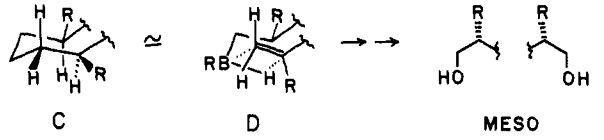
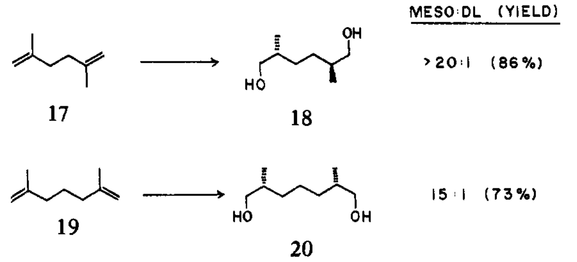
relative stereochemistry of the two asymmetric centers in dihydromyoporone has not been previously reported, this synthesis establishes the stereochemistry of the natural product as threo.

Although the extension of this method to the formation of more widely separated asymmetric centers seemed possible, we encountered substantial difficulties in accomplishing this goal. In particular, hydroboration of several homologues of **3** at various dilutions led to no obvious stereochemical control. The hydroborations thus far described are ones which proceed via a fused transition state (A). Some of the related bridged transition states (B, D) appear somewhat less flexible and have the interesting and useful property of resembling a low-energy conformational substructure found in a number of rings having more than six atoms (C). This geometrical similarity would suggest that transition state D should not experience substantially more strain than that inherent to the ring being formed, and to the extent that the hydroboration is intramolecular, the product should be meso. Results with thexylborane (0.1 M, THF; −78–25 °C) seem to bear out this prediction. Thus hydroboration of dienes **17** and **19** proceeded by formation of seven- and eight-membered boracycles and gave the *meso*-diols with high 1,4- and 1,5-asymmetric induction. Here authentic mixtures of diastereomers were prepared from **17** and **19** with 9-borabicyclononane and samples of pure **18** and **20** were prepared by coupling enantiomerically pure fragments.[25] Product compositions could be determined only by high-resolution ^{13}C NMR.[26] Several attempts to extend the reaction to formation of a boracyclononane with 1,6-asymmetric induction have been unsuccessful.





A direct application of the last reaction is the preparation of the vitamin E side chain **2**. This synthesis is carried out by statistical monotosylation (p-TsCl, C_5H_5N; 0 °C) of **20** and bromide exchange (LiBr, DMF; 25 °C; 18 h), followed by coupling with excess isoamylmagnesium bromide (THF, Li_2CuCl_4; 0 °C; 1 h). The (±)-alcohol thus prouduced was identical by ^{13}C NMR with authentic (+)-**2**.[27]

Although numerous cyclic hydroborations are shown above to proceed with synthetically useful remote asymmetric induction, diene hydroboration as presented here provides only a partial solution to the general problem of remote stereocontrol. The most serious synthetic limitation is that relative asymmetric induction operates here only in a mechanistic sense, since the first, controlling asymmetric center is produced in the same overall reaction which subsequently creates the second. The key point, however, is that the stereochemistry associated with the intramolecular hydroboration step can be efficiently controlled by a remote chiral center. We believe that the generality of the cyclization approach to remote asymmetric induction is now firmly established and that examination of other intramolecular reactions in this context will reveal similar stereochemical controls.[28]

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[24] Dihydromyoporone: ^{1}H NMR ($CDCl_3$) δ 8.00 (br s, 1 H), 7.40 (t, 1 H, J = 1.7 Hz), 6.74 (br s, 1 H), 3.75 (m, 1 H), 2.75 (br t, 2 H, J = 6 Hz), 2.0–1.1 (m), 0.89 (m, 9 H). ^{13}C NMR ($CDCl_3$) δ 195.6, 147.0, 144.1, 108.6, 67.4, 47.0, 45.5, 37.8, 30.0, 29.1, 24.5, 23.4, 22.0, 20.3. Epidihydromyoporone: ^{13}C NMR ($CDCl_3$) δ 195.4, 147.0, 144.1, 108.6, 67.7, 47.7, 45.1, 38.0, 32.0, 29.2, 25.9, 24.6, 23.2, 18.8. We wish to thank Dr. L. T. Burka at Vanderbilt University for a sample of authentic dihydromyoporone.

[25] Authentic optically active **18** (for ^{13}C NMR identification of *dl*-**18**) was prepared by Wurtz-like dimerization of (R)-$BnOCH_2CH(CH_3)CH_2Br$ (Mg, Li_2CuCl_4, THF) followed by deprotection (Li/NH_3). Authentic *meso*-**20** was prepared by a dithiane alkylation sequence: (1) 2-lithiodithane, THF, (S)-$THPOCH_2CH(CH_3)CH_2Br$; (2) *sec*-BuLi, (R)-$BnOCH_2CH(CH_3)CH_2Br$, THF; (3) RaNi, EtOH; (4) H_2O–HOAc; (5) Li/NH_3.

[26] **18**: IR (neat) 3300, 2920, 1480, 1400, 1050, 1000, 950 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.48 (d, 4 H, J = 6 Hz), 1.75–1.1 (m), 0.90 (d, 6 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 67.3, 35.6, 30.0, 16.5 (cf. *dl*-**18**: 67.5, 35.7, 30.2, 16.4). **20**: IR (neat) 3300, 2920, 1460, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.45 (dd, 4 H, J = 6, 2 Hz), 1.75–1.1 (m), 0.90 (d, 6 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 67.9, 35.5, 33.3, 24.1, 16.5 (cf. *dl*-**20**: 68.0, 35.4, 33.2, 24.0, 16.4).

[27] We wish to thank Dr. N. Cohen at Hoffmann-La Roche, Nutley, NJ, for a sample of authentic (±)-**2**.

[28] This work was supported by grants from the National Science Foundation (NSF CHE7801769) and the National Institutes of Health (RO1 HL 25634).

[29] Fellow of the Sloan Foundation, 1978–1980.

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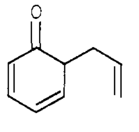
Ultraviolet Photoelectron Spectrum of the Phenoxy Radical

Sir:

We believe we have measured the ultraviolet photoelectron (UPE) spectrum of phenoxy radical (**1**) and, with the aid of MNDO[1] calculations, assigned the bands below 12 eV. To our knowledge this would be the first time that the UPE spectrum of a complex organic radical has been assigned in detail.

The MNDO calculations were carried out by both the spin-unrestricted[2] (UMNDO) and "half-electron"[3] (MNDO/HE) versions. Using Koopmans' theorem,[4] MNDO/HE gives good estimates of the first ionization energies of radicals while UMNDO gives first ionization energies that are usually larger by ~1 eV, due to the overestimation of correlation. Analogous results may be expected for the higher ionizations.

Phenoxy radical was obtained by thermolysis of allyl phenyl ether (**2**).[5] Comparisons for known compounds indicated the absolute values for IPs to be correct to ±0.02 eV. The resolution (Ar) was 20–30 meV. Spectra for several radicals (Et, t-Bu, allyl, $PhCH_2$) closely resembled those reported by Beauchamp et al.[6] Full experimental details will be given elsewhere. Besides ally radical (**3**), the only other products that might normally be expected under our conditions are phenol (**4**) (from **1**), 1,5-hexadiene (**5**), the dienones **6** and **7**, and o-allylphenol (**8**) (**2** → **6** → **7** or **8**). The bands in our spectrum (Figure 1) do not correspond to



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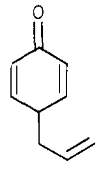

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[1] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

[2] Pople, J. A.; Nesbet, R. H. *J. Chem. Phys.* **1954**, *22*, 571.

[3] (a) Longuet-Higgins, H. C.; Pople, J. A. *Proc. Phys. Soc., London* **1955**, *68*, 591; (b) Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953.

[4] Koopmans, T. *Physica (Utrecht)* **1935**, *1*, 104.

[5] Fisher, I. P.; Palmer, T. F.; Lossing, F. P. *J. Am. Chem. Soc.* **1964**, *86*, 2742. Electron impact IP for **1**, 8.84 eV.

[6] (a) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290; (b) *Ibid.* **1979**, *101*, 4069.

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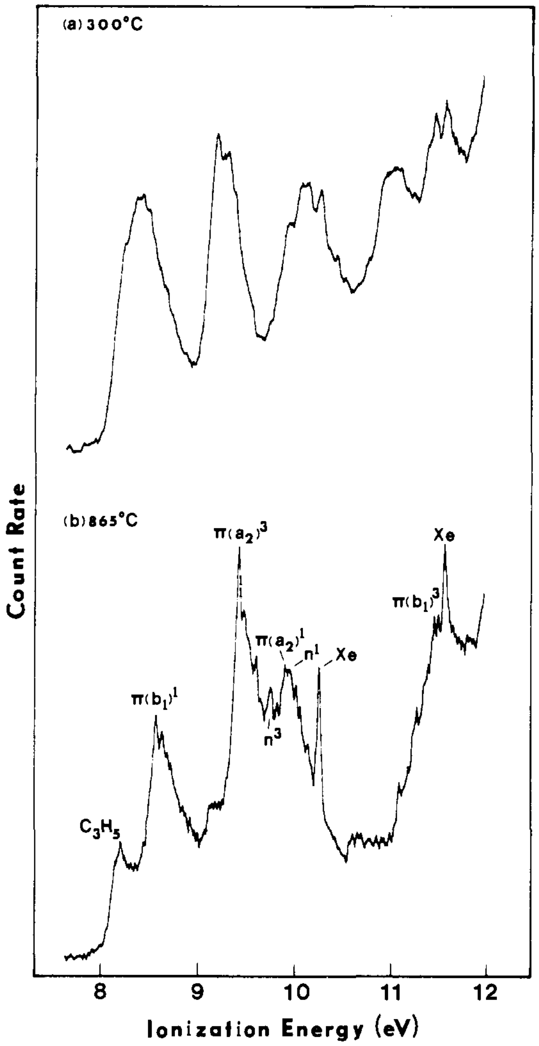


Figure 1. UPE spectra of allyl phenyl ether at various (external) temperatures of the pyrolysis tube: (a) 300 °C, (b) 865 °C. The room temperature spectrum was essentially identical with (a), corresponding to the ether itself.

4, **5**, or the ionization energies and band shapes expected for **6** or **7**. The main bands in the spectrum, below 12 eV, are therefore likely to derive from **1** + **3**. The following arguments support this conclusion and lead to the assignments indicated in Figure 2.

The band with a maximum at 8.20 eV and a distinct shoulder at 8.13 eV clearly corresponds to **3**.[6a] Its profile differs from that observed by Beauchamp et al.[6a] and by us, at lower temperature, the vibrational band at 8.13 eV being the most intense. Such a difference could well be due to thermal excitation of vibrations at the higher temperature.

The band at 8.56 eV (cf. 8.84 eV[5]) would be expected to correspond to ionization from the perturbed b_1 π MO of the ring, in agreement with the calculations. The small shoulder at 9.15 eV in the 865 °C spectrum is due to residual **2**, still present in small amount.

The remaining bands of **1** should occur in pairs, corresponding to the singlet (S) and triplet (T) species formed by ionization from the same doubly occupied (RHF approximation) MO. Since the S and T species are expected to have similar geometries, the two bands in the UPE spectrum are expected to have similar vibrational structures, the intensity of the T being the greater.[7]

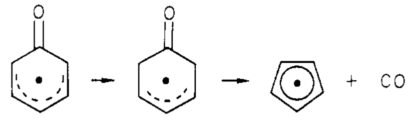
The bands at 9.42 and 9.90 eV are similar in shape and are predicted to arise from the unperturbed a_2 π MO of the ring. Their shapes resemble those of the corresponding bands for a_2 ionizations of monosubstituted benzenes, and their positions and splitting are in agreement with prediction. Finally, the band at lower energy is clearly the more intense.

The S–T separation corresponds to the S–T splitting in the first excited state of the phenoxy cation. This is double the exchange integral between the two singly occupied π MOs of b_1 and a_2 symmetry. In the phenoxy anion, the lowest singly excited states have one electron in the same b_1 MO as the cation while the other occupies an antibonding a_2 π MO. Since oxygen should leave both a_2 MOs unperturbed, their orbital coefficients should be numerically the same. The exchange integrals between one or the other a_2 MO and the b_1 MO should therefore be equal. Therefore the S–T separations in phenoxy cation and phenoxy anion should be the same. The latter can be estimated to be 0.49 eV from spectral data.[8] The separation between the bands in the UPE spectrum of **1** is 0.48 eV. This agreement strongly supports our assignment.

The next pair of bands should correspond to ionizations from an MO predominantly derived from the in-plane oxygen lone pair.[11] UMNDO calculates little unpaired electron density to be on the oxygen, suggesting that the S–T splitting for this MO should be small. On this basis, the sharp peak at 9.75 eV is tentatively assigned to the T and the small peak at 9.96 eV, which does not seem to be part of the vibrational structure of the 9.90 eV band, to the S. A more definite assignment will become possible when the vibrational structures have been analyzed.

The peaks at 10.26 and 11.57 eV correspond to xenon. The next intense peak is then the one centered at 11.56 eV. MNDO predicts this to correspond to formation of a T species by ionization from the (perturbed) third benzene π MO.

The part of the spectrum above 12 eV is not sufficiently resolved for individual ionizations to be identified, apart from peaks corresponding to Xe and Ar, and one other, at 14.01 eV. The position of this peak and its fine structure allow it to be assigned unequivocally to carbon monoxide. The only reasonable way in which this could be formed is by cyclization of **1** to an intermediate **8** which then fragments into CO + $(CH)_5\cdot$ (**9**).



1 **8** **9** (1)

Indeed, mass spectrometry[13] has shown **9** to be a pyrolysis product of **2**. Therefore, a band should be seen corresponding to **9**. All our spectra gave some indication of ionizations in the regions 8.3–8.5 eV and 8.8–8.9 eV which might correspond to the

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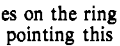
[7] Cox, P. A.; Orchard, F. A. *Chem. Phys. Lett.* **1970**, *7*, 273.

[8] The excitation energy to the first singlet excited state of phenoxy anion (4.01 eV) was determined by averaging the band maxima of its absorption (34 950 cm^{-1}, 4.33 eV) and fluorescence (29 750 cm^{-1}, 3.69 eV) spectra,[9] the corresponding value for the triplet state (36 300 cm^{-1}, 4.50 eV) being determined from its phosphorescence spectrum.[10]

[9] Wehry, E. L.; Rogers, L. B. *J. Am. Chem. Soc.* **1965**, *87*, 4234.

[10] Lim, E. C.; Chakrabarti, S. K. *J. Chem. Phys.* **1967**, *47*, 4721.

[11] No such ionization is seen in the UPE spectrum of phenol[12] because the in-plane oxygen 2p AO is tied up in the OH bond. According to UMNDO, **1** approximates in structure to



The UMNDO structure for **1** is also supported by its ESR spectrum (Lloyd, R. V.; Wood, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 659) which indicates that 92% of the unpaired spin resides on the ring (methine) carbon atoms. We are grateful to the referee for pointing this out. The oxygen lone pair in ketones appears in the region 9–10 eV; see, for example, (a) Tam, W.; Yee, D.; Brion, C. E. *J. Electron Spectrosc.* **1974**, *4*, 467. (b) Koenig, T.; Smith, M.; Snell, W. *J. Am. Chem. Soc.* **1977**, *99*, 6663.

[12] For the assignment of this spectrum, see: Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 521.

[13] (a) Harrison, A. G.; Honnen, L. R.; Danben, H. J., Jr.; Lossing, F. P. *J. Am. Chem. Soc.* **1960**, *82*, 5593. (b) Hedaya, E.; McNeil, D. *J. Am. Chem. Soc.* **1967**, *89*, 4213.

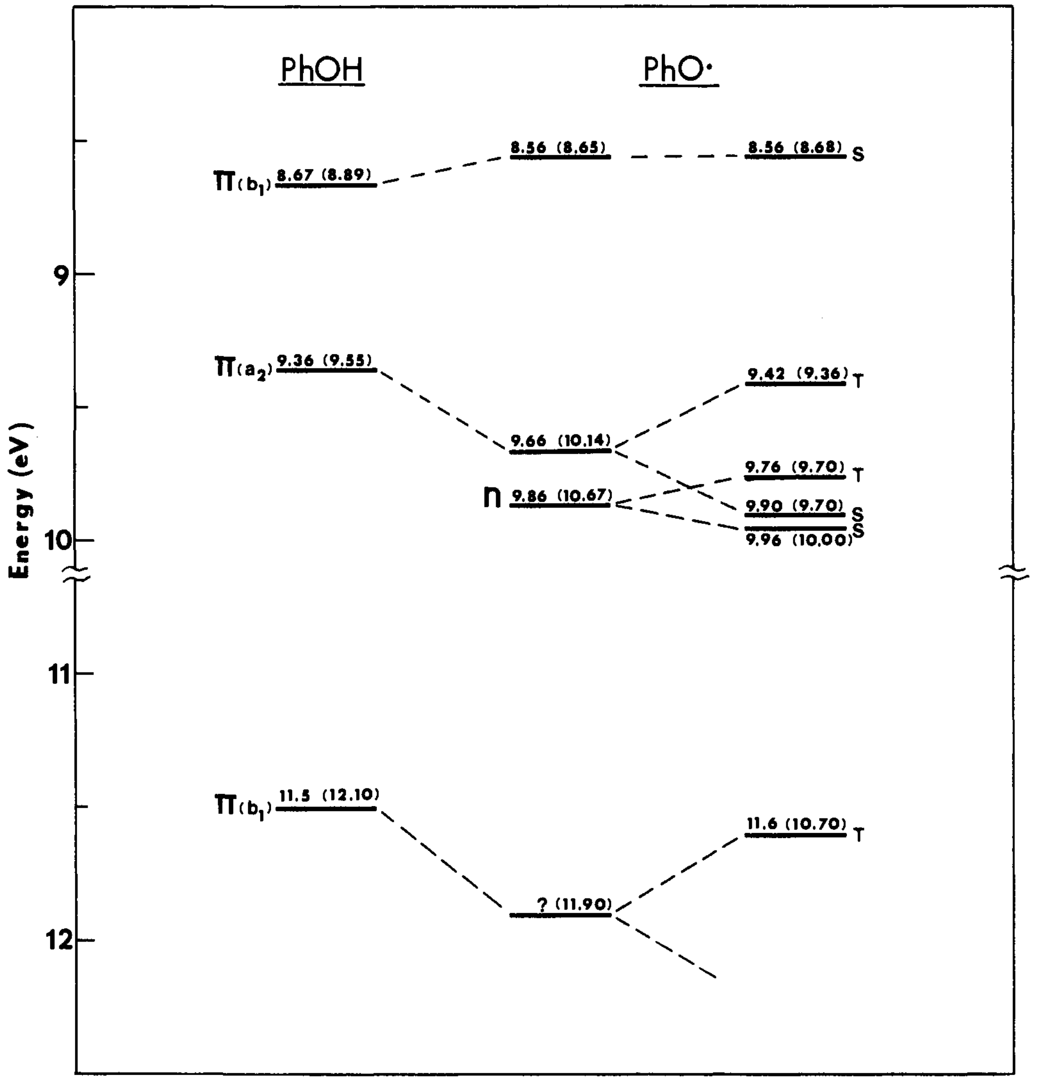


Figure 2. Correlation diagram relating the observed ionization energies (MNDO values in parentheses) for PhOH with those of PhO· (**1**). The central column compares means of corresponding S–T pairs with (in parentheses) MNDO values while the last column compares the observed ionization energies with (in parentheses) those calculated by UMNDO and reduced by 1 eV to allow for the systematic error noted in the text. For a discussion of the high-lying oxygen lone-pair orbital in **1** see ref 11.

first T and S ionizations of **9**.[14]

The heat of formation of phenoxy cation [$\Delta H_f(\mathrm{PhO}^+)$] can be calculated from the adiabatic ionization energy and heat of formation of phenoxy radical. Using our value (8.56 ± 0.02 eV; 197.4 ± 0.5 kcal/mol) for the former and the most recent value (11.6 ± 2.3 kcal/mol[18]) for the latter, we find

$$\Delta H_f(\mathrm{PHO}^+) = 209.0 \pm 2.8\ \mathrm{kcal/mol} \qquad (2)$$

This compares with values calculated by MNDO (203.2 kcal/mol) and estimated by mass spectrometry (≤224 kcal/mol[5]).

Our conclusions are currently being tested by further studies of the thermolysis of **2** and its derivatives and of the analogous phenyl benzyl ethers.

Acknowledgment. This work was supported by grants from the Air Force Office of Scientific Research (Grant 79-0008), the National Science Foundation (Grant CHE-7803213), and the Robert A. Welch Foundation (Welch F-126).

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[14] The first ionization energy of **9** has been estimated by mass spectrometry to be 8.56,[15a] 8.69 ± 0.1,[15b] or 8.41 eV.[15c] The S–T separation of the resulting ion is estimated by MINDO/3 to be 1.6 kcal/mol for the ground states[16] and 14.7 kcal/mol for ions with D_{5h} symmetry.[17] The difference between the two vertical ionizations of **9** is estimated by UMNDO to be 0.22 eV.

(15) (a) Schissel, P.; McAdoo, D. J.; Hedaya, E.; McNeil, D. W. *J. Chem. Phys.* **1968**, *49*, 5061. (b) Harrison, A. G.; Hannen, L. R.; Danben, H. J., Jr.; Lossing, F. P. *J. Am. Chem. Soc.* **1960**, *82*, 5593. (c) Lossing, F. P.; Traeger, J. C. *Ibid.* **1975**, *97*, 1579.

(16) Dewar, M. J. S.; Haddon, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 5836.

(17) Dewar, M. J. S.; Haddon, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 255.

(18) DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.

Asymmetric Synthesis in a Spinning Vessel

Sir:

A recent communication[1] claims the achievement of asymmetric synthesis in a spinning vessel. This result is very surprising because it violates the gravitational analogue of de Gennes' theorem[2,3] on

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(1) Edwards, D.; Cooper, K.; Dougherty, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 381.

(2) de Gennes, P.-G. *C. R. Hebd. Seances Acad. Sci., Ser. B.* **1970**, *270*, 891.

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