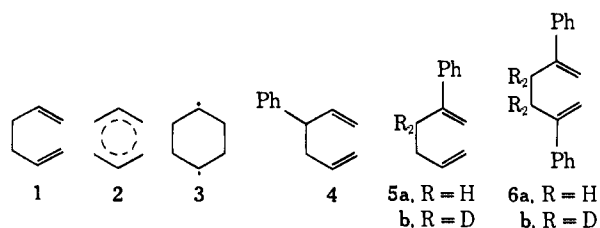this would be 1,4-cyclohexylene (3). They estimate the difference in heat of formation between **1** and **3** to be 35 kcal/mol, barely more than the observed activation energy (34 kcal/mol[1]) for rearrangement of **1**.



1    2    3    4    5a, R = H    6a, R = H
                        b, R = D    b, R = D

The mechanisms of reactions involving alternant hydrocarbons can often be elucidated by comparing the observed rates with those predicted by MO theory.[2] Indeed, for this purpose, calculations based on simple perturbational procedures[3] often suffice. In the present communication it is easily seen that $\pm E$ substituents[3] (e.g., phenyl) in the 3 position of **1** should have little effect on the rate of rearrangement if this takes place via **3** but should accelerate it if it takes place via **2**. In the latter case, comparison of the effects of different $\pm E$ substituents in the 2 or 5 positions of **1** should show a cumulative accelerating effect if the reaction takes place via **3** but little or no effect if it takes place via **2**.

We have been engaged in a detailed study of the Cope rearrangement using this approach. While the work is not yet complete, we are reporting some preliminary results which have an immediate bearing on the possible intermediacy of the biradical **3**.

These results refer to the rearrangements of the 3-phenyl (**4**), 2-phenyl (**5**), and 2,5-diphenyl (**6**) derivatives of **1**. The rearrangement of **4** was studied in the gas phase using glc; the product contained both cis- and trans-1-phenyl-1,5-hexadiene. The rearrangements of **4**, **5**, and **6** were followed by an nmr procedure, using the deuterated derivatives **5b** and **6b** with o-dichlorobenzene as the solvent. Comparison of these rates with the gas-phase value reported for **1** by Doering, et al.,[1] led to the results shown below

| Compd | Rel rate of rearrangement at 189.8 ± 0.1° |
|---|---|
| 1 | 1 |
| 4 | 18 |
| 5b | 41 |
| 6b | 2000 |

It will be seen that **5b** rearranges much faster than **1** and indeed faster than **4**. The rate of rearrangement of **6b** is greater again and the ratio of rates for **6b** and **5b** (49) is close to that for **5b** and **1** (41). There can therefore be little doubt that the rearrangements of **5** and **6** are not pericyclic reactions but involve derivatives of 1,4-cyclohexylene (**3**) as intermediates.

If the biradicals were transition states, the difference in activation energy between **1** and **5**, or between **5** and **6**, should be equal to the difference in stabilization energy between the benzyl radical and styrene (8

kcal/mol[4]). The rate differences in the table correspond to much smaller differences than this. The biradical must therefore be a stable intermediate, not the transition state.

While **5** and **6** thus seem to rearrange by the biradical mechanism, the rearrangement of **4** cannot take place in this way since it is also much faster than that of **1**. Moreover, the rearrangement of 3,4-diphenyl-1,5-hexadiene is faster again.[8] These reactions most probably do occur by the conventional pericyclic path via cyclic transition states analogous to **2**. It therefore seems likely that **1** itself may be more or less poised between the biradical and pericyclic mechanisms and that the balance can be displaced either way by appropriate substitution.

(4) The difference in CH bond dissociation energy between ethane and toluene is ca. 13 kcal/mol.[5] If the Ph–C bond in toluene were localized,[6] the CH bond energy in toluene would be reduced by ca. 5 kcal/mol, due to the conversion of a sp³–sp² C–C bond in toluene to a sp²–sp² C–C bond in the benzyl radical.[7] The extra stabilization (8 kcal/mol) of the benzyl radical must then be ascribed to resonance stabilization.[6] In the conversion of styrene to benzyl radical the Ph–C bond remains of unchanged type (sp²–sp²). The exocyclic bonds in styrene are moreover localized.[6] Consequently the conversion of styrene to benzyl radical should be resonance assisted to the extent of 8 kcal/mol.

(5) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(6) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(7) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962, p 66.

(8) R. P. Lutz, S. Bernal, R. J. Boggio, R. O. Harris, and M. W. McNicholas, *J. Amer. Chem. Soc.*, **93**, 3985 (1971).

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## Photoelectron Spectra of Cyclic Ethers

*Sir:*

For over 30 years there has been widespread interest in the interactions of nonadjacent groups.[1] In the past, electronic absorption spectroscopy was very useful in determining if such interactions existed. However, ground-state and excited-state interactions could not be distinguished by uv spectroscopy. Recently photoelectron spectroscopy (PES) has proven to be extremely useful in evaluating these interactions in the ground state, assuming the validity of Koopmans' theorem.[2] Heilbronner and coworkers[3] have clearly demonstrated the use of PES in studying $\pi_{CC}, \pi_{CC}$ interactions in dienes, $n_N, n_N$ interactions in nitrogen compounds, and $n_O, n_O$ interactions in dicarbonyl compounds. We[4] and others[5] have found PES useful in the study of the $\pi_{CC}$ and $n_O$ levels in unsaturated ketones. Now we would like to report our results of a

(2) See, e.g., M. J. S. Dewar and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956); M. J. S. Dewar and R. J. Sampson, *ibid.*, 2789 (1956); M. J. S. Dewar and R. Scott Pyron, *J. Amer. Chem. Soc.*, **92**, 3098 (1970); M. D. Bentley and M. J. S. Dewar, *ibid.*, **92**, 3991 (1970).

(3) M. J. S. Dewar, *ibid.*, **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(1) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(2) T. Koopmans, *Physica*, **1**, 104 (1934); W. G. Richards, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 419 (1969).

(3) E. Haselbach, E. Heilbronner, H. Muso, and A. Schmelzer, *Helv. Chim. Acta*, **55**, 302 (1972), and previous papers.

(4) (a) D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **93**, 4320 (1971); (b) *ibid.*, **93**, 4962 (1971).

(5) M. D. Brown, J. Hudec, and J. M. Mellor, *Chem. Commun.*, 1640 (1971).

study of $\pi_{CC},n_O$ interactions in unsaturated ethers. The measured ionization potentials (IP's) for the compounds studied are given in Table I.[6]

Table I. Vertical Ionization Potentials (eV)[a] of Ethers **1–4**

| Tetrahydro-furan (**1**) | 2,5-Dihydro-furan (**2**) | 7-Oxabicyclo-[2.2.1]heptane (**3**) | 7-Oxabicyclo-[2.2.1]heptene-2 (**4**) |
|---|---|---|---|
| 9.57 | 9.14 | 9.57 | 9.44 |
|  | 10.59 |  | 9.83 |
| 10.0[b] | 11.4[b] | 10.4[b] | 10.9[b] |

[a] Ionization potentials ($\pm0.02$ eV) are measured relative to the IP's of methyl iodide at 9.52 and 10.14 eV; F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **54**, 1423 (1971). [b] This band includes several ionizations. The figure quoted is the adiabatic value of the lowest IP.

The first IP of tetrahydrofuran (**1**) at 9.57 eV is readily assigned to ionization from one of the oxygen nonbonding levels. This compares favorably with the first *adiabatic* IP of ethyl ether at 9.61 eV.[7] The first two IP's of 2,5-dihydrofuran (**2**) are at 9.14 and 10.59 eV. The first band is assigned to ionization from a
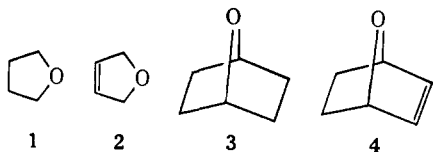


level which is mainly a $\pi_{CC}$ orbital, and the second band is assigned to ionization from a level which corresponds mainly to the oxygen nonbonding orbital. This ordering of levels and the $\pi_{CC},n_O$ mixing (*vide infra*) is corroborated by CNDO and INDO calculations.[8] The average of the first two IP's of 1,3-dioxolane is 10.37 eV[8,9] which leads to a shift of 0.8 eV due to the inductive effect of oxygen. Introducing an additional double bond in cyclohexene to give 1,4-cyclohexadiene produces a shift of 0.2 eV.[10] If we assume that similar inductive shifts apply to dihydrofuran, we obtain[11]

$$A_\pi = 9.2 + 0.8 = 10.0 \text{ eV}$$

$$A_n = 9.6 + 0.2 = 9.8 \text{ eV}$$

The mean $(A_\pi + A_n)/2 = 9.9$ eV agrees with the observed mean of $(9.14 + 10.59)/2 = 9.87$ eV. Although this crude estimation inverts the $\pi_{CC},n_O$ ordering suggested by calculations,[8] it does suggest a large $\pi_{CC},n_O$ interaction $(B_{\pi,n})$ and small interactions of $n_O$ and $\pi_{CC}$

(6) We note that there is some uncertainty in assigning the vertical IP where the two or more highest vibrational peaks in a band are of approximately the same intensity. Minor variations in peak intensities from instrument to instrument can possibly affect the precise assignment of the "vertical" IP. At present we feel the best way to estimate the vertical IP from, for instance, an ionization such as the first band in **3**, which contains several peaks of similar intensity, is to estimate the maximum of the band contour

(7) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).

(8) A. D. Bain, M.Sc. Thesis, University of British Columbia, Vancouver, B. C., 1972.

(9) D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5599 (1972).

(10) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).

(11) This terminology follows that recently suggested for unsaturated hydrocarbons[12a] and other systems.[12b] The value for the unperturbed $\pi_{CC}$ level is $A_\pi{}^0 = 9.18$ eV from the PES of cyclopentene.[10]

(12) (a) E. Heilbronner, *Isr. J. Chem.*, **10**, 143 (1972); (b) personal communication, 1972.

levels with lower $\sigma$ levels. Calculations indicate that these latter interactions are negligible.[8] Thus we conclude that $B_{\pi,n}$ is 0.8 eV which is similar to the interactions in cyclopenten-3-one,[4a] cyclohexadiene,[13] and 1,3-dioxolane.[8,9]

The first IP of 7-oxabicyclo[2.2.1]heptane (**3**) at 9.57 eV[6] is due to ionization from one of the oxygen nonbonding levels. It is well known that alkyl substitution tends to lower IP's of analogous levels and hence, on preliminary comparison of **1** and **3**, one might expect the first IP of **3** to be lower than that of **1**. However, the changes in geometry around the oxygen atom in **1** *vs.* **3** probably result in different inductive effects and different $n_O,\sigma$ interactions which offset the alkyl effect. The first two IP's of 7-oxabicyclo[2.2.1]heptene-2 (**4**) at 9.44 and 9.83 eV have been assigned to ionization from a level which is mainly $\pi_{CC}$ and $n_O$, respectively. If we again neglect the effect of interactions involving the $n_O$ and $\pi_{CC}$ levels with the $\sigma$ levels,[14] then we obtain

$$-I_1 = \epsilon_\pi = A_\pi{}^0 + \delta A_\pi - B_{\pi,n}$$

$$-I_2 = \epsilon_n = A_n{}^0 + \delta A_n + B_{\pi,n}$$

or

$$\delta A_\pi - B_{\pi,n} = 0.47 \text{ eV}^{15}$$

$$\delta A_n + B_{\pi,n} = 0.26 \text{ eV}$$

Taking a value of $\delta A_\pi/\delta A_n = 4$ (*vide supra*), then $\delta A_\pi = 0.6$, $\delta A_n = 0.15$, and $B_{\pi,n} = 0.1$ eV which indicates that the interaction of the $\pi_{CC}$ and $n_O$ levels in **4** is quite small, contrary to the case of **2**. In the solvolysis of 2-halo-7-oxabicyclo[2.2.1]heptanes, there was no indication of any interaction between the oxygen "lone pair" and the developing p orbital.[16] Rate effects were ascribed entirely to oxygen inductive effects. This analysis of the PES of **4** parallels the solvolysis data.

(13) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Horung, *Tetrahedron Lett.*, 1033 (1970).

(14) In actuality, we are neglecting *differences* in the $n_O,\sigma$ interactions and $\pi_{CC},\sigma$ interactions between **4** and **3** or norbornene.

(15) The value of $A_\pi{}^0$ is the IP of norbornene (8.97 eV): P. Bischof, J. A. Hasmall, E. Heilbronner, and V. Horung, *Helv. Chim. Acta*, **52**, 1745 (1969).

(16) J. C. Martin and P. D. Bartlett, *J. Amer. Chem. Soc.*, **79**, 2533 (1957); for the 2-oxabicyclo[2.2.1]heptan-6-ol systems, where oxygen participation is important, *cf.* L. A. Spurlock and R. G. Fayter, Jr., *ibid.*, **94**, 2707 (1972).

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## New Synthetic Reactions. Allylic Alkylation

*Sir:*

The activation of the $\alpha$ position by a carbonyl group provides the key to the most important synthetic method for formation of carbon–carbon bonds in complex molecules. The ready accessibility of many ole-