

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 $n \rightarrow \pi^*$ absorption at 2920 Å (4.25 eV), whereas **2** has $n \rightarrow \pi^*$ 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^* orbital in **2**.⁷ Our above calculations of the interactions between the π levels would imply that the π_{CO}^* level should be destabilized by at least 0.4 eV due to the $\pi_{CC}-\pi_{CO}^*$ interaction. However, we expect any $\pi_{CO}^*-\sigma^*$ interactions to stabilize the π_{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 $n-\pi_{CC}$ 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 $n-\pi_{CC}$ 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 $n \rightarrow \pi^*$ transitions in the uv spectra of compounds of this type.¹³ It is interesting to note that neither **2** nor **5** has exalted $n \rightarrow \pi^*$ 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 stabilized by 1.13 eV relative to the π_{CC} level in **6** (8.97 eV).⁵ If the $n-\pi_{CC}$ 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 $\pi_{CC}-\pi_{CO}^*$ interaction is dominant even though $\sigma-\pi$ 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 destabilize the π_{CC} level.^{13,15} We do not find experimental support for this proposal.

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(15) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962).

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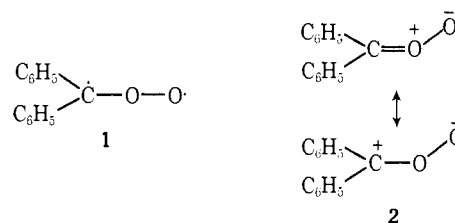
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Ozonides from the Photooxidation of Diphenyldiazomethane in the Presence of Aldehydes

Sir:

The suggestion¹ that the photooxidation of diphenyldiazomethane proceeds through the intermediacy of a carbonyl oxide has received support from the work of Bartlett and Traylor² 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 process³ 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 Giacini⁴ 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**.



(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.

(13) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959).

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

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

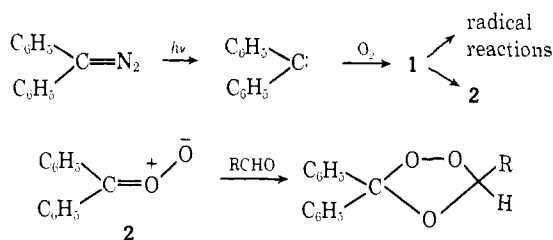
(2) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **84**, 3408 (1962).

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

(4) G. A. Hamilton and J. R. Giacini, *J. Amer. Chem. Soc.*, **88**, 1584 (1966).

We have now found that photooxidation of diphenyldiazomethane in an aldehyde solvent leads to the formation of the appropriate ozonide, incorporating the aldehyde and zwitterion, **2**, and the suppression of diperoxide formation. This ozonide formation represents a duplication of the Criegee ozonolysis mechanism⁵ under conditions where no ozone is involved.

It seems likely that the intermediate involved in the ozonide formation has the zwitterion form, **2**, inasmuch as the carbonyl oxides produced in ozonolysis, and presumably duplicated here, do not show radical character.⁵ On the other hand, the low yields of ozonide and the earlier results of Hamilton and Giacini⁴ suggest that the diradical species, **1**, is produced initially. This intermediate could then be converted to **2** for the ozonide reaction or undergo further radical reactions.



When a solution of 18.9 g of diphenyldiazomethane in 125 ml of chlorobenzene was photooxidized⁶ using an oxygen flow of 240 ml/min the diazo compound was completely decomposed in 2 hr. After removal of the solvent the yellow residue was recrystallized from acetone to give 1.26 g of solid benzophenone diperoxide, mp 210–212° (lit.² mp 213.5–214°). A solution of 9.70 g of diphenyldiazomethane in 200 ml of freshly distilled acetaldehyde was photooxidized for 130 min with an oxygen flow rate of 300 ml/min. After removal of excess acetaldehyde under reduced pressure the yellow residue was chromatographed on silica gel. Elution with hexane–benzene (80:20) gave 0.95 g (7.8%) of 1,1-diphenylpropene ozonide. This material was identical with that obtained from ozonolysis of 1,1-diphenylpropene and had nmr absorptions⁸ at 2.7 (multiplet, 10 H), 4.50 (quartet, 1 H), and 8.60 (doublet, 3 H), and infrared absorptions at 1220 and 1120 cm⁻¹. Further elution of the column with benzene–hexane (50:50) gave 8.23 g (90.5%) of benzophenone. The absence of benzophenone diperoxide in the photooxidation in the presence of acetaldehyde is presumably due to the successful competition of the aldehyde for the zwitterions at the expense of the dimerization process.

Similar photooxidations using propionaldehyde and benzaldehyde as solvents led to the formation of 1,1-diphenyl-1-butene (0.8%) and triphenylethylene (11.8%) ozonides, respectively. The 1,1-diphenyl-1-butene ozonide had nmr absorptions at 2.7 (multiplet, 10 H), 4.57 (triplet, 1 H), 8.0–8.9 (multiplet, 2 H), and 9.02 (triplet, 3 H). The triphenylethylene ozonide had nmr absorp-

(5) R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

(6) The photooxidation apparatus used was similar to that described in the literature.⁷ A General Electric DWY 650-W lamp was used without filter.

(7) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, **90**, 975 (1968).

(8) Nmr values given are τ values relative to internal TMS and were taken in CCl₄.

tions at 2.7 (multiplet, 15 H) and 3.73 (singlet, 1 H) and mp 97° (lit.⁹ mp 95°).

These observations lend additional support to the mechanism proposed¹ for the photooxidation of diphenyldiazomethane. At the same time they can provide a unique confirmation of the proposal of Criegee⁵ that ozonides arise from the addition of carbonyl oxides to carbonyl compounds. This process also provides a synthetic route to ozonides which does not involve ozonolysis. Because of our interest in the mechanism of ozonolysis¹⁰ we intend to conduct similar photooxidations of diazo compounds under conditions where ozonide cis–trans pairs can be expected. The stereochemical results so obtained could then be compared to those obtained from the ozonolysis of the suitable olefin.

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(9) J. Castonguay, M. Bertrand, J. Carles, S. Fliszar, and Y. Rousseau, *Can. J. Chem.*, **47**, 919 (1969).

(10) See, for example, R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).

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Lattice Spacings of Pseudobinary Solid Solutions of Silver Bromide and Silver Iodide

Sir:

Laboratory and cloud-seeding experiments in the natural atmosphere have established that silver iodide particles are effective in nucleating the formation of ice crystals in supercooled water and in regions supersaturated with respect to ice. It is recognized that the close similarity of the crystal structure of silver iodide to that of ice may be one of the factors that make it a good nucleus.¹

In the close packing of the cubic system the atomic layers are stacked along the body diagonal in an ABCABC... arrangement, while in the case of close packing in the hexagonal system the atoms are stacked along the hexagonal direction in the ABAB... sequence. Both structures have the same atomic arrangement in the planes; that is, each atom has 12 equidistant nearest neighbors, 6 in its own plane and 3 in each adjacent layer. The next-nearest neighbors are arranged differently in the two cases. Each structure can be made equivalent to the other by a rotation of half the crystal of 30° about the crystallographic directions defined above. Thus, at the ice–AgI interface, lattice coherence can be achieved between the two crystal structures but two effects now prevail. There is a misfit strain between the ice–AgI interface due to a small difference in the lattice spacings between these two structures, and a stacking fault is introduced at the interface. The implications of the dislocations at the interface have been discussed by Turnbull and Vonnegut.² In the same publication, Turnbull and

(1) B. Vonnegut, *J. Appl. Phys.*, **19**, 959 (1948); *Bull. Amer. Meteorol. Soc.*, **31**, 151 (1950); B. Vonnegut and K. Maynard, *ibid.*, **33**, 420 (1952); B. Vonnegut, *ibid.*, **50**, 248 (1969).