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THE EFFECT OF ARYL SUBSTITUENTS ON ARYLCARBENE REACTIVITY

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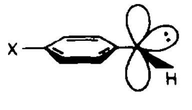
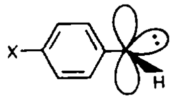
Abstract—Substituted (*p*-MeO, *p*-Me, H, *p*-Cl, *p*-Br, *m*-Br, *m*-MeO, 3,4-Cl_2, *p*-CO_2Me, *m*-CN and *p*-CN) monophenylcarbenes are generated in a binary mixture of substrates (methanol, *cis*-4-methyl-2-pentene and cyclohexane) and the relative rate of O—H insertion into methanol to stereospecific cyclopropanation of the olefin to C—H insertion into cyclohexane are calculated from the ratios of products and substrates. It is found (i) that the reactivities of the substrates decrease in the order of methanol, olefin and cyclohexane and (ii) that electron-donating substituents generally lead to reaction with the more reactive substrates while the reaction with the less reactive substrates is favoured in the case of electron-withdrawing substituents. These results are interpreted in terms of the change in the electrophilicity of the singlet arylcarbene by the substituents rather than the change in the singlet–triplet equilibrium.

Quantitative correlations between structure and reactivity of carbenes have been the subjects of increased interest and many pertinent facts as to the nature of the carbene reaction are now available.[1] However, it is rather surprising to note that, in contrast to the impressive histories of the effect of ring substituents on the reactivity of the benzyl carbocation[2] and benzyl carbanion,[3] only a limited number of studies[4–12] have been devoted to the problem in carbene chemistry. *A priori*, it can be said that, since a singlet carbene has both a vacant *p*-orbital and an electron-rich σ-orbital, the singlet state can be stabilized either by electron-donating or electron-withdrawing substituents.

However, these carbenes are usually represented as in **A**, where the π system is seen to be isoelectronic with a benzylic cation. This means that arylcarbenes with electron-donating substituents (e.g. X = OMe) should be the most stabilized and selective species, while those with electron-withdrawing substituents (e.g. X = CN) should be destabilized (less selective) owing to less favourable electronic interactions. In other words, ring-substituents should influence the intersystem crossing of arylcarbenes: with electron-donating substituents, the degree of singlet involvement can be increased while with electron-withdrawing substituents, increasing amounts of triplet chemistry can be seen. The argument has been supported by the findings[10] that the stereospecificity in the addition of arylcarbenes to *cis*-2-butene was decreased as the substituents were changed from electron-donating to electron-withdrawing groups. Similarly it was found[10] that in the addition of arylcarbenes to 1,1-dimethylallene electron-donating substituents lead to a much more regioselective reaction, while selectivity becomes quite low in the case of electron-withdrawing substituents.



A



B

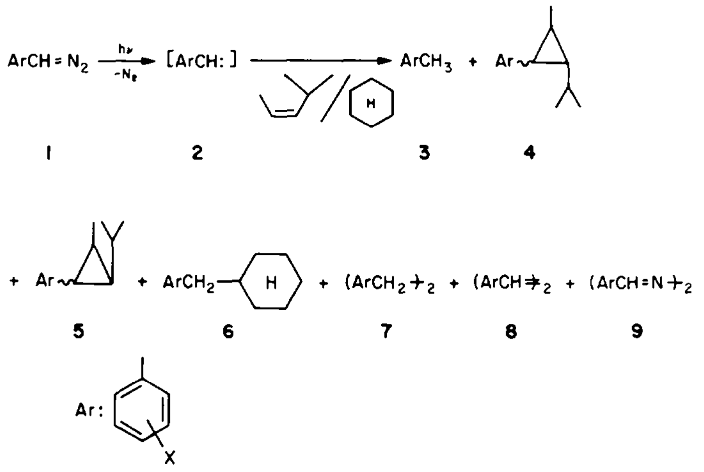
More recently, however, Shechter and co-workers have proposed[7–9] that although electron-donating substituents indeed favour a planar conformation for a singlet carbene in order to stabilize the vacant *p*-orbital, electron-withdrawing substituents are presumed to enhance twisting of the phenyl group to a perpendicular conformation as in **B** in which the electron-rich, carbenic σ-orbital is also favourably delocalized. The argument is mainly based on the observation[7,8] that the thermolyses of substituted diphenyldiazomethanes were facilitated either by electron-donating or electron-withdrawing substituents. Further support was lent by the finding[9] that stereochemistry in the conversion of *p*-substituted 1-phenyl-1-propylidenes to the corresponding propenylbenzenes is significantly dependent on the nature of substituents: an electron-withdrawing group increases the conversions to *cis*-propenylbenzene. This is interpreted as indicating that the steric repulsion of the phenyl and methyl groups in the carbene conformer leading to *cis*-olefin is relatively small in electron-withdrawing group since the phenyl group may twist from the vacant *p*-orbital and overlap with the filled carbenic orbital. Calculations[7,8] of net atomic charges of singlet phenylcarbenes also support the interaction of their non-bonded orbitals with both types of substituents. One would expect, then, that ring substituents influence the reactivity of singlet arylcarbenes by changing their 'philicity'.

This paper reports our efforts to clarify the nature of the interaction between ring substituents and arylcarbene orbitals by studying the effect of ring substituents on the relative rates of addition and O—H and C—H insertion of arylcarbenes.

RESULTS

Addition-insertion selectivity

The reaction which we first utilized to examine the effect of ring substituents on arylcarbene reactivity was the competition reaction between the addition to the double bond and the insertion into the C—H bond of a hydrocarbon. Thus, ring-substituted monophenylcarbenes (**2**) were generated by irradiation of the corresponding diazomethanes (**1**) using a high-pressure mercury lamp through a Pyrex filter at 10° in a degassed binary mixture (1 : 1.16) of *cis*-4-methyl-2-pentene and cyclohexane. GC–MS analysis as well as isolation of individual components by column chromatography



(1)

followed by characterization of the reaction mixture showed that cyclopropanes (**4** and **5**) and benzylcyclohexane (**6**) were formed as major products along with toluene (**3**), bibenzyl (**7**), stilbenes (**8**) and aldazine (**9**). The product distributions in the reaction of some typical arylcarbenes are listed on Table 1. From the data in Table 1, it is seen that cyclohexane is a less reactive substrate than the pentene toward arylcarbenes and that the product ratio is quite substituent dependent; the ratio of insertion into the C—H bond of cyclohexane to the addition to the double bond of pentene tends to increase as the ring substituents are changed from electron-donating to electron-withdrawing groups (Table 2). In order to obtain more quantitative information about the effect of ring-substituents on arylcarbene reactivity, we assume here that the stereospecific cyclopropanation of olefin and C—H insertion into cyclohexane are mostly derived from the singlet state of the arylcarbene and the relative rates (k_{rel}) of addition to insertion are calculated by means of a well-established equation:

$$k_{rel} = \frac{k_{addin}}{k_{insert}} = \frac{P_a}{P_i} \times \frac{I_i}{I_a} \tag{2}$$

where P_a and P_i are the moles of stereospecific cyclopropanation product and C—H insertion product and I_i and I_a are the initial moles of cyclohexane and olefin respectively.[13] The relative rate constant data correlate well with the Hammett equation using σ (σ^+ for electron donor group) values (Fig. 1) and the ρ-value was computed by a least-squares analysis to be -0.96, with a correlation coefficient of 0.96. In other words, electron-donating substituents such as *p*-methoxy and *p*-methyl lead to the reaction with olefin which is a more reactive substrate, while the reaction with a less reactive substrate, i.e. cyclohexane, is favoured in the case of electronegative substituents.

Table 1. Effect of substituent on product distribution in the photolysis of monoaryldiazomethanes (**1**) in a binary mixture of *cis*-4-methyl-2-pentene and cyclohexane

X in **1**	Relative yield (%)						
	3	**4**	**5**	**6**	**7**	**8**	**9**
p-Me	1	4.3	47.8	16.9	3.2	8.9	9.8
H	1	1.1	62.1	22.0	2.4	3.3	5.9
m-Br	1	3.2	48.9	31.7	4.8	5.5	3.9

Table 2. Product distribution in the photolysis of **1** in a binary mixture (1:1.16) of degassed *cis*-4-methyl-2-pentene and cyclohexane

X in **1**	Relative yield (%)[a]	
	5 (syn:anti)	**6**
p-MeO	89.4 (1:1.01)	10.6
p-Me	74.2 (1:0.73)	26.1
H	73.8 (1:0.69)	26.2
p-Cl	65.7 (1:0.69)	34.3
m-MeO	68.3 (1:0.64)	31.7
m-Br	60.7 (1:0.55)	39.3
3,4-Cl	59.6 (1:0.67)	40.4
m-CN	56.8 (1:0.55)	43.2
p-CN	54.6 (1:0.48)	45.4

[a] Yields are based on **1** and are averages of duplicate experiments; reproducibilities are ±5%. Total product yields (60–70%) are essentially invariant regardless of substituents.

O—H *versus* C—H *insertion selectivity*

The reaction which we next utilized to examine the effect of ring substituents on arylcarbene reactivity was the insertion selectivity into O—H and C—H bonds of

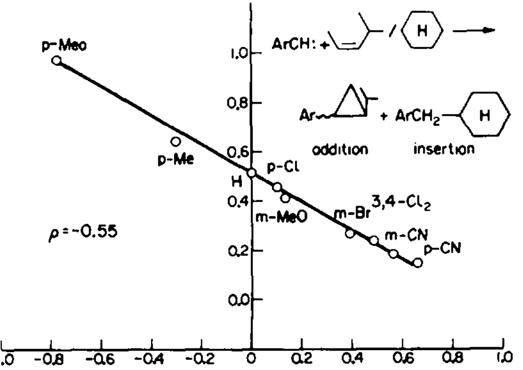


Fig. 1. Hammett plots of cyclopropanation–C—H insertion selectivity. The correlation coefficient is 0.96.

Table 3. Product distribution in the photolysis of **1** in a degassed 2-propanol

X in **1**	Relative yield (%)^{a} **10**	**11**	**12**
p-MeO	97.6	2.4	—^{b}
p-Me	95.5	4.5	—^{b}
H	90.7	9.3	—^{b}
p-Cl	87.2	12.8	—^{b}
p-Br	87.1	12.9	—^{b}
p-CO_2Me	86.4	12.5	1.1
p-CN	79.5	17.8	2.7

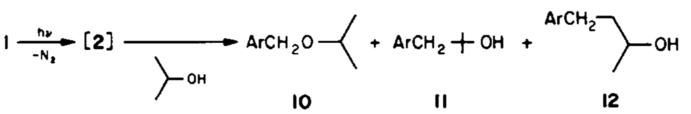
^{a}See footnote to Table 2.
^{b}Trace.

Table 4. Product distribution in the photolysis of **1** in a binary mixture (1 : 3.27) of degassed methanol and *cis*-4-methyl-2-pentene

X in **1**	Relative yield (%)^{a} **13**	**5** (syn : anti)
p-MeO	63.2	36.8 (1 : 1.12)
p-Me	57.1	42.9 (1 : 0.94)
H	51.0	49.0 (1 : 0.82)
p-Cl	44.7	55.3 (1 : 0.77)
m-Br	31.4	68.6 (1 : 0.65)
m-CN	25.8	74.2 (1 : 0.64)

^{a}See footnote to Table 2.

alcohols. When a series of arylcarbenes are generated in degassed 2-propanol at 20°, O—H insertion product (**10**) was obtained as a major product along with a small amount of two C—H insertion products (**11** and **12**), but the product ratio is again quite substituent dependent (Table 3). The data are shown in Fig. 2 as a Hammett plot of log k_{OH}/k_{CH} *vs* σ (σ^+), which gives a fairly linear correlation. The results again indicate that the arylcarbene favours reaction with the more reactive centre of the alcohol, i.e. O—H bond, as electron-donating substituents are introduced on the phenyl ring, while electron-withdrawing substituents lead to the reaction with the less reactive centre, i.e. C—H bond.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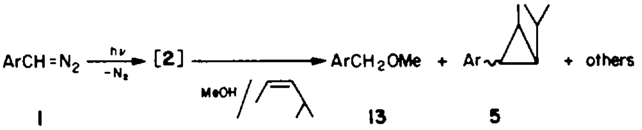

(4)

O—H *Insertion-addition selectivity*

Finally, we have examined the competition between O—H insertion into alcohol and stereospecific addition to olefin. The reaction system is especially important in that it is generally believed[14,15] that both reactions are characteristic for a singlet carbene. Since the C—H insertion products formed in the former two reaction systems may be derived from the singlet carbene or result from the triplet,[15] the observed effect of substituents on the arylcarbene reactivity can be explained either in terms of the effect on the singlet carbene reactivity or by the effect on the singlet–triplet equilibrium. Thus, a series of arylcarbenes are generated in a binary mixture of methanol and *cis*-4-methyl-2-pentene and the relative rates ($k_{rel} = k_i/k_a$) of insertion into the O—H bond of methanol to stereospecific addition to olefin are calculated from the product ratio (**13** and **5**) listed in Table 4. The data are shown as a Hammett plot in Fig. 3, which gives a fairly linear correlation; electron-donating substituents lead to more O—H insertion product, while cyclopropanation increases in the case of electron-withdrawing substituents.

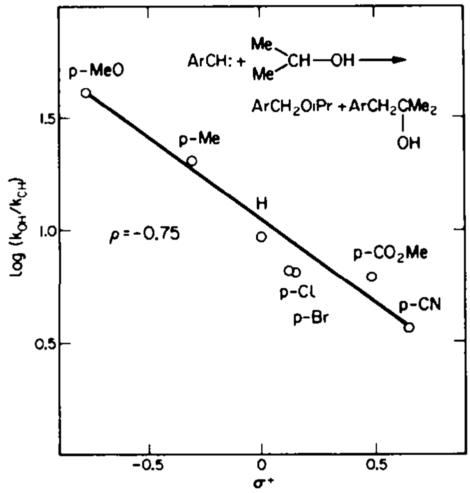


Fig. 2. Hammett plots of O—H/C—H insertion selectivity. The correlation coefficient is 0.97.

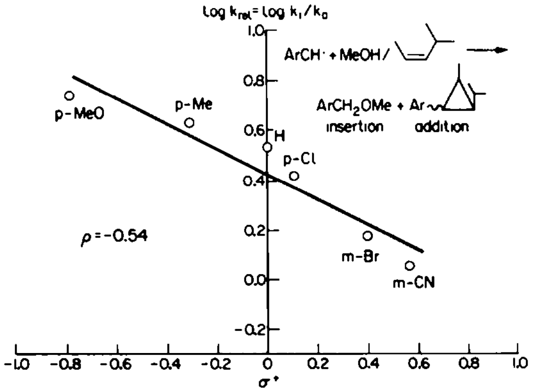
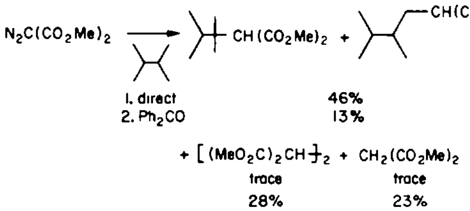


Fig. 3. Hammett plot of O—H insertion–cyclopropanation selectivity. The correlation coefficient is 0.98.

DISCUSSION

Although most arylcarbenes have a triplet ground state,[16] arylcarbenes generated photolytically from diverse sources are shown[4,11,12] to react mainly in the singlet states. This is chiefly because the reaction of the singlet carbene is substantially faster than the competing intersystem crossing processes. Although rates of intersystem crossing can be expected to be influenced by substituents, to date a limited number of arylcarbene intersystem crossing efficiencies have been investigated in terms of substituent effects. Closs and Moss[4] estimated the involvement of the triplet state to be not more than 5% based on the degree of loss of stereospecificity in the substituted (*m*-Cl, *p*-Cl, H, *p*-CH_3 and *p*-CH_3O) monophenylcarbenes addition to olefin. This means intersystem crossing processes are relatively insensitive to the nature of the substituents employed. Goh and Gian[5] showed that the amount of non-stereospecific addition was significantly increased only with much more electronegative substituents such as the nitro group. Judging from the stereospecificity of the addition to 4-methyl-2-pentene in the present reaction system, we would also like to suggest that the degree of triplet intervention seems not to be increased significantly by the substituents employed.

The fact that the C—H insertion into C—H bonds of cyclohexane increases as the ring substituents are changed from electron-donating to electron-withdrawing groups would imply the increase in the degree of the triplet intervention since the C—H insertion is not only derived from the singlet state but also formed from the triplet. Although the C—H insertion of the singlet carbene is generally believed to proceed *via* a one-step mechanism, the C—H 'insertion' of the triplet is known to proceed *via* abstraction of a hydrogen atom followed by coupling of the radical pair[15] and therefore is usually accompanied by a large amount of the products derived from all possible radical coupling reactions. For example, Jones *et al.*[17] found in the reaction of singlet and triplet *bis*-carbomethoxycarbene with 2,3-dimethylbutane that the yields of 'insertion products' are sharply reduced in the triplet carbene reaction concomitant with the formation of the products expected from free-radical dimerization and H-abstraction. Although the free-radical products are also observed in the present reaction system, no significant increases in the radical products are noted with an increase in the C—H insertion product. This is again interpreted as indicating that a significant increase in the triplet intervention is not attained by the substituents employed.



(5)

More importantly, similar trends are also observed in the competitive reactions between alcohol and olefin. Since it is generally accepted that insertion into the O—H bond of an alcohol and stereospecific cycloaddition to the double bond of an olefin are both characteristic reactions for the singlet carbene, the observed trends must reflect the change in the singlet carbene reactivity caused by ring-substituents. Although alcohols and olefins are usually equally-efficient trapping reagents for the singlet carbenes, the product ratio indicates that methanol is slightly more reactive than *cis*-4-methyl-2-pentene at least toward phenylcarbene. It is then important to note that the trend of electron-donating substituents leading to reactions with more reactive substrates, in this case methanol, is also the same trend as observed in other reaction systems.

Thus, we would like to interpret these results in terms of the effect of substituents on the singlet arylcarbene reactivity rather than on the singlet–triplet equilibrium. Singlet carbenes can be experimentally classified as electrophiles, nucleophiles, or ambiphiles depending on their selectivity toward alkenes. Although the crucial determination of 'philicity' for phenylcarbene addition seems not to have been made, an electrophilic character has been suggested[4] in the effect of a carbenic aryl substituent on the isobutene–*trans*-2-butene reactivity ratio. For O—H insertion, on the other hand, at least three plausible reaction paths are conceivable: (a) one-step insertion, (b) electrophilic attack of the carbene on the lone-pairs of electrons of the O atom and (c) protonation of the carbene to give a carbocation,[18] most electrophilic carbenes are likely to follow path (b).[19] The C—H insertion of the singlet carbene is generally considered[15] to proceed *via* a 'one-step' mechanism, but the fact that, in their reaction with olefins, the significant amount of C—H insertion products has been generally formed in the case of strongly electrophilic carbenes such as cyclopentadienylidene[20] and dicyanocarbene[21] suggests that the driving force for the reaction must be a 'voracious appetite of singlet carbenes for electrons'.[22] The observed change in the reactivity of arylcarbenes with ring substituents can, then, be interpreted in terms of the change in the electrophilicity of singlet arylcarbene by the substituents. Thus, electron-donating substituents interact with the vacant *p*-orbital by donating electrons so that the carbene becomes less electrophilic. Electron-withdrawing substituents, on the other hand, interact with the electron rich σ orbital by withdrawing electrons so that the carbene becomes more electrophilic. The electron-pairs of the substrates which are attacked by the vacant *p*-orbital of the singlet carbene are σ-electrons of C—H bonds, π-electrons of C—C double bonds and lone-pair electrons on oxygen atoms of alcohols. Apparently, the σ-electrons of C—H bonds are tightly held and hence weaker sources of electrons than loosely held π-electrons of double bonds and O atoms. Consequently, singlet carbenes attack on C—C double bonds or O—H bonds more efficiently than on the C—H bond. Thus, as the carbene becomes less electrophilic, its selectivities become higher due to the reduced ability to attack on the weaker electron sources, whereas more electrophilic carbenes attack the weaker sources more significantly and therefore become less selective.

Presumably, the 'hard and soft, acid and base' (HSAB) principle could be applied to understand the singlet carbene reactivities at least qualitatively: the carbenes can be classified as soft (less electrophilic or nucleophilic) and hard (more electrophilic) acids depending on the nature of their substituents and a wide

Table 5. NMR data for cyclopropane (5), benzylcyclohexane (6) and benzyl methyl ether (13)[a]

Compound	(*X* in Ar)		NMR spectra in CCl_4, δ
5	(*p*-MeO)	Syn	0.55–1.56 (m, 12H), 1.90 (t, 1H), 3.64 (s, 3H), 6.45–7.11 (m, 4H)
		Anti	0.63–1.55 (m, 12H), 1.93 (t, 1H), 3.69 (s, 3H), 6.54–7.21 (m, 4H)
	(*p*-Me)	Syn	0.58–1.49 (m, 13H), 2.24 (s, 3H), 6.52–7.00 (m, 4H)
		Anti	0.66–1.47 (m, 12H), 1.94 (t, 1H), 2.28 (s, 3H), 6.96–7.15 (m, 4H)
	(H)	Syn	0.56–1.49 (m, 13H), 6.65–7.27 (m, 5H)
		Anti	0.58–1.48 (m, 12H), 1.98 (t, 1H), 6.80–7.25 (m, 5H)
	(*p*-Cl)	Syn	0.59–1.46 (m, 12H), 1.94 (t, 1H), 6.67–7.23 (m, 4H)
		Anti	0.62–1.64 (m, 12H), 1.95 (t, 1H), 6.72–7.28 (m, 4H)
	(*m*-MeO)	Syn	0.57–1.36 (m, 13H), 3.59 (s, 3H), 6.23–7.11 (m, 4H)
		Anti	0.64–1.35 (m, 13H), 3.51 (s, 3H), 6.38–7.16 (m, 4H)
	(*m*-Br)	Syn	0.64–1.56 (m, 12H), 2.00 (t, 1H), 6.80–7.44 (m, 4H)
		Anti	0.72–1.39 (m, 12H), 2.02 (t, 1H), 6.94–7.48 (m, 4H)
	(3,4-Cl_2)	—[b]	0.44 ~ 1.55 (m, 12H), 1.95–1.96 (m, 1H), 6.55–7.36 (m, 3H)
	(*m*-CN)	Syn	0.76–1.46 (m, 12H), 2.02 (t, 1H), 7.02–7.59 (m, 4H)
		Anti	0.78–1.43 (m, 12H), 1.96 (t, 1H), 7.16–7.62 (m, 4H)
	(*p*-CN)	Syn	0.68–1.44 (m, 13H), 6.96–7.63 (m, 4H)
		Anti	0.79–1.22 (m, 13H), 7.20–7.58 (m, 4H)
6	(*p*-MeO)		0.72–1.98 (m, 11H), 2.35 (d, 2H), 3.65 (s, 3H), 6.49–7.14 (m, 4H)
	(*p*-Me)		0.68–1.89 (m, 11H), 2.30 (s, 3H), 2.45 (d, 2H), 6.65–7.40 (m, 4H)
	(H)		0.71 ~ 1.90 (m, 11H), 2.24 (d, 2H), 7.00 (bs, 5H)
	(*p*-Cl)		0.76–1.95 (m, 11H), 2.40 (d, 2H), 6.66–7.35 (m, 4H)
	(*m*-MeO)		0.70–1.96 (m, 11H), 2.45 (d, 2H), 3.73 (s, 3H), 6.50–7.18 (m, 4H)
	(*m*-Br)		0.62–2.00 (m, 11H), 2.44 (d, 2H), 6.85–7.51 (m, 4H)
	(3,4-Cl_2)		0.77–1.93 (m, 11H), 2.42 (d, 2H), 6.80–7.47 (m, 3H)
	(*m*-CN)		0.77–1.93 (m, 11H), 2.50 (d, 2H), 7.24–7.61 (m, 4H)
	(*p*-CN)		0.63–1.99 (m, 11H), 2.56 (d, 2H), 6.97–7.73 (m, 4H)
13	(*p*-MeO)		3.20 (s, 3H), 3.65 (s, 3H), 4.23 (s, 2H), 6.57–7.16 (m, 4H)
	(*p*-Me)		2.28 (s, 3H), 3.18 (s, 3H), 4.22 (s, 2H), 6.47–7.30 (m, 4H)
	(H)		3.28 (s, 3H), 4.25 (s, 2H), 7.08–7.24 (m, 5H)
	(*p*-Cl)		3.34 (s, 3H), 4.35 (s, 2H), 6.89–7.57 (m, 4H)
	(*m*-MeO)		3.30 (s, 3H), 3.74 (s, 3H), 4.34 (s, 2H), 6.37–6.98 (m, 4H)
	(*m*-Br)		3.29 (s, 3H), 4.31 (s, 2H), 7.00 ~ 7.45 (m, 4H)
	(3,4-Cl_2)		3.30 (s, 3H), 4.28 (s, 2H), 6.90–7.49 (m, 3H)
	(*m*-CN)		3.40 (s, 3H), 4.44 (s, 2H), 7.29–7.70 (m, 4H)
	(*p*-CN)		3.36 (s, 3H), 4.42 (s, 2H), 7.20–7.65 (m, 4H)

[a] In CCl_4.

[b] Syn : anti mixture.

variety of substrates which will be attacked by this very reactive intermediate are also classified as soft and hard bases according to the nature of the electron-pairs they have. Soft carbenes will react only with soft substrates and hence will be more selective, but hard carbenes can react even with hard substrates and hence become less selective.

EXPERIMENTAL

General

IR spectra were recorded on a JASCO IR-G recording spectrometer. ^{1}H-NMR spectra were determined on a JEOL JNM-MH-100 spectrometer with an internal $(CH_3)_4Si$ standard. GC–MS spectra were obtained on a Shimadzu GC–MS 1000 spectrometer using a column consisting of Silicone OV-17 on Shimalite (4.0 mm × 1.0 m). GC work was done on a Yanagimoto G-180 gas chromatograph using a 4.0 mm × 2.0 m column packed with OV-17 (5%) on 60–80 mesh Diasolid L.

Materials

The aryldiazomethanes (**1**) were prepared according to the literature[10] immediately before use. Preparations of insertion products (**10** to **12**) into O—H and C—H bonds of 2-propanol have been published elsewhere.[12] All other reagents were obtained from commercial sources and purified by distillation before use.

Irradiations for product identification

In a typical run, a soln of **1** (300 mg) in substrate (5 ml) was placed in a Pyrex tube and irradiated with a high-pressure, 300 W, Hg lamp at room temp until all of the diazo compound was destroyed. The irradiation mixtures were concentrated on a rotary evaporator below 25°. Individual components were isolated either by column chromatography or by gas chromatography and identified by NMR and MS. NMR data for cyclopropanes (**5**), benzylcyclohexanes (**6**) and methyl ether (**13**) are given in Table 5.

Irradiation for analytical purposes

All irradiations outlined in Tables 1 to 4 were carried out on a 25 mM soln of **1** in a binary mixture of substrates in a Pyrex tube of 5.0 ml capacity at 20°. In order to avoid ambiguity of the relative yields due to the oxidation, the soln was degassed by subjecting the samples to a minimum of three freeze–degas thaw cycles at a pressure near 10^{-5} mmHg before irradiation. Irradiation was generally continued until all the diazo compound was destroyed. Product identifications were established either by GC as well as GC–MS comparisons using authentic samples and product distributions were conveniently determined by standard GC techniques.

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