mp 178–80 °C (from ethanol). ^{1}H-NMR δ 3.7 (AB system, J_{CH_2CH} = 6, CH_2), 5.25 (dd, J_{gem} = 2, J_{trans} = 15), and 5.35 (dd, J_{gem} = 2, J_{cis} = 8) (=CH_2), 5.9 (ddd, J_{CH_2CH} = 6, J_{trans} = 15, J_{cis} = 8, =CH–), 7.8 (s, H-6), 8.05 (s, H-3). Anal. Calcd for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.50; H, 3.60; N 21.85.

From BTN (142 mg, 0.1 M) in dichloromethane after 8 h of irradiation. Unreacted starting material (92 mg); product **11** (46 mg, 85%). In an identical experiment, the solvent was evaporated, and the residue was submitted to bulb-to-bulb distillation at reduced (30 mmHg) pressure. From the distillate were obtained two volatile compounds separated by VPC. *trans*-1,2-Bis[(trimethylsilyl)methyl]cyclobutane (**12**, 25 mg): M$^+$ m/z 228: ^{1}H-NMR ($CDCl_3$) δ 1.35, 1.8 and 1.95 (three m, AA′BB′CC′ system), 0.5 (dd, J_{gem} = 14, J_{CH_2CH} = 10), and 0.83 (dd, J_{gem} = 14, J_{CH_2CH} = 4) (CH_2Si); ^{13}C-NMR ($CDCl_3$) δ −0.8 (Me_3Si), 24 (CH_2Si), 28.3 (C-3), 43.1 (C-1). Cis isomer of compound **12** (**13**, 20 mg), M$^+$ m/z 228: ^{1}H NMR ($CDCl_3$) δ 1.5, 2.0, and 2.4 (three m, AA′BB′CC′ system), 0.5 (dd, J_{gem} = 14, J_{vic} = 5), 0,62 (J_{gem} = 14, J_{vic} = 10) (CH_2Si); ^{13}C-NMR ($CDCl_3$) δ −0.9 (Me_3Si), 17.3 (CH_2Si), 27.3 (C-3), 35.3 (C-1). Compare with tabulated values for *cis*- and *trans*-1,2-dimethylcyclobutane δ 26.6 (C-3) and 32.2 (C-1) and, respectively, 26.8 (C-3) and 39.2 (C-1).

Irradiation of Compound 4. Compound **4** (8 mg) in 25 mL of acetonitrile was irradiated as above for 90 min. Evaporation of the solvent gave compound **5** (quantitative yield) identical in its spectroscopic properties to the sample obtained in the NN-ATMS irradiation.

Quantum Yield of Reaction. Aliquots (5 mL) of solution in quartz tubes were prepared as above and irradiated in a merry-go-round apparatus inserted in the multilamp apparatus described above. Chemical reaction was evaluated by VPC and light intensity by ferrioxalate actinometry.

Fluorescence Measurements. Fluorescence intensities were measured by means of an Aminco-Bowman MPF spectrofluorimeter using 1-cm optical path spectrophotometric cells degassed by five freeze–degas–thaw cycles.

Acknowledgment. Support of this research by Consiglio Nazionale delle Ricerche, Roma, is gratefully acknowledged.

Photochemistry of Matrix-Isolated (α-Diazobenzyl)phosphonate. Observation and Reactions of Phosphonylphenylcarbene, Phosphonyl Phenyl Ketone Oxide, and Phenylphosphonyldioxirane

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Photolysis of dimethyl α-diazobenzylphosphonate (**1**) in an Ar matrix at 10 K resulted in the appearance of new absorption bands at 1268, 788, and 536 cm^{-1}, attributable to the carbene **2**. The assignment was based on the observation that the new absorptions disappeared upon thawing of the CO-containing matrix to produce the ketene **3**, which can be generated by photolysis of (α-diazophenacyl)phosphonate **4**. Photolysis of **1** in an Ar matrix doped with 20% O_2 at 10 K produced benzoylphosphonate **5** along with benzoyl phosphate **8**. Generation of **2** in a 0.3% O_2-containing matrix, followed by warming of the matrix to 35 K in the dark, resulted in the total disappearance of the band arising from **2** and the concurrent appearance of a new intermediate, identified as the carbonyl oxide **6**. Photolysis of **6** with visible light ($\lambda > 480$ nm) gave the corresponding dioxirane **7**, which was converted to the ester **8** by further irradiation ($\lambda > 350$ nm); none of the phosphate **9**, expected to arise via phenyl migration in the photoisomerization of **7**, was detected.

Phosphorylcarbenes, readily available from the photolysis or thermolysis of phosphoryl diazo compounds, have been the focus of considerable interest because they can be used not only to introduce the phosphoryl function into organic compounds,[1] as in the phosphorylcyclopropanation of alkenes or arenes, but also as potential photolabile mimics of phosphate derivatives.[2] In this regard, the chemistry of phosphorylcarbenes seems to have been thoroughly investigated. However, the direct observation and characterization of phosphorylcarbenes has not yet been accomplished, to the best of our knowledge, in spite of the fact that there has been an increasing number of reports concerning the direct observation, characterization, and kinetic analysis of many fundamental types of carbenes using either laser flash photolysis techniques[3] or matrix isolation spectroscopy.[4] In the course of our studies on the chemistry of phosphorylcarbenes,[5] we explored the photochemical generation of phenylphosphonylcarbene under matrix isolation conditions. We wish to report herein the characterization of this carbene, its thermal reactions with CO and O_2, and spectroscopic evidence for the sequential formation from it of a carbonyl oxide and a dioxirane.

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(2) (a) Bartlett, P. A.; Carruthers, N. I. *J. Chem. Soc., Chem. Commun.* **1982**, 536. (b) Bartlett, P. A.; Carruthers, N. I.; Winter, B. M.; Long, K. P. *J. Org. Chem.* **1982**, *47*, 1284. (c) Bartlett, P. A.; Long, K. P. *J. Am. Chem. Soc.* **1977**, *99*, 1267.

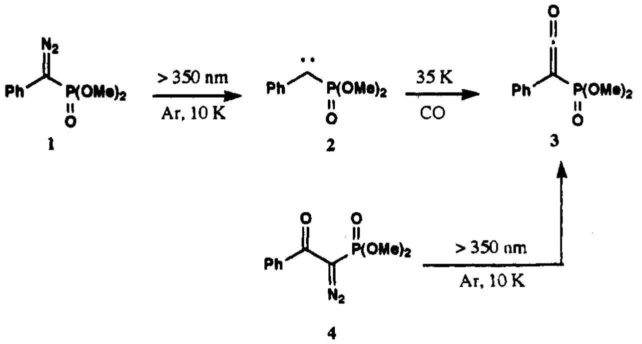
(3) See, for example: (a) Regitz, M., Ed. *Methoden der Organischen Chemie* (*Houben-Weyl*); Thieme: Stuttgart, 1989; Vol. E19b. (b) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Acc. Chem. Res.* **1984**, *17*, 283. (c) Platz, M. S., Ed. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum Press: New York, 1990.

(4) See, for review: (a) Dunkin, I. R. *Chem. Soc. Rev.* **1980**, *9*, 1. (b) Sheridan, R. S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1987; Vol. 8, pp 159–248. (c) Tomioka, H. *Photochem. Photophys.*; Rabek, J. F., Ed.; CRC press: Boca Raton, FL, in press.

(5) (a) Tomioka, H.; Inagaki, T.; Izawa, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 1023. (b) Tomioka, H.; Inagaki, T.; Nakamura, S.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 1* **1979**, 130. (c) Tomioka, H.; Hirai, K. *J. Chem. Soc., Chem. Commun.* **1989**, 362; **1990**, 1611. (d) Tomioka, H.; Watanabe, M.; Kobayashi, N.; Hirai, K. *Tetrahedron Lett.* **1990**, *31*, 5061.

0022-3263/92/1957-6216$03.00/0

Scheme I



Results

The phenyl(dimethylphosphonyl)carbene (2) employed in this study is easily generated by photolysis and/or thermolysis of the precursory diazomethane 1. Its chemistry seems to have been thoroughly studied not only in fluid solution phase at ambient temperatures but also in the gas phase at high temperatures and in organic matrices at low temperatures. In solution phase, for example, it behaves as a typical phenylcarbene, undergoing addition to double bonds and insertion into C–H and OH bonds.[1] In the gas phase at high temperature, it undergoes intramolecular C–H insertion, forming an oxaphosphetane which subsequently undergoes cleavage to give styrene and metaphosphate.[5d] This is not typical behavior for a phenylcarbene, which usually undergoes carbene–carbene rearrangement using the phenyl ring as a conduit to transmit a divalent center.[6] In organic matrices at 77 K, the carbene undergoes C–H insertion reactions with the matrix host molecules when possible, most probably via H abstraction–recombination of the triplet state molecule through H atom tunneling mechanisms.[5b] When 1 is irradiated in frozen matrices saturated with O_2, the generation of a carbonyl compound formed in the reaction of triplet carbene with O_2 is observed.[5b]

Generation and Characterization of Phenylphosphonylcarbene 2. The starting material, dimethyl (α-diazobenzyl)phosphonate (1), was synthesized according to the procedure of Seyferth and co-workers[7] as a rather stable yellow oil.

Deposition of 1 in an argon matrix at 20 K gave an IR spectrum with absorptions at 2088 and 2076 $\mathrm{cm^{-1}}$ arising from the diazo group (Figure 1a) and a UV absorption at 265 nm (Figure 3a). Broad-band irradiation ($\lambda > 350$ nm) of the sample at 10 K resulted in a rapid decrease in the bands attributable to starting material and the concurrent appearance of new bands in the IR (Figure 1a). These new absorptions were all assigned to the phenylphosphonylcarbene 2 since the strong sharp absorption band characteristic of the diazo group disappeared, while the C–H deformations of the phenyl group, as well as the P=O stretching and P—O—C vibrations, changed very little in the transformation from 1 to 2. This conclusion was further supported by trapping experiments. The diazo compound 1 was deposited in an argon matrix containing 6.0% CO. Irradiation gave mainly the carbene 2 and a small amount of carbonyl phosphonate 3 (Figure 1b). The identitiy of 3 was ascertained by comparison of the IR spectra of 3 and authentic material, generated by photolysis of (α-diazophenacyl)phosphonate 4[8] in an argon matrix at 10 K (Figure 1c). Warming the matrix to 35 K caused the bands of 2 to disappear, with concomitant growth of the bands of 3. Carbene 2 proved to be remarkably photostable. Prolonged irradiation of 2 even with short wavelength light (22 h, 254 nm) did not lead to any appreciable changes in the spectra (Scheme I).

Table I. IR Spectroscopic Data of 6 and [$^{18}O_2$]-6 Matrix-Isolated in Ar at 10 K (Wavenumbers in $\mathrm{cm^{-1}}$)

6	[$^{18}O_2$]-6	Δ[a]
1300 (m)	1297	3
1204 (w)	1201	3
1189 (m)	1187	2
1069 (s)	1068	1
1058 (s)	1058	0
947 (w)	945	2
	897	50
885 (w)	872	13
853 (m)	852	1
680 (w)	680	0
577 (w)	573	4
540 (m)	535	5

[a] Isotopic shifts.

Oxidation of Phenylphosphonylcarbene 2. When 1 was irradiated ($\lambda > 350$ nm) in oxygen-doped matrices (0.3–20% O_2 in Ar, 10 K), carbene 2 and several oxidation products were formed. The ratio of 2 to its oxidation products was strongly dependent on the O_2 content of the matrix. In 0.3% O_2-doped matrices, 2 was the main product, whereas at high O_2 concentrations the oxidation was nearly complete and no 2 could be detected by IR spectroscopy.

Thus, irradiation of 1 in Ar matrices doped with 20% O_2 resulted in the formation of two oxidation products plus ozone with no sign of the formation of carbene 2. The oxidation products were easily identified as benzoylphosphonate 5[9] and benzoyl phosphate 8[10] by comparison with the authentic matrix-isolated compounds. Direct comparison of the spectra obtained with those of authentic compound 9[11] indicated, once again, that none of this potential oxidation product was formed, to the limits of our IR sensitivity.

Irradiation of 1 in Ar matrices doped with 0.3% O_2 at 10 K, on the other hand, gave free carbene 2 almost exclusively (Figure 2a). Warming the matrix containing 2 and excess O_2 from 10 to 35 K caused a decrease in the band arising from 2 and a simultaneous increase in the absorptions at 1300, 947, and 577 $\mathrm{cm^{-1}}$ (Figure 2b and Table I). The matrix also took on a distinct yellow hue upon warming. In the UV–vis spectra, the disappearance of the carbene absorption and the formation of an intense, broad band with a maximum at 378 nm was observed (Figure 3c).

The product was remarkably photolabile and completely disappeared upon irradiation with visible light ($\lambda > 480$ nm) to form an intermediate with absorption bands at 844, 786, and 691 $\mathrm{cm^{-1}}$ (Figure 2c). Simultaneously, the color in the matrix was bleached; the visible absorption due to the initial product disappeared. No new UV–vis maximum

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(6) For reviews, see: (a) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353. (b) Jones, W. M. *Rearrangement in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, pp 95–160. (c) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980; Chapter 5, pp 115–163. (d) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. I, pp 263–320.

(7) Marmor, R. S.; Seyferth, D. *J. Org. Chem.* **1971**, *36*, 128.

(8) Synthesis and photolysis forming ketene 3 of 4 is reported: (a) Regitz, M.; Bartz, W. *Chem. Ber.* **1970**, *103*, 1477. (b) Regitz, M.; Anshchurtz, W.; Bartz, W.; Liedhegener, A. *Tetrahedron Lett.* **1968**, 3171.

(9) Berlin, K. D.; Hellwege, D. M.; Nagabhushanman, M. *J. Org. Chem.* **1965**, *30*, 1265.

(10) Cramer, F.; Gatner, K. G. *Chem. Ber.* **1958**, *91*, 704.

(11) Phosphate (9) was prepared by the reaction of PhOCOCl with $P(OMe)_3$.

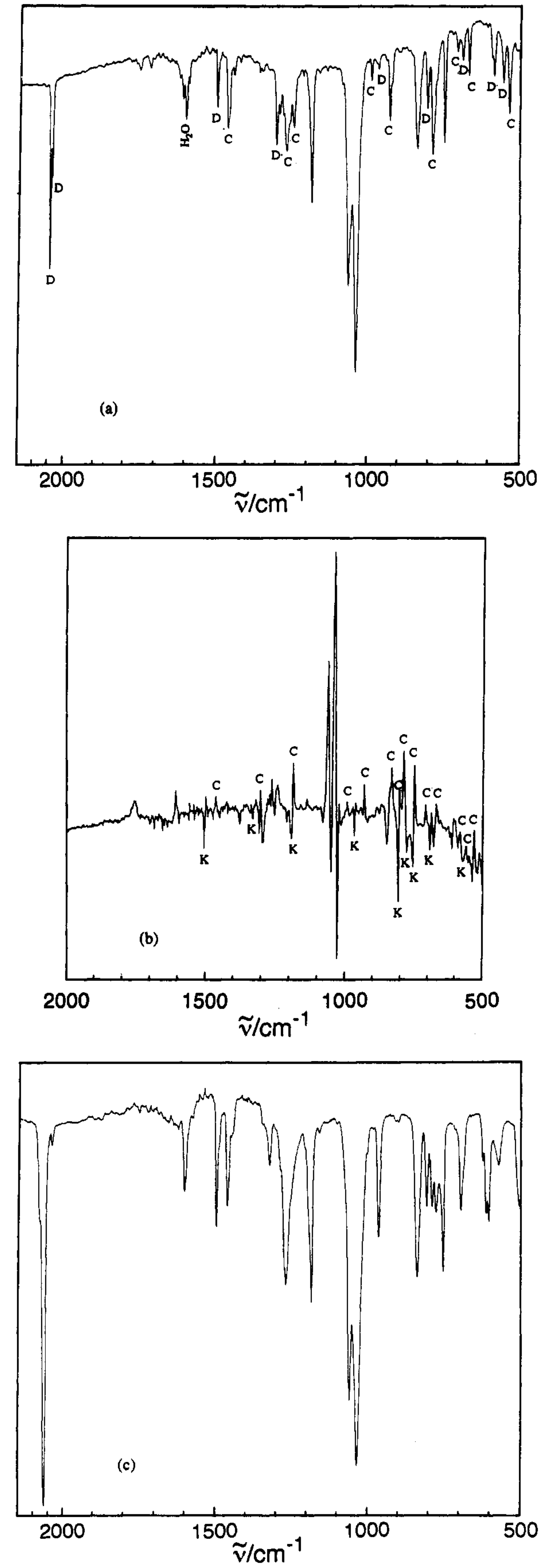
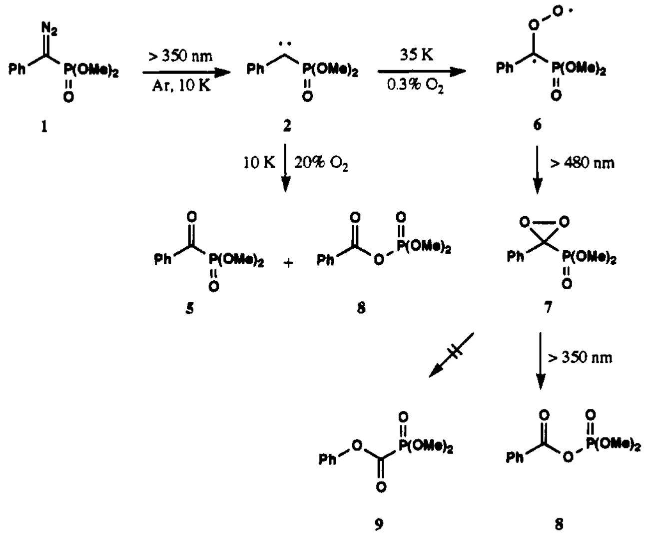


Figure 1. (a) IR spectrum produced on irradiation (λ > 350 nm) of (α-diazobenzyl)phosphonate 1 in an argon matrix at 10 K. (b) Difference IR spectrum obtained after irradiation of 1 in a 6.0% CO-containing argon matrix at 10 K. (c) Spectrum obtained on irradiation (λ > 350 nm) of argon matrix-isolated (benzoyldiazo)phosphonate 4. D = 1, C = 2, and K = 3.

Scheme II



corresponding to the secondary product was observed in the region between 400 and 300 nm (Figure 3d). Subsequent irradiation (λ > 350 nm) rapidly converted the secondary product into benzoyl phosphate 8 almost exclusively (Figure 2d).

A reasonable mechanistic scenario incorporating the above observations is outlined in Scheme II. Several workers have reported the UV and IR observations of intermediates formed on reaction of triplet carbenes with O_2.[12] The intermediates, suggested to be carbonyl oxides, all have $\pi \rightarrow \pi^*$ absorptions with maxima in the range of 390–460 nm and ν(O–O) in the range of 900–1050 cm^{-1}. Accordingly, the yellow intermediate was assigned as carbonyl oxide 6. Isotopic labeling supports the structure assignment for 6. Thus, when $^{18}O_2$ was used in the experiment, the band at 947 cm^{-1} showed an isotopic shift of 50 cm^{-1} to longer wavelength (Table I). The large isotopic shift, as well as the intensity and frequency of the band at 947 cm^{-1}, are both characteristic of the O–O stretching vibrations of carbonyl oxides.[12]

The intermediate which is formed photochemically from 6 and which produces the final product 8 is assigned as the dioxirane 7, as photochemical isomerization of carbonyl oxides to dioxiranes and their subsequent photochemical rearrangement to esters are well-documented.[12] The structure of 7 was further confirmed by IR spectroscopy. Dimethyldioxirane[13] exhibits several weak absorptions in the region 1080 to 1030 cm^{-1} and a strong absorption at 784 cm^{-1}, and diphenyldioxirane[14] exhibits its O–O deformation absorption at 588 cm^{-1}. The intermediate 7 exhibits absorptions at 844, 786, 691, 568, 536, and 522 cm^{-1}. Presumably, the band at 536 cm^{-1} is caused by the O–O deformation mode of the dioxirane moiety, since this band alone is affected by ^{18}O labeling (9 cm^{-1}), although the isotopic shift is smaller than that observed (13 cm^{-1}) for diphenyldioxirane.[14] The ester 8, on the other hand, formed from 7, shows large isotopic shifts at 1752 (31) and 1270 cm^{-1} (5 cm^{-1}).

Discussion

The primary product obtained in the photolysis of (α-diazobenzyl)phosphonate 1 in an argon matrix at 10 K is

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[12] See, for review: Sander, W. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.

[13] Murray, R. W.; Heyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

[14] Sander, W. W. *J. Org. Chem.* **1989**, *54*, 333.

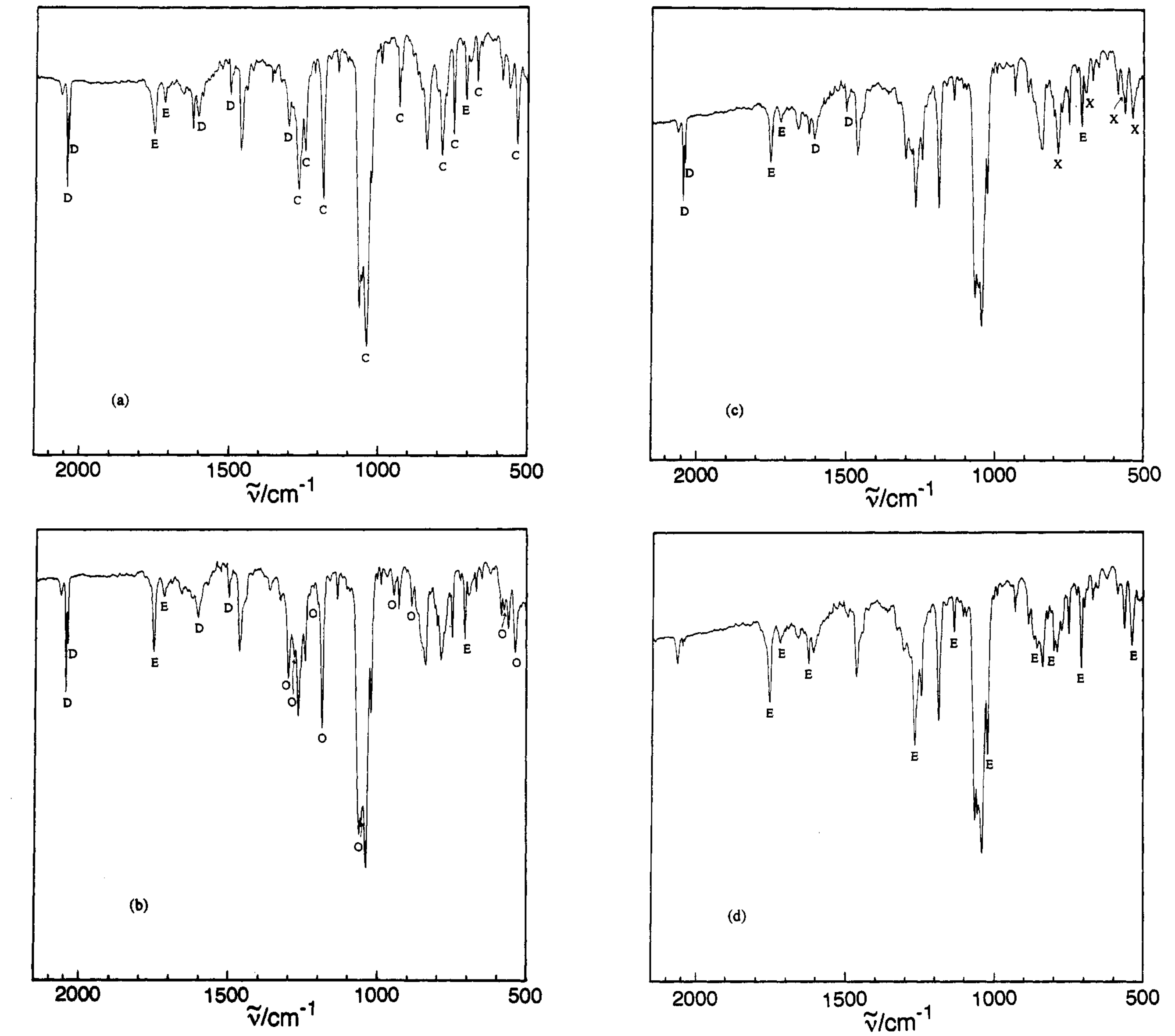

Figure 2. (a) IR spectrum produced on irradiation ($\lambda > 350$ nm) of **1** in an argon matrix doped with 0.3% O_2 at 10 K. (b) Spectrum on the same sample after warming to 35 K. (c) Spectrum obtained after irradiation of b for 15 min at $\lambda > 480$ nm. (d) Spectrum obtained after irradiation of c for 4 h at $\lambda > 350$ nm. D = **1**, C = **2**, O = **6**, X = **7**, and E = **8**.

thus unambiguously identified as the corresponding carbene (**2**) presumably in the triplet ground state,[15] on the basis of trapping experiments using CO and O_2. UV as well as IR absorptions of the phosphonylcarbene have been recorded for the first time.

The remarkable photostability of this carbene under these conditions is worthy of comment in light of the fact[16,17] that most monophenylcarbenes investigated to date, e.g., phenylcarbene,[16a,b] (*o*-fluorophenyl)carbene,[16c] (*o*-chlorophenyl)carbene,[16c,17] tolylmethylenes,[16d,e] pyridylmethylene,[16f–h] and phenyl(chloro)carbene,[17] usually undergo ring expansion to form the corresponding 1,2,4,6-cycloheptatetraene derivatives upon irradiation in matrices. Chapman and co-workers have presented evidence showing that the photoring-expansion of phenylmethylene under matrix conditions does not occur via a bicyclo[4.1.0]hepta-2,4,6-triene intermediate but rather occurs directly upon excitation, presumably by a 1,2 shift to the carbenic center.[16] The inability of **2** to undergo the ring expansion reaction may be partly explained in terms of delocalization of the carbenic orbital onto the adjacent phosphonyl moiety. Support is lent to this explanation by the ESR spectra,[15] which show a considerably smaller D value for the phosphonylcarbene **2** than for the parent phenylcarbene.[16c] The complete lack of Wolff-type 1,2-methoxy migration, another reaction channel[1,18] available to **2**, may also be related to this delocalized nature. It is very interesting to note in this regard that (methoxycarbonyl)phenylcarbene (**11**) generated in Ar matrices at 10 K undergoes both Wolff rearrangement forming ketene

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[15] ESR study shows that the carbene **2** has the triplet ground state: Tomioka, H.; Murata, S.; Hirai, K. To be published.

[16] (a) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779. (b) Chapman, O. L.; Abelt, C. J. *J. Org. Chem.* **1987**, *52*, 1218. (c) McMahon, R. T.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456. (d) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683. (e) Chapman, O. L.; Jonson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 501. (f) Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *Recl. Trav. Chem. Pays-Bas* **1979**, *98*, 334. (g) Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 6245. (h) Chapman, O. L.; Sheridan, R. S. *J. Am. Chem. Soc.* **1989**, *101*, 3690.

[17] Sander, W. W. *Spectrochimica Acta* **1987**, *43A*, 637.

[18] Phosphorylcarbenes with suitable substituents on the phosphorous atom usually undergo migration of a substituent to the carbene center to form methylenephosphane.

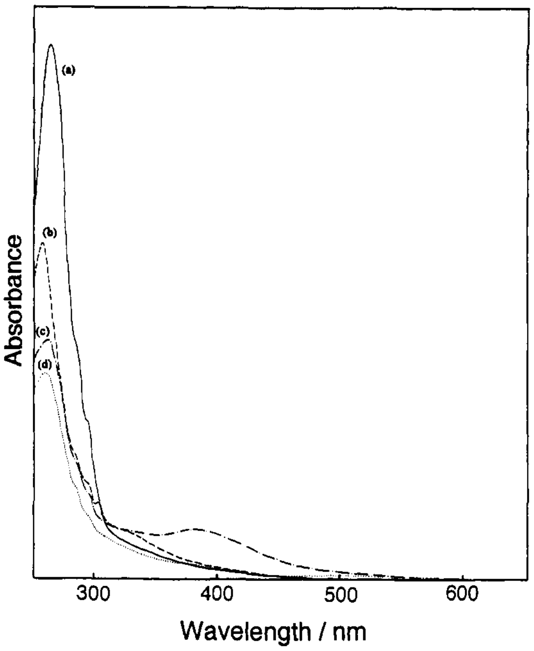
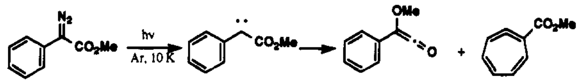


Figure 3. (a) (—) UV spectra of 1 matrix isolated in Ar at 10 K. (b) (- -) UV spectra of carbene 2 obtained after 3 h of irradiation ($\lambda > 350$ nm) of 1. (c) (-·-) UV spectra of carbonyl oxide 6 obtained after warming the matrix containing 2 and O_2 to 35 K. (d) (- - -) UV spectra obtained on irradiation ($\lambda > 480$ nm) of carbonyl oxide 6.

12 and ring expansion leading to the cycloheptatetraene derivative 13 simultaneously upon irradiation (eq 1).[19]



(1)

10 11 12 13

The thermal reaction of carbene 2 with CO produces a secondary product which was identified as the ketene 3 by direct comparison with an authentic sample. The trapping study using CO has been demonstrated to be diagnostic for the presence of carbenes.[16,20,21] This is an interesting reaction because both CO and the ketenes are singlet-state species whereas carbene 2 has a triplet ground state. Thus, an electronic spin-inversion must occur at some point on the reaction pathway. Actually, the reaction of the carbene 2 with CO was found to be less efficient than with the triplet ground-state molecule O_2. Thus, 2 can be generated in Ar matrices containing 6% CO at 10 K and seems to be stable under these conditions indefinitely. Only upon warming the matrices to about 35 K does the thermal, ketene-forming reaction take place at a reasonable rate. It is very difficult, on the other hand, to generate a detectable concentration of the carbene in matrices containing even 2% O_2. Thus, there is a great difference in the reactivity of 2 toward CO, on the one hand, and O_2 on the other. These types of reactivity differences have been noted in the reactions of other triplet ground-state carbenes, e.g., indenylidene[21,22] and fluorenylidene,[21,22] and can be explained in terms of rate limitation due to spin-inversion.

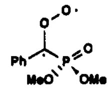
Table II. Characteristic IR and UV Spectroscopic Data for Some Carbonyl Oxides (RR′C–OO)

R	R′	ν(O–O), cm^{-1}	Δ,[a] cm^{-1}	$\pi \rightarrow \pi^*$, nm	ref
Ph	Ph	896	−35	422	23c
Ph	H	915	−30	387	23c
		890	−21		
Ph	CF_3	1009	−20	378	24
		943	−35		
Ph	$P(O)(OMe)_2$	947	−50	378	this work
		885	−13		

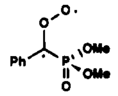
[a] Isotopic shifts.

The thermal reaction of the carbene with O_2 is very smooth. Thus, photolysis of the diazomethane precursor 1 in an Ar matrix doped with 20% O_2 produces the corresponding ketone 5 and the ester 8, with no detection of 2, indicating that 2 is trapped by O_2 instantly under these conditions. The formation of 5 can be explained in terms of reaction of the carbonyl oxide with excess O_2 with extrusion of O_3,[23] while 8 must be produced through dioxirane intermediate 7. These oxidation intermediates can only be observed under highly controlled conditions.

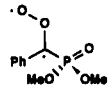
The carbonyl oxide 6 has a strong characteristic band in the IR at 947 cm^{-1} which exhibits an isotopic shift of 50 cm^{-1} when 6 is doubly ^{18}O-labeled and is therefore assigned to the O–O stretching mode. A band at 885 cm^{-1} also shows a marked ^{16}O–^{18}O isotopic shift (13 cm^{-1}) and is therefore assigned to the O–O vibration of 6. For carbonyl oxide 6, four possible isomers, **6at**, **6ac**, **6st**, and **6sc** can be formulated. The observation of only one O–O stretching vibration in the IR spectrum might be explained by the fact either that only one isomer is formed or that all four isomers show the same O–O stretching vibration. Characteristic spectroscopic data for some typical carbonyl oxides are listed in Table II. It is noteworthy that electron-withdrawing groups shift the bands to higher frequencies. Thus, if one uses benzophenone oxide as a reference, substitution of one Ph by CF_3 induces a shift of 44 cm^{-1}. This means that the O–O bond is stabilized by electron acceptors (π-acceptors), giving rise to larger effects than σ-acceptors.[24] The fact that the phosphonyl group induces a shift of 50 cm^{-1} indicates that it has a considerable effect on stabilizing the O–O bond in carbonyl oxide. From the frequency of the O–O stretching vibration, the O–O bond order can be estimated. In H_2O_2 the O–O stretching vibration is found at 863 cm^{-1} (bond order 1), in O_2 at 1580 cm^{-1} (bond order 2). Thus in carbonyl oxides a bond order of slightly more than 1 is estimated between oxygen atoms. It is difficult to assign the IR band due to the C–O stretching absorption of the carbonyl oxide moiety because of strong overlapping of the P–O–C absorption bands, although one may assign the bands appearing at 1300–1200 cm^{-1} to the C–O stretching absorption since these bands undergo an isotopic shift. At higher frequencies, and especially in the carbonyl region, no bands were found. This indicates a bond order of substantially less than 2 and is in accordance with findings in other carbonyl oxides.[12]



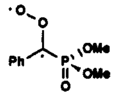
6ac



6at



6sc



6st

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Table III. Some Ground-State Properties of Carbonyl Oxides Calculated by PM3-UHF (P)[a,b]

carboxyl oxide	R(CO)	R(OO)	∠COO	atomic charges C(1)	atomic charges O(1)	atomic charges O(2)	NπC	Pπ spin densities[d] C(1)	Pπ spin densities[d] O(1)	Pπ spin densities[d] O(2)
CH_2OO	1.326	1.270	117.4	−0.164	0.215	−0.288	4.000	0.753	−0.216	−0.537
	(1.281)	(1.269)	(124.0)	(0.074)	(0.183)	(−0.331)	(4.000)	(0.653)	(−0.253)	(−0.400)
PhCHOO	1.349	1.263	120.9	−0.105	0.196	−0.268	4.020	0.655	−0.247	−0.569
(syn)	(1.298)	(1.279)	(125.2)	(0.113)	(0.118)	(−0.296)	(4.006)	(0.619)	(−0.285)	(−0.491)
6ac[e]	1.375	1.259	117.8	−0.426	0.188	−0.227	4.031	0.684	−0.242	−0.609

[a] Data in parentheses are those calculated by MINDO/3-UHF (M) method. [b] Bond lengths R in angstroms, bond angles in degree, charges q in electrons. [c] Number of π-electrons. [d] Negative (positive) values denote an excess of $\alpha(\beta)$-spin density. [e] Essentially similar results are obtained for **6at**, **6sc**, and **6st**.

The carbonyl oxide 6 exhibits a rather strong absorption at 378 nm in the UV spectrum. According to CNDO/S calculations, carbonyl oxides have two characteristic absorptions; a very strong $\pi \rightarrow \pi^*$ transition and a weak n $\rightarrow \pi^*$ transition.[25] Most carbonyl oxides studied thus far exhibit $\pi \rightarrow \pi^*$ transitions with $\log \epsilon = 4$ between 378 and 582 nm, depending on the size of the π system and the electronic properties of the substituents.[12] Generally, π donors lead to a red shift of the $\pi \rightarrow \pi^*$ transition, while the opposite is true for electron acceptors. Again, a CF_3 group exerts the strongest effect on the $\pi \rightarrow \pi^*$ transition among the electron-attracting substituents thus far examined, as manifested by the observation that $Ph(CF_3)CO_2$ has its absorption maximum at 378 nm. The blue-shifted absorption observed for 6 is thus in line with these trends. The calculated, extremely weak n $\rightarrow \pi^*$ transitions were not observed directly in the spectra, but some indirect evidence for them comes from the photochemistry of 6 (vide infra).[12]

Semiempirical calculations employing the MINDO/3-UHF method have been carried out on a variety of substituted carbonyl oxides, providing a reasonable description of the ground-state properties of carbonyl oxides.[25] Since attempts to calculate the properties of 6 were unsuccessful, presumably due to a lack of suitable parameters, the calculations were carried out using the PM3-UHF(P) method.[26] The results are summarized in Table III. The table also includes the data for CH_2OO and PhCHOO calculated by the PM3-UHF (P) as well as by the MINDO/3-UHF (M) methods. Bearing in mind these differences, the following characteristic features emerge for 6: Negative charge is transferred from the two O atoms to the C atom. A phosphonyl group gives more weight to these resonance structures, which all furnish the C atom with a formal negative charge. In this way, negative charge can delocalize onto the substituents, thus leading to an overall stabilization of the molecule. The biradical character of 6, on the other hand, is maintained. Thus, the overall features of 6 are in line with the MINDO/3 results for the carbonyl oxide with a typical π-acceptor substituent such as CHO.[25]

As with many other carbonyl oxides,[12] 6 is also extremely photolabile. Thus, exposure to visible light readily produced dioxiranes 7 along with a small amount of ketone 5. It has been shown that the reaction patterns of carbonyl oxides upon irradiation with visible light depend on the substituents.[12] Thus, many carbonyl oxides, e.g., the oxides of benzophenone,[23] 1,1,1-trifluoroacetophenone,[24] benzoyl chloride,[27] cyclopentadienone,[28] p-quinone,[29] and bicyclo[6.3.0]undeca-2,4,6,8,11-pentaenone[30] undergo photoisomerization to give the corresponding dioxiranes, while the carbonyl oxides of benzaldehyde[23b] and bis(trifluoromethyl) ketone[24] extrude an oxygen atom to give the corresponding carbonyl compounds. However, it is not clear whether dioxirane is not formed or whether it is simply not observable under the experimental conditions. Dioxirane 7 is identified not only by IR spectroscopy but also by its subsequent photochemistry. Upon irradiation, dioxirane 7 produces the phosphate 8 almost exclusively, while no phosphonate 9 is detected. This rearrangement likely occurs via O–O cleavage followed by a phosphonyl shift. The observed selectivity in the migration is in accord with that seen previously in the photoisomerizations of analogous unsymmetrically substituted dioxiranes, but the large preference for phosphonyl migration over phenyl is rather surprising in light of the fact that phenyl migration is usually favored in the photoisomerizations of phenylchloro-[27] and phenyl(trifluoromethyl)dioxiranes.[24] A systematic study of the decomposition of dioxiranes using ketone-free methyl(trifluoromethyl)dioxirane in the gas, solution, and matrix phases has recently been presented by Adam and co-workers,[31] who based their conclusions primarily on product analysis. This report suggested that, while both gas- and liquid-phase photolyses involve a radical chain process, initiated by attack of CH_3 and CF_3 radicals on the dioxirane, the matrix-phase (CCl_4–$CDCl_3$, 77 K) photolyses form only trifluoroacetate along with CF_3CH_3 and CO_2. This is explained in terms of β-scission of the intermediary dioxyl diradical, followed by in-cage coupling of the resulting acetyloxy and methyl radical pairs. A similar explanation cannot be applied, however, to the present reaction, since no in-cage coupling products, i.e., CO_2 and $PhP(O)(OMe)_2$, were detected. Presumably, other factors such as product stability, matrix effect on migration, and affinity of the radicals to oxygen must also be considered in order to explain the observed selectivity.

Experimental Section

General Method. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-700 recording spectrophotometer, and ^1H NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer in CCl_4 or $CDCl_3$ with Me_4Si as the internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 ev).

Matrix-Isolation Experiments. Matrix experiments were performed by standard techniques[2b] using an Iwatani Cryo-Mini closed cycle helium cryostate. For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing parts of a vacuum shroud surrounding the cold head were fitted with KBr windows for spectroscopic viewing, and the

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remaining parts were fitted with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For UV experiments, a sapphire cold window and quartz window were used. The temperature of the matrix was controlled by an Iwatani TCCl controller (gold vs Chromel thermocouple).

Argon (Seitetsu Chemicals, 99.999%), oxygen (Seitetsu Chemicals, 99.9995%), $^{18}O_2$ (Isotech, 97% isotopic purity), carbon monoxide (Seitetsu Chemicals, >99.9%) and volatile organic compounds were mixed in a gas handling system by standard manometric techniques. Less volatile compounds were directly sublimed on the cold window while a large excess of the host gas was deposited simultaneously.

Irradiations were carried out using a Wacom 500 W xenon high pressure arc lamp or a Ushio 500-W mercury high pressure arc lamp. For broad-band irradiation, Toshiba cut-off filters were used (50% transmittance at the wavelength specified).

Materials. Dimethyl (α-diazobenzyl)phosphonate (1)[7] and dimethyl α-(diazophenacyl)phosphonate (4)[8] were synthesized according to the literature procedures. Benzoyl phosphate 8[10] was prepared by the reaction of 1,3-diethoxy-3-(dimethylphosphenyl)prop-2-en-1-one with benzoic acid. Dimethyl (phenoxycarbonyl)phosphonate (9) was obtained by treating phenyl chloroformate with $P(OMe)_3$ followed by distillation: bp 104 °C/0.5 Torr; ^1H NMR (CCl_4) δ 3.94 (d, $J = 12.0$ Hz, 6 H), 7.02–7.44 (m, 5 H); IR (KBr) 1735, 1480, 1272, 1028, 797, 735 cm^{-1}. Benzoylphosphonate 5[7] was prepared by reaction of benzoyl chloride with $P(OMe)_3$. All other chemicals were used as received or distilled before use as specified.

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Stereoselective Photocyclization of Some Phenolic, Highly Congested Benzophenones and Benzaldehydes. Use of *cis*-2-Arylbenzocyclobutenol Methyl Ethers for the Synthesis of Lignans

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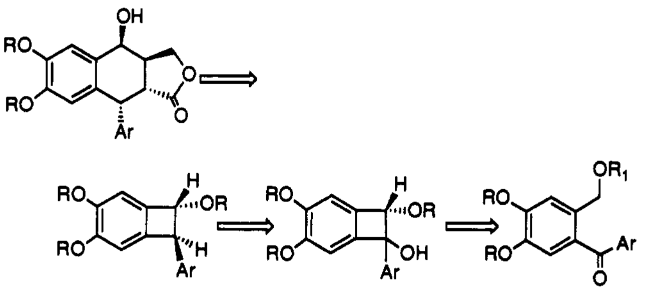
Irradiation of some highly congested, phenolic 2-(methoxymethyl)benzophenones provides a rapid, efficient and stereoselective entry to the corresponding 1-aryl-1-hydroxy-2-methoxybenzocyclobutenes in high chemical yield. The analogous photocyclization reaction of phenolic benzaldehydes appears to be more limited in scope. According to semiempirical (AM1) calculations on the thermal ring opening of a large number of benzocyclobutene derivatives, α,α′-dioxygenated *o*-quinodimethanes are significantly more stable (5–7 kcal/mol) than the corresponding benzocyclobutene derivatives, thereby suggesting that 1-hydroxy-2-alkoxybenzocyclobutenes are unlikely to be thermally derived from the corresponding *o*-QDM's during photolysis of *o*-(methoxymethyl)benzophenones. Hydrogenolysis (H_2, Pd/C) of either the cis or trans isomers of 1-aryl-1-hydroxy-2-methoxybenzocyclobutenes gives rise to cis–trans mixtures of 1-methoxy-2-arylbenzocyclobutenes enriched in the cis isomer. These enriched mixtures undergo thermal isomerization to the desired trans 1-methoxy-2-arylbenzocyclobutenes. The cis-enriched mixture directly derived from the hydrogenolysis step can be used as a precursor of the required (*E*,*E*)-α-aryl-α′-methoxy-*o*-quinodimethane for the synthesis of lignanes via the intermolecular Diels–Alder approach.

The antitumor properties[1] shown by synthetically derived podophyllotoxin glycosides etoposide and teniposide (in clinical use[2]) have spurred a great deal of synthetic effort toward the naturally occurring lignan podophyllotoxin[3] and related analogs.[4] Among the recently developed synthetic approaches,[5] that of Durst and Macdonald[6] is notable because the stereochemical control of the four contiguous chiral centers was achieved in a single operation. The authors' tactic was to utilize an intramolecular Diels–Alder cycloaddition between an in situ generated *o*-quinodimethane[7] and the appropriate dienophile appended in the side chain.

Scheme I



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