Chemistry and Kinetics of α- and β-Naphthyl(phosphonyl)carbenes. Effects of Positions on Neighbouring Phosphonate Participation

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A series of naphthyldiazomethanes **1** having either (dimethyl)phosphonyl [**a**: $(MeO)_2P(O)$–] or sodium (monomethyl)phosphonate [**b**: $(MeO)(NaO)P(O)$–] groups at positions α or β have been prepared and the effects of these substituents on the naphthylcarbenes (**2**) generated by photolysis of the corresponding diazo compounds have been investigated both by product analysis and by spectroscopic means.

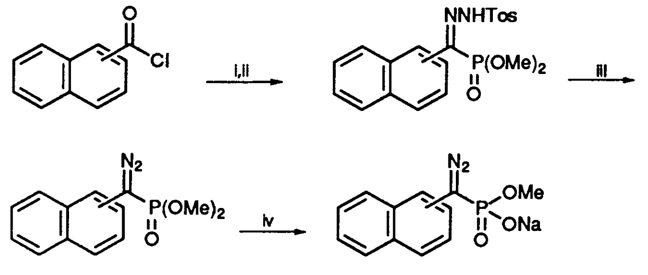
A marked difference in the reaction patterns and reactivities between the α- and β-isomers of **2a** can be explained in terms of differences in electrophilicity of the carbenic centre due to the naphthyl moiety HOMO and of the interaction between the carbene centre and the *peri*-hydrogen. On the other hand, the dramatic increase in the reactivity towards the OH bond relative to the alkenic double bond of the phosphonate anion indicates that the neighbouring phosphonate group must interact with the vacant p-orbital of a singlet carbene and thus reduce the electrophilicity of the carbene.

One of the most dramatic effects of substituents in organic reactions is neighbouring group participation where the intramolecular association of one group in a molecule exerts a significant effect on the reactivity of another.[1–3] The neighbouring-group participation has been particularly well studied in nucleophilic displacement reactions, where the reactions proceed particularly rapidly and/or with retained stereochemistry when the nucleophile and the leaving groups are in the same molecule. In marked contrast, the effect of the neighbouring group on the reactivity of carbenes has been found to be much less dramatic than in carbenium-ion chemistry.[4,5] This is apparently because carbenes are much less electrophilic than carbenium ions. Another reason may be that the internal nucleophiles that have been used in carbene reactions are heavily weighted with neutral heteroatom substituents, *e.g.*, ether, carbonyl and halogens.[5] Recently, however, we have found that neighbouring anionic groups such as carboxylates,[6,7] known to be among the most effective participants in nucleophilic displacement reactions,[1–3] also exert a marked effect on the reactivity of carbene.

As part of our work on the effect of neighbouring anionic groups on the reactivities of carbenes, we have generated naphthylcarbene having phosphonyl or phosphonate groups at either the α or β position and have studied their reactivities both by product analysis and by spectroscopic techniques. Our results indicate that there are significant differences between the α- and β-isomers of the carbene not only in the reactivity of the phosphonyl carbene itself, but also in the magnitude of the participation by the neighbouring phosphonate group.

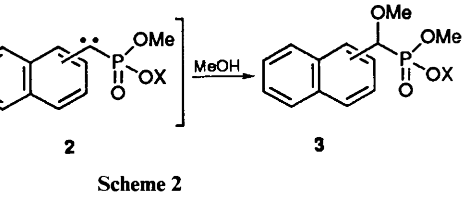
Results

Synthesis of the Precursor Naphthyl(phosphonyl)diazomethanes **1**.—The phosphonyl diazomethanes **1a** were prepared by a slightly modified procedure of Seyferth[8] (Scheme 1). Thus, the treatment of the tosylhydrazone of the naphthoylphosphonates, obtained by the reaction of the naphthoyl chloride with trimethyl phosphite, with either Na_2CO_3 or KOH in water resulted in the formation of **1a** but in a poor yield. The reaction with Na–ethylene glycol at 65 °C for a short time gave superior results. The diazomethanes **1a** were obtained as stable orange crystals. The treatment of **1a** with NaI in refluxing acetone[9] gave the monosodium salt **1b** of the diazomethane as stable yellowish solid.



Scheme 1 *Reagents:* i, $P(OMe)_3$; ii, $TosNHNH_2$; iii, Na–$HOCH_2CH_2OH$; iv, NaI–Me_2CO

Product Analysis Studies: Photolysis in MeOH.—Irradiation ($\lambda > 300$ nm) of the diazomethanes **1** in MeOH afforded the methyl ethers **3** as the major products, regardless of the position and of the charge on the phosphonyl groups (Scheme 2). These products are apparently derived from photolytically generated carbenes **2** which must undergo insertion into the O–H bond of methanol[4] since the diazo compounds **1** were completely recovered unchanged in the dark under otherwise the identical conditions.



Scheme 2

Photolysis in the Presence of Alkenes.—Irradiation of **1** in the presence of alkenes, resulted in the formation of products the structures of which were sensitively dependent on the position and on the charge on the phosphonyl groups.

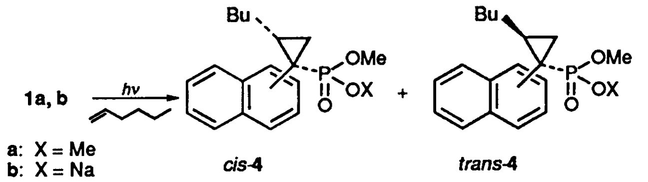
Thus, photolysis of **1a** in hex-1-ene afforded cyclopropanes

Table 1 Photolysis[a] of diazophosphonate **1** in benzene

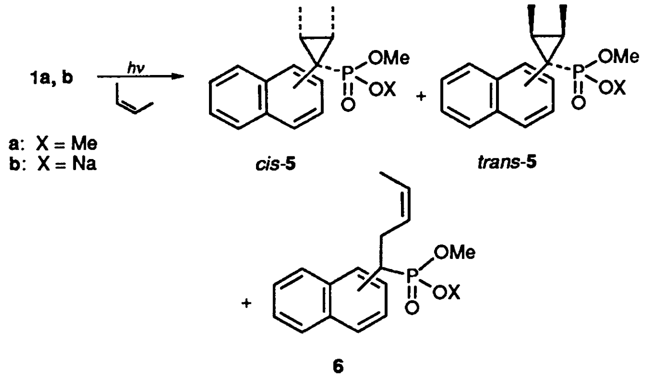
Diazo compound	X	Yield (%)[b] 7	8	9	10
α-**1a**	Me	0.9	96.6	0	0
α-**1b**	Na	43.2	7.7	0	0
β-**1a**	Me	2.4	0	52.6	23.5
β-**1b**	Na	44.8	0	3.9	1.8

[a] Irradiations were carried out on 10 mmol dm^{-3} degassed solution of **1** in benzene at 20 °C. [b] Determined by GLC.

4a in 65–71% yield as a mixture of geometrical isomers, which could be separated by gel permeation chromatography into two fractions, *syn*- and *anti*-**4a** (Scheme 3).* In order to obtain information on the multiplicities of the carbene undergoing cyclopropanation, the carbene was generated in an alkene having a stereochemical handle, *i.e.*, (*Z*)-but-2-ene. Thus, irradiation of α-**1a** in the butene resulted in the formation of cyclopropanes α-**5a** again as a mixture of geometrical isomers. ^1H NMR analysis clearly indicated that the cyclopropanes were formed almost exclusively with retention of stereochemistry of the butene, suggesting the participation of the singlet-state carbene. Essentially similar results were obtained in the photolysis of β-**1a** in the presence of but-2-ene, although an appreciable amount (*ca.* 10%) of the product β-**6a** in which the carbene had inserted into the C–H bond of the Me group was detected in this case (Scheme 4). This can be explained in terms of the difference in electrophilicity between α- and β-**2a** (*vide infra*).



Scheme 3



Scheme 4

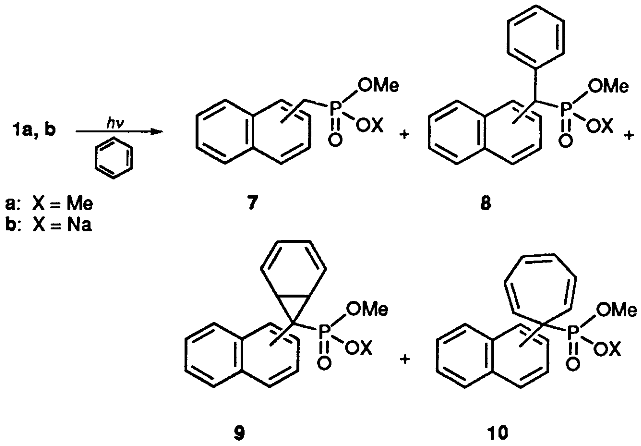
In marked contrast, irradiation of the sodium salt of the diazophosphonate, *i.e.*, **1b** in the presence of an alkene did not result in the formation of the corresponding cyclopropane to an extent which enabled us to examine the stereochemistry of the reaction.

Table 2 Photolysis[a] of diazophosphonate **1** in methanol–hex-1-ene: effect of neighbouring phosphonate groups on insertion–addition selectivities

Diazo compound	X	Yield (%)[b] 3	4	$k_{OH}/k_{add}(k_{rel})$
α-**1a**	Me	41.7	48.7	3.96 (1.00)
α-**1b**	Na	81.0	2.3	163 (41.2)
β-**1a**	Me	19.5	72.6	1.24 (1.00)
β-**1b**	Na	69.9	20.1	16.1 (13.1)

[a] Irradiations were carried out on 10 mmol dm^{-3} degassed solution of **1** in a binary mixture of methanol–hex-1-ene (1:4.2) at 20 °C. [b] Determined by GLC.

Photolysis in Benzene.—Irradiation in benzene resulted in the formation of products which were much more dramatically affected by the subtle changes in the carbenic structure. Thus, photolysis of α-**1a** in benzene afforded the α-(naphthyl)benzylphosphonate α-**8a**, formally an insertion product of the carbene α-**2a** into the C–H bond of the solvent, as major product along with a trace amount of the (naphthyl)methylphosphonate α-**7a**, whereas similar irradiation of β-**1a** resulted in the formation of a mixture of the norcaradiene β-**9a** and cycloheptatriene β-**10a**, no C–H insertion product, *i.e.*, β-**8a** being detected in this case. Introduction of the phosphonate monoanion group again resulted in a dramatic decrease in the product obtained in the corresponding diester carbene. Thus, irradiation of **1b** in benzene resulted in the formation of **7** at the expense of either α-**8** or β-**9** and β-**10** (Scheme 5, Table 1).



Scheme 5

OH *Insertion–Cyclopropanation Selectivity.*—Product analysis studies clearly indicate that the reactivities of naphthyl(phosphonyl)carbenes are highly sensitive to the position as well as the charge of the phosphonyl group. In order to obtain more quantitative information, competitive experiments were carried out. Thus, the carbene was generated in a binary mixture of methanol and hex-1-ene (1:4.2) and the product yields were determined by GC. The O–H insertion–addition selectivities (k_{OH}/k_{add}) were conveniently calculated by means of the well-established equation of Doering–Henderson[10] from the ratios of the products and substrates. Inspection of the data summarized in Table 2 immediately indicates that the α-diester carbene α-**2a** is some three times more reactive towards MeOH relative to the hexene than is the corresponding β isomer (β-**2a**), while the magnitude of the effect of neighbouring phosphonate group is much greater in the α-isomer than in the β-isomer as judged from the increase in the relative reactivities by replacing the function with a monoester + monoanion.

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* *syn* and *anti* refer to the mode of the carbene addition with reference to the methyl groups of the alkene.

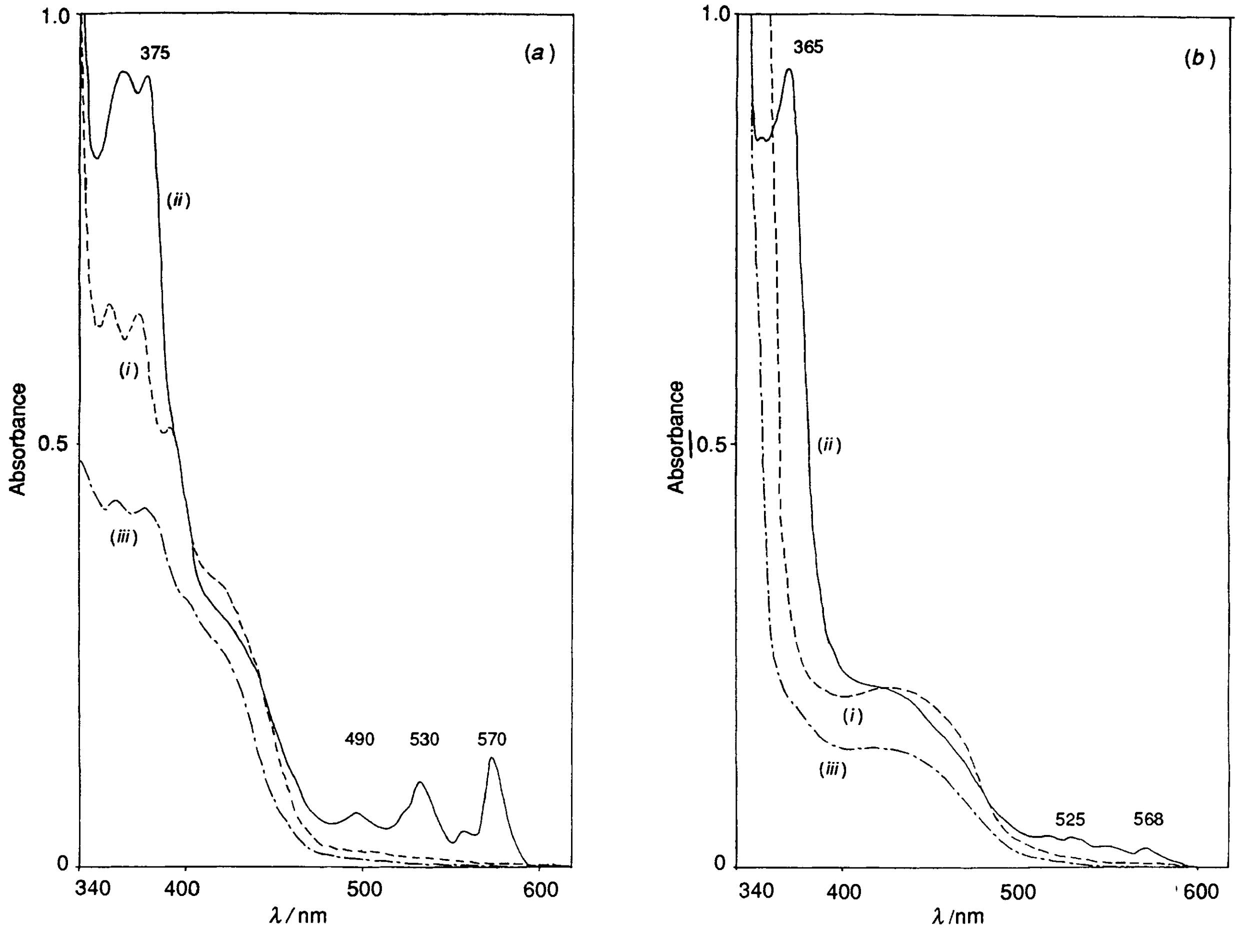


Fig. 1 UV–VIS spectrum of transient products obtained by photolysis of α-**1a** (*a*) and α-**1b** (*b*): (i) UV–VIS spectrum of α-**1** in 2-MTHF at 77 K; (ii) same sample after irradiation (λ > 300 nm); (iii) same sample after thawing the matrix

Table 3 Spectra of carbenes **2** in 2-methyltetrahydrofuran matrix at 77 K

Carbene	λ_{max}/nm
α-**2a**	375, 490, 530, 570
α-**2b**	365, 525, 568
β-**2a**	370, 510, 543, 590
β-**2b**	378, 498, 535, 575

Spectroscopic Studies: Steady-state Irradiation of **1** *in Frozen Media.*—Irradiation (λ > 300 nm) of α-**1a** in a 2-methyltetrahydrofuran (MTHF) glass at 77 K resulted in the appearance of new absorption bands as the absorption due to α-**1a** was consumed, as is shown in Fig. 1(*a*). The new absorption consisted of two identifiable features. There were sharp, intense UV bands centred at 375 nm and the visible portion of the spectrum showed two weak and broad overlapping bands with apparent maxima at 490, 530 and 570 nm. The glassy solution did not exhibit any spectral change for several hours if kept at 77 K. However, warming to room temperature and refreezing at 77 K led to complete disappearance of the characteristic absorption bands. The optical absorption spectra of several arylcarbenes in frozen media have been assigned and typically they consist of an intense UV band and a weak visible transition.[11] These features are present in the spectrum obtained in the photolysis of α-**1a**. Thus, the absorption spectrum is attributable to the phosphonylcarbene α-**2a**.

Photolysis of the monosodium salt of the diazomethane, *i.e.*, α-**1b** under similar conditions also resulted in essentially similar absorption bands at the expense of the original absorption due to the precursor compound [Fig. 1(*b*)]. Thus, again there were sharp, intense UV bands at 365 nm and weak visible bands with apparent maxima at 527 and 568 nm and all the absorption bands completely disappeared when the matrix was thawed to room temperature. Thus, the transient absorption was ascribable to the carbenic phosphonate α-**2b**.

Essentially similar absorptions were observed with the β isomer of the carbenes β-**2** and the absorption maxima are summarized in Table 3. There were no significant changes in the spectrum of the carbene on changing from the diester group to the monoanion. However, the thawing experiment indicated an appreciable difference in thermal stability between the ester **2a** and anion–carbene **2b**. Thus, gradual thawing of the matrix containing the carbenes **2** at identical warming rates indicated that the characteristic absorption of the ester carbene disappeared at around 90 K while the absorption bands due to the anion–carbene **2b** remained even at 110 K. Thus, carbenes seem to be thermodynamically stabilized by anionic phosphonate groups.

Laser Flash Photolysis in Fluid Solution.—Flash photolysis of **1a** (3.8×10^{-4} mol dm^{-3}) in a degassed benzene solution at room temperature with the output of a XeCl excimer laser (308 nm, pulse width 12 ns) gave the transient absorption spectrum shown in Fig. 2. The transient spectrum consisted of two identifiable features, a sharp, relatively intense UV absorption with a maximum at 380 nm and a broad, weak absorption extending from 500 to 600 nm, all of which appeared to rise within the pulse width of the laser and disappeared with similar kinetic behaviour over a period of *ca.* 100 μs. The spectrum is

Table 4 Spectra and lifetime of transient species in benzene

Diazo compound	D/A[a]	Carbene 2		Peroxide 11	
		λ_{max}/nm	Lifetime/μs	λ_{max}/nm	Lifetime/μs
α-**1a**	D	380	20	420	3.0
	A	380	3.0		
α-**1b**	D	380	26	410	4.5
	A	380	4.0		
β-**1a**	D	370	37	420	2.1
	A	370	2.0		
β-**1b**	D	380	27	420	2.9
	A	380	2.3		

[a] D, degassed; A, aerated.

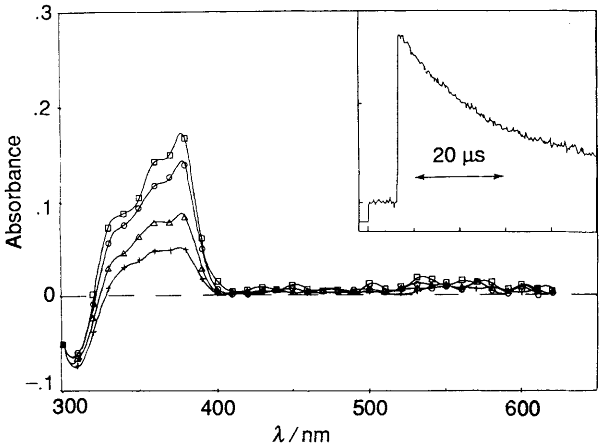
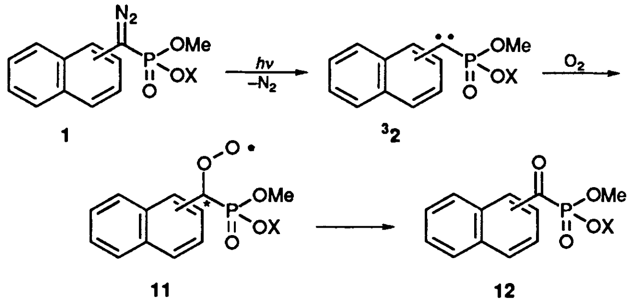


Fig. 2 Time-resolved absorption spectra obtained upon 308 nm excitation of dimethyl (α-naphthyl)diazomethylphosphonate α-**1a** in degassed benzene at room temperature: □, 1.2 μs; ○, 5.9 μs; △, 20 μs; +, 41 μs delay from 308 nm laser pulse. Inset: oscillogram trace monitored at 380 nm.



Scheme 6

similar to that measured during the photolysis of **1a** in a 2-methyltetrahydrofuran (MTHF) glass at 77 K and was therefore assigned to the carbene **2a**. The oscillogram trace of the transient absorption due to **2a** monitored at 380 nm is shown in the inset of Fig. 2. The decay was found to be first order and the lifetime was determined to be 30 μs.[12] This assignment was further supported by a trapping experiment using oxygen. Thus, when flash photolysis of **1a** was carried out in aerated benzene solution, the transient absorption bands due to the carbene were observed but decayed very fast and the lifetime was now only 3.0 μs. A broad absorption band with a maximum at 420 nm appeared (Table 4). The rate of increase in absorbance at 420 nm was practically identical with that of decay of the peak at 380 nm, showing that the carbene **2a**, most likely in its triplet ground states, was quenched by O_2 to form a new species. Analysis of the spent solution showed the presence of a large amount of the ketone **12**. It is now well documented[13] that arylcarbenes with the triplet ground state are readily trapped by O_2 to give the corresponding aryl carbonyl oxide, which are observed directly either by matrix-isolation techniques or by flash photolysis. These carbonyl oxides usually show rather broad absorption bands centred at around 390–450 nm. Thus, the observations can be interpreted as indicating that the triplet carbene **2a** is trapped by O_2 to generate the carbonyl oxide **11**, thus, confirming that the transient absorption at 380 nm quenched by O_2 is due to the triplet **2a**.

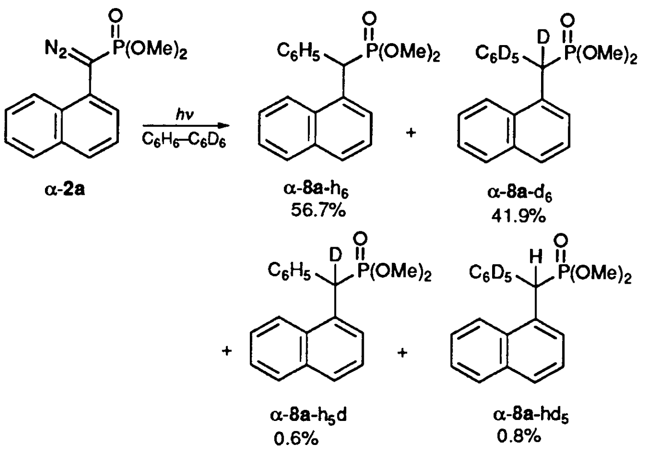
Essentially similar observations were made with the sodium salt of the diazophosphonate **1b**. Thus, laser flash photolysis of **1b** in degassed benzene produced a transient spectrum consisting of a sharp UV absorption at 380 nm along with broad visible absorption extending from 500 to 600 nm with lifetime of 26 μs ascribable to the carbene **2b**. The transient absorption was quenched with O_2 to give a characteristic absorption (λ_{max} at 410 nm) due to the corresponding peroxide **11**. The key difference noted was in the intensities of the transient absorption. Thus, the absorbance of transient absorption due to the carbenic phosphonate **2b** was only a tenth of that of the ester carbene **2a**. On the assumption that all the transient absorptions observed in time ranges of the order of microseconds are due to the triplet-state carbene, the marked decrease in the absorbance can be explained, at least in part, as indicating that the reaction of the singlet carbene is much faster than the rate of intersystem crossing in **2b** than in **2a**, so that most of the carbene is quenched before it decays to the triplet state.

Discussion

The chemistry of 'parent' naphthylcarbenes (NC) has been examined by product analysis and also by laser flash photolysis.[14–16] A comparison of the data available on the reactions of α-NC and β-NC with hydrocarbons shows that α-NC exhibits the lower reactivity and the higher singlet character and possesses the smaller singlet–triplet energy gap. Two key molecular structural differences are responsible for the observed difference in the reactivity. First, the α-position of the naphthyl moiety has the largest HOMO orbital coefficient (Hückel, 0.425 *vs.* 0.263). This will lead to greater stabilization of the carbene centre by π–p overlap thus making the carbenic centre less electrophilic. A second factor which should be taken into account is the interaction between the carbene centre and the *peri*-hydrogen, which as clearly shown from an EPR experiment[16] shows a preference for the *syn* conformation of α-NC.

The marked difference in the reaction patterns as well as in the reactivities between the α- and β-isomers of naphthyl(phosphonyl)carbene **2a** can also be explained in terms of either or both of these two factors. Thus, in the reaction with (*Z*)-but-2-ene (Scheme 4), α-**2a** produces only stereospecific cyclopropanation products **5**, while β-**2a** affords the cyclopropanes **5** and C–H insertion products **6**, the formation of which can be explained as indicating either that the β-isomer is more electrophilic and hence can attack even the C–H bonds of the alkene or that, because of the higher singlet–triplet energy gap, the singlet state of β-isomer decays to the triplet which reacts by abstracting allylic hydrogens from the alkene before it undergoes intersystem crossing to regenerate the singlet. A significant increase in the reactivity of the carbene **2a** towards MeOH relative to hex-1-ene on going from the β to the α isomer can, again, be interpreted in terms of decreasing electrophilicity of the carbenic centre due to the higher electron density in the α-position of the naphthyl moiety HOMO, since it has been shown[17] that MeOH is a 'softer' substrate towards carbenes than are alkenes, and tends to react with less electrophilic carbenes, and even with nucleophilic carbenes, by a protonation mechanism.[18,19]

The dramatic difference in the reaction patterns in the reaction of α- and β-**2a** with benzene (Scheme 5) is rather surprising. The less electrophilic α-**2a** produced product **8** which is formally an insertion into the C–H bonds of benzene, while the more electrophilic β-**2a** afforded a mixture of the norcaradiene **9** and cycloheptatriene **10**. Most carbenes react with benzene by initial attack on the π electrons on the aromatic ring to result in the formation of a norcaradiene and/or cycloheptatriene[4] and the C–H insertion product is observed only in the reaction of highly electrophilic carbenes, *e.g.*, $(CF_3)_2C\colon$.[20] It is likely that **8** is produced from the triplet state of α-**2a** by an abstraction–recombination mechanism. In order to check this possibility, the irradiation of α-**1a** was carried out in a 1:1 mixture of C_6H_6 and C_6D_6, and the deuterium distributions in the product **8** were determined by the mass spectrometric analysis, which clearly showed that direct insertion products, *i.e.*, α-**8a**-h_6 and -d_6 were formed almost exclusively (>98%) while the yield of scrambled products detected was less than 2% (Scheme 7). The kinetic isotope effect (k_H/k_D) for the formation of **8** was determined to be 1.35 from the product distributions. The results clearly indicate that the C–H insertion product is formed almost exclusively from the singlet carbene α-**2a**. Recently Olah and his co-workers have studied the mechanism of the C–H insertion of methylene ($CH_2\colon$) into benzene using kinetic hydrogen isotope effects as well as theoretical calculations and concluded that, while the insertion of the triplet methylene ($k_H/k_D = 12.1 \pm 1.0$) proceeds through a stepwise mechanism which may involve an intermediate, the mechanism for the singlet methylene ($k_H/k_D = 1.34 \pm 0.04$) seems to follow a concerted pathway although initial formation of π-complexes cannot be excluded.[21] Direct attack of the singlet α-**2a** at the C–H bond of benzene is however rather unlikely in the light of the decreased electrophilicity as well as increased steric crowding due to the *peri*-hydrogen. Presumably it is possible that, as the carbenic centre of α-**2a** approaches to the π-electrons on the aromatic ring in a manner to form norcardiene, it will experience severe steric hindrance due to the *peri*-hydrogen and to the phosphonyl group and thus the carbene will be forced to follow the pathway to generate π-complex or a neutral zwitterionic species which will ultimately cascade to **8**. Alternatively, a norcaradiene may be formed which readily undergoes rearrangement to give the insertion product owing to steric repulsion either as it is formed or during the work-up, although all attempts to detect the norcaradiene (*i.e.*, α-**10a**) have been unsuccessful to date.

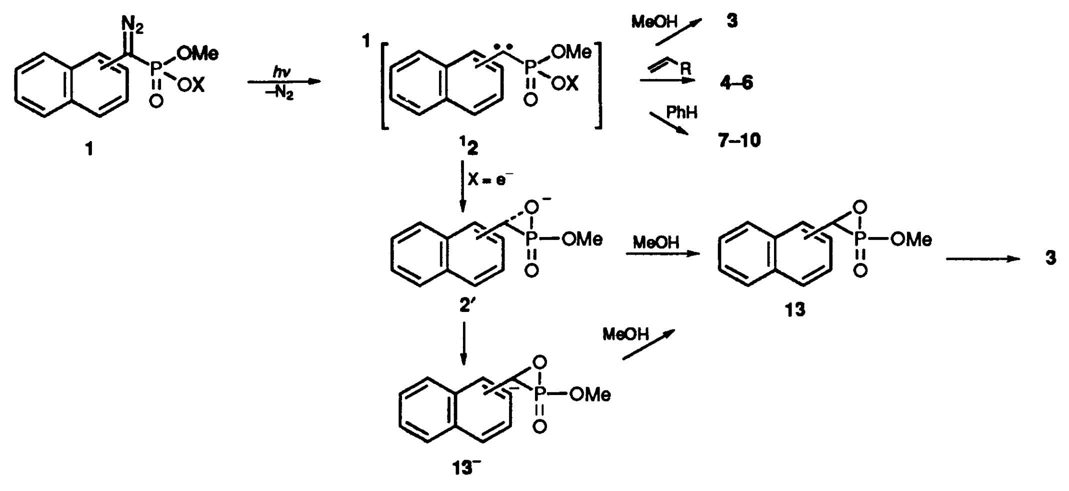


Scheme 7

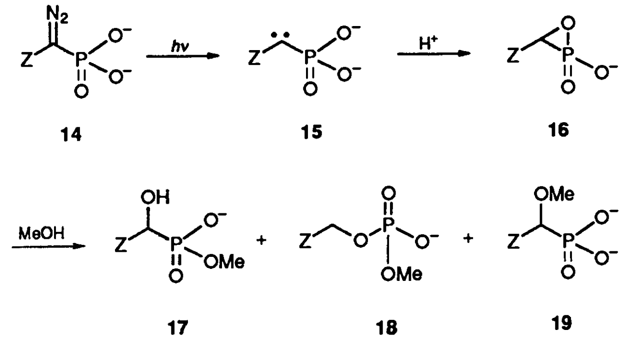
Replacement of the phosphonyl ester group by the phosphonate anion on either the α- or β-position resulted in a drastic decrease in the formation of both cyclopropanation products with alkenes and adducts with benzene, while the formation of OH-insertion products remained little affected (Table 2). The observed increase in the reactivity caused by the phosphonate group is obviously too great to be attributable to differences in inductive, conjugative or steric effects, and can better be explained in terms of neighbouring-group participation. It is quite reasonable to assume that the neighbouring phosphonate group can interact with the vacant p orbital of a singlet carbene. Such an interaction should greatly reduce the electrophilicity of the carbene towards external electron-rich reagents by filling its vacant p-orbital. Naphthylcarbenes are classified as typically electrophilic carbenes and therefore react by accepting electrons from external substrates, *e.g.*, alkenes and benzene, into the vacant p-orbital. When a phosphonate group is introduced, the vacant p-orbital interacts effectively with the internal phosphonate oxygen anion and therefore is no longer available to the external reagents. Simple alkenes such as hex-1-ene or benzene are trapping agents for many electrophilic carbenes, but are not always reactive toward nucleophilic carbenes.[22] On the other hand, methanol is known to be very reactive towards both electrophilic and nucleophilic carbenes, since the former carbene can attack the lone-pair electron on the oxygen while the latter undergoes protonation.[18] Thus, the phosphonate carbene **2b** showed enhanced reactivity towards the alcohol relative to the alkenes. It may be that carbene **2b** can be covalently bonded to the internal phosphonate group leading to the formation of an oxaphosphirane anion **13**$^-$ which then undergoes protonation to give the oxaphosphirane **13**. Subsequent nucleophilic cleavage of **13** by a nucleophile, *e.g.*, methanol, affords the formal OH-insertion product (Scheme 8).

It is very important to compare our results with those of Bartlett who reported that similar phosphonate carbenes **15** generated from the mono- or di-sodium salts of the phosphonate **14** in methanol do not undergo insertion into the alcohol OH, which would form **19**, but give rise to the α-hydroxy phosphonate **17** and/or phosphate **18**. They explained their results in terms of the oxaphosphirane **16** intermediate resulting from intramolecular trapping of the carbenes by phosphonate anion (Scheme 9).[23] This observation supports the above idea that the phosphonate anion can interact with the carbenic centre. However, we were unable to detect the product analogous to **17** and **18** in our reaction mixtures. The reason for this difference probably lies partly in the difference in the carbene substituents. We have shown, for instance, the reaction products of the carbene **15** with methanol changed from **17** to **18** to **19** as one changes the carbenic substituents (Z) from MeO_2C to H to Ph and the results are interpreted in terms of the extent of the interaction between the carbenic centre and oxygen anion.[7]

The difference in the magnitude of participation caused by



Scheme 8



Z = Et_2NSO_2, $Pr^i_2O_3P$, Me_2NCO

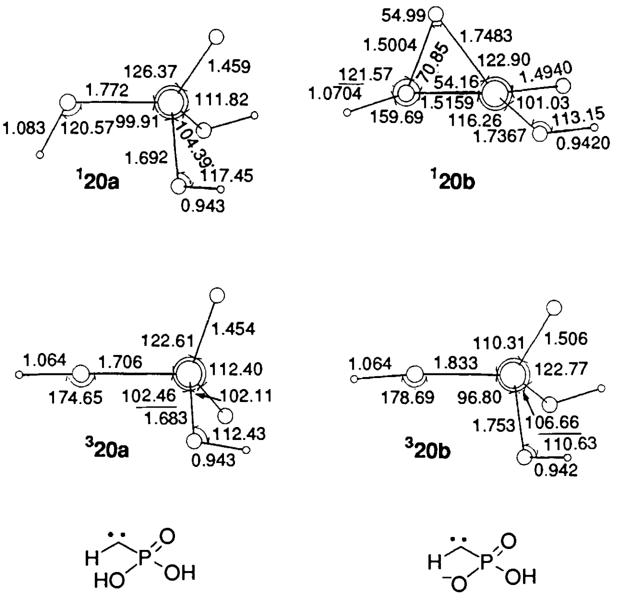
Scheme 9

phosphonate group between the α- and β-isomers of the carbenes **2** is again explicable in terms of electronic and steric factors. Thus, α-**2a** itself is already less electrophilic than β-**2a** because of the higher electron density in the α-position of the naphthyl HOMO. Introduction of a phosphonate anion on the α-position will result in further decrease in the electrophilicity of the carbenic centre as a result of the intramolecular interaction. Steric factors involved in the reaction should play a more important role. Presumably, approach of the carbenic centre to the alkene in a concerted manner must be sterically more hindered than that to an alcohol oxygen given the substituents involved in the reaction centre.[24] The difference must be much more dramatic if the protonation mechanism is operative in the reaction with methanol. Such steric problems already present in the reaction of the ester carbene **2a** must become more important in the reaction of the anionic carbene **2b** where the reactive intermediate undergoing the reaction is not a free carbene but oxaphosphirane-anion-type intermediate. Therefore, in the reaction of α-**2b**, protonation by methanol is presumably greatly favoured over cyclopropanation of the alkene.

In spite of those impressively large differences in reactivity on going from the ester to the anionic carbenes, subtle differences in the spectroscopic behaviour between the two carbenic systems are rather surprising. However, careful examination of the data provides important information which supports the involvement of neighbouring phosphonate participation. First, there is no significant difference in the spectrum of the carbenes observed in MTHF matrix in terms of the intensity on changing the phosphonyl group to the phosphonate anion. Only slight changes in the maximum are observed but no systematic shifts are apparent (Table 3). On the assumption that these transient absorption bands observed in organic matrix at 77 K are due to the triplet carbenes, these results can be interpreted as indicating that the neighbouring phosphonate group exerts little effect on the triplet state of the carbene. This is reasonable since in the singlet, phosphonate anion can effectively interact with the vacant p-orbital involving a two-electron stabilization while for the triplet, the interaction is only a one-electron one, if any, and should be much less effective. The apparent thermal stability of the triplet phosphonate carbene **2b** may be explicable in terms of the stabilization by the neighbouring phosphonate group even by the one-electron net interaction.

Flash photolysis provided more intriguing information. There is no significant difference in the lifetime of the triplet carbene between the α- and β-isomers of the ester carbenes **2a** in benzene. This is rather surprising in the light of the significantly different reaction patterns with benzene of α-**2a** and β-**2a** (Table 1, Scheme 5). However, as most of the reactions occur with the singlet-state carbene, direct observation of the singlet state with much faster time-resolution spectroscopy provided data reflecting its chemical reactions. For instance, there are significant differences in the reaction patterns between α- and β-naphthylnitrenes, obviously because of the similar electronic steric factors as described above and this difference has been nicely explained in terms of the lifetime of the azirine intermediates which are directly observed by laser flash photolysis.[25]

Finally, semiempirical theoretical calculations offer further corroborating evidence for neighbouring participation of the phosphonate group on phosphonylcarbene chemistry. The geometries of the singlet state of the parent phosphonic acid **20a** and the phosphonate anion carbene **20b** optimized by the PM3-UHF(P) method[26] are shown in Fig. 3. Inspection of the optimized geometries immediately reveals that the geometry changes dramatically on going from acid–carbene to anion–carbene. Thus, in the phosphonate carbene, the C–P=O bond angle is expanded to 141.4° whereas the C–P–O⁻ bond angle is contracted to 54.2° and consequently the distance between carbenic carbons and oxygen anions is calculated to be 1.50 Å, which is as short as that of a carbon–phosphorus single bond. The whole geometry of **20b** is then very much like that of oxaphosphirane anion, supporting the idea that an oxaphosphirane-anion-type intermediate is involved in the reaction of phosphonate carbene. No such interaction is expected from the inspection of the geometry of acid carbenes **20a**. Optimized geometries of the corresponding triplet carbene were also calculated and are shown in Fig. 3. It is immediately clear that no significant change in geometry is seen on going from acid– to anion–carbene in the case of the triplet. This is again in



20a **20b**

Fig. 3 Optimized geometries for the singlet and triplet acid carbenes **20a** and acid anion carbenes **20b** (bond lengths are in Å and angles are in deg)

accord with the spectroscopic observations that the triplet states are little affected by the neighbouring phosphonate anion group.

Experimental

General Methods.—UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-G recording spectrophotometer and ^1H NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer for solutions in $CDCl_3$ with $SiMe_4$ as an internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). The GC analyses were performed on a Yanagimoto Instrument, Model G-180. The GC column was prepared from 5% PEG-20M on Diasolid L (5.0 mm × 1.0 m). Thin-layer chromatography was carried out on Merck Kieselgel 60 PF_{254}. Column chromatography was carried out on silica gel (Fuji Davison for column chromatography). Gel permeation chromatography (GPC) was performed on a JASCO, Model HLC-01 instrument. The GPC column was a Shodex H-2001.

Preparation of Dimethyl (Naphthyl)diazomethylphosphonate **1a**.—*Dimethyl α-naphthoylphosphonate toluene-*p*-sulfonylhydrazone was prepared from dimethyl α-naphthoylphosphonate and toluene-*p*-sulfonyl hydrazide by the procedure of Seyferth,[8] as a white solid in 50% yield: m.p. 112–115 °C; δ($CDCl_3$) 2.45 (s, H), 3.62 (d, *J* = 12.0 Hz, 6 H), 7.20–7.51 (m, 7 H) and 7.70–7.86 (m, 4 H).

The tosylhydrazone (300 mg, 0.69 mmol) was added in one portion to a solution of sodium (24 mg, 1.0 mmol dm^{-3}) in ethylene glycol (2.3 cm^3) at 65 °C. The solution was stirred for 13 min at 65 °C, cooled rapidly to 30 °C and extracted with six portions of diethyl ether (5 cm^3 each). The combined ether extracts were washed with 5% aqueous NaOH and saturated aqueous NaCl, dried (Na_2SO_4) and evaporated to give dimethyl (α-naphthyl)diazomethylphosphonate (α-**1a**) as a yellow crystalline solid in 75% yield.

The β-isomer β-**1a** was prepared by essentially the same procedure as orange crystals in 89.7% yield.

Preparation of Sodium Methyl (α-Naphthyl)diazomethylphosphonate **1b**.—The diazomethane **1b** was prepared by reaction of dimethyl (naphthyl)diazomethylphosphonate **1a** with sodium iodide according to the method of Goldstein.[9] A solution of α-**1a** (200 mg, 0.72 mmol) and sodium iodide (160 mg, 1.07 mmol) in dry acetone (5 cm^3) was refluxed for 30 min. The resulting solution was cooled to 0 °C to precipitate pale yellow crystals of α-**1b**, which were filtered, washed with a small amount of cold dry acetone and dried under reduced pressure (10^{-1} Torr) at room temperature, yield 127 mg, 0.45 mmol, 62.3%, m.p. > 250 °C. The β-isomer β-**1b** was prepared by essentially the same procedure as a pale yellow solid in 69.8% yield, m.p. > 250 °C.

Irradiations for Product Identification.—In a typical run, a solution of the diazo compounds (*ca.* 100 mg) in a Pyrex tube was irradiated with a high-pressure, 300 W, mercury lamp at room temperature until all the diazo compound was destroyed. The sodium salts of the diazophosphonate **1b** were dissolved in solvents with the minimum amount of 12-crown-4. The resulting solution with the salt of diazophosphonate **1b** was neutralized and treated with diazomethane shortly after the irradiation. The irradiation mixtures were then concentrated on a rotary evaporator below 20 °C. Individual components were isolated by column chromatography, preparative TLC or GPC and identified by NMR and MS. These fully characterized products were then used as 'authentic' compounds for product identification by co-injection GC–MS.

The Cycloadducts of **2**.—A solution of the diazo compounds (**1**, *ca.* 50 mg) in the alkene (3 cm^3) in a Pyrex tube was irradiated at 10 °C. After evaporation of the solvent under reduced pressure, the reaction mixture was separated by preparative TLC to give isomerically pure cyclopropanes. ^1H NMR and MS data are given in Table 5.

The OH *Insertion Product* **3**.—A solution of the diazo compounds (**1**, *ca.* 5 mg) in dry methanol (2 cm^3) in a Pyrex tube was irradiated. The reaction mixture was separated by preparative TLC to afford pure methyl ether **3** in 90–95% yields. α-**3a**: colourless liquid: δ($CDCl_3$) 3.40 (s 3 H), 3.54 (d, *J* = 10.2 Hz, 3 H), 3.70 (d, *J* = 10.6 Hz, 3 H), 5.37 (d, *J* = 16.2 Hz, 1 H), 7.48–7.58 (m, 3 H), 7.75–7.79 (m, 1 H), 7.84–7.90 (m, 2 H) and 8.17 (d, 8.3 Hz, 1 H); *m*/*z* 280 (M^+, 3%) and 171 (100). β-**3a**: colourless liquid: δ($CDCl_3$) 3.43 (s, 3 H), 3.62 (d, *J* = 10.6 Hz, 3 H), 3.73 (d, *J* = 10.6 Hz, 3 H), 4.72 (d, *J* = 15.5 Hz, 1 H), 7.39–7.60 (m, 3 H) and 7.85–7.90 (m, 4 H); *m*/*z* 280 (M^+, 3%) and 171 (100).

Photolysis of **1a** *in Benzene.*—A solution of **1a** (50 mg) in benzene (5 cm^3) was irradiated and the irradiated mixture was separated by preparative TLC (ether–hexane 3:2) to give the following benzene adducts: α-**8a**: 22.5% white crystals; δ(CCl_4) 3.38 (d, *J* = 11.0 Hz, 3 H), 3.45 (d, *J* = 11.0 Hz, 3 H), 5.11 (d, *J* = 27.0 Hz, 1 H) and 7.10–8.18 (m, 12 H); *m*/*z* 326 (M^+, 20%) and 217 (100). β-**9a**: 4.6% pale yellow oil; δ(CCl_4) 3.53 (d, *J* = 11.0 Hz, 6 H), 3.68–3.76 (m, 1 H), 3.83–3.92 (m, 1 H), 5.64–5.74 (m, 2 H), 5.98–6.20 (m, 2 H) and 7.10–7.70 (m, 7 H); *m*/*z* 326 (M^+, 45%) and 217 (100). β-**10a**: 11.7% pale yellow oil; δ(CCl_4) 3.63 (d, *J* = 11.0 Hz, 3 H), 3.70 (d, *J* = 11.0 Hz, 3 H), 5.40–5.60 (m, 2 H), 6.20–6.32 (m, 2 H), 6.77–6.88 (m, 2 H) and 7.20–7.78 (m, 7 H); *m*/*z* 326 (M^+, 30%) and 217 (100).

Irradiations for Analytical Purposes.—All irradiations outlined in Tables 1–3 were carried out on solutions contained in Pyrex tubes of 2.0 cm^3 capacity at below 10 °C. In order to

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* Throughout the paper α and β have been used to refer to the 1 and 2 positions of naphthalene, respectively.

Table 5 NMR and MS data of 1-naphthyl(dimethylphosphonyl)cyclopropanes (**4**, **5**)

		NMR, δ			
Cyclopropanone	(*syn*/*anti*)[a]	Ar	OMe	Other	m/z (rel. intensity)
α-**4a**	*syn*	7.37–7.63 (m, 4 H) 7.74–7.85 (m, 2 H) 8.36 (d, J = 8.3 Hz, 1 H)	3.53 (d, J = 10.6 Hz, 3 H) 3.62 (d, J = 11.2 Hz, 3 H)	0.95 (t, J = 6.9 Hz, 3 H) 1.28–2.15 (m, 8 H) 2.18–2.33 (m, 1 H)	332 (M^+, 55) 289 (48) 250 (69) 179 (78)
	anti[b]	7.40–7.55 (m, 4 H) 7.78–7.86 (m, 2 H) 8.32–8.37 (m, 1 H)	3.50, 3.55, 3.60, 3.61 (d, J = 10.6 Hz, 6 H)	0.10–0.53 (m, 1 H) 0.75, 0.82 (t, J = 7.1 Hz, 3 H) 0.95–2.13 (m, 8 H)	152 (100)
β-**4a**	*syn*	7.41–7.53 (m, 3 H) 7.75–7.81 (m, 4 H)	3.66 (d, J = 10.6 Hz, 6 H)	0.96 (t, J = 7.1 Hz, 3 H) 1.33–1.61 (m, 7 H) 1.78–1.88 (m, 1 H) 1.96–2.08 (m, 1 H)	332 (M^+, 60) 289 (56) 250 (90) 179 (100) 165 (54)
	anti	7.45–7.51 (m, 3 H) 7.78–7.83 (m, 4 H)	3.65 (d, J = 10.6 Hz, 3 H) 3.71 (d, J = 10.6 Hz, 3 H)	0.48–0.58 (m, 1 H) 1.15–1.54 (m, 6 H) 1.71–1.80 (m, 2 H)	152 (43)
α-**5a**	*syn*	7.30–8.20 (m, 7 H)	3.42 (d, J = 11.0 Hz, 3 H) 3.55 (d, J = 11.0 Hz, 3 H)	1.55–1.78 (m, 8 H)	304 (M^+, 45) 179 (100)
	anti	7.32–7.42 (m, 4 H) 7.62–7.79 (m, 2 H) 8.11–8.22 (m, 1 H)	3.44 (d, J = 11.0 Hz, 3 H) 3.54 (d, J = 11.0 Hz, 3 H)	0.96 (d, J = 6.0 Hz, 3 H) 1.05 (d, J = 6.0 Hz, 3 H) 1.87–2.23 (m, 2 H)	304 (M^+, 45) 179 (100)
β-**5a**	*syn*	7.31–7.92 (m, 7 H)	3.64 (d, J = 11.0 Hz, 6 H)	1.55–1.88 (m, 8 H)	304 (M^+, 55) 179(100)
	anti	7.20–7.50 (m, 3 H) 7.60–7.90 (m, 4 H)	3.60 (d, J = 11.0 Hz, 6 H)	0.93–1.12 (m, 6 H) 1.70–2.11 (m, 2 H)	304 (M^+, 55) 179 (100)
β-**6a**[c]	—	7.32–7.87 (m, 7 H)	3.72 (d, J = 11.0 Hz, 6 H)	1.43–1.90 (m, 5 H) 5.05–5.42 (m, 2 H)	

[a] Phosphonyl group is *syn* or *anti* with respect to the alkyl groups. [b] Mixture of rotational isomers. [c] Dimethyl 1-(β-naphthyl)pent-3-enylphosphonate.

avoid any ambiguity concerning the relative yields due to the oxidation, the solution was degassed by subjecting the samples to a minimum of five freeze–degas–thaw cycles at *ca.* 10^{-5} mmHg before irradiation. Irradiation was generally continued until all the diazo compound was destroyed. Product identifications were established either by GC or GC–MS comparisons with authentic samples and product distributions were conveniently determined by standard GC techniques.

General Comments Concerning the Competition Experiments.—These were carried out on binary mixtures of two substrates under the carefully controlled conditions. The precursor diazo compounds (0.05 mmol) were dissolved in the solvent (2 cm^3) which consisted of a large excess of the two substrates. Generally no other solvents were used to avoid possible solvent effects on the reactivities of carbene.[23] The reaction mixtures were degassed and irradiated as described above and product ratios were determined on a Yanagimoto gas chromatograph equipped with a calibrated flame ionization detector, coupled to a Shimadzu C-R1B digital electronic integrator. The reaction mixtures with the diazo phosphonate **1b** were treated with diazomethane before the GC analysis. Control experiments excluded the possible photoconversion of the products during the irradiation period and also demonstrated that no reaction had occurred in the absence of light. Experiments were run in duplicate, and average deviations from the mean values were all $< 3\%$.

Low-temperature UV–VIS Spectra.—Low-temperature spectra (77 K) were obtained by using an Oxford variable-temperature liquid nitrogen cryostat (DN1704) equipped with quartz outer windows and sapphire inner windows. The sample was dissolved in dry 2-methyltetrahydrofuran, placed in a long-necked quartz cuvette of 1 mm pathlength and degassed by repeated freeze–degas–thaw cycles at *ca.* 10^{-5} Torr. The cuvette was placed in the cryostat and cooled to 77 K. After a baseline had been recorded, the sample were irradiated for several minutes in the spectrophotometer with a Halos 300 W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instruments intelligent temperature controller (ITC4).

Laser Flash Photolysis.—The sample (10^{-3} ~ 10^{-4} mol dm^{-3}) was dissolved in dry benzene (over diphenyl ketyl), placed in a long-necked 10 × 10 mm (3 ~ 5 cm^3) quartz fluorescence cuvette, and degassed by a minimum of four freeze–degas–thaw cycles at pressure near 10^{-5} Torr immediately prior to the flash. Laser flash photolysis was carried out by means of an excimer laser (Lambda Physik EMG-50E, 308 nm) and a xenon arc lamp as excitation and probe light sources, respectively. A transient signal was detected by a combined monochromator, photomultiplier and storagescope (Iwatsu TS-8123) and fed into a microcomputer (Fujitsu FM-11BS) for analysis.

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References

1 J. B. Lambert, H. W. Mark, A. G. Holcomb and E. S. Magyar, *Acc. Chem. Res.*, 1979, **12**, 317.

2 B. Capon and S. P. McManus, *Neighboring Group Participation*, Plenum, New York, 1976, vol. 1.

3 H. C. Brown, *The Nonclassical Ion Problem*, Plenum, New York, 1977.

4 (*a*) Eds. R. A. Moss and M. Jones, Jr., *Carbenes*, Wiley, New York, 1973, 1975; vols. 1 and 2; (*b*) W. Kirmse, *Carbene Chemistry*, Academic Press, New York, 1971; (*c*) C. Wentrup, *Reactive Molecules*, Wiley, New York, 1984, ch. 4; (*d*) ed. M. Regitz, *Methoden der Organischen Chemie* (Houben-Weyl), Thieme, Stuttgart, 1989, vol. E19b.

5 For a pertinent review: K. G. Taylor, *Tetrahedron*, 1982, **38**, 2751.

6 H. Tomioka, K. Tabayashi and Y. Izawa, *Chem. Lett.*, 1985, 1103; H. Tomioka, K. Hirai, K. Tabayashi, S. Murata, Y. Izawa, S. Inagaki and T. Okajima, *J. Am. Chem. Soc.*, 1990, **112**, 7692.

7 H. Tomioka and K. Hirai, *J. Chem. Soc., Chem. Commun.*, 1989, 362; 1990, 1611.

8 D. Seyferth, R. S. Marmor and P. Hilbert, *J. Org. Chem.*, 1971, **36**, 1379.

9 J. A. Goldstein, C. McKenna and F. H. Westheimer, *J. Am. Chem. Soc.*, 1976, **98**, 7327.

10 W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, 1958, **80**, 5274.

11 See for reviews (*a*) A. M. Trozzolo, *Acc. Chem. Res.*, 1968, **1**, 329; (*b*) A. M. Trozzolo and E. Wasserman, in ref. 4(*a*), vol. 2, ch. 5.

12 See for a pertinent review on the detection and kinetics of arylcarbenes using flash photolysis techniques: ed. M. S. Platz, *Kinetics and Spectroscopy of Carbenes and Biradicals*, Plenum, New York, 1990.

13 For a review, see W. W. Sander, *Angrew. Chem., Int. Ed. Engl.*, 1990, **29**, 344; see also J. C. Scaiano, W. G. McCimpsey and H. L. Casal, *J. Org. Chem.*, 1989, **54**, 1612.

14 (*a*) L. M. Hadel, M. S. Platz and J. C. Scaiano, *Chem. Phys. Lett.*, 1983, **97**, 446; (*b*) R. L. Barcus, L. M. Hadel, L. J. Johnston, M. S. Platz, T. G. Savino and J. C. Scaiano, *J. Am. Chem. Soc.*, 1986, **108**, 3928.

15 (*a*) J. E. Chateauneuf and K. A. Horn, *Tetrahedron*, 1985, **41**, 1465; (*b*) G. W. Griffin and K. A. Horn, *J. Am. Chem. Soc.*, 1987, **109**, 4919; J. E. Chateauneuf, K. A. Horn and T. G. Savino, *J. Am. Chem. Soc.*, 1988, **110**, 539.

16 See also (*a*) B. B. Wright and M. S. Platz, *J. Am. Chem. Soc.*, 1984, **106**, 4175; (*b*) V. P. Senthilnathan and M. S. Platz, *J. Am. Chem. Soc.*, 1981, **103**, 5503; (*c*) V. P. Senthilnathan and M. S. Platz, *J. Am. Chem. Soc.*, 1980, **102**, 7637; (*d*) M. S. Platz, V. P. Senthilnathan, B. B. Wright and C. W. McCurdy, Jr., *J. Am. Chem. Soc.*, 1982, **104**, 6494.

17 H. Tomioka, K. Tabayashi, Y. Ozaki and Y. Izawa, *Tetrahedron*, 1985, **41**, 1435.

18 W. Kirmse, K. Loosen and H.-D. Sluma, *J. Am. Chem. Soc.*, 1981, **103**, 5935.

19 It has been shown that 'simple' arylcarbenes usually regarded as being electrophilic also undergo protonation when generated in MeOH: (*a*) H. Tomioka, N. Hayashi, T. Sugiura and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, 1986, 1364; (*b*) K. Friedlich, U. Jansen and W. Kirmse, *Tetrahedron Lett.*, 1985, **25**, 1936; (*c*) W. Kirmse, J. Kilian and S. Steenken, *J. Am. Chem. Soc.*, 1990, **112**, 6399.

20 D. M. Gale, W. J. Middleton and C. G. Krespan, *J. Am. Chem. Soc.*, 1965, **87**, 657; 1966, **88**, 3617.

21 N. Hartz, G. K. Surya-Prakash and G. A. Olah, *J. Am. Chem. Soc.*, 1993, **115**, 901.

22 (*a*) R. Richter and H. Ulrich, *J. Org. Chem.*, 1971, **36**, 2005; (*b*) J. M. Brown and B. D. Place, *J. Chem. Soc., Chem. Commun.*, 1971, 533; (*c*) H. Quast and S. Hunig, *Chem. Ber.*, 1966, **99**, 2017; (*d*) H. D. Hartzler, *J. Am. Chem. Soc.*, 1973, **95**, 4379.

23 (*a*) P. A. Bartlett, N. I. Carruthers, B. M. Winter and K. P. Long, *J. Org. Chem.*, 1982, **47**, 1284; (*b*) P. A. Bartlett and N. I. Carruthers, *J. Chem. Soc., Chem. Commun.*, 1982, 536.

24 (*a*) H. Tomioka, Y. Ozaki and Y. Izawa, *Tetrahedron*, 1985, **41**, 4987; (*b*) H. Tomioka, N. Hayashi and Y. Izawa, *Chem. Lett.*, 1986, 695.

25 A. K. Schrock and G. B. Schuster, *J. Am. Chem. Soc.*, 1984, **106**, 5234.

26 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209, 221. MOPAC version 6.01 (JCPE#PO44) was used.

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