

EQUILIBRATION STUDIES: A 2-PYRONE AND A 4-PYRONE

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(Received 4 March 1963)

A synthetic and structural interest in some naturally occurring 2-pyrone<sup>1</sup> has influenced us to further investigate the chemistry of the pyrone molecule. We wish to report the direct conversion of a 4-pyrone to a 2-pyrone by a method which is conceptually applicable to the equilibration of a variety of isomeric compounds.

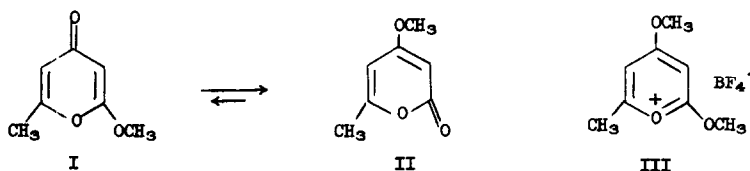
Traditionally 4-pyrones have been considered to be aromatic while the 2-pyrones have been represented as non-aromatic.<sup>2</sup> Presumably this order should be reflected in the relative ground state energies of these compounds; *i.e.* a 4-pyrone would be of lower energy than a 2-pyrone. However recent investigators<sup>3</sup> have reported evidence which indicates that the order of thermodynamic stabilities of the pyrones is not that predicted on traditional grounds. Conclusive information on the relative stabilities of one set of isomeric pyrones has been obtained by the direct equilibration of 2-methoxy-6-methyl-4-pyrone<sup>4</sup> (I) and 4-methoxy-6-methyl-2-pyrone<sup>4</sup> (II) through the agency of 2,4-dimethoxy-6-methyl-pyrylium fluoroborate (m.p. 152-154°)<sup>5</sup> (III) as a catalyst.

<sup>1</sup>P. Beak and H. Abelson, J. Org. Chem. **27**, 3715 (1962).

<sup>2</sup>G. M. Badger, "The Chemistry of Heterocyclic Compounds," Academic Press, New York, 1961, pp. 428-429.

<sup>3</sup>D. Herbst, W. B. Mors, O. R. Gottlieb and C. Djerassi, J. Am. Chem. Soc. **81**, 2427 (1959); J. D. Bu'Lock and H. G. Smith, J. Chem. Soc. 502 (1960); H. Nakata, Bull. Chem. Soc. Japan **33**, 1683 (1960); and references cited therein.

<sup>4</sup>W. B. Mors, M. T. Magalhães and O. R. Gottlieb, "Fortschritte Der Chemie Organischer Naturstoffe," IX, Springer-Verlag, Vienna, 1962, p. 141.



In a typical experiment 10.0 mg. of the 4-pyrone, I, and 1.2 mg. of the pyrylium salt, III, were heated in a sealed tube at  $140^\circ$  for five minutes to give 9.3 mg. of an ether soluble product which was shown by melting point and infrared and ultraviolet<sup>6</sup> spectral criteria to be at least 98% of the 2-pyrone, II. The ether insoluble product was 1.0 mg. of the pyrylium salt, III. I was not converted to II in the absence of III. The substantial conversion of 2-methoxy-6-methyl-4-pyrone to 4-methoxy-6-methyl-2-pyrone indicates that the 2-pyrone, II, is more stable than the 4-pyrone, I, by at least 3 Kcal./mole at  $140^\circ$ . This result is clearly important to the chemistry of the pyrones<sup>7</sup> and to the general problem of the relative stabilities of a number of heterocyclic systems. Furthermore this conversion illustrates a method of equilibration which is in principle applicable to any isomers which have a common alkylated derivative. Experiments are underway to extend these observations.

The author is grateful to Dr. S. G. Smith for incisive and productive discussion.

<sup>6</sup>This compound was prepared from I or II and methyl iodide by the method of H. Meerwein, V. Henderick and K. Wunderlich, *Arch. Pharm.* **291**, 541 (1958). The structure of the pyrylium salt was confirmed by infrared, ultraviolet and proton magnetic resonance spectroscopy and by satisfactory analytical data.

<sup>7</sup>M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.* 345 (1957).

<sup>7</sup>The chemical and spectral significance of this will be discussed in a forthcoming publication.