Tetrahedron Vol. 41, No. 21, pp. 4987 to 4993, 1985
Printed in Great Britain

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

MODIFICATION OF SINGLET CARBENE REACTIVITIES BY SOLVENT

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(*Received in Japan* 12 *January* 1984)

Abstract—The solvent effect on the reactivity of singlet carbenes has been investigated. Competition reactions between pairs of alcohols for arylcarbenes in various solvents indicates that the O—H insertion selectivity is influenced only by 1,4-dioxane. Thus, phenylcarbene is some 33 times more reactive toward methanol relative to t-butyl alcohol in 90 mol% dioxane than without solvent. Similar competition reactions between alcohol and olefin indicate that the O—H insertion–addition selectivities of arylcarbenes are considerably altered by dioxane. These results are interpreted as indicating that dioxane stabilizes singlet carbenes by complexing with its lone pairs of electrons.

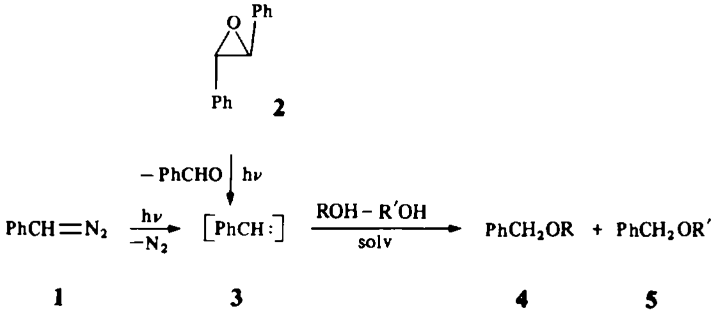
It is well known that solvation of ionic reactive intermediates such as carbocations and carbanions is very important and hence often has a fatal effect on the course of their reactions.[1] It is equally well recognized that reactivity of neutral reactive intermediates such as free radicals and carbenes is generally insensitive to the nature of solvent. A distinct solvent effect on the reactivity of free radicals is rare indeed, but not unprecedented. For instance, it has been shown[2–5] that selectivity of radical chlorination of hydrocarbons is considerably enhanced in aromatic solvents and carbon disulphide. This is interpreted as indicating that chlorine radical is stabilized by the complexation with these solvents. Although a considerable number of studies have been reported[6] on the effect of solvent in carbene chemistry, they are mainly focussed upon the so-called "dilution effect",[6,7] namely collisional deactivation of singlet carbene to the triplet by *inert* solvents such as C_6F_6. It is rather surprising to note that few efforts[8] have been previously made to reveal the possible interaction of singlet carbene with solvents in spite of the facts that the complexation of carbenes by salts and metals (carbenoids) has been well recognized[6] to modify the reactivity of carbenes and has been utilized in a wide variety of synthetic processes. With these precedent facts in mind and inspired by current laser flash photolysis studies[9,10] suggesting the possible stabilization of singlet 1-naphthylcarbene in acetonitrile by reversible complexing with a solvent, we investigated the effect of solvents on the singlet carbene reactivities. In this paper we wish to report that, among many electron-pair donor solvents studied, only 1,4-dioxane interacts effectively with singlet arylcarbene and hence considerably alters reactivities of singlet carbenes in its O—H insertion selectivities as well as insertion–addition selectivities.

RESULTS AND DISCUSSION

O—H *Insertion selectivity*

The reaction which we have first utilized to probe the interaction of singlet carbene with solvents is the insertion of carbene into the O—H bond of alcohols to yield the corresponding ether, since it is generally accepted[6] that the key intermediate leading to the O—H insertion product is singlet carbene. A recent pulsed-laser spectroscopic analysis[11] of transient products in the photolysis of diazo compounds provided direct evidence for the above assignments.

Irradiation of phenyldiazomethane (**1**) in a large excess of two different degassed alcohols compared to **1** using a high-pressure mercury lamp through a Pyrex filter at 10° gave two benzyl ethers (**4** and **5**) in 75–80% yields along with small amounts of toluene, bibenzyl, stilbenes and aldazine. Similar irradiation of **1** in the presence of a solvent (60 mol%) also afforded the benzyl ethers as main product. The relative rates of insertion of singlet monophenylcarbene (**3**) into the alcohols in various solvents were calculated by means of the well-established Eq. 1,[12]



$$k_{rel} = \frac{k_{ROH}}{k_{R'OH}} = \frac{PhCH_2OR}{PhCH_2OR'}\,\frac{[R'OH]_0}{[ROH]_0} \quad (1)$$

where $PhCH_2OR$ and $PhCH_2OR'$ are the mols of the ethers **4** and **5** and $[ROH]_0$ and $[R'OH]_0$ are the initial mols of alcohols, respectively. The results are presented in Table 1.

Inspection of the results in Table 1 indicates immediately that the selectivity of phenylcarbene is markedly influenced only by 1,4-dioxane among the solvents studied. Thus, as 1,4-dioxane was added, k_{rel} increased rather gradually at low dioxane concen-

Table 1. Effect of solvent on relative reactivities $k_{rel} = k_{MeOH}/k_{ROH}$ of monophenylcarbene toward alcohols[a]

Carbene precursor	ROH	Solvent[b]	Total yield (%) of ethers[c]	k_{MeOH}/k_{ROH}[d]
1	t-BuOH	None	79.0	1.85
2		None	e	1.84
1		Cyclohexane	60.6	1.89
1		PhH	58.5	1.70
1		MeCN	75.5	1.90
1		1,4-Dioxane	76.3	16.5
2		1,4-Dioxane	e	14.2
1		1,4-Dioxane[f]	70.0	61.4
1	i-PrOH	None	76.9	1.45
1		MeCN	70.2	1.46
1		1,4-Dioxane	75.6	6.57
1		1,4-Dioxane[f]	73.0	13.3
1	EtOH	None	76.5	1.31
1		1,4-Dioxane	76.1	3.23

[a] Phenylcarbene was generated by photolysis of **1** or **2** in a binary mixture (1 : 3) of degassed MeOH–ROH through a Pyrex filter at 10°.

[b] Unless otherwise indicated, 60 mol % of solvent was used.

[c] Determined by GC.

[d] Determined according to Eq. 1.

[e] Not determined.

[f] About 90 mol % of dioxane was added.

tration and steeply at the higher concentration (Fig. 1); the singlet phenylcarbene is some 33 times more reactive toward methanol relative to t-butyl alcohol in 90 mol% 1,4-dioxane than without solvent. The insertion selectivity was essentially unaltered on dilution with other solvents employed. Similar, but less dominant, increase in the reactivity toward methanol caused by dioxan was also observed for the competition reaction using ethyl and isopropyl alcohols (Table 1). Since the total absolute yields of the ethers were essentially unaltered on dilution with dioxane (Table 1 and Fig. 1), the ratio of benzyl ethers produced in dioxane reflects the selectivity of phenylcarbene for the alcohols. Moreover, the fact that the carbene generated from 2,3-diphenyloxirane (**2**)[13] underwent similar increase in the insertion selectivity by dioxane also support that singlet carbene is involved in the reaction.

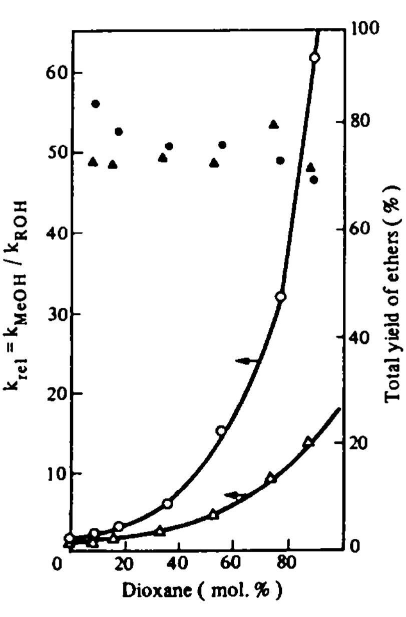


Fig. 1. Effect of dioxane concentration on the relative rates of insertion of monophenylcarbene into alcohol and total yield of the O—H insertion products. △, ▲ MeOH–i-PrOH; ○, ● MeOH–t-BuOH.

Since 1,4-dioxane showed a marked effect on the O—H insertion selectivity of singlet phenylcarbene, we next examined the effect of other cyclic as well as acyclic ethers in order to find the nature of interaction of singlet carbenes with these electron pair donor solvents. To our surprise, however, a very small or no appreciable increase in the insertion selectivity was observed in these solvents (Table 2). Thus, neither simple acyclic ether nor polyether like 2-ethoxyethyl ether altered the reactivity of singlet phenylcarbene. Furthermore, even cyclic polyethers which are structurally closely related to 1,4-dioxane, e.g. 1,3-dioxolane or 1,3,5-trioxane, did not cause a significant change in the selectivity. It is noteworthy that a sizeable amount of the solvent-incorporated products were formed in these solvents, as is evident from a decrease in the total absolute yields of the O—H insertion products with increase in the proportion of the solvents. For example, phenylcarbene generated in a solution of 40 mol % alcohols and 60 mol % THF afforded, in addition to the O—H insertion products (29.0%), a C—H insertion product (**6**, 35%) and a C—O insertion product (**7**, 8%). Similarly $PhCH_2OEt$ (3.0%) and $PhCH_2CH(CH_3)OEt$ (17.2%) were formed when the carbene was generated in a solution of 4:6 alcohol–diethyl ether. This is in apparent contrast with that observed in 1,4-dioxane, where the yield of insertion product **8** of carbene into

Table 2. Effect of ether structure on relative reactivities ($k_{rel} = k_{MeOH}/k_{ROH}$) of monophenylcarbene and carbomethoxyphenylcarbene toward alcohols[a]

Carbenes	Solvent[b]	Total yield (%) of ethers[c]	k_{rel}[d]
PhCH:	None	79.0	1.85
	Et_2O	67.3	2.76
	Diethyl cellosolve	48.9	2.62
	THF	29.0	3.92
	1,4-Dioxane	76.3	16.5
	1,3,5-Trioxane[e]	62.5	1.78
$Ph\ddot{C}CO_2Me$	None	78.3	6.87
	None[f]	90.0	24.4
	Et_2O	80.4	5.48
	THF	32.6	7.21
	1,3-Dioxolane[g]	50.6	6.89
	1,4-Dioxane	76.1	17.8
	1,3,5-Trioxane[e]	69.4	6.13
	18-Crown-6[e,g]	68.9	5.92

[a] Carbenes were generated by photolysis of diazo compound in a binary mixture (1 : 3) of MeOH–t-BuOH through a Pyrex filter at 10°.

[b] Unless otherwise indicated, 60 mol % of solvent was used.

[c] Determined by GC.

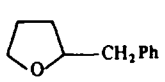
[d] $k_{MeOH}\ k_{t\text{-}BuOH}$ determined according to Eq. 1.

[e] Et_2O was used as co-solvent.

[f] $Cu(OT_f)_2$ catalyzed reaction in dark.

[g] Monophenyldiazomethane decomposed in these solvents in dark.

the solvent was less than 5% even in the presence of 90 mol % of 1,4-dioxane.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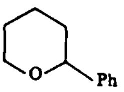
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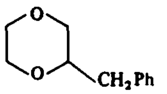
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Examination of the effect of 1,4-dioxane on the reactivity of other arylcarbenes revealed that the O—H insertion selectivity of these carbenes was also affected by 1,4-dioxane, but that the magnitude of increase in the selectivity caused by dioxane was somewhat sensitive to the carbenic substituents (Table 3). Thus, although the selectivity of monoarylcarbenes was similarly increased by addition of 1,4-dioxane irrespective of the ring-substituents, the magnitude tends to decrease as the carbenic carbon becomes more crowded; the selectivity of diphenylcarbene was essentially unaffected by dioxane.

The above results clearly indicate that 1,4-dioxane has a remarkable effect on the apparent reactivity of singlet arylcarbenes towards alcohol. An explanation

Table 3. Effect of carbene structure on 1,4-dioxane-modified relative reactivities ($k_{rel} = k_{MeOH}/k_{ROH}$) of arylcarbenes toward alcohols[a]

Carbenes	ROH	Total yields (%) of ethers[b]	k_{rel}[c]
PhH:	i-PrOH	75.6 (76.9)	6.57 (1.45)
	t-BuOH	76.3 (79.0)	16.5 (1.85)
$p\text{-}MeC_6H_4CH$:	t-BuOH	80.7 (93.0)	7.75 (1.62)
$p\text{-}ClC_6H_4CH$:	t-BuOH	81.9 (96.1)	14.4 (2.19)
$Ph\ddot{C}CO_2Me$	t-BuOH	76.1 (78.3)	17.8 (6.85)
Ph_2C:	t-BuOH	75.8 (83.1)	2.49 (1.91)
Fl:[d]	t-BuOH	71.9 (85.9)	4.16 (1.55)

[a] Carbenes were generated by photolysis of diazo compound in a binary mixture (1 : 3) of MeOH–ROH in the presence of 60 mol % of 1,4-dioxane.

[b] Determined by GC. Yields in parentheses were determined in the absence of dioxane.

[c] Determined according to Eq. 1. Values in parentheses were obtained in the absence of dioxane.

[d] Fluorenylidene.

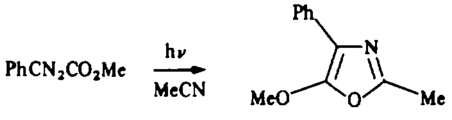
of the observation must include, at least in part, the stabilization of singlet carbene in dioxane presumably by reversible interaction of the vacant p orbital of singlet carbene with the lone pair electrons of dioxane. It is quite reasonable to assume that singlet carbene can form such a complex with electron-pair donor solvent like 1,4-dioxane since most singlet carbenes are known to act as an electrophile and hence generally reacts with ether to give the products resulting from initial attack on the oxygen atom.[6,14] A change in reactivity of carbene due to such a complexation with ether oxygen has been invoked[15] to explain a high selectivity in cyclopropanation of olefin bearing ketal group. It was suggested[15] that a ketal oxygen–carbene complex might "deliver" the carbene to the favorably located double bond, enhancing its reactivity. Moreover, similar modification of reactivity by the complexation with electron-pair donor solvents, e.g. ether, has been shown in other analogous neutral divalent reactive intermediates such as nitrenes[16] and silylenes.[17]

The observed change in the reactivity of carbenes was brought about, then, by increase in the size of attacking species as a result of the complex formation. Thus, the reaction of the complex with the crowded t-butyl alcohol is much more retarded by steric hindrance in the transition state compared to a free carbene. Support is lent to the above suggestion by the findings that the more a carbenic center is crowded, the less its reactivity is affected by dioxane.

What is the reason for the fact that only 1,4-dioxane shows a marked effect on the reactivity of singlet carbene, then? A possible reason must lie partly in the difference in basicity between the ethers employed. The order of basicity in solution increases in the order dioxane < diethyl ether < THF.[18,19] Steele and Weber[17] found that dimethylsilylene is more selective in THF than in ethyl ether for the competition reaction between pairs of alcohols. This difference has been explained by assuming that the complex between silylene and a more basic ether, i.e. THF, is stronger than the complex between silylene and a less basic ether. Presumably, the interaction of singlet carbenes with more basic ethers, e.g. THF, is, on the other hand, strong enough to give rise to the solvent-incorporated products, while the interaction with less basic 1,4-dioxane is weak and reversible, resulting in an effective stabilization in the reaction with alcohol. The formation of an appreciable amount of solvent adducts formed in THF and ethyl ether supports the above explanation.

Recently it has been demonstrated[20] by a pulsed-laser spectroscopic analysis that H-bonding in alcohols plays an important role in the O—H insertion of some carbenes into alcohols. Thus, the reactions of phenylchlorocarbene (Ph—$\ddot{\mathrm{C}}$—Cl) with alcohols were not first order with respect to the substrate and oligomers of methanol reacted more rapidly with Ph—$\ddot{\mathrm{C}}$—Cl than their monomer, while the converse was true for t-butyl alcohol. The observed effect of solvent, then, might be ascribed to changes in the nature of the O—H bond of the alcohols due to hydrogen bonding with the solvent ethers. A simple test for this possibility is to examine the effect of substrate ratio on product ratio. The product ratio is a linear function ($r > 0.99$) of the substrate ratio for the competition reaction between methanol and iso-propyl alcohol in dioxane and acetonitrile, indicating that the insertion reaction is first order in alcohol concentration, at least in the concentration ranges studied. Thus, we think it more likely that the observed effects are mostly due to altered carbene reactivity rather than altered substrate reactivity.

It is noteworthy that acetonitrile, which has been shown[20] to affect the reactivity of methanol toward Ph—$\ddot{\mathrm{C}}$—Cl by H-bonding, was not effective in the present system. Recent spectrophotometric investigations showed[9,22] that acetonitrile is a highly reactive solvent toward carbenes and that the interaction with carbenes giving rise to ylidic intermediates plays an important role in some carbene reactions. Photolysis of methyl phenyldiazoacetate (**9**) in acetonitrile afforded oxazole (**10**), which apparently arises from ylidic interaction of the carbene with the lone-pair electrons of acetonitrile. Addition of alcohol caused a decrease in the formation **10**, but the O—H insertion selectivity was identical within experimental error to that obtained without acetonitrile. This indicates that the interaction of carbene with acetonitrile is not so important as to change its reactivity toward alcohol.

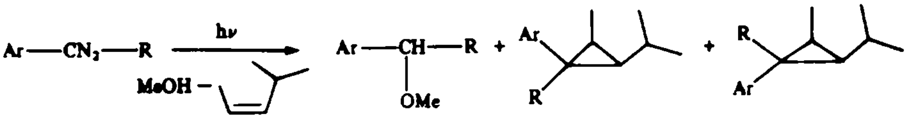


9 **10**

In order to get more insight into the nature of the interaction, we next examined the effect of dioxane on the reactivity of singlet carbenes in the reaction with olefins.

Insertion–addition selectivity

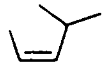
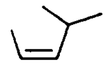
The reaction which we next utilized to probe the interaction of singlet carbenes with dioxane is the insertion–addition selectivity. Thus, carbenes were generated in a binary mixture of degassed alcohol–olefin and the insertion selectivities (k_i/k_a) were calculated by means of an equation similar to (1) using the ratios of products **12**/**13** and substrates.



11 **12** **13**(syn) **13**(anti)

Ar = p-X—C$_6$H$_4$; R = H, CO$_2$Me

Table 4. Effect of 1,4-dioxane on insertion–addition selectivities (k_i/k_a) of arylcarbenes[a]

Carbenes	Olefin	Solvent[b]	Total yields[c] (%)	k_i/k_a[d]	*syn/anti*[e]
PhCH:		None	80.1	1.04	0.81
		PhH	61.0	1.14	0.80
		1,4-DO	68.6	6.49	0.85
p-Me—C_6H_4—CH:		None	73.0	1.46	0.93
		1,4-DO	63.8	5.12	1.08
p-Cl—C_6H_4—CH:		None	76.5	0.97	0.77
		1,4-DO	62.6	6.11	0.70
$\mathrm{Ph\ddot{C}CO_2Me}$		None	68.4	4.50	2.1
		None[f]	g	~50	g
		1,4-DO	62.5	6.42	2.7

[a] Carbenes were generated by photolysis of diazo compound in a binary mixture (1 : 10) of MeOH–olefin through a Pyrex filter at 10°.

[b] About 60 mol% of solvent was added.

[c] Determined by GC.

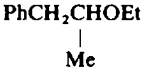
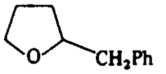
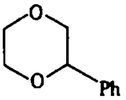
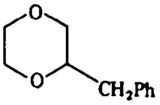
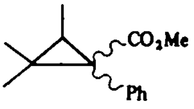
[d] $k_{\mathrm{MeOH}}/k_{\mathrm{olefin}}$.

[e] Stereoselectivity of cyclopropanation, *syn*-aryl *syn*-hydrogen.

[f] Decomposed in the presence of $\mathrm{Cu(OTf)_2}$.

[g] Not determined.

Table 5. NMR spectra (δ) in CCl_4

Compound		NMR spectra
10		2.21 (s, 3H), 3.80 (s, 3H), 7.06–7.70 (m, 5H)
 $\mathrm{PhCH_2\underset{\underset{Me}{\mid}}{C}HOEt}$		1.10 (t, 3H), 1.12 (d, 3H), 3.42 (q, 2H), 3.70 (d, 2H), 4.20 (m, 1H), 7.08 (bs, 5H)
	**6**	1.4–1.8 (m, 4H), 2.75 (dd, 2H), 3.2–4.0 (m, 3H), 7.0 (bs, 5H)
	**7**	1.4–1.8 (m, 4H), 3.2–3.6 (m, 3H), 3.8–4.0 (m, 1H), 6.9–7.3 (m, 5H)
	**8**	7.1 (bs, 5H), 3.8–3.4 (m, 5H), 3.5–3.0 (m, 2H), 2.6, 2.5 (dd, 2H)
13 (R = X = H)	*syn*	1.03 (d, 6H), 1.20 (bs, 3H), 0.6–2.5 (m, 3H), 6.7–7.2 (m, 5H)
	anti	0.95 (d, 3H), 1.08 (bs, 6H), 0.7–2.3 (m, 3H), 6.9–7.2 (m, 5H)
13 (R = H, X = Me)	*syn*	0.9–1.3 (m, 9H), 0.8–1.8 (m, 3H), 2.4 (s, 3H), 6.7–6.8 (m, 5H)
	anti	0.87–1.1 (m, 9H), 0.6–2.0 (m, 3H), 2.43 (s, 3H), 6.7–7.0 (m, 5H)
13 (R = H, X = Cl)	*syn*	0.8–1.3 (m, 9H), 0.7–2.6 (m, 3H), 6.7–7.2 (m, 5H)
	anti	0.9–1.4 (m, 9H), 0.8–2.5 (m, 3H), 6.8–7.3 (m, 5H)
	*syn*	0.92 (s, 6H), 0.98 (s, 3H), 1.80 (q, 1H), 3.45 (s, 3H), 7.0–7.4 (m, 5H)
	anti	1.23 (s, 6H), 1.29 (s, 3H), 1.62 (q, 1H), 3.45 (s, 3H), 7.0–7.4 (m, 5H)

The results summarized in Table 4 again indicate that only dioxane shows a considerable effect on k_i/k_a. Thus, phenylcarbene generated in 60 mol % of 1,4-dioxane was some 6 times more reactive toward methanol relative to 4-methyl-2-pentene than that generated without a solvent, while the reactivity was essentially unaltered on dilution with benzene. Similar trends were observed with other carbene–olefin–methanol systems.

The observed change in the reactivity of carbenes would be attributable to a change in steric as well as electronic nature of the carbene as a result of the complex formation. Assuming that the reactions of singlet phenylcarbene with olefin (cyclopropanation) and methanol (O—H insertion) take place via its initial electrophilic attack on π-electrons of carbon–carbon double bonds and lone pair electrons of methanol oxygen, it is reasonable to suggest that the transition state for the cyclopropanation is more crowded than that for the O—H insertion. Thus, the reaction of the carbene–dioxane complex with olefin is much more retarded by steric hindrance compared to the free carbene. On the other hand, the complexation of carbene to dioxane is expected to reduce its electrophilicity as a result of the weak interaction of empty p orbitals of the carbene with the oxygen lone pair. A less electrophilic carbenoid intermediate would prefer to attack a more nucleophilic center. Olefins and alcohols are generally known to act as equally efficient traps for singlet carbenes. The value of k_i/k_a for phenylcarbene generated without a solvent, however, indicates that methanol is slightly more reactive than olefins at least toward the arylcarbenes studied. Thus, as the electrophilicity of singlet carbenes is reduced by the complexing with dioxane, the carbene becomes more discriminate since its reaction with a less activated substrate beomes unfavored.

CONCLUDING REMARKS

The present study indicates that 1,4-dioxane stabilizes singlet carbene by reversible complexing with its lone pair electrons so that the reactivity of carbene is considerably altered. It is very important to note in this connection that the metal-catalyzed decomposition of diazo compound often generates a reactive species (carbenoid) which is different from the free carbene.[6] For example, the reaction of cyclohexene with catalytically (Cu) generated carboethoxycarbenoid affords cyclopropanes with high stereoselectivity, while the reaction of the corresponding free carbene gives an allylic C—H insertion product along with the cyclopropane.[23] The differences are generally attributable to the intervention of a carbene–metal complex.[6] It is thus very interesting to compare the reactivity of metal–carbenoid with that of dioxane–carbenoid. The results (Tables 2 and 3) indicate that the reactivity of the carbene was modified by Cu and dioxane in the same direction, although the magnitude of the modification was not the same.

EXPERIMENTAL

Instruments. IR spectra were recorded on a JASCO IR-G recording spectrometer. ^{1}H-NMR spectra were determined on a JEOL JNM-MH-100 spectrometer as $CDCl_3$ or CCl_4 solns with an internal Me_4Si standard (see Table 5). GC-MS spectra were obtained on a JEOL JMS D-300 spectrometer using a column consisting of Silicone OV-1 on Diasolid L (4.0 mm × 1.0 m). GC work was done on a Tanagimoto G-180 using a 4.0 mm × 2.0 m column packed with OV-17 (5%) on 60–80 mesh Diasolid L. Preparative GC was done on a Hitachi 167 using a 4.0 mm × 2.0 m column packed with OV-17 (10%) on 60–80 mesh Diasolid L.

Materials. Monoaryldiazomethanes,[24] diphenyldiazomethane,[25] diazofluorene,[26] and methyl phenyldiazoacetate[27] were prepared according to literature procedures immediately before use. All of the solvents used were of GR grade and distilled before use.

Benzyl (**4**,**5**) *and benzhydryl ethers* were prepared[28] by adding the corresponding chloride to a refluxing mixture of NaOH and alcohol, followed by extraction with Et_2O–H_2O and distillation.

Methyl α-alkoxyphenylacetates were prepared[29] by the reaction of α-bromo-α-phenylacetate with sodium alkoxide, followed by ester exchange.

Fluorenyl ethers were prepared by the reaction of fluorenyl bromide[30] in refluxing alcohol.

5-Methoxy-4-phenyl-2-methyloxazole (**10**). This compound was made by a BF_3 catalyzed reaction[31] of a diazo carbonyl compound in acetonitrile. Thus, a soln of **9** (0.3 g) in anhyd acetonitrile (3 ml) was added dropwise to acetonitrile (10 ml) containing BF_3-etherate (1.0 ml) under magnetic stirring at 10°. After complete gas evolution, the mixture was poured into H_2O (50 ml) and ether (50 ml). The ether layer was extracted with dil HCl, the aqueous soln was made basic with NaOH, and extracted with ether. The ether was distilled under reduced pressure to leave the oxazole as a yellow oil (0.214 g, 66.5%).

1-Phenyl-2-propanol ethyl ether. 1-Phenyl-2-propanol (1.36 g) was added to a stirred suspension of finely powdered NaOH (1.0 g) in DMSO (10 ml). To the resulting mixture was added EtI (3.0 g) at room temp, and the soln was stirred overnight. After dilution with water (25 ml) the product was extracted with ether. Evaporation of the ether left the crude product which was purified by column chromatography to afford colorless oil (1.36 g, 83%).

Benzyldioxane. This compound was prepared by the reaction of chlorodioxane[32] with benzylmagnesium chloride according to the lit. procedure.[33]

Photolysis of monophenyldiazomethane (**1**) *in THF.* A soln of **1** (*ca* 500 mg) in THF (10 ml) was irradiated with light from a 300-W Hg lamp filtered through Pyrex until all diazo compound was destroyed. GC-MS analysis of the mixture showed the presence of toluene, benzaldehyde, bibenzyl, stilbenes, aldazine and two phenylcarbene–THF adducts. The photolysate soln was concentrated, and the residue was passed through GC to give **6** (30.8%) and **7** (19.2%).

Photolysis of **1** *in 1,4-dioxane.* A soln of **1** (*ca* 500 mg) in dioxane (10 ml) was irradiated as described above. Preparative GC gave **8** (240 mg, 32%).

Photolysis of monoaryldiazomethane in the presence of cis-*4-methyl-2-pentene.* A soln of **1** (*ca* 200 mg) in *cis*-4-methyl-2-pentene (3 ml) was irradiated as described above. After removal of the excess olefin preparative gas chromatography gave *syn* and *anti*-cyclopropanes. No *trans* isomer was isolated from the reaction mixture.

Photolysis of methyl α-diazo-α-phenylacetate in the presence of 2-methyl-2-butene. In similar fashion, a reaction of the diazo compounds with 2-methyl-2-butene was shown to yield *syn*- and *anti*-1,1,2-trimethyl-3-phenyl-3-carbomethoxycyclopropane.

Irradiation for analytical purposes. All irradiations outlined in Tables 1–4 and Fig. 1 were carried out using a Halos 300-W high-pressure mercury lamp with a water-cooled quartz jacket. In a typical run, 0.005 mmol of the freshly prepared diazo compound was added to 2.0 ml of the appropriate solvent in Pyrex tubes of 5.0-ml capacity. The sample was degassed by subjecting it to a minimum of three freeze-degas-thaw cycles at a pressure near 10^{-5} mmHg and irradiated at 10° until all the diazo compound was destroyed.

Product identifications were established either by GC as well as GC-MS comparisons using authentic samples synthesized as described above or by isolating individual components followed by spectroscopic identification. Product distributions were conveniently determined by standard GC technique. Control experiments exclude the possible photoconversion of the product during the irradiation period and also demonstrate that no reaction occurs in the absence of light.

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