Photoelectron Spectrum of Bicyclo[2.1.0]pent-2-ene: Electronic Destabilization of a Homo[4*n*]annulene

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Rotational Zeeman spectroscopy may afford experimental measures for anisotropies in the diagonal values of magnetic susceptibility tensors; the out-of-plane minus the average in-plane susceptibilities, $\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$, for bicyclo[2.1.0]pent-2-ene is positive, $+3.6 \times 10^{-6}$ erg/(G^2 mol), a finding suggestive of a positive ("paramagnetic") nonlocal contribution to χ_{cc}.[1-4] This most simple of homo[4*n*]annulenes may accordingly exhibit physical properties characteristic of the antiaromatic [4*n*]-annulenes.[5,6]

We now report the photoelectron spectrum of bicyclopentene and estimate the magnitude of the destabilizing interaction of cyclobutenyl π and cyclopropyl e_s orbitals, filled orbitals of comparable energies.

The helium(I) photoelectron spectrum of bicyclopentene was obtained with a Perkin-Elmer PS-18 spectrometer using a standard gas-inlet system and argon as an internal calibration standard. The observed band maxima (Figure 1) at 8.6, 10.8, 11.2, 11.9, 12.6, and 14.7 eV were taken to be vertical ionization potentials, IP_v.

Molecular orbital calculations using Gaussian-type orbitals[7] in combination with Koopmans' approximation[8] and HAM/3 calculations which do not depend on Koopmans' theorem[9,10] agree in assignments for the observed bands: the three of lowest energy stem from 12a′ ($\pi - e_s$), 11a′ ($\pi + e_s$), and 6a″ orbitals[7] of bicyclopentene. These data and assignments may be combined with an orbital interaction analysis[11] to provide a rough estimate of the electronic destabilization associated with interaction between the cyclobutenyl π and the cyclopropyl e_s orbitals. The energy of the π level of cyclobutene is 9.6 eV;[12] the e_s and e_a levels of the cyclopropane moiety in the absence of interaction with the olefinic unit could be as much as 0.8 eV apart,[13,14] and the lower e_a level would not be expected to shift much through interaction with the cyclobutenyl π^* orbital. An orbital interaction diagram may be constructed accordingly, as shown in Figure 2.

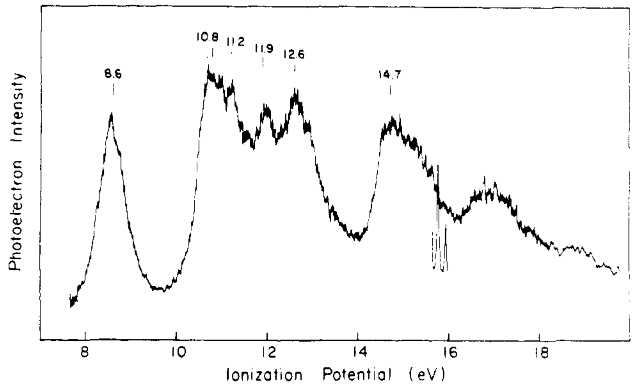

Figure 1. Photoelectron spectrum of bicyclo[2.1.0]pent-2-ene.

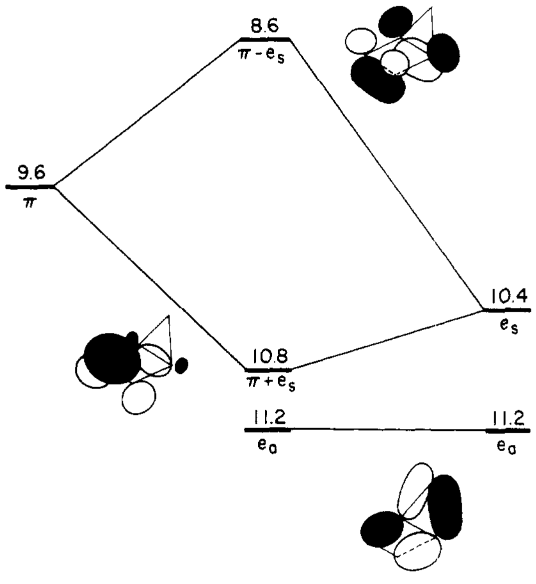

Figure 2. Molecular orbital interaction diagram for the combination of cyclobutene π and cyclopropyl e_s levels in bicyclo[2.1.0]pent-2-ene (orbital perspective drawings based on ref 7).

The electronic destabilization of the two orbitals implied by the interaction model is 1.2 eV, or 28 kcal mol^{-1}. The homoantiaromaticity of bicyclopentene[4] discussed by Borden and Jorgensen[15-17] entails, then, a substantial energetic consequence. A comparable destabilization is not evident in the photoelectron spectrum of bicyclo[2.2.0]-hex-2-ene (first IP_v = 9.4 eV).[18]

The electronic destabilization of the bicyclopentene molecule may be estimated by comparing calculated and experimentally derived heats of formation. The $\Delta H_f°$ value reckoned[19] without consideration of the homoantiaromaticity of the molecule is 67.6 kcal mol^{-1}; the experimental $\Delta H_f°$ derived from the heats of hydrogenation of bicyclopentene,[20] 42.5 kcal mol^{-1}, and $\Delta H_f°$ (bicyclopentane),[21,22] 36.6 kcal mol^{-1}, is 79.1 kcal mol^{-1}. The dif-

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ference, 11.5 kcal mol^{-1}, approximates the molecular electronic destabilization associated with the homoantiaromaticity of bicyclopentene.

The hot-molecule effects observed in the thermal isomerizations of bicyclopentenes[23-25] have been analyzed in terms of RRKM theory and the Benson-O'Neal estimate of $\Delta H_f°$ for bicyclopentene.[19] The higher energy of the molecule connected with homoantiaromaticity implies that a reanalysis would need to employ a more efficient collisional deactivation parameter and a more negative $\Delta H°$: the transition-state region for the bicyclopentene-to-cyclopentadiene thermal isomerization[26] is some 73.6 kcal mol^{-1} above ground-state cyclopentadiene.

Further study of bicyclopentene and consideration of the concepts of antiaromaticity[27] and homoantiaromaticity seem warranted.

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Registry No. bicyclo[2.1.0]pent-2-ene, 5164-35-2.

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2,5-Dimethyl-3-furoic Acid, a Companion to Feist's Acid in the Reaction of 3-Bromo-5-(carboethoxy)-4,6-dimethyl-2-pyrone with Alkali

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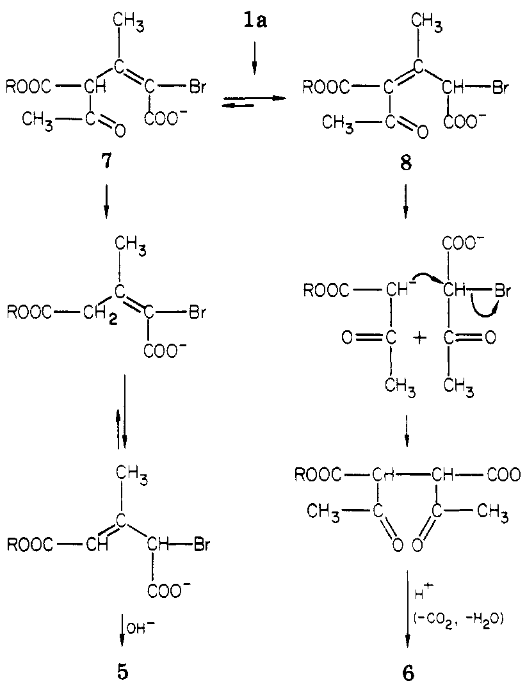
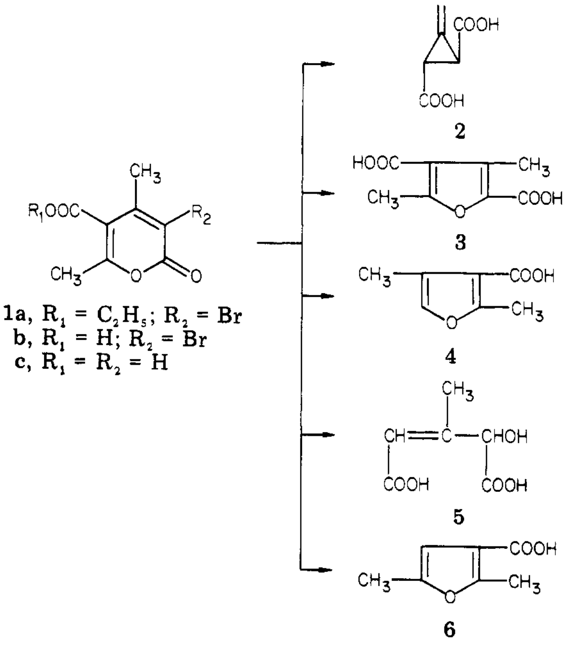
In 1893 Feist described the isolation of a dicarboxylic acid containing a three-membered ring from the treatment of ethyl bromoisodehydroacetate (3-bromo-5-(carboethoxy)-4,6-dimethyl-2-pyrone, **1a**) with alkali[1] but the structure of this acid (Feist's acid) was not securely established until 1952 when Ettlinger proved it to be 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid (**2**).[2,3]

Feist also reported that the bromo acid **1b** yielded 2,4-dimethylfuran-3,5-dicarboxylic acid (**3**) upon treatment with alkali and that the bromination in water of isodehydroacetic acid (**1c**) itself yielded 2,4-dimethyl-3-furoic acid (**4**).[1] More recently, a reinvestigation of the reaction of 3-bromo-2-pyrones with bases confirmed the earlier results and further disclosed that 3-hydroxy-2-methylpropene-1,3-dicarboxylic acid (**5**) was also formed in the reaction of **1a** in 20% aqueous KOH at 20 °C.[4] No explanation was provided for this transformation.

Scheme I



We now report that yet another furoic acid is obtained when **1a** is treated with boiling 16% aqueous KOH and the reaction products are esterified and distilled. The lower boiling fraction yields one major component, which gives crystalline 2,5-dimethyl-3-furoic acid (**6**) after saponification. This product was identified by direct comparison with an authentic sample.[5]



1a, $R_1 = C_2H_5$; $R_2 = Br$
b, $R_1 = H$; $R_2 = Br$
c, $R_1 = R_2 = H$

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