Generation and Reactions of 2-Alkoxydiphenylcarbenes in Fluid Solution and Rigid Matrices

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Irradiation of 2-alkoxydiphenyldiazomethanes **1** in cyclohexane at room temperature produced 3-phenyldihydrobenzofurans **3** presumably as a result of intramolecular C–H insertion of 2-alkoxydiphenylcarbenes **2**. Irradiation of compounds **1** in cyclohexane matrix at −196 °C gave intermolecular C–H insertion products **4** at the expense of benzofurans **3**. The formation of products **4** is explicable in terms of H-atom tunnelling to the triplet state of carbenes **2**, followed by coupling of the resulting radical pairs. Product ratios **3**:**4** were somewhat sensitive to the bulk of the alkoxy group at the 2-position. This can be explained in terms of the matrix effect on the relative population of the rotational isomers of the carbene **2**.

Irradiation of compounds **1** in methanol at room temperature afforded O–H insertion products **5** almost exclusively, whereas irradiation in methanol matrix at −196 °C gave C–H insertion products **6** along with other products **3** and **5**.

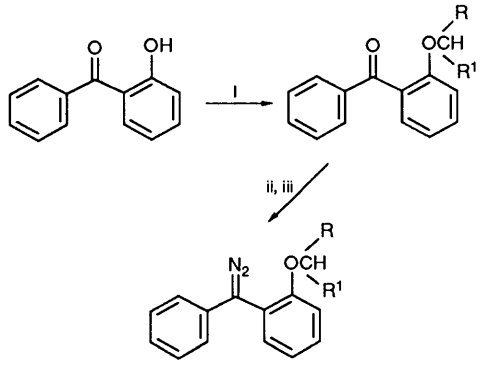
Reactions of 2-substituted arylcarbenes have been attracting continued attention from the synthetic viewpoint. Thus, arylcarbenes bearing appropriate substituents at the 2-position, generated either directly or formed *via* carbene-to-carbene rearrangement, usually react with the proximate group to give many useful benzocyclic compounds which are otherwise not easily prepared.[1] For example, indane derivatives having such heteroatoms as oxygen,[2,3] sulphur,[2] nitrogen,[3,4] silicon,[5–7] germanium[8] and lead[5] have been obtained from the reaction of 2-heteroalkyl arylcarbenes as a result of intramolecular insertion into the C–H bond of the substituent. On the other hand, the carbenes can efficiently interact with 2-positional functional groups such as phenyl,[9] alkenyl[10] and alkyl[11] groups, leading to polycyclic compounds, as well as with carbonyl and heteroatom[12] substituents to form the products resulting from ylide intermediates. These reactions have attracted much attention from the mechanistic viewpoint and useful information concerning the mechanism of C–H insertion,[3,13] internal rotational barriers[10] and intermediates (*e.g.*, ylide)[11,12–14] involved in the reaction and the proximity effect on the reactivity[12] has been obtained.

As part of our recent project on neighbouring-group participation in carbene chemistry,[15] we studied the chemistry of 2-substituted diphenylcarbenes and found that the carbenes generated by photolysis of diazo compounds undergo intramolecular insertion into C–H bonds, leading to dihydrobenzofurans, competitively with intermolecular reactions with the solvent.

Results and Discussion

Synthesis of 2-Alkoxydiphenyldiazomethanes **1**.—2-Alkoxydiphenyldiazomethanes **1** were easily prepared as relatively stable red oils by oxidation of the corresponding hydrazones, which were obtained from anisic acid by way of 2-hydroxybenzophenones (Scheme 1).

Irradiation of Compounds **1** *in Cyclohexane*.—Irradiation of compound **1a** in a degassed cyclohexane solution at 10 °C with the light from a 300 W high-pressure Hg lamp through a Pyrex filter produced 3-phenyl-2,3-dihydrobenzofuran **3a** as the sole isolable product in 85% isolated yield. Formation of product **3a** is reasonably explained in terms of insertion of the photolytically generated carbene **2a** into a C–H bond of the methoxy group. Similar irradiation of other alkoxyphenyldiazomethanes **1b–1d** also afforded the corresponding dihydrofurans **3b–3d** in very good yield (Table 1).

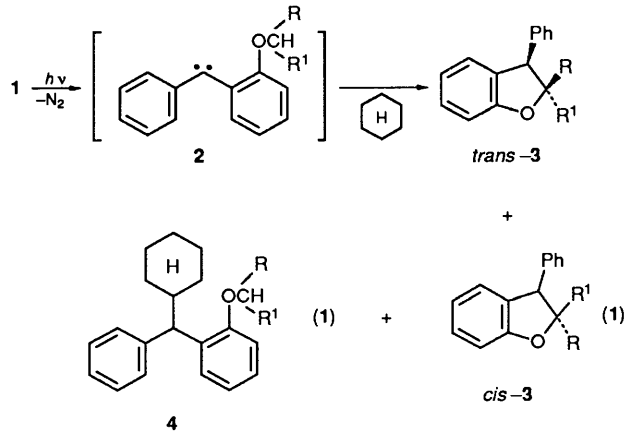


1a; R = R¹ = H
b; R = H, R¹ = Me
c; R = R¹ = Me
d; R = H, R¹ = Ph

Scheme 1 *Reagents:* i, RR^1CHBr, NaOH; ii, N_2H_4-H_2O; iii, HgO

Intriguingly, no products formed by insertion into a β-CH bond of the alkoxy group were detected in the reaction mixture from the carbenes **2b** and **2c**, although these hydrogens are statistically more available. This can be interpreted in terms of the effect of the ether oxygen as well as the carbenic substituents on the intramolecular C–H insertion selectivities. Thus, it is generally recognized[16] that the order of reactivity of carbenes toward the C–H bonds of simple alkanes is tertiary (3°) > secondary (2°) > primary (1°) C–H bonds. Ether substituents usually enhance the insertion of carbenes into a proximate C–H bond by resonance electron donation when the transition state is attained later on the reaction co-ordinate, although they deactivate the C–H insertion having an early transition state presumably due to an inductive effect (ground-state effect).[16,17] Almost exclusive formation of benzofurans **3** clearly suggests that α–CH bonds are highly activated by the combined effects of alkyl (R) groups and the ether oxygen on the later transition state. On the other hand, discriminatory ability is sensitive to carbenic substituents. For instance, methylene itself shows no or only slight discrimination between

1°, 2° and 3° C–H bonds, while phenylcarbene exhibits a quotient of 6.0 ± 0.3 between 1° and 2° C–H bonds.[18] The phenyl ring apparently stabilizes the carbene sufficiently to allow it to show a rather large discriminatory ability. Thus, almost exclusive formation of the furan **3** can be attributable to a combination of stabilization of carbene by the two phenyl rings and activation of C–H bonds by the ether substituents.



The carbenes **2b** and **2d** afforded the furans **3b** and **3d** as a mixture of geometrical isomers, the *trans*-isomer being the major product. Rather selective formation of the *trans*-isomer suggests the intramolecular C–H insertion of the carbene **2** is relatively sensitive to steric factors. There are at least two mechanisms proposed for the singlet carbene C–H insertion processes: one known as the Doering–Prinzbach mechanism[19] which asserts that a triangular transition state is involved, while the other, known as the Benson–DeMore mechanism,[20] asserts that attack by carbene is on the hydrogen through a linear transition state. Obviously the triangular transition state is more sensitive to steric factors than is the linear transition state. Thus, as has been verified in many experimental works, the present results are more easily explicable in terms of the perpendicular approach of the carbenic centre to the C–H bond.

No C–H insertion products **4** formed by reaction with the solvent hexane could be isolated in any case, although GC-MS analysis of the reaction mixtures showed the presence of compounds **4** in trace amounts. This is not surprising since even diphenylcarbene itself appears to be unreactive to such unreactive bonds as those in cyclohexane.[18]

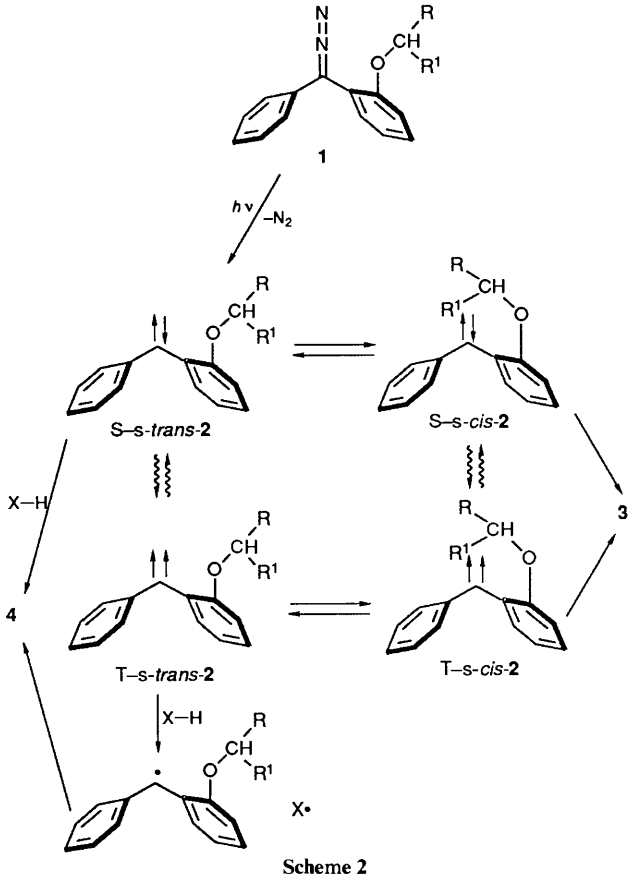
In marked contrast, when the carbenes **2** were generated in cyclohexane matrix at −196 °C, the C–H insertion products **4** formed by reaction with the matrix molecules appeared at the expense of the intramolecular products **3** (Table 1). What is the origin of the marked increase in products **4** at low temperature? It is now well documented[21,22] that, in the case of carbenes with triplet ground states, there are profound differences between the chemistry observed in fluid solution at elevated temperature and that obtaining in solids at −196 °C and that, usually, low-temperature solid-state conditions dramatically enhance the yields of formal C–H insertion adducts between the carbene and the matrix host. Kinetic analysis of the decay of triplet arylcarbenes in a rigid matrix using EPR has demonstrated[22] that these C–H insertion products are formed *via* hydrogen-atom abstraction–recombination of the triplet carbene and that the hydrogen-atom abstraction from the matrix is not a classical process but is a quantum mechanical tunnelling effect. A similar mechanism can be applied to explain the present observations. Thus, direct irradiation of the diazomethanes **1** at room temperature gives rise to the singlet state carbenes S-**2** which reacts with α–CH bonds of the ether group at the *ortho* position to give products **3** (Scheme 2). As the reaction

Table 1 Product distributions obtained in photolysis of compounds **1** in cyclohexane[a]

				Product distribution (%)[b]	
1	R	R¹	*T*/°C	**3** (*trans*:*cis*)[c]	**4**
a	H	H	10	>99	<1
			−196	59.6	40.4
b	H	Me	10	>99 (88:12)	<1
			−196	74.1 69:31)	25.9
c	Me	Me	10	>99	<1
			−196	81.0	19.0
d	H	Ph	10	>99 (77:23)	<1
			−196[d]	37.0 (49:51)	29.9

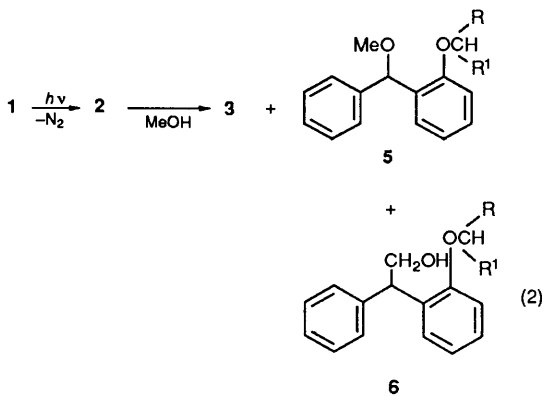
[a] Irradiations were carried out on a 10 mmol dm^{-3} solution of compound **1** in cyclohexane. [b] Determined by GC. Absolute yields were 80–90%. [c] *trans*- or *cis*-relative to the 3-phenyl group. [d] *o*-Benzyloxyphenyl(phenyl)methane was formed in 33.1% yield.

temperature is lowered and the reaction phase becomes solid tunnelling of hydrogen atoms from the matrix cyclohexane to the triplet T-**2**, which is in equilibrium with the singlet species S-**2**, becomes important and eventually competes efficiently with the singlet reaction. The members of the radical pairs formed by the hydrogen-atom abstraction usually diffuse apart in fluid solution but, in the matrix environment, they recombine with high efficiency due to their limited diffusibility to give the C–H insertion products, *i.e.* products **4** in this case.



Scheme 2

Inspection of the data in Table 1 clearly indicates that the ratio of intermolecular to intramolecular C–H insertion products (*i.e.*, **4**:**3**) is sensitive to the bulk of the ether alkyl group and decreasing as more methyl groups are introduced on R and R′. This can be explained in terms of the effect of the



(2)

matrix on the relative populations of the rotational isomers of the carbenes **2**. The nascent singlet carbene S-**2** generated from substrates **1** would be the rotational S-*trans*-isomer where the ether alkyl group is lying *anti* to the carbenic centre because of the steric repulsion between the alkyl group and the diazo group in the precursory diazo compounds. It has been shown[23] in ESR studies that when a carbene is generated in a rigid glass, it has the geometry and the conformation dictated by those of its precursor. This conformer would either undergo intermolecular reaction (*e.g.*, C–H insertion forming compounds **4**) or would rotationally isomerize to the other conformer (s-*cis*) where the alkyl group is lying *syn* to the carbene centre and hence where intramolecular C–H insertion leading to benzofurans **3** is feasible. The carbene generated in a fluid solution would follow the pathway leading to benzofurans **3** because the rates of the rotational isomerization and the intramolecular C–H insertion are considered to be faster than that of intermolecular C–H insertion of the *trans*-isomer. In a rigid matrix at low temperature, however, the rotational isomerization becomes slow due to the rigidity of the matrix and, at the same time, H-atom tunnelling from the matrix host to the triplet T-s-*trans*-**2** comes to compete with the singlet carbene reaction as mentioned above. The observed decrease in the yield of products **4** in going from **2a** to **2c** can now be interpreted as indicating that the approach of the matrix host to the carbenic centre of T-s-*trans*-**2** is more severely prevented due to the steric repulsion between the host and the ether alkyl group as one introduces more methyl groups on R. It has been pointed out[24] that the rate of H-atom tunnelling is dependent upon the barrier height and width, where the barrier height is the classical activation energy and the barrier width is the distance the H atom must tunnel from a matrix molecule to the arylcarbene. It is reasonable to assume that the height will be relatively constant for carbenes **2a–2c**, and therefore the reactivity of the carbene toward the matrix hexane will be affected mainly by the width. Molecular models suggest the carbene centre of species **2a** should have a more accessible H-atom, hence a smaller barrier width and therefore higher reactivity, as is observed.

Finally, a significant change in *trans*:*cis* ratios of benzofurans **3b** and **3d** in going from liquid to solid phase runs is also worthy of comment. The observed change in stereochemistry apparently reflects the difference in rotational barrier between fluid solution and rigid matrix.

Irradiation of Compounds **1** *in Methanol.*—In order to get a deeper insight into the mechanism of the intramolecular C–H insertion, we next studied the reaction of the carbenes **2** in methanol at different temperatures. When carbenes **2** were generated in methanol at 10 °C, most of the carbene was trapped by the O–H bond of the alcohol, giving rise to the formation of O–H insertion product **5** as the major product

Table 2 Product distributions obtained in photolysis of compounds **1** in methanol[a]

				Product distribution (%)[b]		
1	R	R^1	*T*/°C	**3** (*trans*:*cis*)[c]	**5**	**6**
a	H	H	10	<1	>99	0
			−196	9.1	75.6	15.3
b	H	Me	10	2.1 (95:59)	97.9	0
			−196	22.2 (65:35)	63.9	13.9
c	Me	Me	10	8.4	91.6	0
			−196	46.2	42.5	11.3
d	H	Ph	10	9.4 (79:21)	90.6	0
			−196	23.0 (59:41)	56.7	20.3

[a–c] See footnotes *a–c* in Table 1.

along with a small amount of the furan **3**, the yield of which, however, increased in going from **2a** to **2d** (Table 2). This is expected since methanol is used as one of the most efficient trapping reagents for singlet carbenes. For example, the absolute rate constant for the reaction between singlet diphenylcarbene and methanol in acetonitrile was determined[25] to be $(3.5 \pm 0.5) \times 10^{10}$ dm^3 mol^{-1} s^{-1} which is very close to the value for diffusion-controlled reaction in MeCN. Thus, almost exclusive formation of the ether **5** indicates that the nascent singlet **2** is trapped immediately by the O–H bond before it reacts with the intramolecular ether C–H bonds which are apparently less reactive. A slight but significant increase in yield of the benzofuran **3** in going from **2a** to **2d** can be explained in terms of the steric effects of the bulky alkyl group of the *ortho* ether on the approach of the solvent.

The generation of carbenes **2** in methanol matrix at −196 °C again resulted in a completely different product distribution compared with that obtained in fluid solution but the change in the product ratios in going from liquid to solid was interestingly reversed compared with that observed in cyclohexane. Thus, the intramolecular C–H insertion products **3** were found in increased yield at the expense of adducts **5** in matrix run. At the same time, the C–H 'insertion' products **6** also appeared. It is well documented that generation of arylcarbenes in alcoholic solution at room temperature results in the exclusive formation of the O–H insertion product, the singlet reaction product, whereas similar generation in rigid matrices of the alcohol at −196 °C results in a marked increase in the C–H insertion product presumably as a result of H-atom abstraction *via* quantum mechanical tunnelling of the triplet carbene. So, the observed appearance of products **6** in the low-temperature matrix runs is clearly explained in terms of H-atom tunnelling to the triplet followed by coupling of the resulting radical pairs.

What is the origin of the marked increase in the yield of benzofurans **3** at low temperature? Accepting that the benzofuran **3** is derived from the singlet carbene **2**, a decrease in yield of product **5** simply means that intermolecular O–H insertion becomes less favourable in the matrix at low temperature than does intramolecular C–H insertion. Comparing the nature of the bonds between O–H and C–H, one can easily expect that the insertion of carbenes **2** into an O–H bond will need a more polar transition state than that into a C–H bond and therefore will be favoured by solvation by a polar medium, *viz.* an alcohol. Thus, it has been shown[26] that a typically nucleophilic carbene undergoes protonation in alcohols with the formation of a carbocation while most electrophilic carbenes are likely to attack on the oxygen, leading to an ylide intermediate. Apparently, the OH insertion will be favoured by the solvation of these intermediates, but such solvation is not attained in a matrix environment, where C–H insertion becomes dominant.

An alternative possibility is that H-atom tunnelling is

occurring not only from matrix molecules but also from intramolecular alkoxy groups. To date no clear evidence has been advanced for intramolecular H-atom tunnelling in carbene reactions. However, intramolecular H-atom tunnelling has been observed[27] in the reaction of sterically hindered aryl radicals, *e.g.* 2,4,6-tri-t-butylphenyl. It is tempting, then, to suppose that, as the carbene centre becomes sterically more crowded in going from **2a** to **2c**, intramolecular H-atom tunnelling comes to dominate the intramolecular one. Significant changes in *trans*:*cis* ratio of benzofurans **3b** and **3d** in going from fluid solution to matrix runs may reflect, at least in part, the change in mechanism for the formation of compounds **3**, although the difference may also be ascribed to the difference in the rigidity between the two states. More sophisticated experiments are needed to differentiate between these two explanations.

Conclusions.—2-Alkoxydiphenylcarbenes are shown to be excellent precursors for the synthesis of dihydrobenzofuran derivatives when generated in inert solvents at room temperature, while the carbenes undergo intermolecular insertion into the C–H bonds of the solvent, producing substituted diarylmethane derivatives when generated in rigid matrix at −196 °C. Thus, the reaction patterns of the carbenes having multiple reaction channels can be conveniently controlled by simply changing the solvent and the reaction temperature. The evidence presented above also suggests that the relative populations of the carbene conformers play an important role in determining the fate of the carbene, especially in rigid matrices.

Experimental

Apparatus.—UV–visible spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured with a JASCO IR-G recording spectrometer. Measurement of ^{1}H NMR was on a JEOL JNM-MH-100 NMR spectrometer for solutions in $CDCl_3$ or CCl_4 with Me_4Si as internal reference. Mass spectra were run using a Shimadzu QP-1000 mass spectrometer by electron impact (70–20 eV). GLC analyses were carried out on a Yanagimoto instrument, Model G-80, using 5% PEG-20 M on Diasolid L and 5% OV-17 on Diasolid L, and utilizing flame ionization detection. Silica gel (ICN for dry-column chromatography) was used for all column chromatographic separations, and TLC was done on Merck Kiesel gel 60 PF 254.

Materials.—*2-Alkoxybenzophenones: General procedure.* To a vigorously stirred solution of 2-hydroxybenzophenone (5 g, 25 mmol) and pulverized NaOH (1 g, 26 mmol) in dimethyl sulphoxide (30 cm^3) at 40 °C was added an alkyl iodide (35 mmol) and the mixture was kept at 40 °C until all the ketone was consumed; it was then cooled, poured onto water and extracted with diethyl ether. The extract was dried (Na_2SO_4) and evaporated, and the residue was either distilled under reduced pressure or recrystallized.

2-Methoxybenzophenone (96.9%); b.p. 126–128 °C (0.9 mmHg); $\delta_H(CCl_4)$ 3.06 (3 H, s, OMe) and 6.62–7.76 (9 H, m, ArH); *m/z* 212 (M^+, 35%), 195 (18), 135 (100), 121 (32), 105 (40) and 77 (82).

2-Ethoxybenzophenone (92.5%); b.p. 131–132 °C (0.6 mmHg); $\delta_H(CCl_4)$ 1.01 (3 H, t, *J* 12 Hz, Me), 3.88 (2 H, q, *J* 12 Hz, CH_2O) and 6.78–7.80 (9 H, m, ArH); *m/z* 226 (M^+, 20%), 197 (42), 181 (19), 121 (100), 105 (41) and 77 (52).

2-Isopropoxybenzophenone (69.2%); b.p. 125–126 °C (0.7 mmHg); $\delta_H(CCl_4)$ 1.20 (6 H, d, *J* 14 Hz, Me), 4.30 (1 H, sep, *J* 14 Hz, CH) and 6.70–7.65 (9 H, m, ArH); *m/z* 240 (M^+, 20%), 211 (40), 135 (100), 105 (50) and 77 (43).

2-Benzyloxybenzophenone (77.3%); m.p. 63–65 °C; $\delta_H(CCl_4)$ 4.86 (2 H, s, CH_2) and 6.78–7.76 (14 H, m, ArH); *m/z* 289 ($M + 1$, 8%), 288 (M^+, 48), 270 (13) and 91 (100).

2-Alkoxybenzophenone hydrazones: General procedure. A solution of the ketone (10 mmol) and hydrazine hydrate (40 mmol) in anhydrous EtOH (10 cm^3) was refluxed overnight: it was then evaporated to *ca.* 3 cm^3, poured onto water and extracted with diethyl ether. The extract was dried (Na_2SO_4) and evaporated to give the hydrazone as an oily solid. The ^{1}H NMR spectrum showed that both *syn* and *anti* isomers were present. Most of the hydrazone was used without further purification.

2-Methoxybenzophenone hydrazone (98.1%); $\delta_H(CCl_4)$ 3.50 and 3.72 (3 H total, s, MeO), 5.26 (2 H, br s, NH_2) and 6.44–7.00 (9 H, m, ArH).

2-Ethoxybenzophenone hydrazone (90.8%); $\delta_H(CCl_4)$ 0.83 and 1.16 (3 H total, t, *J* 14 Hz, Me), 3.60 and 3.89 (2 H total, q, *J* 14 Hz, CH_2), 5.20 and 5.32 (2 H total, br s, NH_2) and 6.46–7.68 (9 H, m, ArH).

2-Isopropoxybenzophenone hydrazone (74.5%); $\delta_H(CCl_4)$ 0.83 and 1.12 (6 H total, d, *J* 6 Hz, Me), 4.05 and 4.21 (1 H, total, q, *J* 6 Hz, CH), 5.24 and 5.38 (2 H total, br s, NH_2) and 6.50–7.60 (9 H, m, ArH).

2-Benzyloxybenzophenone hydrazone (74.9%); m.p. 70–74 °C; $\delta_H(CCl_4)$ 4.66 and 4.92 (2 H, s, CH_2), 5.22 (2 H, br s, NH_2) and 6.76–7.50 (14 H, m, ArH).

2-Alkoxydiphenyldiazomethanes: General procedure. The hydrazone (4.4 mmol), anhydrous diethyl ether (20 cm^3), anhydrous sodium sulphate (1.0 g), yellow mercury(II) oxide (4.6 mmol) and saturated ethanolic potassium hydroxide (0.5 cm^3) were placed in a 100 cm^3 round-bottom flask equipped with a magnetic stirring bar and drying tube. The mixture was stirred in the dark at room temperature for 10 h. After filtration, the solvent was removed on a rotary evaporator, with the water bath at room temperature, to afford essentially a quantitative yield of the crude diazo compound as a dark red oil. The crude material was dissolved in a small portion of pentane (5–10 cm^3). The solution was cooled to −10 °C and decanted from any solid ketazine and hydrazone. The solvent was removed on a rotary evaporator to afford the diazo compound as a viscous oil.

2-Methoxyphenyl(phenyl)diazomethane **1a**; $\delta_H(CCl_4)$ 3.36 (3 H, s, OMe) and 6.74–7.78 (9 H, m, ArH); ν_{max}(neat)/cm^{-1} 2060.

2-Ethoxyphenyl(phenyl)diazomethane **1b**; $\delta_H(CCl_4)$ 0.95 (3 H, t, *J* 12 Hz, Me), 3.66 (2 H, q, *J* 12 Hz, CH_2O) and 6.73–7.78 (9 H, m, ArH); ν_{max}(neat)/cm^{-1} 2070.

2-Isopropoxyphenyl(phenyl)diazomethane **1c**; $\delta_H(CCl_4)$ 1.01 (6 H, d, *J* 12 Hz, Me), 4.10 (1 H, sep, *J* 12 Hz, CH) and 6.70–7.70 (9 H, m, ArH); ν_{max}(neat)/cm^{-1} 2070.

2-Benzyloxyphenyl(phenyl)diazomethane **1d**; $\delta_H(CCl_4)$ 4.65 (2 H, s, CH_2) and 6.53–7.68 (14 H, m, ArH); ν_{max}(neat)/cm^{-1} 2060.

Preparative Irradiation of Compounds **1**.—In a typical run, a solution of a diazomethane **1** (*ca.* 100 mg) in a solvent (10 cm^3) was placed in a Pyrex tube and irradiated with a high-pressure, 300 W mercury lamp at room temperature until all the diazomethane was destroyed according to the TLC monitoring. When irradiation was performed in the solid phase at −196 °C, the tube was suspended in a transparent Pyrex Dewar flask filled with liquid nitrogen and was then irradiated. The mixture was periodically warmed in the dark until the rigid glass or solid melted so that mixing could occur. The irradiation mixture was concentrated on a rotary evaporator below 20 °C. Individual components were isolated by preparative TLC (PLC) and identified by NMR and mass spectrometry. These fully characterized products were then used as 'authentic' compounds for product identification by co-injection in GC-MS.

Irradiation of compounds **1** *in cyclohexane:* (a) *At* 10 °C. Irradiation was carried out as described above and the

following benzofurans **3** were isolated almost quantitatively by PLC.

3-Phenyl-2,3-dihydrobenzofuran **3a**; $\delta_H(CCl_4)$ 4.14–4.78 (1 H, m, CH), 5.66 (2 H, d, *J* 4 Hz, CH_2) and 6.50–7.50 (9 H, m, ArH); *m/z* 197 ($M^+ + 1$, 20%), 196 (M^+, 100), 195 ($M^+ - 1$, −30), 166 (23) and 149 (18).

2-Methyl-3-phenyl-2,3-dihydrobenzofuran **3b**; $\delta_H(CCl_4)$ *trans*-**3b**: 1.02 (3 H, d, *J* 6 Hz, Me), 4.04 (1 H, br s, C*H*Ph), 4.44 (1 H, q, *J* 6 Hz, C*H*Me) and 6.50–7.34 (9 H, m, ArH); *cis*-**3b**: 0.92 (3 H, d, *J* 6 Hz, Me), 3.96 (1 H, br s, C*H*Ph), 4.84 (1 H, q, *J* 6 Hz, C*H*Me) and 6.50–7.34 (9 H, m, ArH); *m/z* 212 ($M^+ + 2$, 8%), 211 ($M^+ + 1$, 15), 210 (M^+, 100), 209 ($M^+ - 1$, 35), 195 (55), 181 (20), 167 (21) and 165 (48).

2,2-Dimethyl-3-phenyl-2,3-dihydrobenzofuran **3c**; $\delta_H(CCl_4)$ 0.87 (3 H, s, Me), 1.46 (3 H, s, Me), 4.16 (1 H, s, CH) and 6.56–7.12 (9 H, m, ArH); *m/z* 225 ($M^+ + 1$, 13%), 224 (M^+, 100), 223 ($M^+ - 1$, 22), 209 (57), 181 (35) and 165 (75)

2,3-Diphenyl-2,3-dihydrobenzofuran **3d**; $\delta_H(CCl_4)$ *trans*-**3d**: 4.40 (1 H, d, *J* 8 Hz, CH), 5.40 (1 H, d, *J* 8 Hz, CH) and 6.46–7.44 (14 H, m, ArH); *cis*-**3d**: 4.64 (1 H, d, *J* 8 Hz, CH), 5.78 (1 H, d, *J* 8 Hz, CH) and 6.40–7.40 (14 H, m, ArH); *m/z* 273 ($M^+ + 1$, 20%), 272 (M^+, 100), 271 ($M^+ - 1$, 52), 194 (37), 181 (38) and 165 (62).

(b) *At* −196 °C. Irradiation was carried out as described above and the following cyclohexyl derivatives **4** were isolated by PLC in addition to the benzofurans **3**.

Cyclohexyl(2-methoxyphenyl)phenylmethane **4a**; $\delta_H(CCl_4)$ 0.73–2.01 (10 H, m, c-C_6H_{10}), 2.30–2.58 (1 H, m, CH), 3.48 (3 H, s, OMe), 3.96 (1 H, d, *J* 4 Hz, C*H*Ph) and 6.73–7.50 (9 H, m, ArH); *m/z* 281 ($M^+ + 1$, 10%), 280 (M^+, 75), 262 (30), 247 (20), 198 (20), 197 (100) and 91 (32).

Cyclohexyl(2-ethoxyphenyl)phenylmethane **4b**; $\delta_H(CCl_4)$ 1.10 (3 H, t, *J* 12 Hz, Me), 0.81–2.20 (10 H, m, c-C_6H_{10}), 2.35–2.66 (1 H, m, CH), 3.72 (2 H, q, *J* 12 Hz, CH_2O), 3.86 (1 H, d, *J* 4 Hz, C*H*Ph) and 6.75–7.78 (9 H, m, ArH); *m/z* 295 ($M^+ + 1$, 12%), 294 (M^+, 70), 212 (15), 211 (72), 107 (85) and 105 (100).

Cyclohexyl(2-isopropoxyphenyl)phenylmethane **4c**; $\delta_H(CCl_4)$ 1.10 (6 H, d, *J* 12 Hz, Me), 0.81–2.03 (10 H, m, c-C_6H_{10}), 2.30–2.65 (1 H, m, CH), 3.90 (1 H, d, *J* 4 Hz, C*H*Ph), 4.15 (1 H, sep, *J* 12 Hz, C*H*Me_2) and 6.77–7.80 (9 H, m, ArH); *m/z* 310 ($M^+ + 2$, 15%), 309 ($M^+ + 1$, 15), 308 (M^+, 80), 226 (10), 225 (100), 184 (8) and 183 (82).

2-Benzyloxyphenyl(cyclohexyl)phenylmethane **4d**; $\delta_H(CCl_4)$ 0.80–1.92 (10 H, m, c-C_6H_{10}), 2.45–2.75 (1 H, m, CH), 4.00 (1 H, d, *J* 4 Hz, C*H*Ph), 4.73 (2 H, s, CH_2) and 6.56–7.7 (14 H, m, ArH); *m/z* 356 (M^+, 28), 274 (12), 273 (60) and 91 (100).

Irradiation of compounds **1** *in methanol.* (a) *At* 10 °C. Irradiation was carried out as described above and the following methyl ethers **5** were isolated almost quantitatively by PLC.

2-Methoxyphenyl(phenyl)methyl methyl ether **5a**; $\delta_H(CCl_4)$ 3.24 (3 H, s, OMe), 3.64 (3 H, s, MeOAr), 5.56 (1 H, s, CH) and 6.60–7.44 (9 H, m, ArH); *m/z* 228 (M^+, 12%), 214 (10), 213 (100), 197 (48), 196 (49), 195 (30), 151 (45), 135 (15), 121 (20), 105 (14) and 91 (95).

2-Ethoxyphenyl(phenyl)methyl methyl ether **5b**; $\delta_H(CCl_4)$ 1.20 (3 H, t, *J* 16 Hz, Me), 3.16 (3 H, s, MeO), 3.68 (2 H, q, *J* 16 Hz, CH_2), 5.44 (1 H, s, CH) and 6.32–7.30 (9 H, m, ArH); *m/z* 242 (M^+, 10%), 227 (65), 213 (50), 195 (25), 181 (38), 165 (35), 121 (50), 107 (60) and 105 (100).

2-Isopropoxyphenyl(phenyl)methyl methyl ether **5c**; $\delta_H(CCl_4)$ 1.02 (3 H, d, *J* 6 Hz, Me), 1.21 (3 H, d, *J* 6 Hz, Me), 3.18 (3 H, s, OMe), 4.32 (1 H, sep, *J* 6 Hz, CH), 5.44 (1 H, s, CH) and 6.50–7.38 (9 H, m, ArH); *m/z* 256 (M^+, 8%), 214 (9), 213 (43), 183 (7), 182 (25) and 181 (100).

2-Benzyloxyphenyl(phenyl)methyl methyl ether **5d**; $\delta_H(CCl_4)$ 3.18 (3 H, s, OMe), 4.76 (2 H, s, CH_2), 5.54 (1 H, s, CH) and 6.56–7.46 (14 H, m, ArH); *m/z* 304 (M^+, 10%), 272 (8), 213 (10), 182 (28), 181 (50) and 191 (100).

(b) *At* −196 °C. Irradiation was carried out as described above and the following C–H insertion products **6** were isolated along with the benzofurans **3** and the methyl ethers **5**.

2-(2-Methoxyphenyl)-2-phenylethanol **6a**; $\delta_H(CCl_4)$ 1.92 (1 H, s, OH), 3.64 (3 H, s, MeO), 3.95–4.10 (3 H, m, CH_2CH) and 6.60–7.45 (9 H, m, ArH); *m/z* 228 (M^+, 5%), 138 (13), 137 (50) and 91 (100).

2-(2-Ethoxyphenyl)-2-phenylethanol **6b**; $\delta_H(CCl_4)$ 1.21 (3 H, t, *J* 16 Hz, Me), 2.20 (1 H, s, OH), 3.66 (2 H, q, *J* 16 Hz, CH_2), 3.90–4.12 (3 H, m, CH_2CH) and 6.33–7.29 (9 H, m, ArH); *m/z* 242 (M^+, 8%), 212 (25), 211 (26), 165 (20), 152 (13), 107 (75) and 105 (100).

2-(2-Isoproxyphenyl)-2-phenylethanol **6c**; $\delta_H(CCl_4)$ 1.12 (6 H, d, *J* 6 Hz, Me), 2.05 (1 H, s, OH), 4.03–4.12 (3 H, m, CH_2CH), 4.30 (1 H, sep, *J* 6 Hz, CH) and 6.50–7.53 (9 H, m, ArH); *m/z* 256 (M^+, 13%), 226 (15), 225 (45), 184 (15), 183 (100), 181 (10) and 165 (16).

2-(2-Benzyloxyphenyl)-2-phenylethanol **6d**; $\delta_H(CCl_4)$ 2.10 (1 H, s, OH), 3.90–4.10 (3 H, m, CH_2CH), 4.73 (2 H, s, CH_2) and 6.56–7.52 (14 H, m, ArH); *m/z* 304 (M^+, 20%), 275 (21), 273 (99), 183 (32) and 91 (100).

Irradiation for Analytical Purposes.—All irradiations outlined in Tables 1 and 2 were carried out in a Pyrex tube of 5.0 cm^3 capacity. In order to avoid ambiguity in the relative yields due to oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze–degas–thaw cycles at a pressure near 10^{-5} mmHg before irradiation and the tube was sealed under reduced pressure. Irradiation was generally continued until all the diazomethane was destroyed. When irradiation was performed in the solid phase, a second Pyrex tube was inserted into the sample tube in order to maximize exposure and utilization of radiation. The mixture was periodically warmed in the dark until the rigid glass or solid melted, so that mixing could occur. Control experiments ruled out the interconversion of the products during the irradiations and also showed that no reaction occurred in the absence of light over the range of temperature studied. Product indentifications were established either by GC or by GC-MS comparison with authentic samples prepared independently or separated as described above, and product distributions were conveniently determined by standard GC techniques.

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