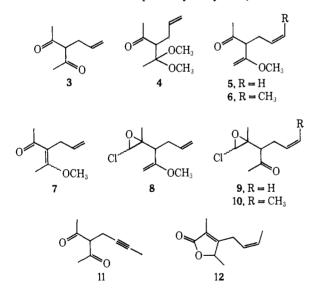
of crude ketal over a catalytic amount of anhydrous ptoluenesulfonic acid produced a mixture of the vinyl ether 5 (64%) (ir (CCl₄) 1720 cm⁻¹; nmr (CDCl₃) δ 3.00 (m, 1), 4.06 (s, 2), etc.) and the stereoisomeric β -methoxy- α , β -unsaturated ketones 7 (18%) (ir (CCl₁) 1665 cm⁻¹; uv (95% EtOH) 273 nm (ϵ 14,200)) separable by vapor phase chromatography. The distribution of isomers 5 and 7 observed is the result of a kinetic effect because *p*-toluenesulfonic acid catalyzed equilibration in refluxing tetrahydrofuran leads to an equilibrium mixture containing 65% of the conjugated (7) and 35% of the unconjugated isomer (5) (uv and vpc analysis). Condensation of the ketone 5 with dichloromethyllithium⁵ gave the sensitive chloroepoxide 8 which was hydrolyzed directly (20°, 45 min) in 2:1 tetrahydrofuran-10% aqueous hydrochloric acid to the equally sensitive ketone 9 (ir (CCl₄) 1720 cm⁻¹). While the enol ether 8 was stable to 0.1 M aqueous methanolic barium hydroxide at room temperature, cyclization of the corresponding ketone 9 under identical conditions was complete within 1 hr giving allethrolone (1) (72%)based on 5) (ir (CCl₄) 3430, 1705, 1645 cm⁻¹; uv (95%EtOH) 231 nm (ϵ 13,300)).⁶ Its nmr spectrum was identical with that reported.7 The synthesis can be performed with crude vinyl ether 5 because the vinylogous ester 7 does not combine with dichloromethyllithium. The latter is transformed to the β -diketone 3 readily separable from the rethrolone 1 by base extraction, in the course of the two subsequent hydrolytic operations.



Alkylation of acetylacetone with 2-butynyl-p-toluenesulfonate⁸ in aqueous methanol containing 1 equiv of Hünig's base⁹ gave the cinerolone precursor 11 (44%; yield not optimized); uv (95% EtOH) 287 nm (e 3200); uv (EtOH, NaOH) 303 nm (e 21,000). Ketal exchange and elimination of methanol, as described for allethrolone, were followed by catalytic hydrogenation over

(5) Method of G. Köbrich and W. Werner, Tetrahedron Lett., 2181 (1969).

(6) For a recent synthesis of allethrolone which, however, has not been applied to the preparation of a natural rethrolone, see M. Vandewalle and E. Madeleyn, *Tetrahedron*, 26, 3551 (1970).
(7) A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M.

Elliot, and N. F. James, ibid., 25, 1738 (1969).

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(9) Method of K. W. Rosenmund and H. Bach, Chem. Ber., 94, 2394 (1961).

Lindlar's catalyst. The resulting cis olefin 6 was transformed to rac-cis-cinerolone (2) in similar yield by methods detailed for allethrolone. Both ir and nmr spectra⁷ were identical with those of natural (+)- and synthetic¹⁰ (\pm)-cis-cinerolone (2) and identity was confirmed by thin-layer chromatography.

Parenthetically, thermolysis of the chloroepoxide 10 in refluxing xylene did not yield the corresponding α chloroaldehyde⁵ but the lactone 12 (62%) (ir (CCl₄) 1755 cm⁻¹; nmr (CCl₄) δ 1.33 (d, 3, J = 7 Hz), 1.70 (d, 3, J = 6.5 Hz), 1.77 (s, 3), 3.07 (d, 2, J = 6 Hz), 4.73 (q, 1, J = 6.5 Hz), and 5.1-5.8 (m, 2)). This seemingly new synthesis of α -butenolides is being explored further.

Acknowledgment. The authors are grateful to Hoffmann-La Roche, Inc., Nutley, N. J., for financial support and to Drs. A. Brossi and R. A. LeMahieu of that firm for samples of synthetic and natural cinerolone.

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G. Büchi,* D, Minster, J, C, F. Young Department of Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts 02139 Received June 16, 1971

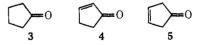
Photoelectron Spectra of Cyclopentanone and Cyclopentenones

Sir:

It is well known that the π bonds of a 1,3-unsaturated system of type 1 interact very strongly provided the two π bonds can approach coplanarity. However, when the two π bonds are "insulated" by any number of saturated

$$C = C - C = X \qquad C = C - (C)_n - C = X$$
1 2

atoms as is 2 then the experimental results are not always interpretable.¹ Recently, however, Heilbronner and coworkers² have demonstrated the utility of photoelectron spectroscopy (pes) in determining the interaction of the π bonds in systems of type 1 and 2 where X = C. Hoffmann³ has given an extensive theoretical analysis of this phenomenon. We have been investigating the interaction of an ethylenic π bond with a carbonyl π bond, 1 and 2 where X = O, and we wish to report our results of a study of the pe spectra⁴ of the series of cyclopentane derivatives 3-5 (Table I).



The first ionization potential (IP) of 3 at 9.25 eV which we assign to ionization from one of the nonbonding (n) levels has vibrational spacings of 710 and 1220 cm⁻¹. The spacing of 710 cm⁻¹ in the ion is assigned to the symmetric skeletal ring breathing which is observed at 711 cm⁻¹ in the Raman spectrum of the neutral molecule.³ The vibrational spacing of 1220

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- (2) E. Haselbach, E. Heilbronner, and G. Schröder, Helv. Chim. Acta, 54, 153 (1971), and previous papers.
 - (3) R. Hoffmann, Accounts Chem. Res., 4, 1 (1971).
- (4) The pe spectra were obtained using a 584-Å spectrometer with a

²⁻in. radius hemispherical electrostatic energy analyzer.
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Table I, Vertical Ionization Potentials $(eV)^{\alpha}$ 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°	10.10 (1089 and 1417 cm ⁻¹)	9.98 (1204 cm ⁻¹)
15.94	11.9-15.3	12.0-15.1
16.56	16.23	16.22

 $^{a} \pm 0.02 \text{ eV}$. ^b The vibrational spacings are given in parentheses, and are ± 40 cm⁻¹. • 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 sp^2 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 $\pi_{\rm CO}$ 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 $\pi_{\rm CC}$ level is in fact stabilized on conjugation with the $\pi_{\rm CO}$ levels.14

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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 pe band of 5¹⁵ 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 $n \rightarrow \pi^*$ transition¹⁶ and 5 has a band at 2850 Å (4.35 eV)¹⁷ due to an $n \rightarrow \pi^*$ 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 $\pi_{\rm CC}^{14}$ 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_{CH_2} 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 $\pi_{\rm CC}$ 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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(19) We are grateful to the NRC of Canada for financial grants, to Professor C. A. McDowell for advice and encouragement, and to Mr. B. Cornford for invaluable experimental assistance. One of us (D. C.) is grateful to the SRC of Great Britain for the award of a NATO fellowship.

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Conversion of Natural Phthalideisoguinolines into **Benzazepine Alkaloids**

Sir:

We wish to report the successful conversion of the opium alkaloid nornarceine (1) into the benzazepine (\pm) -11-methyl-2,3-methylenedioxy-4.6,7,8-tetramethoxyrheadan¹(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 rhoeadine 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.