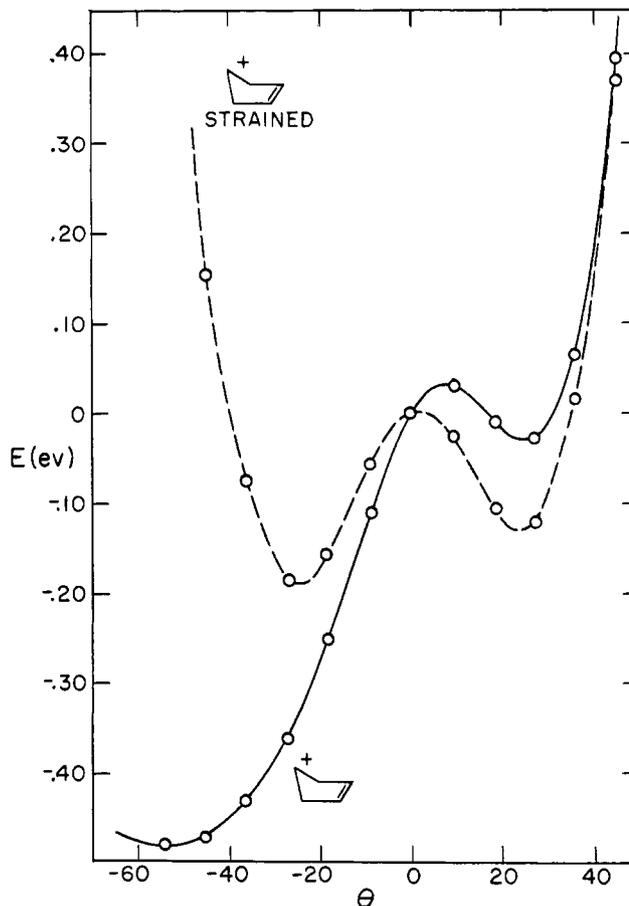

Fig. 4.—Potential energy curves for 4-cyclopentenyl cation. Angle θ, measured in degrees from position in norbornane fragment, with zero of energy set at this angle for both forms. Planar molecule at $\theta = -54.5°$. On an absolute scale the unstrained curve should be displaced down by 1.103 e.v.

double bond, but also by the assumption of an advantageous planar geometry with respect to the other double bond. The very interesting feature of the double minimum in the cyclopentenyl cation raises the possibility of a new type of isomerism.[10]

Acknowledgment.—The author wishes to thank E. J. Corey for numerous discussions.

(10) The nonclassical minimum of unstrained cyclopentenyl is probably so energetically unfavorable relative to the planar ion that it does not influence normal reactions. Experimentally, the absence of activation in 4-bromocyclopentene solvolysis was recently demonstrated by P. D. Bartlett and M. R. Rice, J. Org. Chem., 28, 3351 (1963).

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A Dicarbonium Ion as a Solvolysis Intermediate

Sir:

The formation of a stable dipositive carbonium ion from trichloromethylpentamethylbenzene in concen-