Epoxides of Bicyclic Phospholane Derivatives. Stereochemistry of Epoxidation of 2- and 3-Phospholene Oxides[1]

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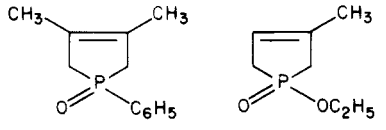
3-Phospholene oxides fused at the *b* or *c* faces to cyclohexano or cyclopentano rings were smoothly epoxidized by *m*-chloroperbenzoic acid in a stereospecific manner. 2-Phospholene oxides joined to cycloalkano groups at the *b* face were also easily epoxidized, again with stereospecificity, but with the opposite orientation of incoming oxygen relative to the phosphoryl oxygen. This was determined by converting epoxides of each type in the 1-methylperhydrophosphindole 1-oxide system to a common structure (1-methyl-3a-hydroxyperhydrophosphindole 1-oxide) which, however, had different stereochemical features. ^{13}C NMR evidence was gathered to support an earlier suggestion that epoxidation of 1-substituted 3-phospholene 1-oxides occurs anti to the phosphoryl oxygen. Several epoxyphospholane oxides were deoxygenated to give the first examples of epoxyphosphines, and from them were formed 1,1-dibromides, 1-sulfides, and methiodides. The epoxy ring from a bicyclic 2-phospholene oxide gave an amino alcohol from attack at the α-position by cyclohexylamine; the epoxide from the isomeric 3-phospholene oxide was rearranged to the allylic alcohol under the same conditions or with triethylamine or Li–ethylenediamine, although pyrrolidine did give some amino alcohol by attack at the 3-position.

Epoxidation of the double bond in 3-phospholene derivatives was first reported in 1968 by Arbusov et al.[2] Peracetic acid gave good yields of epoxides from phosphine oxide **1** and phosphinate **2**. The reactions were stereo-

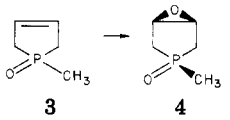
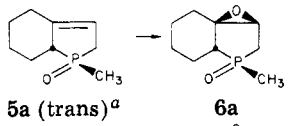
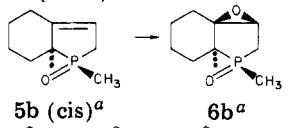
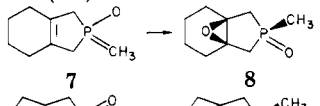
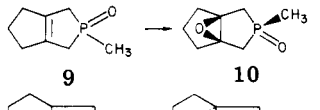
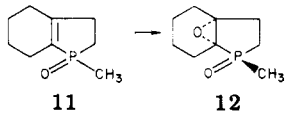
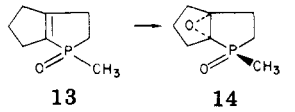
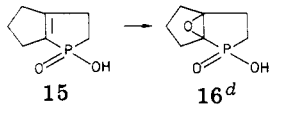


1 **2**

specific; since the phosphorus function is tetrahedral, oxygen can be delivered from above or below the ring, but only one isomer was observed in each case. From results of dipole moment measurements,[3] it was proposed that the single isomer of **1** formed has the anti arrangement of the two oxygen atoms, as a result of dipolar repulsions on approach of the reactants. Other workers have attempted to epoxidize the double bond when in the 2,3-position but with very poor[4] or negative[5] results. It was shown in the latter study, however, that 2-phospholene oxides formed bromohydrins that readily reacted with base to give the epoxide grouping. Acyclic α,β-unsaturated phosphine oxides are also said to be inert to direct epoxidation with *m*-chloroperbenzoic acid.[6]

In exploring the properties of some newly created bicyclic phospholene derivatives,[7] we attempted epoxidation with *m*-chloroperbenzoic acid and found not only that the reaction proceed very smoothly with 3-phospholene oxides but that it took place with comparable ease with 2-phospholene oxides as well. In both cases, stereospecificity was present; spectroscopic examination of the products failed to reveal the presence of an isomer resulting from the alternative approach. These observations led to a study of the stereochemistry of epoxidation of phospholene oxides and to further development of the chemistry of the epoxides as precursors of new derivatives of this system. Our results are presented in this paper.[8]

Table I. Epoxidation Results

results	product: yield, %	product: bp, °C (mm)
 **3** **4**	81	81-82 (0.05)
 **5a** (trans)[a] **6a**	76[a]	120-123 (0.1)[a]
 **5b** (cis)[a] **6b**[a]	*a*	*a*
 **7** **8**	74	115-119 (0.03)[b]
 **9** **10**	64	*c*
 **11** **12**	63	89-92 (0.05)
 **13** **14**	73	115-120 (0.05)
 **15** **16**[d]	65	

[a] The ratio of isomers **5a** and **5b** formed on hydrolysis of the cycloadduct[7] is variable from about 1:1 to 3:1. The mixture in this experiment was 72:28; epoxides **6a** and **6b** are formed in the same ratio. [b] Mp 90-93 °C. [c] Mp 115 °C. [d] Stereochemistry not determined; mp 114-117 °C.

Synthesis of Epoxides. In Table I are given the structures of the various epoxyphospholane oxides prepared in this study by direct epoxidation. In each case,

(1) Supported in part by Public Health Service Research Grant CA-05507, National Cancer Institute.

(2) Arbusov, B. A.; Rakov, A. P.; Vizel, A. O.; Shapshinskaya, L. A.; Kulikova, N. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 1313.

(3) Arbusov, B. A.; Anasteseva, A. P.; Vereshchagin, A. N.; Vizel, A. O.; Rakov, A. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 1729.

(4) Hunger, K. *Ber. Dtsch. Chem. Ges.* **1968**, *101*, 3530.

(5) Smith, D. G.; Smith, D. J. H. *Tetrahedron Lett.* **1973**, 1249.

(6) Postle, S. R.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2084.

(7) Symmes, C., Jr.; Quin, L. D. *J. Org. Chem.* **1976**, *41*, 238.

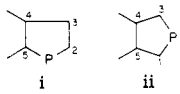
(8) A preliminary report on the directive effect in 3,4-phospholene oxides and on epoxyphosphines has appeared: Symmes, C., Jr.; Quin, L. D. *Tetrahedron Lett.*, **1976**, 1853.

0022-3263/80/1945-4688$01.00/0

Table II. Spectral Properties of Epoxyphospholane Derivatives[a]

no.	^{31}P NMR, δ [b]	^1H NMR, δ [c,d]		^{13}C NMR, δ [d,e]					
		PCH_3	OCH	C-1	C-2	C-3	C-4	C-5	CH_3
4	60.5	1.66 (14)	3.70 (26), H-3,4		30.1 (65)	53.5 (5)	53.5 (5)	30.1 (65)	20.4 (60)
4a					30.8 (62)	55.0 (3)	55.0 (3)	30.8 (62)	17.5 (60)
6a[f]	62.4	1.63 (14)	3.45 (25), H-3						
6b[f]	61.4	1.56 (14)	3.62 (22), H-3						
8	59.8	1.64 (13)		35.6 (67.8)		35.6 (67.8)	64.7 (3.7)	64.7 (3.7)	19.4 (67.1)
10	81.6	1.61 (13)		32.2 (65.1)		32.2 (65.1)	70.7 (3.0)	70.7 (3.0)	19.8 (64.1)
12	60.6	1.55 (13)			22.7 (69.5)	28.6 (s)	68.5 (12.6)	59.9 (103.2)	12.1 (65.3)
14	54.4	1.74 (14)			30.5 (70)	22.5 (12)	78.5 (13)	67.2 (107)	13.4 (68)
16	57.2				28.5 (136.1)	g	74.8 (23)	64.4 (150)	
17	−36.4	1.10 (4)	3.66 (4), H-3,4		28.2 (15)	60.2 (5)	28.2 (15)	60.2 (5)	15.0 (18)
17a					30.8 (18)	62.8 (3)	30.8 (18)	62.8 (3)	12.0 (15)
18a		1.10 (4)	3.56 (m), H-3						
18b		1.00 (4)	3.64 (m), H-4						
19	−20.2	1.15 (3)			20.6 (12.8)	g	68.8 (8.6)	67.6 (18.9)	7.63 (17.7)
20					28.1 (52)[h]	59.3 (s)	28.1 (52)	59.3 (s)	10.4 (50), anti; 13.7 (50), syn
21					g	61.7 (2)	68.3 (s)	37.3 (5.6)	7.4 (50), 13.5 (52)
22	49.2	2.42 (19)							7.1 (50.6)
		2.56 (19)			17.8 (45.2)	29.4 (2.4)	70.5 (14.0)	60.1 (82.5)	8.2 (46.2)
23	59.9	1.81 (12)			22.7 (77.4)	29.0 (s)	69.1 (14.6)	63.9 (81.0)	17.4 (63.3)

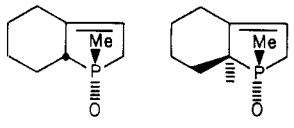
[a] Satisfactory analytical data (±0.4% for C, H, and P) were obtained for all compounds except phosphines **17–19**, where analysis of the corresponding salts (**20–22**) was performed. [b] 85% H_3PO_4 as reference, with positive values for downfield shifts and negative values for upfield shifts. Taken on $CDCl_3$ solutions. [c] Values in parentheses are ^{31}P–^1H coupling constants in hertz. In general, protons on ring carbons other than those bearing the epoxy function were poorly resolved. [d] For convenience, positions are numbered according to i for monocyclic and cycloalkano[*b*]phospholanes and ii for cycloalkano[*c*]phospholanes.



i ii

[e] Values in parentheses are ^{31}P–^{13}C coupling constants in hertz. $CDCl_3$ was used as solvent unless otherwise noted. [f] Analysis performed on a **6a,b** mixture. [g] Not clearly assignable. [h] CH_3OH solvent.

the corresponding phospholene oxide was reacted with 1 equiv of *m*-chloroperbenzoic acid in refluxing methylene chloride. The coproduct *m*-chlorobenzoic acid was removed by $NaHCO_3$ extraction, and the epoxides were recovered in good yield (60–80%) from the organic layer as crystalline solids or distillable oils. One phosphinic acid also was epoxidized successfully (providing **16**), but a typical phosphine sulfide (corresponding to oxide **5**) lost sulfur during the reaction. Compounds **12**, **14**, and **16** represent the first epoxides prepared by direct reaction of a peracid with a phospholene bearing the double bond in the 2,3-position. In every case, the oxygen was delivered specifically to one face of the phospholene ring; examination of the products by ^1H, ^{31}P, and ^{13}C NMR spectroscopy failed to detect the presence of an isomeric epoxide. This was also true in the case of one phospholene oxide that was used in the reaction as a mixture of trans (**5a**) and cis (**5b**) isomeric forms. The isomer ratio at the start was maintained in the epoxide product.



5a 5b

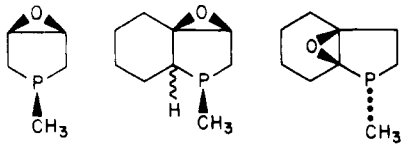
^{13}C NMR spectroscopy was especially useful in confirming the structure of the products, since the carbons of the epoxy function appear in a clear region of the spectrum (δ 55–80). Data for some of the compounds are given in Table II. Coupling to ^{31}P was of great help in assigning signals; carbons α to phosphoryl are strongly coupled (50–100 Hz; the coupling is greatly increased in the α,β-epoxyphospholane derivatives) while those β are more moderately coupled (10–20 Hz). Other features of the ^{13}C NMR as well as the ^1H and ^{31}P NMR spectra are included in Table II but require no comment. Techniques for the assignment of the anti relation of the oxygens in the products from 3-phospholene oxides and the syn relation of those from the 2-phospholene oxides are discussed in a later section.

Synthesis and Properties of Epoxyphosphines. The literature contains no prior report on the existence of epoxyphosphines[8] as a family of compounds. Indeed, it is known that at elevated temperatures phosphines deoxygenate epoxides to form olefins.[9] However, we found that stable, distillable liquids were formed on P-deoxygenation with phenylsilane of phosphine oxides **4**, **6**, and **12** (forming phosphines **17–19**, respectively, with **18** as a cis–trans mixture). This reducing agent is stereospecific in its action and gives phosphines with retention of the configuration of the starting oxides.[10]

These new compounds have the normal chemistry expected for each functionality. The phosphine group is easily quaternized to form another new family, epoxy-

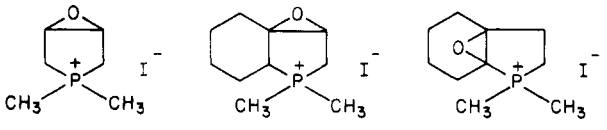
(9) See, for example: (a) Baskin, M. J.; Denney, D. B. *Chem. Ind. (London)* **1959**, 330; (b) Wittig, G.; Haag, W. *Ber. Dtsch. Chem. Ges.* **1955**, *88*, 1654.

(10) Marsi, K. L. *J. Org. Chem.* **1974**, *39*, 265.



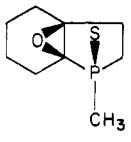
17 18 19

phosphonium salts (20–22), which also have good stability



20 21 22

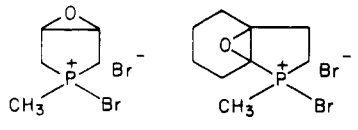
at room temperature. Sulfuration (retention) also takes place readily, and epoxyphosphine sulfides may be formed in excellent yield. Compound **23** so obtained was a stable,



23

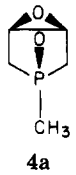
crystalline solid. This process is of practical importance since direct epoxidation of a phospholene sulfide failed to give an epoxy derivative.

The epoxyphosphines also react with bromine in a hydrocarbon solvent, whereupon the bromophosphonium bromide precipitates from solution. Two examples of this new type of epoxide (**24** and **25**) have been prepared. Such



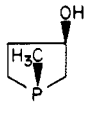
24 25

compounds are of potential value as a source of derivatives with both syn and anti structures with respect to the epoxy group, which is denied by the stereospecificity of the epoxidation reaction. Thus, hydrolysis of the related halophospholenium halides is known to occur without stereospecificity,[11] and this was indeed found to be true for hydrolysis of **24**. Although the major (90%) product proved to be identical with that (**4**) from direct epoxidation of **3**, enough of the anti isomer (**4a**) was formed to allow comparison of spectroscopic properties for assignment of structure, which will be seen to provide confirmation of the syn structure for the single product of epoxidation.



4a

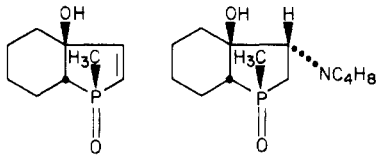
The epoxyphosphines can undergo ring opening with lithium aluminum hydride, forming hydroxyphospholane derivatives. Thus, phospholanol **26** was formed in 81%



26

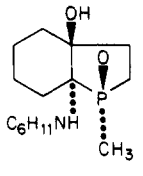
yield from epoxyphosphine **17**. The product was identical with that obtained from a different route and to which the cis structure had been assigned.[12] While this reaction therefore plays a role in deducing the steric structure of the original epoxyphosphine oxide (**4**), additional evidence was also gathered and is presented in the final section of this paper.

Reaction of Amines with Epoxyphospholane Oxides. From the work of Arbusov et al.[13] it would be expected that the epoxide of a 3-phospholene oxide would undergo isomerization to the allylic alcohol structure when refluxed with a tertiary amine. This proved to be the case for epoxide **6**. From a 28% cis/72% trans mixture of **6** there was obtained a 75% yield of a single crystalline product. The product derivable from the minor isomer (**6b**) either failed to form under the conditions used or was lost in the workup. Its epimerization to **6a** is also a possibility. That the product has structure **27a** was easily established by its ^{13}C NMR spectrum, which had a signal at δ 79.3 for a tertiary alcohol and two signals for olefinic carbons in the α,β-position to phosphoryl (δ 123.6, J = 83.8; δ 159.6, J = 13.7 Hz). The ^1H NMR spectrum also showed that there was no proton on the carbinol carbon and that two olefinic protons were present. The same result was obtained when epoxide **6** (cis, trans) was refluxed with cyclohexylamine; a 70% yield of **27a** was achieved. However, a quite different result was obtained on refluxing epoxide **6** with pyrrolidine in toluene; while some allylic alcohol **27a** was isolated, the major product, easily separated by its solubility in benzene from the insoluble **27a**, was crystalline nitrogen-containing compound **28** (49%). That the back-side attack of the nucleophile had occurred at the least-hindered position was evident from the ^{13}C NMR spectrum, which as for **27a** showed a tertiary alcohol carbon (δ 79.9, J = 9.2 Hz) and also a carbon for a secondary amine (δ 70.0, J = 3 Hz). Again, only products from the major isomer of **6** were isolated.



27a 28

When the isomeric epoxide **12** derived from the 2-phospholene oxide was refluxed with neat cyclohexylamine, the only product isolated was the crystalline amino alcohol **29** (60%). Attempts to perform the reaction in alcohols as solvents were unsuccessful. That attack of the nucleophile had occurred at the α-position to phosphorus was clearly established by ^{13}C NMR spectroscopy, since the carbon of the tertiary alcohol structure had the expected chemical shift and possessed the moderate C–P coupling for location β to phosphorus (δ 79.1, $^2J_{PC}$ = 16.5 Hz), while the more upfield carbon attached to nitrogen had the large coupling for α location (δ 62.7, $^1J_{PC}$ = 71.3 Hz). This mode of ring opening is not common in phosphorus chemistry; with α,β-epoxyphosphonates, attack occurs at the β-position,[14] a characteristic also of α,β-epoxy carbonyl com-



29

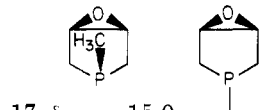
(11) (a) Quin, L. D.; Barket, T. P. *J. Am. Chem. Soc.* **1970**, *92*, 4303. (b) Quin, L. D.; Stocks, R. C. *Phosphorus Sulfur* **1977**, *3*, 151.

(12) Quin, L. D.; Stocks, R. C. *J. Org. Chem.* **1974**, *39*, 1339.

(13) Arbusov, B. A.; Rakov, A. P.; Vizel, A. O. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 85.

pounds.[15] However, with strong electron-attracting groups on the α-carbon, this direction of ring opening can be reversed;[16] this may be the explanation for the regiospecificity we have observed, since phosphonates have less positive character on phosphorus than do phosphine oxides as a result of back-donation of electrons from alkoxy groups.

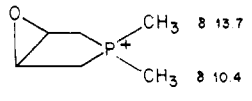
Stereochemistry of Epoxidation. In their assignment of the anti arrangement of oxygens in epoxidation products of 3-phospholene derivatives, Arbusov[3] et al. had only one isomer available for their dipole moment study; their treatment of the data also required the assumption of ring planarity, which is not consistent with fact. Nevertheless, the calculated values for the two possible isomers were quite different, and the experimental value agreed with the anti calculated value. We have gathered several pieces of evidence that are in agreement with their assignment. (1) Having both isomers **4** and **4a** available from hydrolysis of the corresponding bromophosphonium bromide **24**, it was possible to use ^{13}C NMR, which immediately showed that the major isomer had the P–CH_3 group syn to the epoxide oxygen since its chemical shift was significantly downfield (2.9 ppm) of that for the minor isomer. We attribute this deshielding to the known[17] δ effect of the epoxide group in cyclic compounds. The effect is also present in the phosphines (**17** and **17a**) which were formed



17, $\delta_{^{13}CH_3}$ 15.0

17a, $\delta_{^{13}CH_3}$ 12.0

with retention of configuration by silane deoxygenation of the **4**–**4a** mixture. (2) The methiodide (**20**) formed from



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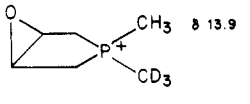
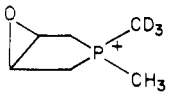


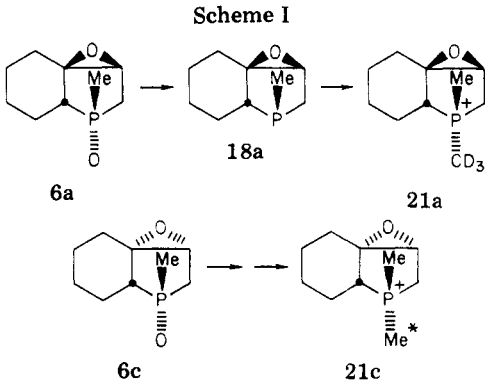
30a



30b

phosphine **17** more clearly reveals the operation of the δ effect of the epoxide function. The methyls would be identical were it not for this effect; in fact, the methyls have a chemical shift difference of 3.3 ppm. Again, the downfield methyl is assigned to the syn methyl. If structure **17** is correct for the phosphine derived from the oxide resulting from the original epoxidation reaction, then methylation (retention[11a]) with CD_3I, rather than CH_3I, would give a salt (**30a**) whose only P–CH_3 signal would correspond to the downfield signal (δ 13.7) in methiodide **20**, whereas structure **17a** would give a deuteriomethyl salt whose P–CH_3 signal would occupy the relatively upfield position (δ 10.4). The CD_3 carbon would not give a detectable signal since it is weak because of the absence of nuclear Overhauser enhancement and is coupled with the D atoms. When the epoxide product (**4**) from phospholene oxide **3** was reduced with phenylsilane and the product

Scheme I



quaternized with CD_3I (both retention), the product (**30a**) had the relatively downfield P–CH_3 signal, which means that the oxygen on phosphorus had occupied the anti position in the original **4**. (3) Reduction of phosphine **17** with lithium aluminum hydride gave, as noted, the same alcohol (**26**) as that assigned the cis structure in another investigation.[12] Since hydride attacks from the rear of the epoxide function, methyl and oxygen had the syn relation in the epoxyphosphine and its oxide.

The deuteriomethylation technique was also applied to the cyclohexano[*b*]phospholane system. The major isomer of the phosphine pairs (**18**), derived from reduction of epoxyphospholane oxides **6a,b**, gave a deuteriomethyl salt in which the upfield signal of the nondeuteriated salt **21** (δ 13.5 and 7.4) was absent (Scheme I). This reveals that, just as in the monocyclic system, the original CH_3 group of the epoxide occupied the more deshielded of the two possible positions. This is again consistent with the syn orientation of epoxy oxygen and P–CH_3 in the phosphine oxide formed from direct epoxidation and provides the assignment of stereochemical structure **6a** to the major isomer (with **6b** epimeric at C-7a). However, this assignment is not on the same firm ground that has been established for the monocyclic system and must be considered only tentative at this time. The presence of the cyclohexano group, specifically the carbon attached to the α-position of the phospholane ring, introduces a feature that complicates the ^{13}C NMR relations used earlier. This carbon is γ oriented to the P–CH_3 groups and when cis to P–CH_3 can introduce a shielding effect just as that seen in the 3-phospholene isomers **5a** and **5b**. If this shielding effect were greater than the deshielding caused by a syn-epoxide group, then the major isomer (**6c**) from the opposite approach of the epoxidizing agent would give the same relative NMR position of the P–CH_3 signals, with that marked by an asterisk in **21c** the more upfield and hence absent in the deuterio derivative's spectrum. However, there is no obvious reason why the direction of epoxidation would be completely reversed in the bicyclic system, and it is likely that all of the epoxidations of bicyclic 3-phospholenes recorded in Table I proceed anti to the phosphoryl oxygen.

The techniques described above are also inconclusive for proving the structure of the epoxide formed stereospecifically from the 2-phospholene oxide system. Thus, the two methyl carbons of the methiodide (**22**) of phosphine **19** were separated by only 1.1 ppm, and since both are γ oriented to a substituent (either ring CH_2 or O) of uncertain relative shielding strength, it is not feasible to use the CD_3 derivatives of salts or the CH_3 chemical shift differences in the oxides and phosphines as was done for the 3,4-epoxide system. By employing the reactions of Scheme II, however, we developed a proof for the syn orientation of the oxygens in the epoxide **12**. This con-

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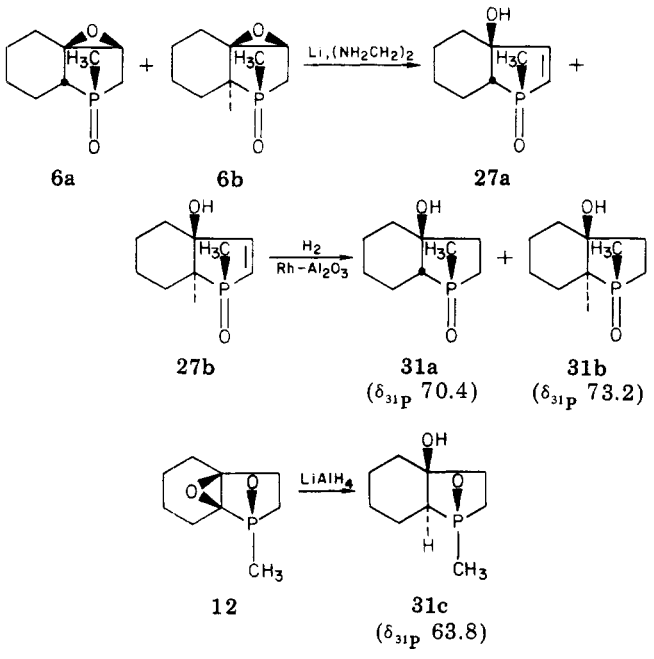
Table III. Yields and Properties of New Phospholene Derivatives from the McCormack Reaction[a]

no.	yield, %[b]	mp, °C	^{31}P NMR, δ[c]	^{13}C NMR, δ[d] C-1	C-2	C-3	C-4	C-5	CH_3
7	82 (12)	75-78	58.5	37.6 (67.3)		37.6 (67.3)	130.6 (9.8)	130.6 (9.8)	16.2 (63.5)
9	76 (1)[e]	127-132	73.5	32.3 (65.3)		32.3 (65.3)	137.8 (10.4)	137.8 (10.4)	16.8 (60.4)
13	47 (2)	64-65	50.3		30.9 (70)	32.7 (13)	166.5 (35)	137.6 (98)	16.6 (68)
15	10 (29)	123-124	64.3						

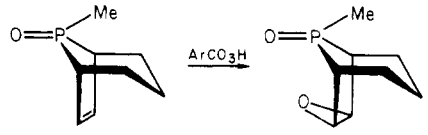
[a] Satisfactory analytical data (±0.4% for C, H, and P) were obtained for all compounds. [b] Values in parentheses are the cycloaddition periods in days. [c] See footnote b of Table II. [d] Numbered as in footnote d of Table II. See also footnote e of Table II. [e] Exothermic cycloaddition.

Scheme II



clusion, the *opposite* of that for epoxidations of a 3-phospholene oxide, depends on the following relations. Epoxide **12** was reductively cleaved by lithium aluminum hydride in 70% yield, with negligible attack on the phosphoryl group, to form a hydroxyphospholane oxide. The trans fusion of the rings is required by the nature of the opening of the epoxides by hydride reagents. There are two possible compounds (**31b** and **31c**) with trans fusion; these differ in the configuration at phosphorus. One of these (**31b**) was made by the sequence shown in Scheme II. This involves first isomerization of the epoxide **6b** (assumed to have anti oxygens from its origin from a 3-phospholene oxide) in admixture with its isomer **6a** to allylic alcohol **27b** and then hydrogenation to the saturated compound **31b**. Whereas triethylamine isomerization of a mixture of **6a** and **6b** led to the isolation of only allylic alcohol **27a**, the lithium–ethylenediamine system gave a mixture of **27a** and **27b**, in the same ratio as for the epoxides. The three diastereomers **31a–c** had different ^{31}P NMR signals as well as different ^{13}C NMR spectra. Compound **31c** resists epimerization by the basic reagents used and thus cannot enter in as a complicating process. That the alcohol from epoxide **12** is different from that derived from epoxide **6b** can only mean that the epoxides had different relations for the oxygen atoms.[18] Thus, if the assumption is correct that the bicyclic 3-phospholene oxide epoxidation occurred anti to the phosphoryl oxygen, then epoxidation must have occurred syn in the bicyclic 2-phospholene oxide.

In considering the cause of the opposing steric pathways taken on epoxidation of a 3- vs. a 2-phospholene oxide, one should first note that even a 3-phospholene oxide moiety, when incorporated in a structure of unusual steric constraint (e.g.,[19] **32**), can be epoxidized preferentially syn to



32

the phosphoryl oxygen. As we have seen, in unhindered 3-phospholene oxides the anti path is exclusively followed. Therefore, any directive influence by the phosphoryl group that involves H bonding, pentacovalent adducts from the peracid,[19] or dipolar repulsions[3] appears easily dominated by other features of molecular geometry. The syn pathway assumed to be followed by the 2-phospholene oxide moiety of **11** could also be the result of such structural influences. Additional examples of such structural effects on the steric pathway of epoxidation are needed to assist in clarifying this point.

Experimental Section

General Methods. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. All manipulations of cycloadducts and phosphines were conducted in a glovebag with N_2. Spectra were taken as follows: ^{1}H, JEOL MH-100 spectrometer, internal Me_4Si reference, $CDCl_3$ solutions; ^{31}P, Bruker HFX-10 at 36.43 MHz, FT proton decoupled, 85% H_3PO_4 external reference with positive values downfield and negative values upfield, $CDCl_3$ solutions; ^{13}C, JEOL FX-60 at 15.0 MHz, FT proton decoupled, internal Me_4Si as reference in $CDCl_3$ solutions as lock.

Synthesis of Dienes. 1-Vinylcyclohexene and 1-vinylcyclopentene were prepared by addition of vinylmagnesium bromide to the ketones, followed by dehydration with $KHSO_4$.[7] 1,2-Dimethylenecyclohexane was prepared, as described elsewhere,[20] by pyrolysis of the *N,N'*-dioxide of 1,2-bis(dimethylamino)-cyclohexane; the same procedure was used for 1,2-dimethylenecyclopentane.

Synthesis of Phospholene Oxides. Available from previous work were phospholene oxides **3**,[21] **5**,[7] and **11**.[7] The following general procedure was used to prepare other phospholene oxides. The diene (0.1 mol) was dissolved in 75–100 mL of hexane, and 0.1 g of copper stearate was added as a polymerization inhibitor. The freshly distilled phosphorus chloride (0.11 mol; CH_3PCl_2, except PCl_3 used for **15**) was added and the solution allowed to stand at room temperature. The adduct that precipitated after the specified interval was filtered off if a solid (or freed of liquid

(18) The possibility that attack of hydride occurred at C-3a of **12**, thus giving a 7a-hydroxy derivative, can be ruled out by the ^{13}C NMR data; the carbons α to P are clearly discerned by their large coupling to ^{31}P (δ 22.9, J = 69.5 Hz; δ 48.4, J = 71.9 Hz), and neither has the downfield chemical shift expected for hydroxy substitution.

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by decantation if an oil) in a glovebag, washed with hexane, and added slowly to an ice–water mixture. The mixture was neutralized with solid $NaHCO_3$ and then continuously extracted with chloroform (48 h). The extract was dried ($MgSO_4$) and concentrated to leave a residue that generally crystallized and was purified either by recrystallization (**15**, ethyl acetate), vacuum sublimation (**9**), or distillation (**7**, **13**). Yield data and other properties are given in Table III.

Epoxidation of Phospholene Derivatives. The following general procedure was used for the tertiary phosphine oxides; the products prepared and melting or boiling point values are given in Table I and spectral properties in Table II. A solution of 0.10 mol of the phospholene derivative in 200 mL of CH_2Cl_2 was treated with 0.11 mol of *m*-chloroperbenzoic acid and the mixture refluxed for 24 h. It was neutralized with a solution of 16.7 g (0.2 mol) of $NaHCO_3$ in 170 mL of water with vigorous stirring for 1 h (omitted in the preparation of **10**). The aqueous layer was then placed in a continuous extractor (chloroform) for 24 h. The extract, along with the original organic layer, was dried ($MgSO_4$) and concentrated to leave an oil that was purified by distillation. Most of the distillates crystallized on being allowed to stand.

For phosphinic acid **16**, a 12-h reflux period was used, following which solvent was removed and the white solid residue taken up in water. The water extract was continuously extracted with chloroform; this extract was dried ($MgSO_4$) and evaporated to leave an oil that formed a solid on trituration with hexane. The solid was recrystallized from acetone–ligroin. Other data are given in Tables I and II.

Epoxyphosphines and Epoxyphosphonium Salts. The following general procedure for the reduction of phosphine oxides[10] was used. A neat mixture of the phosphine oxide (0.050 mol) and phenylsilane (0.035 mol) was stirred while being heated to the initiation of hydrogen evolution (about 70–80 °C). After gas evolution ceased, the mixture was again heated (1 h at 80 °C) and distilled to recover the phosphine. The phosphines (in benzene) were then reacted with methyl iodide to form the quaternary salts for analysis.

17: 67%; bp 60–61 °C (16 mm); methiodide (**20**), mp 190–193 °C dec ($CHCl_3$–pentane).

18 (cis and trans): 82%; bp 115–120 °C (17 mm); methiodide (**21**), mp 178–182 °C dec (methanol–ether).

19: 69.3%; bp 115–116 °C (20 mm); methiodide (**22**), mp 190–191.5 °C (methanol–hexane).

Spectral data of the salts are given in Table II.

Synthesis of *anti*-1-Methyl-3,3a-epoxy-2,3,4,5,6,7-hexahydro-1*H*-phosphindole 1-Sulfide (23). A solution of 5.3 g (0.03 mol) of phosphine **19** in 20 mL of benzene was added slowly to a solution of 5.3 g (0.17 mol) of sulfur in 60 mL of benzene. The mixture was refluxed for 9 h and then stripped of solvent. The phosphine sulfide **23** was extracted from the excess sulfur with hexane and was recovered (4.4 g, 70%) as a white solid, mp 84 °C. Spectral data appear in Table II.

Synthesis of *cis*-1-Methyl-3-phospholanol (26). To a stirred suspension of 0.25 g (6.6 mmol) of $LiAlH_4$ in 160 mL of dry tetrahydrofuran was added 2.32 g (20 mmol) of epoxyphosphine **17**. The mixture was stirred at room temperature for 12 h and then treated cautiously with 1 mL of water, 3 mL of 3 N NaOH, and finally 1 mL of water. Liquid was decanted from the gummy solids, dried ($MgSO_4$), and distilled to give 1.9 g (81%) of **26** whose boiling point [100–101 °C (16 mm)] and ^1H and ^{31}P NMR spectra matched those previously reported.[12]

Reaction of Epoxyphospholane Oxides 6a and 6b with Amines. With Triethylamine. A suspension of 1.0 g of the epoxide (72% **6a**, 28% **6b**) and 8 mL of triethylamine was refluxed for 12 h. Some insoluble solids were present. The amine was stripped from this mixture, and the residual solid was recrystallized from CH_2Cl_2 to yield 0.75 g (75%) of isomer-free allylic alcohol **27a**: mp 189–190 °C; ^1H NMR (D_2O, external Me_4Si) δ 1.69 (d, $^2J_{PH}$ = 13 Hz, CH_3), 6.18 (dd, $^2J_{PH}$ = 23 Hz, $^3J_{HH}$ = 8 Hz, PCH=), 6.85 (dd, $^3J_{PH}$ = 42 Hz, $^3J_{HH}$ = 8 Hz, PCH=C**H**), other signals poorly resolved; ^{13}C NMR ($CDCl_3$) δ 15.4 (d, $^1J_{PC}$ = 68.2 Hz, CH_3), 42.7 (d, $^1J_{PC}$ = 72.2 Hz, C-7a), 79.8 (d, $^2J_{PC}$ = 17.4 Hz, C-3a), 123.6 (d, $^1J_{PC}$ = 83.9 Hz, C-2), 159.6 (d, $^2J_{PC}$ = 13.7 Hz, C-3), other signals not assigned.

Anal. Calcd for $C_9H_{15}O_2P$: C, 58.06; H, 8.12; P, 16.63. Found: C, 58.33; H, 8.23; P, 16.63.

With Cyclohexylamine. Refluxing a mixture of 1.0 g of the **6a**/**6b** mixture with 5 mL of freshly distilled cyclohexylamine for 12 h and then stripping off the amine gave a waxy solid which on trituration with ether was converted to a crystalline solid (0.7 g, 70%). Recrystallization from CH_2Cl_2 gave allylic alcohol **27a** (mp 190–191 °C) with spectra identical with those reported in the preceding experiment.

With Pyrrolidine. The **6a**/**6b** mixture (4.0 g, 0.021 mol) in 40 mL of refluxing toluene was treated with a solution of 4.6 g (0.066 mol) of freshly distilled pyrrolidine in 10 mL of toluene over a 15-min period. Reflux was continued for 15 h, and the mixture was stripped of volatiles to leave a dark yellow solid. Trituration with benzene gave a white crystalline solid and a yellow benzene solution. The solid (0.90 g) had a melting point of 190–191 °C and spectra identical with those of **27a** as prepared above. The benzene solution was concentrated to an orange solid, which gave on acetone recrystallization a white crystalline sample of amino alcohol **28** (2.7 g, 49%). A sample was recrystallized as plates from acetone: mp 194 °C dec; partial ^{13}C NMR ($CDCl_3$) δ 15.8 (d, $^1J_{PC}$ = 62.9 Hz, PCH_3), 21.8 (d, $^1J_{PC}$ = 61.5 Hz, C-2), 44.9 (d, $^1J_{PC}$ = 67.7 Hz, C-7a), 70.0 (d, $^2J_{PC}$ = 3 Hz, C-3), 79.8 (d, $^3J_{PC}$ = 9.2 Hz, C-3a).

Anal. Calcd for $C_{13}H_{24}NO_2P$: C, 60.66; H, 9.40; N, 5.47; P, 12.03. Found: C, 60.89; H, 9.60; N, 5.20; P, 11.88.

Reaction of Epoxyphospholane Oxide 12 with Cyclohexylamine. A solution of 2.5 g (0.013 mol) of **12** in 15 mL of cyclohexylamine was refluxed for 36 h. The mixture was evaporated to dryness and the residual oil triturated with ether to give a white solid. This was recrystallized from THF, providing 2.3 g (60%) of **29**: plates; mp 174.5 °C; ^1H NMR δ 1.50 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 1.20–2.00 (m, CH_2), 2.30–2.90 (m, NH, OH, and NCH); ^{31}P NMR ($CDCl_3$) δ 73.8; partial ^{13}C NMR δ 18.6 ($^1J_{PC}$ = 71.9 Hz, PCH_3), 21.1 ($^1J_{PC}$ = 57.2 Hz, C-2), 31.2 ($^2J_{PC}$= 5.0 Hz, C-3), 79.1 ($^2J_{PC}$ = 16.5 Hz, C-3a), 62.7 ($^1J_{PC}$ = 71.3 Hz, C-7a).

Anal. Calcd for $C_{15}H_{28}NO_2P$: C, 63.12; H, 9.89; N, 4.93; P, 10.88. Found: C, 63.37; H, 9.90; N, 4.64; P, 10.81.

Synthesis of *r*-1-Methyl-*t*-3a-hydroxy-*t*-perhydrophosphindole 1-Oxide (31c). A suspension of 0.27 g (7 mmol) of $LiAlH_4$ in 70 mL of tetrahydrofuran was treated with a solution of 3.0 g (16 mmol) of epoxyphospholane oxide **12** in 20 mL of THF, and the mixture brought to reflux. After 16 h, the mixture was chilled and treated successively with 2.5 mL of water, 3 mL of 20% NaOH, and 3 mL of water. After being stirred for 2 h, the mixture was filtered, and the filtrate was dried ($MgSO_4$) and stripped to a white solid. The solid was washed with ether and recrystallized from acetone, yielding 2.1 g of **31c** (69.8%): mp 161.5–163.0 °C; ^1H NMR ($CDCl_3$) δ 1.56 (d, $^2J_{PH}$ = 13 Hz, CH_3), 1.1–2.5 (m, 13 H), 4.9 (s, OH); partial ^{13}C NMR δ 16.6 (d, $^1J_{PC}$ = 67.7 Hz, PCH_3), 22.9 (d, $^1J_{PC}$ = 69.5 Hz, C-2), 37.3 (d, $^2J_{PC}$ = 8.6 Hz, C-3), 48.4 (d, $^1J_{PC}$ = 71.9 Hz, C-7a), 76.5 (d, $^2J_{PC}$ = 5.6 Hz, C-3a); ^{31}P NMR ($CDCl_3$) δ 63.8.

Anal. Calcd for $C_9H_{17}O_2P$: C, 57.43; H, 9.11; P, 16.46. Found: C, 57.46; H, 9.25; P, 16.66.

Synthesis of the *r*-1-Methyl-*c*-3a-hydroxy Derivatives of *cis*- and *trans*-Perhydrophosphindole 1-Oxides (31a,b). To a solution of 1.86 g (0.01 mol) of a mixture of epoxides **6a** (60%) and **6b** (40%) in 8 mL of ethylenediamine was added 0.21 g (0.030 mol) of freshly cut lithium. Since no visible reaction had occurred after 40 min, the mixture was warmed, whereupon dissolution of the metal commenced. Reaction was complete in about 15 min. After being stirred at room temperature for 40 min, the mixture was quenched with 10 mL of water and then extracted with THF. The extract was dried ($MgSO_4$) and concentrated to give a white solid (1.6 g, 86%) whose ^1H NMR indicated that a **27a** (60%)–**27b** (40%) mixture had been formed. For **27b**: δ 1.72 (d, $^2J_{PH}$ = 12 Hz, PCH_3), 6.22 (dd, $^2J_{PH}$ = 23 Hz, $^3J_{HH}$ = 8 Hz, PCH=C**H**), 6.89 (dd, $^3J_{PH}$ = 37 Hz, $^3J_{HH}$ = 8 Hz, PC**H**=CH). The product (1.60 g, 8.6 mmol) was dissolved in 120 mL of methanol, mixed with 125 mg of rhodium on powdered alumina, and hydrogenated at 45 psi of H_2 for 24 h. The solid (mp 190–192 °C) remaining after stripping of the solvent was a mixture of isomers in approximately the starting ratio. For **31a**: partial ^1H NMR ($CDCl_3$) δ 1.56 (d, $^2J_{PH}$ = 12 Hz, PCH_3); partial ^{13}C NMR ($CDCl_3$) δ 14.9 (d, $^1J_{PC}$ = 59.1 Hz, PCH_3), 48.7 (d, $^1J_{PC}$ = 67.4 Hz, C-7a), 75.6 (d, $^2J_{PC}$ = 11.0 Hz, C-3a); ^{31}P NMR ($CDCl_3$) δ 70.4. For **31b**: partial ^1H NMR δ 1.78 (d, $^2J_{PH}$ = 12 Hz, PCH_3); partial ^{13}C NMR δ 19.5 (d,

$^1J_{PC}$ = 61.5 Hz, PCH_3), 25.6 (d, $^1J_{PC}$ = 57.3 Hz, C-2), 37.6 (d, $^2J_{PC}$ = 8.6 Hz, C-3), 45.3 (d, $^1J_{PC}$ = 67.5 Hz, C-7a), 77.9 (d, $^2J_{PC}$ = 10.4 Hz, C-3a); ^{31}P NMR δ 73.2.

Synthesis and Hydrolysis of 1-Bromo-1-methyl-3,4-epoxyphospholanium Bromide. To a solution of *syn*-1-methyl-3,4-epoxyphospholane (**17**; 5.0 g, 0.043 mol) in 200 mL of cyclohexane at 0 °C was added a solution of bromine (6.9 g, 0.043 mol) in 100 mL of cyclohexane. The resulting slurry was stirred for 0.5 h and then filtered (N_2). The solid was washed with cyclohexane and then added in portions to a slurry of ice in $NaHCO_3$ solution. The solution was extracted continuously with CH_2Cl_2 for 24 h, and the extract was dried ($MgSO_4$) and stripped to a solid mixture (3.1 g, 55%) of epoxyphospholane oxides **4** (90% by ^{31}P NMR) and **4a** (10%). Spectral properties of the latter are included in Table II.

Synthesis of a Mixture of Epoxyphosphines 17 and 17a. A 2.0-g sample of the mixed epoxyphospholane oxides **4** (90%) and **4a** (10%) prepared in the preceding experiment was reduced with phenylsilane as described for the synthesis of **17**. The product was a mixture of phosphines **17** (90%) and **17a** (10%; spectral data are given in Table II).

Quaternization of Epoxyphosphines with Deuteriomethyl Iodide. A 0.8-g (6.9 mmol) sample of **17** in benzene was treated with CD_3I (1.0 g, 6.9 mmol) and the precipitated salt recrystallized from ether–methanol; mp 195–198 °C. Its ^{13}C NMR spectrum (CH_3OH) contained a single P–CH_3 signal at δ 13.9 (d, $^1J_{PC}$ = 50 Hz), a C-2,5 signal at δ 28.4 (d, $^1J_{PC}$ = 54 Hz), and a C-3,4 signal at δ 59.5 (d, $^2J_{PC}$ = 2 Hz).

Anal. Calcd for $C_6H_9D_3IOP$: C, 27.60; H and D, 5.78; P, 11.86. Found: C, 27.71; H and D, 5.31; P, 11.53.

Similarly, the deuteriomethyl salt was formed from the mixture of isomeric phosphines **18**. Its ^{13}C NMR spectrum contained only one P–CH_3 signal, δ 13.4 (d, $^1J_{PC}$ = 50.5 Hz).

Registry No. **3**, 930-38-1; **4**, 61247-91-4; **4a**, 61183-63-9; **5a**, 57065-62-0; **5b**, 57065-63-1; **6a**, 74958-57-9; **6b**, 74958-58-0; **7**, 65482-10-2; **8**, 74925-19-2; **9**, 65489-18-1; **10**, 74925-20-5; **11**, 57065-64-2; **12**, 74925-21-6; **13**, 74925-22-7; **14**, 74925-23-8; **15**, 74925-24-9; **16**, 74925-25-0; **17**, 61183-59-3; **17a**, 61217-62-7; **18** (α-H isomer), 74958-59-1; **18** (β-H isomer), 61183-60-6; **19**, 74925-26-1; **20**, 61183-61-7; **21**, 74925-27-2; **21a**, 74925-28-3; **22**, 74925-29-4; **23**, 74925-30-7; **26**, 51015-54-4; **27a**, 74925-31-8; **27b**, 74958-60-4; **28**, 74925-32-9; **29**, 74925-33-0; **30a**, 74925-34-1; **31a**, 74925-35-2; **31b**, 74958-61-5; **31c**, 74958-62-6; 1-vinylcyclohexene, 2622-21-1; 1-vinylcyclopentene, 28638-58-6; 1,2-dimethylenecyclohexane, 2819-48-9; 1,2-dimethylenecyclopentane, 20968-70-1; CH_3PCl_2, 676-83-5; PCl_3, 7719-12-2; pyrrolidine, 123-75-1; cyclohexylamine, 108-91-8.

Photochemical Reactions of Duroquinone with Cyclic Polyenes. Synthesis of New Cage Compounds

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Photoinduced cycloadditions of duroquinone to cyclic trienes and cylooctatetraene have been studied. When irradiated in the presence of cycloheptatriene, duroquinone afforded two kinds of 1:1 and 2:1 cage products: pentacyclo[7.4.0.0^{2,8}.0^{4,12}.0^{5,11}]tridec-6-ene-3,13-dione (**3**) and a more complex cage compound **4**, by way of the intermediate [2 + 2] cycloadduct **9**. Duroquinone with ethyl bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate produced a 1:1 cage adduct **14** via its valence isomer, a bicyclo[4.3.0]nona-2,5,7-triene derivative. Cyclooctatetraene did not react directly with duroquinone, but a caged dihydrobullvalene (**18**) was obtained by photolysis with the 76 °C melting dimer of COT. Structural and mechanistic investigations of the formations of these new cage compounds have been carried out.

p-Quinones afford cycloadducts upon irradiation in the presence of alkenes and alkynes.[1] Formation of both oxetanes[2] and cyclobutanes[3] has been observed, depending on the substituents present in the quinone. From theoretical and experimental investigations,[4] *p*-benzoquinone is thought to react from a triplet n,π^* excited state to yield exclusively oxetane adducts, while its tetramethyl or tetrachloro derivative, duroquinone or chloranil, whose lowest triplet should be π,π^*,[5] affords only cyclobutanes. These photocyclizations are one of the most convenient methods for synthesis of cage compounds which are a group of interesting energy-rich molecules.[6]

The photodimerization of certain *p*-quinones occurs to give pentacyclo[6.4.0.0^{2,7}.0^{4,11}.0^{5,10}]dodeca-3,6,9,12-tetraone derivatives either in solution or in the solid phase.[7] The photochemical cyclizations of duroquinones to cyclohexa-1,3-dienes,[3b] bicyclo[2.2.1]hepta-2,5-diene,[3b] and related dienes[8] afford several types of cage adducts via double [2 + 2] cyclizations. Also the endo Diels–Alder adducts of *p*-benzoquinone derivatives with cyclic[9] and acyclic 1,3-dienes[10] are well-known to give cage products

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