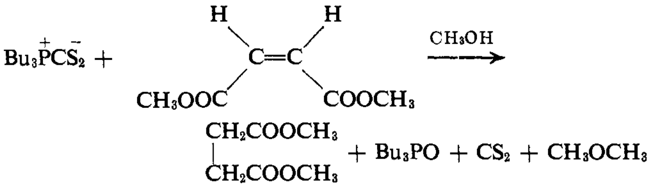
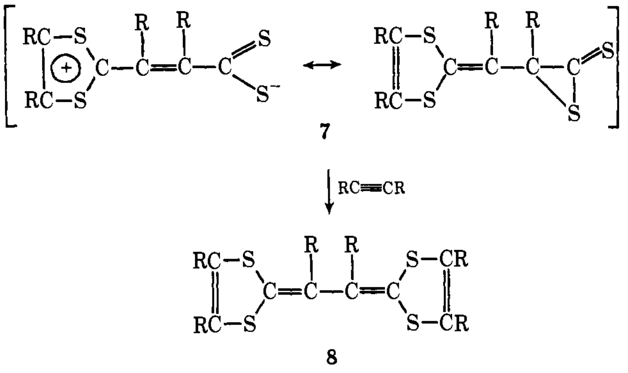
peaks attributable to the exocyclic hydrogen at δ 6.2–7.0 in the nmr spectra of **6**. The importance of the contribution which the dipolar structure makes to **6** is indicated by the low temperatures at which free rotation about the exocyclic double bond occurs. Coalescence of the exocyclic methine hydrogens occurs at 125° for **6a**, at 100° for **6b**, and at 80° for **6c**.

The phosphine–carbon disulfide complexes reacted with electron-poor olefins differently than with acetylenes. In an alcoholic solvent dimethyl maleate was reduced to dimethyl succinate.



$$\mathrm{Bu_3\overset{+}{P}C\overset{-}{S}_2} + \mathrm{(H)(CH_3OOC)C{=}C(COOCH_3)(H)} \xrightarrow{\mathrm{CH_3OH}} \mathrm{CH_2COOCH_3{-}CH_2COOCH_3} + \mathrm{Bu_3PO} + \mathrm{CS_2} + \mathrm{CH_3OCH_3}$$

The reaction observed between acetylenes and the phosphine–carbon disulfide complexes lends support to the suggestion that compounds of type **8** formed in the thermal reaction of carbon disulfide and electron-deficient acetylenes[6] could have arisen by reaction of the intermediate **7** with the acetylene.



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(6) H. D. Hartzler, *J. Amer. Chem. Soc.*, **92**, 1412 (1970).

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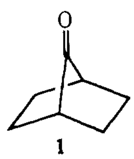
Photoelectron Spectra of Norbornanones and Norbornenones

Sir:

In a recent study we found photoelectron spectroscopy (PES) to be very useful in determining the interaction of the π levels in cyclopentenones.[1] We have now extended our investigations to the series of norbornane derivatives **1–4**. The measured ionization potentials (IP's) from the PE spectra[2] are given in Table I.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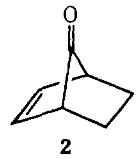
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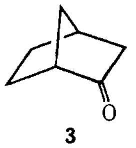
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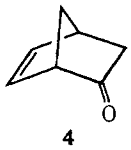
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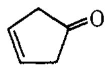
The first IP of norbornan-7-one (**1**)[3] at 9.01 eV is assigned to ionization from one of the oxygen nonbonding orbitals. The vibrational spacings in this band are 430 and 1210 cm^{-1}, which indicate that this n orbital is delocalized to some extent. Unfortunately, no assignment of the ir spectra of any of these molecules (**1–4**) is available. The value for this n ionization is 0.24 eV lower than the corresponding value in cyclopentanone (9.25 eV).[1] It is a well-established observation that the first IP arising from ionization from a similar orbital tends to decrease with increasing size along a homologous series.[4]

Table I. Vertical Ionization Potentials (Electron Volts)[a] of **1–4**[b]

Norbornan-7-one (**1**)	Norbornen-7-one (**2**)	Norbornan-2-one (**3**)	Norbornen-5-one (**4**)
9.01 (430 and 1210 cm^{-1})	9.19	8.94 (410 and 1270 cm^{-1})	8.90
	9.62		10.10
10.3–15.0[c]	11.0–14.6[c]	10.65–14.8[c]	11.0–15.3[c]
	15.12		
15.72	15.90	15.96	15.95
16.82	16.77	16.74	16.87

[a] ±0.02 eV for IP's less than 11 eV and ±0.05 for IP's greater than 11 eV. [b] The vibrational spacings, where measurable, are given in parentheses and are ±40 cm^{-1}. [c] Several ionizations measured from the adiabatic onset.

The first IP of norbornen-7-one (**2**)[3] at 9.19 eV is assigned to ionization from the nonbonding level. The shift of 0.18 eV in the n level of **1** and **2** is attributed to the effect of replacing two sp^3-hybridized carbons in **1** by sp^2 carbons. This agrees very well with the difference of 0.19 eV between the n levels of cyclopentanone and cyclopenten-3-one[1] (**5**). The band at 9.62 eV in the PE spectrum of **2** is attributed to ionization from the π_{CC} level. The π_{CC} IP in norbornene (**6**) occurs at 8.97 eV.[5] This represents a stabilization of the π_{CC} level in **2** of 0.65 eV relative to **6** and it compares with the stabilization of 0.80 eV in **5** (9.98 eV)[1] relative to cyclopentene (9.18 eV).[6] The replacement of an sp^3-hybridized carbon by an sp^2 carbon in the five-membered ring of a norbornene derivative should increase the IP of the π_{CC} level by *ca.* 0.2 eV.[1] Therefore, the major effect in the shift of the π_{CC} level in **2** compared to **6** is the interaction of the π_{CC} level with both π_{CO} levels in **2**. This interaction can occur directly through space[7,8] or through a σ level of the correct symmetry.[8] In **2** the through-space interaction of the two π levels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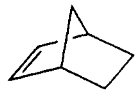
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(1) D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **93**, 4320 (1971).

(2) The PE spectra were obtained using a 584-Å spectrometer with a 2-in. radius hemispherical electrostatic energy analyzer.

(3) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964). We are very grateful to Professors P. G. Gassman and J. Warkentin for generous samples of **2**.

(4) See, for example, K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

(5) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

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

(7) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

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

is mainly a σ-type overlap, whereas in **5**, which is planar,[9] the interaction of the two π levels is mainly a π-type overlap.[7,10] This interaction in **2** is calculated to be 0.4 eV which is slightly smaller than the value obtained for **5** (0.56 eV).[1]

The uv spectrum of **1** has n $\rightarrow$ π^* absorption at 2920 Å (4.25 eV), whereas **2** has n $\rightarrow$ π^* absorption at 2740 Å (4.53 eV).[3] We suggest that a portion of this hypsochromic shift (0.28 eV) *may* be due to the 0.18-eV stabilization of the n level in **2** compared to **1**. Previously, this hypsochromic shift has been ascribed only to a destabilization of the π^* oribtal in **2**.[7] Our above calculations of the interactions between the π levels would imply that the $\pi_{CO}{}^*$ level should be destabilized by at least 0.4 eV due to the π_{CC}–$\pi_{CO}{}^*$ interaction. However, we expect any $\pi_{CO}{}^*$–σ^* interactions to stabilize the $\pi_{CO}{}^*$ level. Cyclopentanone and **5** show a similar effect.[1] It is possible, though unlikely, that the above assignments of the first two IP's of **2** may be reversed. This would lead to an anomalously high value for the n ionization of **2**[11] and the assignment of the first IP to a π ionization would indicate that there is no interaction between the π levels in **2**.

The first PE band of norbornan-2-one (**3**) at 8.94 eV is assigned to the n ionization, and this band has vibrational spacings of 410 and 1270 cm^{-1}, *cf.* the n ionization in **1**. The PE band of norbornen-5-one (**4**) at 8.90 eV is also attributed to ionization from an n level. This IP is rather low and must reflect some effect that is not present in **2**, or in **5**, which has an n ionization at 9.44 eV.[1] The molecular symmetry of these last two β,γ-unsaturated ketones forbids any n–π_{CC} interaction. However, since **4** is nonsymmetric, such an interaction is allowed and it is expected to destabilize the n level and stabilize the π_{CC} level.[8] The inductive effect of two sp^2 carbons in a β,γ-unsaturated ketone increases the n IP by *ca.* 0.2 eV[1,12] (*vide supra*). Therefore, we estimate the n–π_{CC} interaction in **4** to be at least 0.24 eV. This type of interaction in β,γ-unsaturated ketones was first proposed to explain the exalted intensity of the n $\rightarrow$ π^* transitions in the uv spectra of compounds of this type.[13] It is interesting to note that neither **2** nor **5** has exalted n $\rightarrow$ π^* absorption.[3,14] The second band in the PE spectrum of **4** at 10.10 eV is assigned to the π_{CC} ionization. This level has been stablized by 1.13 eV realtive to the π_{CC} level in **6** (8.97 eV).[5] If the n–π_{CC} interaction in **4** stabilizes the π_{CC} level by 0.25 eV (*vide supra*)[8] then the stabilization due to hybridization changes and all other interactions is 0.88 eV. This value compares with the stabilization of 0.65 eV in **2** and of 0.80 eV in **5**.[1] The large stabilization of the π_{CC} level in **4** indicates that the π_{CC}–$\pi_{CO}{}^*$ interaction is dominant even though σ–π interactions are allowed. The hybridization effect may be estimated as follows. Since the π IP of **6** (8.97 eV)[5] and the average of the two π IP's of norbornadiene (9.12 eV)[5] differ by 0.15 eV, then the exchange of two sp^3 carbons for two sp^2 carbons in the six-membered ring increases the π_{CC} IP by 0.15 eV Hence the replacement of one sp^3 carbon by an sp^2 carbon should increase the π_{CC} IP by 0.08 eV. Simple Hückel calculations suggest that the interaction of the π levels in **4** should *destablize* the π_{CC} level.[13,15] We do not find experimental support for this proposal.

Acknowledgment. We are grateful to the National Research Council of Canada for financial grants and to Professor C. A. McDowell for advice and encouragement. One of us (DC) is greatful to the SRC of Great Britain for the award of a NATO fellowship.

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(9) From microwave spectrum; A. C. Legon, private communication to D. C.; C. L. Norris, R. C. Benson, and W. H. Flygare, *Chem. Phys. Lett.*, 10, 75 (1971).

(10) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1962, pp 82–89.

(11) The highest IP we have observed for the nonbonding level in a cyclic ketone is 9.61 eV for cyclobutanone, and most n IP's are in the range 8.9–9.4 eV; D. Chadwick, D. C. Frost, and L. Weiler, unpublished results.

(12) Since this value was obtained from PE data for **2** and **5**, it probably represents a maximum value for the inductive effect in **4** which incorporates the β,γ-unsaturated keto group in a six-membered ring.

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(14) L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967).

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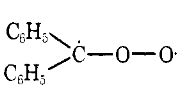
Ozonides from the Photooxidation of Diphenyldiazomethane in the Presence of Aldehydes

Sir:

The suggestion[1] that the photooxidation of diphenyldiazomethane proceeds through the intermediacy of a carbonyl oxide has received support from the work of Bartlett and Traylor[2] who reported that benzophenone diperoxide can be isolated in such photooxidations. The diperoxide presumably arises from the dimerization of the carbonyl oxide or Criegee zwitterion and is reminiscent of a similar process[3] which occurs when suitably substituted olefins are ozonized.

Additional evidence for the intervention of the carbonyl oxide in the photooxidation was presented by Hamilton and Giacin[4] who found that an intermediate is produced in the photooxidation of diphenyldiazomethane which is capable of oxidizing the hydrocarbon solvent. By excluding photoexcited benzophenone as the possible intermediate these authors concluded that the oxidizing agent is the carbonyl oxide in its diradical form, **1**. Bartlett and Traylor, on the other hand, concluded on the basis of an isotopic oxygen technique that the intermediate did not have diradical character, but rather was the benzophenone oxide or Criegee zwitterion form, **2**.



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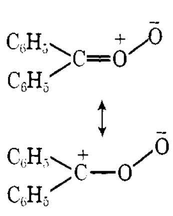

2

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(1) W. Kirmse, L. Horner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **614**, 22 (1958).

(2) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **84**, 3408 (1962).

(3) R. Criegee and G. Lohaus, *Justus Liebigs Ann. Chem.*, **583**, 6 (1953).

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