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 potassium benzoate: the catalyst is not indicated except for the initial steps.

\[
\text{CH}_2\text{COOK} + \text{NaNH}_2 \rightarrow \text{NaCH}_2\text{COOK} + \text{NH}_3
\]

\[
\text{I} \rightarrow \text{NaH} \text{COOK} \rightarrow \text{II} \rightarrow \text{COOK} + \text{NaNH}_2
\]

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

\[
\text{III} \rightarrow \text{COOK} \rightarrow \text{NaH} \text{COOK}
\]

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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, and some controversy.

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

Let the extent of distortion be described by an angle $\theta$ of displacement of the 1,7,4-plane from the symmetrical position, positive $\theta$ 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.
strains,\(^9\) 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 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-

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

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

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-