

Table I. Vertical Ionization Potentials (eV)^a of **3**, **4**, and **5**^b

Cyclopentanone (3)	Cyclopenten-2-one (4)	Cyclopenten-3-one (5)
9.25 (710 and 1220 cm ⁻¹)	9.34 (663 cm ⁻¹)	9.44 (1423 cm ⁻¹)
11.3–15.3 ^c	10.10 (1089 and 1417 cm ⁻¹)	9.98 (1204 cm ⁻¹)
15.94	11.9–15.3 ^c	12.0–15.1 ^c
16.56	16.23	16.22

^a ±0.02 eV. ^b The vibrational spacings are given in parentheses, and are ±40 cm⁻¹. ^c Several ionization potentials measured from adiabatic onset.

cm⁻¹ may be associated with the symmetric methylene group wagging or twisting modes which have been assigned in the 1150–1330-cm⁻¹ region.⁶

The first ionization of **4** at 9.34 eV is assigned to removal of a n electron, and it has a vibrational spacing of 663 cm⁻¹. In **4**, the n level has been stabilized by 0.09 eV relative to the n level in cyclopentanone. This is probably due to the greater inductive effect of the two sp² carbons in **4**. The second band at 10.10 eV is assigned to ionization from a π level. The vibrational progressions of 1089 and 1417 cm⁻¹ on this band are probably due to C=C and C=O stretching modes in the ion which occur at 1593 and 1720 cm⁻¹ in the neutral molecule.⁷ This IP is substantially higher than the π ionization in cyclopentene, 9.18 eV.⁸ The inductive effect of the oxygen atom, the additional sp² carbon in the ring, and the interaction between the π_{CC} and π_{CO} levels would all tend to lower the π level in **4**. We can estimate the effect of replacing one sp³ carbon with an sp² carbon in the following manner. The average of the two π IP's of cyclopentadiene is 9.66 eV,⁸ and hence replacement of two sp³ carbons with sp² carbons in a five-membered ring lowers the average π levels by 0.48 eV relative to cyclopentene. Therefore, the replacement of one sp³ carbon with an sp² carbon should stabilize the π level by ca. 0.24 eV. The inductive effect of the oxygen atom is not expected to be large. Thus the dominant effect in the stabilization of the π level in **4** is the conjugative interaction between the π_{CC} and π_{CO} levels. At first this may appear surprising, since one might expect the interaction in an α,β-unsaturated carbonyl system to be analogous to a 1,3-diene where the highest π level is raised.⁹ However, simple Hückel calculations¹² and more advanced treatments¹³ indicate that, in the case of an α,β-unsaturated ketone, the π_{CC} level is in fact stabilized on conjugation with the π_{CO} levels.¹⁴

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(9) In butadiene the first π level IP occurs at 9.06 eV,¹⁰ whereas the corresponding value in propylene is at 10.01 eV.¹¹

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(14) These are not pure π_{CC} or π_{CO} levels in the conjugated systems, but are combinations of the two. Unfortunately, the π_{CO} IP in compounds **3–5** is obscured by the σ IP's. For example, the π_{CO} ionization in formaldehyde occurs at 14.09 eV: D. W. Turner, A. Baker, C. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970, pp 132–163.

The first πe band of **5**¹⁵ at 9.44 eV with a vibrational spacing of 1423 cm⁻¹ is assigned to ionization from the n level which has been stabilized by 0.19 eV relative to **3**. The uv spectrum of **3** has a band at 3001 Å (4.13 eV) assigned to an n → π* transition¹⁶ and **5** has a band at 2850 Å (4.35 eV)¹⁷ due to an n → π* transition. Part of this hypsochromic shift of 0.22 eV may be ascribed to a stabilization of the n level in **5** rather than only to a shift in the π* level, as was previously thought¹² (*vide infra*). The second band at 9.98 eV is assigned to ionization from a π level, mainly π_{CC}. Cyclopenten-3-one (**5**) has an ir band at 1605 cm⁻¹ which is assigned to the C=C stretch. The corresponding spacing of 1204 cm⁻¹ in the second IP of **5** agrees well with the values of 1320 and 1250 cm⁻¹ in the π ionizations of cyclopentene⁸ and ethylene,¹⁸ respectively. This π_{CC}¹⁴ level in **5** has an IP 0.80 eV greater than the corresponding level in cyclopentene. As in **4**, the most important contribution to this stabilization of the π_{CC} level no doubt is due to the resultant interaction of the π_{CC} with both π_{CO} levels. This interaction may occur directly through space^{3,12} or through a σ_{CH₂} level of the appropriate symmetry.³ If the replacement of an sp³ carbon by an sp² carbon should stabilize the π_{CC} level by 0.24 eV (*vide supra*), then the π_{CC} stabilization due to the π interactions must be ca. 0.56 eV. This implies that the π_{CO}* level has been destabilized.¹⁹

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Conversion of Natural Phthalideisoquinolines into Benzazepine Alkaloids

Sir:

We wish to report the successful conversion of the opium alkaloid nornarceine (**1**) into the benzazepine (±)-11-methyl-2,3-methylenedioxy-4,6,7,8-tetrahydroxyrheadan¹ (**2**). Since **1** is derivable from the phthalide alkaloid (–)-α-narcotine² (**3**), the following reaction sequence³ constitutes the first chemical transforma-

(1) The generic name rheadan is proposed for the basic tetracyclic structure common to rheadine and related alkaloids (T. Kametani, "The Chemistry of the Isoquinoline Alkaloids," Elsevier, Amsterdam, 1969, Chapter 14). Our proposal conforms with *Chemical Abstracts* practices and is exemplified by the numbering and lettering shown for the rheadan **2**. It is suggested that the term isorheadan be used when the 4b and 10b hydrogens are in a trans relationship.

(2) The original procedure of P. Rabe (*Chem. Ber.*, **40**, 3280 (1907)) has been replaced by a new and improved method which will be reported in the full paper.

(3) The absolute configurations indicated in **2**, **7**, **8**, and **9** represent only one of the two possible enantiomers. All compounds gave acceptable elemental analyses.