semiconductor.[23] Excited porphyrins more distant from an electrode (in the bulk phase) are considered to act as charge carriers that simply lower the film resistance.[24a] In contrast, we consider that the bulk of our polyporphyrin films includes a redox potential gradient that contributes significantly to the observed photopotential.

Thus, we believe that there are at least two competing mechanisms for generation of photopotentials in our polyporphyrin films: (1) an electrode hole-injection mechanism, which is expected to be particularly important for films with a nonuniform distribution of excited states—that is, where the optical penetration depth is significantly less than the total film thickness, such as thick films irradiated at a wavelength of high absorptivity (e.g. near the Soret band); and (2) a bulk charge-separation mechanism based on an inherent asymmetry of the polymer structure, which can be most readily observed when the excitation is relatively uniformly distributed across the film, such as with thin films or films irradiated with broad-band light.

Conclusions. Polymeric thin films can be made from porphyrin monomers by the technique of interfacial polymerization. The method leads to a novel structural asymmetry in that opposite surfaces of the films have different concentrations of unreacted functional groups. The surface asymmetry was demonstrated by XPS studies of metalloporphyrin films and by contact angle titrations with aqueous buffers. The films also display a photochemical asymmetry in that irradiation leads to directional charge separation across the film, specifically involving transfer of electrons toward the acid-rich surface of the film. The directionality is consistent with the proposed asymmetric structure of the polymer film, since the redox potentials of the substituted porphyrins become more positive toward the acid side of the film.

Acknowledgment. This research was supported by a grant from the U.S. Department of Energy, Advanced Energy Projects Division, Grant No. DE-FG06-ER85-13389. Excellent assistance with film syntheses was provided by James Brook and Mary Ann Johnson (BRI). Initial contact angle experiments were performed at the Tektronix Research Center, Beaverton, OR, arranged through the courtesy of Dr. Curtis Sheley; later contact angle experiments were performed with the photographic expertise of Brent Schauer (PSU). Indium tin oxide electrodes were provided by Tektronix through the courtesy of Dr. Alan Kawada. Assistance with many of the specialized experimental techniques was provided by the following: XPS experiments, Linda Dake (PNL); AA experiments, Allan Vogel (PSU); transmission electron microscopy, Professor John Dash (PSU); scanning electron microscopy, Robert Barss (BRI). Numerous helpful discussions with Professor David K. Roe (PSU) are gratefully acknowledged.

Reaction of Photochemically Generated Dibromocarbene with 1,2-Dimethylenecycloalkanes. 1,4 Addition Is Real[1]

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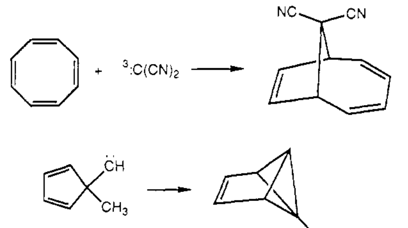
Abstract: Photochemically or thermally generated dibromocarbene adds to a variety of 1,2-dimethylenecycloalkanes and to norbornadiene to give both 1,2 and 1,4 addition products. The ratios of the products of the two addition types match those found from dibromocarbene generated from bromoform. Dibromocarbene is capable of 1,4 addition.

The reactions of carbenes with all manner of 1,3-dienes have been examined over the years in attempts to find 1,4 addition.[2] Despite this attention, only one intermolecular example has survived further scrutiny. This is the reaction of triplet dicyanocarbene with cyclooctatetraene to give, along with the product of 1,2 addition, 8,8-dicyanobicyclo[4.2.1]nona-2,4,6-triene.[3] It has been suggested[4] that this unique case depends upon the presence of *both* the cyclooctatetraene and the cyano groups. Certainly it is not general; dicarbomethoxycarbene gives only 1,2 addition to cyclooctatetraene,[2] and dicyanocarbene does not add in 1,4 fashion to other dienes. An exquisite labeling study from the laboratory of U. Burger revealed an intramolecular example of 1,4 addition in the reaction of cyclopentadienylcarbene to form benzvalene.[5]



One may legitimately wonder why this symmetry-allowed reaction appears so rarely. It has been suggested that the favorable HOMO–LUMO interaction between π_2 of the diene and the empty 2p orbital of the carbene is overwhelmed by the destabilizing interaction between the filled orbitals, π_1 of the diene and the carbene hybrid orbital.[6]

This short list exhausted the proven examples until recently, when it was discovered by two groups that 1,2-dimethylenecycloalkanes reacted with CHX_3 (X = Br, Cl) and alkali or with phenyl(trihalomethyl)mercury reagents to give modest amounts of 1,4 addition.[7,8] The obvious, and suggested, mechanisms were

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[†] Princeton University.
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(1) This work was supported by the National Science Foundation through Grant No. 8800448.
(2) For reviews, see: (a) Jones, M., Jr.; Moss, R. A. *React. Intermed.* **1978**, *1*, 78. (b) Moss, R. A.; Jones, M., Jr. *React. Intermed.* **1981**, *2*, 83. (c) Jones, M., Jr.; Moss, R. A. *React. Intermed.* **1985**, *3*, 62.
(3) Anastassiou, A. G.; Cellura, R. P. *Tetrahedron Lett.* **1970**, 5257.
(4) Hendrick, M. E., 1971, quoted in ref 2b.
(5) Burger, U.; Gandillon, G. *Tetrahedron Lett.* **1979**, 4281.
(6) Schoeller, W. W.; Yurtsever, E. *J. Am. Chem. Soc.* **1978**, *100*, 7549. It should be pointed out, however, that the calculated reaction pathway was not geometry optimized.

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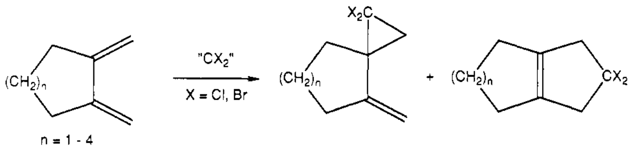
Table I. 1,2 vs 1,4 Addition

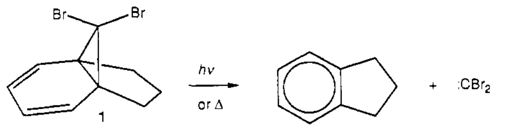
diene	carbene source	1,2 addition	1,4 addition
1,2-dimethylenecyclopentane	CHBr$_3$[7]	96	4
	1($h\nu$)	98	2
1,2-dimethylenecyclohexane	CHBr$_3$[7]	90	10
	1($h\nu$)	88	12
	1(Δ)	83	17
1,2-dimethylenecycloheptane	CHBr$_3$[7]	81	19
	PhHgCBr$_3$[7]	87	13
	PhHgCBr$_3$[7]	89	11
	1($h\nu$)	80	20
	1(Δ)	78	22

1,4 additions of dehalocarbenes. Most recently, the reaction has been shown to be stereospecific. This observation is certainly consistent with the intermediacy of a dihalocarbene, although stereospecificity does not demand a carbene as the reactive intermediate in the reaction.[9] The reaction of dihalocarbenes with 1,2-dimethylenecycloalkanes is the only likely example of intermolecular singlet 1,4 addition, and it is therefore important that there be no question as to the identity of the reacting intermediate.



Identification of the carbene as the reacting species is the more important as wondrous new reactions of "dihalocarbenes" have been claimed before,[10] only to be questioned[11] and finally retracted.[12] The alcoholysis of haloforms clearly yields intermediates capable of isomerizing alkenes[10-12] and some carbenoids—organometallic reagents—can undergo cycloadditions.[13] That phase-transfer catalysis apparently generates free dichlorocarbene[14] does not mean that other reactive intermediates capable of mimicking the carbene are not also formed.[12] The mercury reagent, too, has been shown not to be a straightforward source of free dihalocarbenes.[15] It gives a discernably different ratio of 1,2 to 1,4 addition, for instance (see table). Accordingly, we thought that room for doubt still remained as to the identity of the active ingredient in the 1,4 addition. In this paper we supply a definitive test, which shows that in this case it *is* the carbene that is involved.

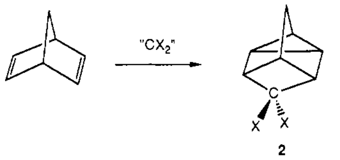
What is needed is an unimpeachable, and very different, source of dihalocarbenes. If the properties of the reactive intermediates generated from bromoform and the new source match, the case for a common intermediate, in this case dibromocarbene, becomes strong. We used **1** as the source of photochemically generated dibromocarbene.[11,16]



The authentic 1,2 and 1,4 adducts to three dienes were prepared by the method of Bickelhaupt.[7] In each case we were able to duplicate the reported data quite closely. We then compared the results from photolysis (mercury arc through Pyrex) or thermolysis (120–163 °C) of **1** with those from the conventional carbene precursors. As shown in the table, not only is the product of 1,4 addition observed but the ratio of 1,2 addition to 1,4 addition is quite similar in the two reactions.

We believe that the conclusion that dibromocarbene is the reactive intermediate responsible for the 1,4 addition is now inescapable.

Another unusual addition reaction of dihalocarbenes is the "homo 1,4 addition" to norbornadiene in which the tetracyclo$[3.3.0.0^{2,8}0^{3,6}]$octane (**2**) appears along with more conventional 1,2 adducts and their further rearrangement products.[17]



2

Here, too, we have shown that the unusual adduct remains when **1** is used as dibromocarbene source. We find 18% relative yield of **2** when bromoform is the source of the carbene and 20% ($h\nu$) and 24% (Δ) when **1** is used.[18] Therefore, the intermediate responsible for **2** must also be dibromocarbene.

Experimental Section

General Procedures. All chemicals were purchased from Aldrich Chemical Co. or synthesized as described below. Preparative gas chromatographic separations were achieved by using a Varian Aerograph A90P chromatograph with helium used as the carrier gas. The 6 ft × $^1/_4$ in. column was constructed to 10% OV-17 silicon oil absorbed on 80/100 mesh Chromosorb WHP. Analytical GC separations were achieved by use of a Hewlett-Packard 5890 chromatograph equipped with a Hewlett-Packard 3390A integrator. The ratio of the peak areas was taken to be the ratio of the products. The column used for obtaining the analytical data was a 60 m × 0.75 mm i.d., 1.0-μm glass capillary SPB-1 column. Gas chromatography/mass spectrometry data were obtained with a Hewlett-Packard 5992B GC/MS machine equipped with a 6 in. × $^1/_8$ in. column of 3% OV-17 silicon oil absorbed on 80/100 mesh Chromosorb W. Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are uncorrected. All photochemical reactions were run in Pyrex tubes using a 450-W medium-pressure Hanovia 679A46 mercury vapor lamp shielded with a Corex filter.

Bicyclo[4.3.0]nona-3,6(1)-diene. Ammonia (500 mL) was condensed in a three-necked flask connected to a cold finger condenser, a liquid addition funnel, and an ammonia tank. A dry ice–acetone bath was needed to maintain the reaction temperature between −60 and −70 °C at all times. Sodium (20.7 g, 0.90 mol) was introduced into the flask in small pieces. A deep blue solution was observed. This solution was then stirred vigorously for an additional 3 h to ensure that the sodium was dissolved completely in the liquid ammonia. A solution of 35.46 g (0.30 mol) of indan and 20 mL of absolute methanol was added to the ammonia–sodium solution dropwise over 1 h. The mixture was stirred for 5–6 h more at low temperature. After the resultant solution was warmed to room temperature and the liquid ammonia completely evaporated, 50 mL of methanol was added to the flask to react with the excess sodium. The brown solution obtained was extracted with three 50-mL portions of petroleum ether. All petroleum ether layers were combined and treated with 20 mL of 5% hydrochloric acid solution to neutralize the

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[7] Turkenburg, A. M.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 769. Mayr, H.; Heigl, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 579. Jenneskens, L. W.; de Wolf, W. H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 585.

[8] Two other groups found that cyclopentadienones were also prone to 1,4 addition, but the intervention of ylides in these cases seems a strong possibility, as cyclopentadiene reacts only in conventional 1,2 fashion: Hart, H.; Raggon, W. *Tetrahedron Lett.* **1983**, *24*, 4891. Mitsuhashi, T.; Jones, W. M. *J. Chem. Soc., Chem. Commun.* **1974**, 103.

[9] Kraakman, P. A.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.*, in press.

[10] Kramer, R.; Dehmlow, E. V. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 706.

[11] Hartwig, J. F.; Jones, M., Jr.; Moss, R. A.; Lawrynowicz, W. *Tetrahedron Lett.* **1986**, *27*, 5907.

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[14] For a discussion, see: Klumpp, G. W. *Reactivity in Organic Chemistry*; Wiley: New York, 1982; p 66ff.

[15] Lambert, J. B.; Larson, E. G.; Bosch, R. J.; TeVucht, M. L. E. *J. Am. Chem. Soc.* **1985**, *107*, 5443.

[16] Warner, P. M.; Lu, S.-L.; Gurumurthy, R. *J. Phys. Org. Chem.* **1988**, *1*, 281.

[17] Jefford, C. W.; Roussilhe, J.; Papadopoulos, M. *Helv. Chim. Acta* **1985**, *68*, 1557.

[18] The products from the reactions of halocarbenes with norbornadiene and quadricyclane are still the subject of some controversy.[17,19] Therefore, we have simply measured the ratio of **2** to "everything else". We hope to use the photolysis of **1** to separate the real products of this reaction from the "wondrous" ones.

[19] Jackson, J. E.; Mock, G. B.; Tetef, M. L.; Zheng, G.-x.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1453.

residual NaOH. The pink petroleum ether layer was separated, treated with decolorizing carbon powder, and dried over $MgSO_4$. After the petroleum ether solvent was evaporated, 37 g of a clear solution containing 90% of bicyclo[4.3.0]nona-3,6(1)-diene and 10% of the unreacted indan was collected.

10,10-Dibromo[4.3.1]propella-3-ene. A mixture of 10 g (0.08 mol) of 10,10-dibromo[4.3.1]propella-3-ene, 17.96 g (0.16 mol) of potassium *tert*-butoxide, and 50 mL of dry ether was introduced into a 250-mL round-bottomed flask. This mixture was stirred vigorously with a stirring motor. An ice–salt bath was needed to maintain the reaction temperature at −10 °C. Bromoform (21.6 g, 0.08 mol) was added to the flask dropwise over 1 h. The reaction was continued for another 2 h at low temperature. After this time 70 mL of water was added. The organic and aqueous layers were separated, and the aqueous layer was washed three times with 20 mL of ether. The organic layer and ether layers were combined and dried over anhydrous $MgSO_4$. The ether solvent was removed under reduced pressure. A brownish mixture of solid and liquid was collected. This mixture was then redissolved in a minimum amount of hot ethyl acetate and was left in the refrigerator overnight. White crystals were observed in the flask. The mother liquor was decanted and the residue washed with cold ethyl acetate three times and dried overnight under reduced pressure. Gas chromatography/mass spectrometry showed that the product [mp 70–71 °C (lit[20] mp 71–72 °C)] was contaminated with a small amount of the diadduct.

10,10-Dibromo[4.3.0]propella-2,4-diene. A mixture of 3.86 g (0.013 mol) of 10,10-dibromo[4.3.0]propella-3-ene, 3.00 g (0.016 mol) of *N*-bromosuccinimide, 20 mg of benzoyl peroxide, and 50 mL of carbon tetrachloride was refluxed under atmospheric pressure for ~15 min. The reaction temperature was maintained between 75 and 80 °C. The solution mixture gradually changed from clear to emerald green. The refluxing was stopped occasionally and the reaction mixture checked by ^1H NMR spectroscopy to ensure that the reaction was still incomplete. The carbon tetrachloride solvent was removed under reduced pressure, and a deep green liquid was collected. This liquid was then passed through a basic aluminum oxide column in hexane solvent. A white crystalline product (2.9 g, 80% yield) was collected, mp 71.5–72 °C (lit.[16] mp 73 °C).

Preparation of 2-[(Dimethylamino)methyl]cycloalkanones.[21] General Procedure. Dimethylamine hydrochloride (1 equiv) was added to an aqueous solution of the cycloalkanone (1 equiv), formaldehyde (1.2 equiv), and 1 mL of concentrated hydrochloric acid. The two-phase mixture was stirred and heated carefully to boiling under a long reflux condenser, refluxed for 2 h at 90–100 °C, and then cooled to room temperature. Saturated brine (125 mL) was added to the solution. The aqueous layer was then washed with four 50-mL portions of ether and then made basic with 30% aqueous KOH (1.3 equiv). The product was separated from the aqueous layer as a dark brown upper layer with a strong amine-like odor. The aqueous layer was extracted with five 30–100-mL portions of ether, and the combined organic layer and ether extracts were dried over anhydrous $MgSO_4$ and distilled through a 10-in. helix-packed column.

2-[(Dimethylamino)methyl]cyclopentanone. A mixture of 84 g (1 mol) of cyclopentanone, 81.5 g (1 mol) of dimethylamine hydrochloride, and 36 g (1.2 mol) of formaldehyde (as a 40% aqueous solution) was refluxed at 80 °C. This temperature is critical. At high temperature the amine product underwent further reaction to form olefin, which polymerized in the flask. In this case, the crude amine product was not distilled.

2-[(Dimethylamino)methyl]cyclohexanone. From 98.15 g (1 mol) of cyclohexanone, 81.5 g (1 mol) of dimethylamine hydrochloride, 36 g (1.2 mol) of formaldehyde (as a 40% aqueous solution), and 1 mL of concentrated hydrochloric acid was obtained 87.3 g (57% yield) of the product amine, bp 91–92 °C (10 mmHg).

2-[(Dimethylamino)methyl]cycloheptanone. From 112 g (1 mol) of cycloheptanone, 81.5 g (1 mol) of dimethylamine hydrochloride, 36 g (1.2 mol) of formaldehyde (as a 40% aqueous solution), and 1 mL of concentrated hydrochloric acid was obtained 123.5 g (73% yield) of the product amine, bp 100–101.5 °C (10 mmHg).

Preparation of 2-[(Dimethylamino)methyl]-1,1-methylenecycloalkanes.[22] General Procedure. To methyltriphenylphosphonium bromide (1.1 equiv) and potassium *tert*-butoxide (1.1 equiv) in dry THF were added 2-[(dimethylamino)methyl]cycloalkanone (1 equiv) and 18-crown-6 ether (catalytic amount). The orange-yellow solution was stirred for 8–10 h under an atmosphere of dry argon. After this time the solvent was evaporated at the water pump. The residue was washed with hexanes, and the washings were filtered through silica gel. Evaporation of the solvent afforded a good yield of pure alkene. Benzyltriethylaluminum (TEBA) could be substituted for 18-crown-6 ether in this reaction and gave comparable yields.

2-[(Dimethylamino)methyl]-1,1-methylenecyclopentane. From 40 g of the unpurified 2-[(dimethylamino)methyl]cyclopentanone, 115 g of methyltriphenylphosphonium bromide, 35 g of potassium *tert*-butoxide, 200 mL of dry THF, and 30 mg of 18-crown-6 was obtained 37 g (90% yield) of the olefin.

2-[(Dimethylamino)methyl]-1,1-methylenecyclohexane. From 21.08 g (0.136 mol) of pure 2-[(dimethylamino)methyl]cyclohexanone, 54 g (0.15 mol) of methyltriphenylphosphonium bromide, 17 g (0.15 mol) of potassium *tert*-butoxide, 100 mL of dry THF, and 30 mg of 18-crown-6 was obtained 20 g (96% yield) of the olefin.

2-[(Dimethylamino)methyl]-1,1-methylenecycloheptane. From 17.9 g (0.11 mol) of pure 2-[(dimethylamino)methyl]cycloheptanone, 13 g (0.12 mol) of potassium *tert*-butoxide, 42 g (0.12 mol) of methyltriphenylphosphonium bromide, 100 mL of dry THF, and 30 mg of 18-crown-6 was obtained 15.6 g (85% yield) of the olefin product.

Preparation of 1,2-Dimethylenecycloalkanes. To a solution of 0.3 mol of methyl iodide in 200 mL of anhydrous ether was added 0.13 mol of 2-[(dimethylamino)methyl]-1,1-methylenecycloalkane with stirring over ~20 min. After standing overnight, the white precipitate was filtered, washed with ether, and dried, yielding 85–100% of the quaternary iodide salt.

To a solution of 0.06 mol of this salt in 300 mL of distilled water were added small portions of Ag_2O (freshly prepared by adding 8 g of NaOH in 25 mL of distilled water to a solution of 34 g of $AgNO_3$ in 100 mL of distilled water, followed by filtration, washing with water and methanol until neutral) during 1 h under nitrogen. The mixture was stirred for 6 h and filtered. The filtrate was concentrated by a rotary evaporator (temperature, <40 °C). A dark brown syrup was collected and transferred to a pyrolysis flask. This residue was concentrated further under vacuum (10^{-3} mmHg) at room temperature. The pyrolysis was carried out at 60–90 °C (10^{-3} mmHg) over ca. 30 min. After this time the temperature was raised slowly to 120 °C. The upper layer in the receiving flask was separated from the pyrolysate and washed successively with 1N HCl and water. Pentane (50 mL) was added to the aqueous solution. After the organic layer was separated and dried over anhydrous $MgSO_4$, the pentane was evaporated by a rotary evaporator to yield the diene. The dienes were identified through a comparison of spectral properties with those reported earlier.[21]

Reaction of Dienes with Dibromocarbene Generated from Bromoform. General Procedure. The method employed was essentially that described by Doering and Hoffmann.[23] Bromoform (1 equiv) was slowly added to a stirred slurry of potassium *tert*-butoxide (1.2 equiv), the diene (1 equiv), and dry *n*-pentane immersed in an ice–salt bath. The amount of pentane was not critical and varied between 200 and 280 mL per mole of bromoform. The addition time was usually 4–6 h. The reaction mixture was left stirring at room temperature overnight. Water was added, and the product was extracted with ether. The ether layer was then dried over anhydrous $MgSO_4$. After the ether solvent was filtered and evaporated at the water pump, the residue was diluted by chloroform. The product mixture was separated by preparative GC and analyzed by ^1H NMR spectroscopy and mass spectrometry.

Thermolysis of 10,10-Dibromo[4.3.1]propella-2,4-diene with 1,2-Dimethylenecycloalkane or Nornbornadiene. General Procedure. Solutions of 10,10-dibromo[4.3.1]propella-2,4-diene in 1,2-dimethylenecycloalkane or norbornadiene (30 equiv) were sealed in Pyrex tubes, which were immersed in an oil bath at three different temperatures for 12 h. The cooled tubes were then opened and the solutions were diluted with chloroform. The product mixture was analyzed by analytical GC and ^1H NMR spectroscopy.

Photolysis of 10,10-Dibromo[4.3.1]propella-2,4-diene with 1,2-Dimethylenecycloalkanes or Norbornadiene. General Procedure. Solutions of 10,10-dibromo[4.3.1]propella-2,4-diene (1 equiv) in 1,2-dimethylenecycloalkane (10 equiv) were transferred to Pyrex photolysis tubes. The tubes were then degassed and irradiated with a Hanovia medium-pressure mercury arc for 20 h. The product mixtures were analyzed by ^1H NMR spectroscopy and by analytical GC.

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