Buttressing Effect in Carbene Chemistry. Effect of 3-Alkyl Groups on the Reactions of 2-Alkoxydiphenylcarbenes

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Irradiation of 2-methoxydiphenyldiazomethane **1a** in diethyl ether at 10 °C gave 3-phenyldihydrobenzofuran **3a** along with a small amount of the ether adduct **4a**, which became the major product when the irradiation was carried out in the ether matrix at −196 °C. The reaction patterns were dramatically changed as an alkyl group was introduced into the 3-position of substrates **1**. Thus, irradiation of 2-methoxy-3-alkyldiphenyldiazomethanes **1b–d** in diethyl ether either at 10 °C or at −196 °C afforded the corresponding benzofurans **3b–d** at the complete expense of the ether adducts **4b–d**. The results are nicely explained in terms of the buttressing effect of the 3-alkyl group, which prevents the 2-methoxy group from lying in the plane of the phenyl ring in the precursor molecules and assists the methoxy group in rotating around the C–O bond toward the carbene centre after elimination of N_2. Generation of carbenes **2** in methanol at 10 °C produced O–H-insertion adducts **5** as the major product at the expense of benzofurans **3**. The ether **5a** was formed as a major product in the reaction of carbene **2a** with the alcohol matrix at −196 °C, but the benzofurans **3** became the major product in the irradiation of substrates **1b–d** in methanol matrix at −196 °C. The results are again explicable in terms of the buttressing effect of 3-alkyl substituents on the relative populations of the rotational isomers of the carbenes **2**.

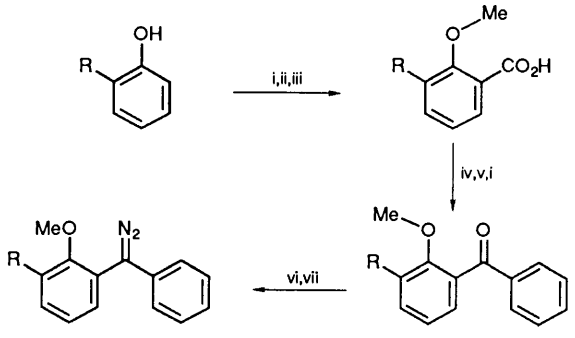
The effect of the 3-alkyl group on the reaction of 2,2′,5′-trimethoxydiphenylcarbenes **7** which form two kinds of intramolecular C–H-insertion products **8** and **9** were studied and the results are again discussed in terms of the buttressing effect.

It is well known that, in 1,2-disubstituted benzene derivatives, introduction of substituents in the 3-position exerts a very large effect not only on the spectroscopic properties but also on the rates of appropriate reactions. For example, the absorption maximum of 2,6-dimethylacetophenone is shifted to shorter wavelength upon introduction of two methyl groups in the 3- and 5-position, although the reverse shift is expected.[1] On the other hand, the rate of racemization of a series of optically active biphenyls derived from 6-carboxy-2′-methoxy-2-nitrobiphenyl are greatly retarded by substituents in the 3′-position, whereas substituents in the 4′-position exert only a small effect on the rate.[2] These data are considered in the light of the importance of bond bending; the 3-substituents 'buttress' the 2-substituents. Thus, the hypsochromic shift in the acetophenones is interpreted as indicating that the 3,5-dimethyl groups 'buttress' the 2,6-dimethyl groups which interact with the acetyl group in the polar excited state and therefore raise its strain energy, whereas the retardation of the biphenyl racemization is understood by assuming that the 3′-substituents 'buttress' the methoxy group and so raise the energy needed to push this group out of the way in the activated state.[3]

The buttressing groups have been shown to play an important role in the reactions involving a reactive intermediate by affecting the stabilization effect of the 2-substituents on the intermediate. For example, in pyrolysis of 2-arylethyl acetates forming styrene and acetic acid, the acetates with buttressed *ortho*-chloro substituents show particularly enhanced reactivity, probably due to enhanced direct p-orbital overlap between the *ortho*-chlorine atom and the incipient side-chain α-carbocation.[4] On the other hand, almost no data are available concerning the buttressing effect in carbene chemistry. During the course of our studies[5] on the effect of substituents on the reaction of 2-methoxydiphenylcarbene, we found that the reactivity is greatly affected by the 3-alkyl group, which is nicely explained in terms of the buttressing effect of the 3-alkyl group on the methoxy group.

Results and Discussion

Synthesis of 3-Alkyl-2-methoxydiphenyldiazomethanes **1**.—Key intermediates for the synthesis of compounds **1** were 3-alkyl-*o*-anisic acids, which were conveniently prepared from 2-alkylphenols by phenoxide-directed *ortho* lithiation, followed by quenching with CO_2.[6] Oxidation of hydrazones could be performed with mercury(II) oxide, but oxidation using $BaMnO_4$[7] usually gave superior results especially with hydrazones bearing more bulky alkyl groups. The diazomethanes **1** (Scheme 1) were obtained as rather stable red oils which could



1
a; R = H
b; R = Me
c; R = Pr^i
d; R = Bu^t

Scheme 1 *Reagents:* i, MeI, NaOH; ii, BuLi, TMEDA; iii, CO_2; iv, $SOCl_2$; v, $AlCl_3$, PhH; vi, N_2H_4·H_2O; vii, HgO or $BaMnO_4$

be kept in a refrigerator (−5 °C) for several months without any appreciable decomposition.

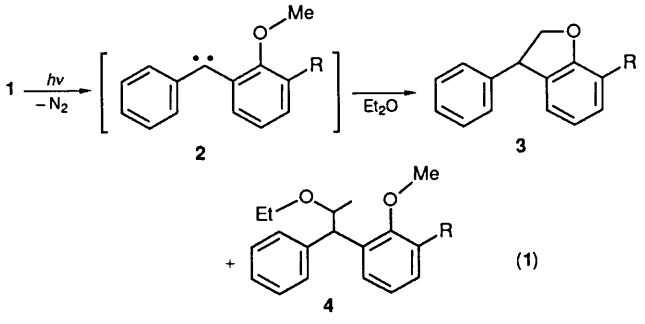
Irradiation of Diazomethanes **1** *in Diethyl Ether.*—Photolysis

Table 1 Product distributions obtained in photolysis of compounds **1** in diethyl ether at 10 and −196 °C[a]

Substrate	R	T/°C	Product distribution (%)[b] 3	4
1a	H	10	62.6	37.4
		−196	4.7	95.3
1b	Me	10	>99	<1
		−196	>99	<1
1c	Pr^i	10	>99	<1
		−196	>99	<1
1d	Bu^t	10	>99	<1
		−196	>99	<1

[a] Irradiations were carried out on a 10 mol dm^{-3} solution of a substrate **1** in diethyl ether. [b] Determined by GC. Absolute yields were 80–90%.

of compound **1a** in a degassed diethyl ether solution at 10 °C with the light from a 300 W high-pressure Hg lamp through a Pyrex filter resulted in the formation of 3-phenyl-2,3-dihydrobenzofuran **3a** and 1-(2-methoxydiphenylmethyl)ethyl ethyl ether **4a** (Table 1). The former product apparently arises from intramolecular C–H insertion of the photolytically generated carbene **2a** into the C–H bonds of the methoxy group, while the latter is explained in terms of intermolecular C–H insertion of the carbene **2a** into the solvent diethyl ether. Formation of compound **4a** in moderate yield under these conditions is in contrast to that observed in cyclohexane[5] where no intermolecular C–H-insertion products are formed, but can be reasonably interpreted in terms of the activation of the C–H bonds of the ether by oxygen[8] [eqn. (1)].



Formation of compound **4a** was dramatically increased at the almost complete expense of the benzofuran **3a**, when the irradiation was carried out in the ether matrix at −196 °C. The dramatic increase in yield of adduct **4a** is explained as indicating that tunnelling of a hydrogen atom from the matrix ether to the triplet state of carbene **2a** comes to compete with the singlet reaction as the reaction temperature is lowered.[9] Thus, as the reaction temperature is lowered and the phase becomes solid, tunnelling of a hydrogen atom from the matrix ether to the triplet **2a**, which is in equilibrium with the singlet, becomes important and competes efficiently with the singlet reaction. Supposing that both products **3** and **4** are formed mostly from the singlet in the liquid phase at room temperature, the dramatic increase in the formation of compounds **4** in the rigid matrix indicates that intermolecular H-atom tunnelling from the solvent ether dominates over intramolecular reaction from the ether at the *ortho* position.

A very different reaction pattern was observed when an alkyl group was introduced at the 3-position. Thus, irradiation of 2-methoxy-3-methyldiphenyldiazomethane **1b** in diethyl ether at 10 °C produced the benzofuran **3b** almost exclusively. The intermolecular C–H-insertion product **4b** was not formed even when the irradiation was carried out in the diethyl ether matrix at −196 °C. Essentially the same trends were observed in the photolysis of substrates **1c** and **1d**. This was rather surprising since it is now generally accepted, for carbenes with triplet ground states, that low-temperature solid-state conditions dramatically enhance the yields of formal C–H-insertion adducts between the carbene and the matrix host as a result of quantum mechanical hydrogen-atom tunnelling.[9]

The results are, however, reasonably understood in terms of the buttressing effect of the 3-alkyl group on the relative populations of the rotational isomers of the carbenes **2**. Thus, the nascent carbene **2a** generated from substrate **1a** would be the *s-trans* rotational isomer because of the steric repulsion between the methoxy and diazo groups in the precursory diazo compound. This conformer would undergo either intermolecular reaction leading to adduct **4** or rotational isomerization to the other, s-*cis*, conformer where intramolecular C–H insertion forming the benzofuran **3a** is feasible. In the diazomethanes having a 3-alkyl group (*e.g.*, compounds **1b–d**), the methoxy methyl group should not be lying in the plane of the phenyl ring due to the steric repulsion not only from the diazo group but also from the alkyl group. In a nascent carbene which has the best geometry and the conformation dictated by those of the precursor, the carbene centre is blocked more effectively by the twisted methyl group from attack of the external substrate compared with that in the nascent carbene **2a**. Moreover, the methyl group is forced to rotate around the C–O bond of the ether against the alkyl group toward the vacant space left after N_2 elimination. In other words, the carbenes generated from substrates **1b–d** take the conformation s-*cis*-**2** almost instantaneously before any reaction can take place, and are forced to react with the proximate methoxy methyl group.*

Exclusive formation of benzofurans **3b–d** even in the rigid matrix at −196 °C initially seemed surprising but can also be reasonably explained in terms of the buttressing effect. Thus, owing to the rapid cooling in the matrix, the diazomethanes did not have time to accommodate themselves to the geometrical requirements imposed by the matrix and were frozen in the most favourable conformer in the fluid state where the methoxy methyl group is twisted out of the plane of the phenyl group. In nascent carbenes generated photolytically in matrices, the carbene centre is blocked effectively by the twisted methyl group since rotational isomerization is retarded due to the rigidity of the matrix. The rate of H-atom tunnelling from the solvent ether will be decreased since the distance the H-atom must tunnel from the matrix to the carbene centre will be increased, whereas H-atom tunnelling from the ether in the *ortho* position will be greatly favoured since the methoxy methyl group is located near the carbene centre at genesis.[10] Alternatively, the buttressed carbenes **2b–d** undergo direct intramolecular C–H insertion, forming benzofurans **3** without suffering from quantum mechanical tunnelling at least over the range of temperatures examined.

Irradiation of Diazomethanes **1** *in Methanol.*—In order to obtain more information concerning the buttressing effects in carbene chemistry, we generated the carbenes **1** in methanol which is known as one of the most reactive reagents toward carbenes. The reactivities of carbenes **1** in methanol at different temperatures clearly reflect the sensitivity of the buttressing effect to the steric factors of the 3-alkyl group (Table 2). Thus,

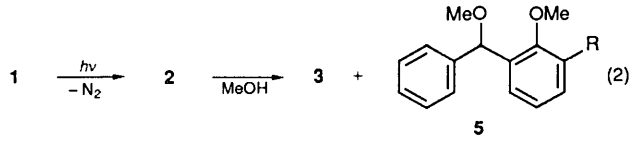
* A referee suggested the possibility of the substituted benzene ring being twisted out of planarity. This bending of the benzene ring would mitigate the buttressing effect of the 3-alkyl group, but presumably the extent of the twist would not be so large as to release all the steric repulsion between the substituents. We thank the referee for this suggestion.

Table 2 Product distributions obtained in photolysis of compounds **1** in methanol at 10 and −196 °C[a]

Substrate	R	T/°C	Product distribution (%)[b] 3	5
1a	H	10	<1	>99
		−196	9.1	90.9[c]
1b	Me	10	2.4	97.6
		−196	76.7	23.3[d]
1c	Pr^i	10	1.9	98.1
		−196	92.9	7.1[d]
1d	Bu^t	10	5.6	94.4
		−196	95.8	4.2[d]

[a,b] See footnotes *a*, *b* in Table 1. [c] C–H-insertion adduct with methanol (15.3%) included. [d] Only trace amounts of the C–H-insertion adducts with methanol were detected by GCMS.

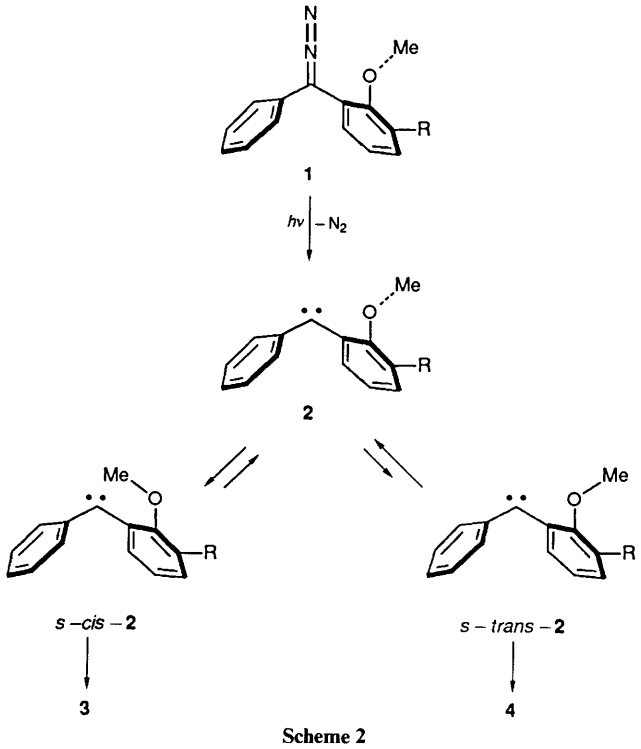
irradiation of substrate **1a** in methanol at 10 °C produced methyl (2-methoxydiphenylmethyl) ether **5a**, probably formed as a result of the insertion of carbene **2a** into the O–H bond of the alcohol at the almost complete expense of formation of the benzofurans **3a**. The generation of carbene **2a** in methanol matrix at −196 °C resulted in a significant increase in products from insertion into the C–H bonds of the methoxy group at the 2-position and the solvent methanol at the expense of the ether **5a** [eqn. (2)].



Similar but more intriguing trends were observed when the diazomethanes **1b–d** were photolysed in methanol at different temperatures. Thus, generation of the carbenes **2b–d** at 10 °C gave the ethers **5** as a major product along with small amounts of the benzofurans **3**, whose yield increased slightly, however, in going from carbenes **2a** to **2d**.

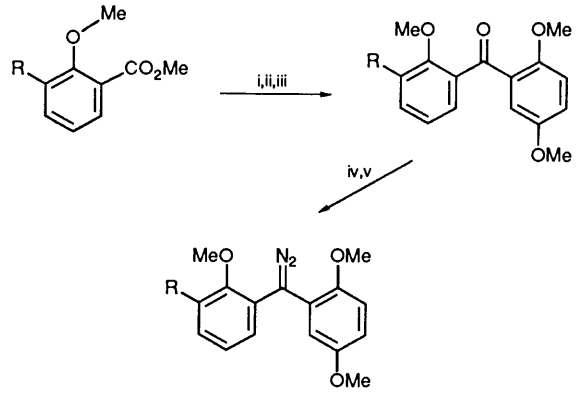
This trend became more obvious when the buttressed carbenes **2** were generated in methanol matrix where the corresponding benzofuran **3** was formed as the major product. Such a dramatic increase in the formation of product **3** again indicates that the carbenic centre of these carbenes is effectively blocked by the buttressed methyl group from the attack of the solvent, and that they are forced to react with the methyl group which is located above the carbenic centre at the instant of formation. The formation of benzofuran **3** in the matrix runs obviously increased in going from carbenes **2b** to **2d**. These trends in the product distribution are reasonably understood as indicating that the extent of buttressing is increased as one introduces more bulky groups in the 3-position. Thus, the methoxy methyl group is forced more severely to lie near the diazo group as more bulky groups are introduced in the 3-position. In a fluid state at 10 °C, most of the carbenes were trapped by the solvent alcohol before they underwent intramolecular C–H insertion. This is presumably because O–H insertion has a lower activation energy than does C–H insertion. Moreover, methanol can react with phenylcarbenes by protonation,[11] which is apparently a much less sensitive process to steric factors than that involving ylide intermediates or a direct O–H insertion process.[12] This explains why methanol acts as an efficient trapping reagent for these buttressed carbenes. In a matrix environment at −196 °C, however, O–H insertion became unfavourable presumably because solvation stabilizing a possible intermediate, *e.g.*, carbocations or ylides, became unimportant in the solid phase. Quantum mechanical H-atom tunnelling from C–H bonds of the matrix methanol to the triplet state of carbenes **2** is possible, but is not attained probably because of the large distance between the H-atom and the carbene centre which is effectively blocked by the buttressed methoxy group. Under these conditions, the carbenes are again forced to react with the methoxy methyl group which is hanging over the carbene centre, either by a direct-insertion mechanism or by quantum mechanical H-atom tunnelling.

The results mentioned above clearly indicate that the reaction patterns are affected by the buttressing substituents which fix the proximate reactive centre near the carbenic centre. In order to get deeper insight into the buttressing effect in this reaction system, we generated diphenylcarbenes **7** having two *ortho* methoxy groups expected to be attacked by the carbene centre, and examined the effect of the buttressing substituents on the reactivity of these two methoxy groups toward the carbene.



Scheme 2

Synthesis of 3-Alkyl-2,2′,5′-trimethoxydiphenyldiazomethanes **6**.—Precursory diazomethanes for the required carbene systems were prepared as summarized in Scheme 3, where hydroquinone



a; R = H; **b**; R = Me; **c**; R = Pr^i; **d**; R = Bu^t

Scheme 3 *Reagents:* i, $SOCl_2$; ii, $AlCl_3$, 1,4-$(MeO)_2C_6H_4$, $PhNO_2$, CCl_4; iii, MeI, NaOH; iv, N_2H_4·H_2O; v, $BaMnO_4$

Table 3 Product distributions obtained in photolysis of compound **6** in diethyl ether at 10 and −196 °C[a]

Substrate	R	T/°C	Product distribution (%)[b] 8	9	10
6a	H	10	37.3	24.5	8.2
		−196	4.1	5.6	90.3
6b	Me	10	<1	>98	<1
		−196	<1	>98	<1
6c	Pr^i	10	<1	>98	<1
		−196	<1	>98	<1
6d	Bu^t	10	<1	>98	<1
		−196	<1	>98	<1

[a,b] See footnotes *a*, *b* in Table 1.

Table 4 Product distributions obtained in photolysis of compound **6** in methanol at 10 and −196 °C[a]

Substrate	R	T/°C	Product distribution (%)[b] 8	9	11
6a	H	10	<1	>1	>98
		−196	<1	<1	>98[c]
6b	Me	10	<1	<1	>98
		−196	<1	77.5	22.5[d]
6c	Pr^i	10	<1	6.4	92.6
		−196	<1	88.9	10.1[d]
6d	Bu^t	10	<1	6.4	92.6
		−196	<1	>98	<1[d]

[a–d] See footnotes *a–d* in Table 2.

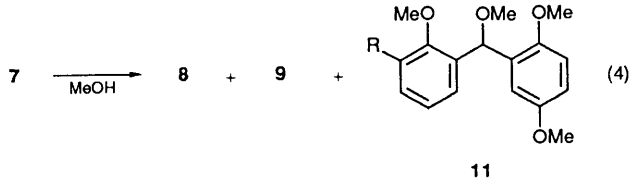
dimethyl ether was used instead of the benzene in Scheme 1. Oxidation of the resulting hydrazone proceeded equally smoothly (as in Scheme 1) when using $BaMnO_4$ to afford the diazomethanes **6** as rather stable, dark red oils. In order to avoid troublesome separation of possible undesired isomers which may be formed when using anisole instead of the dimethoxybenzene, the carbenes **7** which we examined in this study carry another methoxy group at the 5′-position in addition to the two methoxy groups at C-2 and C-2′. This facilitated the differentiation of the two dihydrobenzofurans formed by intramolecular C–H insertion into the two kinds of *ortho* methoxy groups.

Irradiation of Compounds **6** *in Diethyl Ether.*—Photolysis of diazo compound **6a** in degassed diethyl ether solution at 10 °C gave two kinds of dihydrobenzofuran (**8a** and **9a**) in roughly 1:1.5 ratio as the main products along with a small amount of the C–H-insertion adduct with the solvent ether (Table 3) [eqn. (3)]. The benzofurans are obviously formed by the intramolecular insertion of carbene **7a** into the C–H bonds of methoxy methyl groups either at the 2′- or 2-position. A slight but constant preference for the formation of product **9a** over **8a** is not explainable at present. Since inspection of molecular models suggested almost no difference in the steric environment between the two methoxy groups, an electronic effect exerted by the 5′-methoxy group should be taken into account to explain the observed product ratio. Presumably, a 5′-methoxy group might deactivate the C–H insertion into the 2′-methoxy methyl due to an inductive effect, although the effect on the carbenic electrophilicity or on the rate of rotational isomerization of the methoxy group around C–O bond may also be of importance. A considerable decrease in the formation of the solvent adduct **10a** compared with that observed in the reaction of carbene **2a** with the ether under similar conditions (see Table 1) is also noteworthy, and is interpreted as indicating that the carbenic centre in **7a** is sterically more crowded following introduction of one more methoxy group at the 2′-position and is thereby blocked from the attack of the external substrate compared with the situation in carbene **2a**.

A dramatic increase in the formation of the ether adduct **10a** at the expense of the benzofuran was, however, again observed when irradiation was carried out in the ether matrix at −196 °C. This is again explicable in terms of the quantum mechanical H-atom tunnelling from the matrix ether to the triplet state of carbene **7a**. A slight decrease in the proportion of the intermolecular C–H adducts in going from carbene **2a** to **7a** is again interpreted as reflecting the difference in steric crowding of the carbene centres between these two carbenes.

Introduction of alkyl substituents in the 3-position of the carbenes **7** again resulted in a dramatic change in the product distribution (Table 3). Thus, irradiation of the 3-alkyl-2,2′,5′-trimethoxydiphenyldiazomethanes **7b–d** produced the dihydrobenzofurans **9b–d** at the complete expense not only of the isomeric benzofurans **8b–d** but also of the solvent adducts **10b–d** regardless of the reaction temperatures and phases. Obviously the furans formed exclusively were those formed *via* intramolecular insertion of carbene into the C–H bonds of the methoxy group in the 2-position, which is buttressed by the 3-alkyl substituent, and only a trace amount of the other furan formed by the reaction with the methoxy group at the 2′-position was detected in each run. The results are similarly explained in terms of the buttressing effect of the 3-alkyl group on the relative population of rotational isomers of the carbene as advanced above.

Irradiation of Compounds **6** *in Methanol.*—Photolysis of compounds **6** in methanol gave essentially similar but much more obvious trends than those observed for the irradiation of compounds **1**. Thus, irradiation of compound **6a** in methanol at 10 °C afforded O–H-insertion product **11a** almost exclusively [eqn. (4)]. Both benzofurans were detected but only in trace



amounts by GC, but the benzofurans **9** formed by the reaction with the buttressed methoxy group appeared in sizeable yields on the introduction of more bulky buttressing groups in the 3-position (Table 4). The buttressing substituent-aided benzofurans **9** became major products when the carbenes **7** were generated in methanol matrix at −196 °C, where the yield of benzofurans **9** increased continuously in going from carbenes **7b** to **7c** to **7d**, which afforded compound **9a** almost exclusively. Almost exclusive formation of compound **9d** is in contrast with that observed for the carbene **2d** bearing a 3-t-butyl substituent as the buttressing group where the methanol adduct **5** was formed in sizeable amounts. This is, however, in accord with the expectation that the carbene centre in compound **9d** are almost completely blocked not only by the strongly buttressed 2-methoxy group but also by the additional methoxy substituent in the 2′-position even from the attack of a very reactive substrate, *e.g.* methanol.

Conclusions.—The reaction patterns of diphenylcarbenes bearing methoxy substituents are shown to be very sensitive to the 3-alkyl group, which buttresses the methoxy group to hang above the carbenic centre. The extent of buttressing is roughly proportional to the bulk of the 3-alkyl substituent, and in 3-t-butyl derivatives the carbene centre is almost completely covered by the *ortho* substituents so that it becomes unreactive even toward very reactive carbene-trapping reagents, *e.g.* methanol. Our findings not only provide insight into the role of the conformational isomers in the reaction course of the diphenylcarbenes, but also afford important hints for designing sterically crowded carbene systems. Protection of the carbenic centre by sterically bulky *ortho* substituents will be greatly enhanced by introduction of another bulky group at the 3-position, and the lifetime of such carbenes must be prolonged so as to survive for some time even at room temperature. Research along these lines is currently under progress in this laboratory.

Experimental

Materials.—*3-Alkyl-2-methoxybenzoic acid: general procedure.* To a vigorously stirred solution of a 2-alkylanisole (67 mmol) and tetramethylethylenediamine (10.05 cm^3, 67 mmol) in diethyl ether (200 cm^3), was added butyllithium (44.7 cm^3, 67 mmol; 1.6 mol dm^{-3} in hexane) slowly at 0 °C under argon. The lithiation mixture was stirred overnight and was poured onto solid CO_2. The mixture was opened to the atmosphere and allowed to evaporate overnight. The reaction mixture was acidified and the acid was extracted into diethyl ether and then into aq. $NaHCO_3$, from which it was re-extracted after acidification. The solvent was evaporated off to yield crude product which was washed with cold benzene and dried to give the benzoic acid.

3-Isopropyl-2-methoxybenzoic acid (67.4%), m.p. 65–67 °C; $\delta_H(CDCl_3)$ 1.23 (6 H, d, *J* 7 Hz, $CHMe_2$), 3.47 (1 H, sep, *J* 7 Hz, $CHMe_2$), 3.88 (3 H, s, OMe), 7.08 (1 H, dd, *J* 8 and 8 Hz, 5-H), 7.38 (1 H, dd, *J* 2 and 8 Hz, 4-H) and 7.76 (1 H, dd, *J* 2 and 8 Hz, 6-H).

3-t-Butyl-2-methoxybenzoic acid (60.1%), m.p. 118–120 °C; $\delta_H(CDCl_3)$ 1.41 (9 H, s, CMe_3), 3.91 (3 H, s, OMe), 6.92 (1 H, dd, *J* 8 and 8 Hz, 5-H), 7.40 (1 H, dd, *J* 2 and 8 Hz, 4-H) and 7.68 (1 H, dd, *J* 2 and 8 Hz, 6-H).

3-Alkyl-2-methoxybenzophenones: General Procedure.—To a 3-alkyl-2-methoxybenzoic acid (40 mmol) was added thionyl chloride (60 mmol) and the mixture was stirred at 50 °C for 2 h. Excess of thionyl chloride was evaporated off under reduced pressure to give the crude acid chloride, which was dissolved in anhydrous benzene (5 cm^3). The resulting solution was added slowly to a vigorously stirred mixture of anhydrous $AlCl_3$ (40 mmol) and benzene (20 cm^3) at room temperature and the reaction mixture was stirred for 2 h under gentle reflux. Usual work-up followed by distillation under reduced pressure gave 3-alkyl-2-hydroxybenzophenones, which were methylated with methyl iodide and NaOH in dimethyl sulphoxide.

2-Methoxy-3-methylbenzophenone (73.3%), b.p. 149–155 °C (0.7 mmHg); $\delta_H(CCl_4)$ 2.30 (3 H, s, *Me*Ar), 3.58 (3 H, s, OMe) and 6.90–7.80 (8 H, m, ArH); *m/z* 227 (M + 1, 19%), 226 (M^+, 32), 210 (39), 209 (48), 165 (30), 149 (81), 135 (52), 105 (66), 91 (75) and 78 (100).

3-Isopropyl-2-methoxybenzophenone (78.3%), b.p. 155–169 °C (0.7 mmHg); $\delta_H(CCl_4)$ 1.24 (6 H, d, *J* 7 Hz, $CHMe_2$), 3.33 (1 H, sep, *J* 7 Hz, $CHMe_2$), 3.56 (3 H, s, OMe) and 6.98–7.76 (8 H, m, ArH); *m/z* 255 (M + 1, 10%), 254 (M^+, 25) and 213 (100).

3-t-Butyl-2-methoxybenzophenone (35.4%), b.p. 138–145 °C (0.7 mmHg); $\delta_H(CCl_4)$ 1.34 (9 H, s, CMe_3), 3.72 (3 H, s, OMe) and 6.85–7.68 (8 H, m, ArH); *m/z* 268 (M^+, 9%), 253 (46), 211 (92), 135 (100) and 77 (62).

3-Alkyl-2,2′,5′-trimethoxybenzophenone: General Procedure.—These ketones were prepared using a similar procedure as described above using hydroquinone dimethyl ether as substrate and CCl_4–nitrobenzene (1:1) as solvent. The ketone was easily isolated from the solvent by distillation under reduced pressure after usual work-up.

2,2′,5′-Trimethoxybenzophenone (61.8%), b.p. 170–182 °C (1.0 mmHg); $\delta_H(CCl_4)$ 3.46 (3 H, s, OMe), 3.58 (3 H, s, OMe), 3.74 (3 H, s, OMe) and 6.64–7.44 (7 H, m, ArH); *m/z* 273 (M + 1, 16%), 272 (M^+, 88), 165 (45), 151 (75) and 135 (100).

2,2′,5′-Trimethoxy-3-methylbenzophenone (80.3%), b.p. 165–175 °C (0.2 mmHg); $\delta_H(CCl_4)$ 2.24 (3 H, s, MeAr), 3.50 (3 H, s, OMe), 3.54 (3 H, s, OMe), 3.76 (3 H, s, OMe) and 6.64–7.22 (6 H, m, ArH); *m/z* 287 (M + 1, 20%), 286 (M^+, 100), 165 (69), 152 (43), 151 (54), 150 (18), 149 (99) and 135 (62).

3-Isopropyl-2,2′,5′-trimethoxybenzophenone (69.3%), b.p. 170–178 °C (0.3 mmHg); $\delta_H(CCl_4)$ 1.22 (6 H, d, *J* 7 Hz, $CHMe_2$), 3.38 (1 H, sep, *J* 7 Hz, $CHMe_2$), 3.46 (3 H, s, OMe), 3.52 (3 H, s, OMe), 3.74 (3 H, s, OMe) and 6.65–7.26 (6 H, m, ArH); *m/z* 314 (M + 1, 21%), 314 (M^+, 100), 297 (22), 283 (19), 177 (24), 165 (88), 152 (54) and 151 (52).

3-t-Butyl-2,2′,5′-trimethoxybenzophenone (38.5%), b.p. 175–180 °C (0.3 mmHg); $\delta_H(CCl_4)$ 1.36 (9 H, s, CMe_3), 3.50 (3 H, s, OMe), 3.58 (3 H, s, OMe), 3.77 (3 H, s, OMe) and 6.67–7.33 (6 H, m, ArH); *m/z* 328 (M^+, 10%) and 57 (100).

Benzophenone Hydrazones.—The following hydrazones were prepared according to the procedure reported in the preceding paper.[5]

2-Methoxy-3-methylbenzophenone hydrazone (91.0%), δ_H (CCl_4) 2.32 (3 H, s, Me), 3.62 (3 H, s, OMe), 5.44 (2 H, br s, N_2H_2) and 6.86–7.54 (8 H, m, ArH).

3-Isopropyl-2-methoxybenzophenone hydrazone (88.7%), $\delta_H(CCl_4)$ 1.22 (6 H, d, *J* 8 Hz, $CHMe_2$), 3.36 (1 H, sep, *J* 8 Hz, $CHMe_2$), 3.60 (3 H, s, OMe), 5.44 (2 H, br s, N_2H_2) and 6.78–7.50 (8 H, m, ArH).

3-t-Butyl-2-methoxybenzophenone hydrazone (73.3%), δ_H (CCl_4) 1.21 (9 H, s, CMe_3), 3.60 (3 H, s, OMe), 5.10 (2 H, br s, N_2H_2) and 6.83–7.32 (8 H, m, ArH).

2,2′,5′-Trimethoxybenzophenone hydrazone (80.5%), m.p. 101–104 °C; $\delta_H(CCl_4)$ 3.50–3.88 (9 H total, 6 s, OMe), 5.60 (2 H, br s, N_2H_2) and 6.72–7.56 (7 H, m, ArH).

2,2′,5′-Trimethoxy-3-methylbenzophenone hydrazone (68.9%), $\delta_H(CCl_4)$ 3.30–3.74 (9 H total, 6 s, OMe), 5.66 (2 H, br s, N_2H_2) and 6.56–7.20 (6 H, m, ArH).

3-Isopropyl-2,2′,5′-trimethoxybenzophenone hydrazone (73.2%), m.p. 91–98 °C; $\delta_H(CCl_4)$ 1.26 (6 H, d, *J* 7 Hz, $CHMe_2$), 3.28 (3 H, s, OMe), 3.30 (1 H, sep, *J* 7 Hz, $CHMe_2$), 3.75 (3 H, s,

OMe), 3.78 (3 H, s, OMe), 5.66 (2 H, br s, N_2H_2) and 6.60–7.13 (6 H, m, ArH).

3-t-Butyl-2,2′,5′-trimethoxybenzophenone hydrazone (74.0%), m.p. 85–96 °C; $\delta_H(CCl_4)$ 1.40 (9 H, s, CMe_3), 3.27 (3 H, s, OMe), 3.79 (6 H, s, OMe), 5.67 (2 H, br s, N_2H_2) and 6.66–7.24 (6 H, m, ArH).

Diphenyldiazomethanes.—The following diazomethanes were prepared according to the procedure reported in the preceding paper.[5] $BaMnO_4$ was used instead of HgO as oxidation reagent.

2-Methoxy-3-methylphenyl(phenyl)diazomethane **1b** (78.0%),$\delta_H(CCl_4)$ 2.32 (3 H, s, Me), 3.68 (3 H, s, OMe) and 6.80–7.60 (8 H, m, ArH); ν_{max}/cm^{-1} 2050.

3-Isopropyl-2-methoxyphenyl(phenyl)diazomethane **1c** (95.7%), $\delta_H(CCl_4)$ 1.25 (6 H, d, *J* 8 Hz, $CHMe_2$), 3.38 (1 H, sep, *J* 8 Hz, $CHMe_2$) and 3.68–7.30 (8 H, m, ArH); ν_{max}/cm^{-1} 2050.

3-t-Butyl-2-methoxyphenyl(phenyl)diazomethane (91.2%), $\delta_H(CCl_4)$ 1.30 (9 H, s, CMe_3), 3.82 (3 H, s, OMe) and 6.76–7.24 (8 H, m, ArH); ν_{max}/cm^{-1} 2060.

2,5-Dimethoxyphenyl(2′-methoxyphenyl)diazomethane **6a** (98.3%), $\delta_H(CCl_4)$ 3.62 (3 H, s, OMe), 3.72 (3 H, s, OMe), 3.78 (3 H, s, OMe) and 6.56–7.20 (7 H, m, ArH); ν_{max}/cm^{-1} 2050.

2,5-Dimethoxyphenyl(2′-methoxy-3′-methylphenyl)-diazomethane **6b** (68%), $\delta_H(CCl_4)$ 2.28 (3 H, s, Me), 3.60 (3 H, s, OMe), 3.68 (3 H, s, OMe), 3.72 (3 H, s, OMe) and 6.50–7.10 (6 H, m, ArH); ν_{max}/cm^{-1} 2050.

2,5-Dimethoxyphenyl(3′-isopropyl-2′-methoxyphenyl)-diazomethane **6c** (97.7%), $\delta_H(CCl_4)$ 1.24 (6 H, d, *J* 8 Hz, $CHMe_3$), 3.35 (1 H, sep, *J* 8 Hz, $CHMe_2$), 3.67 (3 H, s, OMe), 3.77 (3 H, s, OMe), 3.78 (3 H, s, OMe) and 6.53–7.04 (6 H, m, ArH); ν_{max}/cm^{-1} 2060.

3-t-Butyl-2-methoxyphenyl(2′,5′-dimethoxyphenyl)-diazomethane **6d** (85.4%), $\delta_H(CCl_4)$ 1.38 (9 H, s, CMe_3, 3.61 (3 H, s, OMe), 3.75 (3 H, s, OMe), 3.77 (3 H, s, OMe) and 6.40–7.16 (6 H, m, ArH); ν_{max}/cm^{-1} 2055.

Irradiation of Diazo Compounds **1** *and* **6** *in Diethyl Ether at* 10 °C.—Irradiation was carried out as described in the preceding paper[5] and the following dihydrobenzofurans were isolated by preparative TLC (PLC).

7-Methyl-3-phenyldihydrobenzofuran **3b**, $\delta_H(CCl_4)$ 2.22 (3 H, s, Me), 4.20–4.88 (3 H, m, $CHCH_2$) and 6.54–7.16 (8 H, m, ArH); *m/z* 211 (M + 1, 17%), 210 (M^+, 100), 209 (M − 1, 43), 195 (41), 165 (22) and 105 (16).

7-Isopropyl-3-phenyldihydrobenzofuran **3c**, $\delta_H(CCl_4)$ 1.28 (6 H, d, *J* 7 Hz, $CHMe_2$), 3.11 (1 H, sep, *J* 7 Hz, $CHMe_2$), 4.23–4.93 (3 H, m, $CHCH_2$) and 6.65–7.47 (8 H, m, ArH); *m/z* 239 (M + 1, 15%), 238 (M^+, 83), 237 (M − 1, 2) 223 (100), 195 (17), 145 (23) and 81 (43).

7-Butyl-3-phenyldihydrobenzofuran **3d**, $\delta_H(CCl_4)$ 1.29 (9 H, s, CMe_3), 4.26 (1 H, dd, *J* 7 and 7 Hz, $CHCH_2$), 4.55 (1 H, dd, *J* 7 and 9 Hz, HC*H*CH), 4.79 (1 H, dd, *J* 7 and 9 Hz, *H*CHCH) and 6.62–7.25 (8 H, m, ArH); *m/z* 253 (M + 1, 11%), 252 (M^+, 62), 237 (100), 195 (30), 167 (15) and 119 (36).

5-Methoxy-3-(2-methoxyphenyl)dihydrobenzofuran **8a**, δ_H (CCl_4) 3.58 (3 H, s, OMe), 3.64 (3 H, s, OMe), 4.26–4.28 (3 H, m, $CHCH_2$) and 6.44–7.12 (7 H, m, ArH); *m/z* 257 (M + 1, 16%), 256 (M^+, 100), 241 (9), 225 (23), 213 (13), 181 (10), 152 (11) and 91 (18).

3-(2,5-Dimethoxyphenyl)dihydrobenzofuran **9a**, $\delta_H(CCl_4)$ 3.74 (3 H, s, OMe), 3.80 (3 H, s, OMe), 4.68–5.02 (3 H, m, $CHCH_2$) and 6.40–7.12 (7 H, m, ArH); *m/z* 257 (M + 1, 17%), 256 (M^+, 100), 241 (9), 225 (15), 121 (13), 107 (15) and 91 (16).

3-(2,5-Dimethoxyphenyl)-7-methyldihydrobenzofuran **9b**, $\delta_H(CCl_4)$ 2.20 (3 H, s, Me), 3.60 (3 H, s, OMe), 3.78 (3 H, s, OMe), 4.15 (1 H, dd, *J* 7 and 7 Hz, $CHCH_2$), 4.59 (1 H, dd, *J* 7 and 9 Hz, HC*H*CH), 4.86 (1 H, dd, *J* 7 and 9 Hz, HC*H*CH) and 6.40–7.86 (6 H, m, ArH); *m/z* 271 (M + 1, 18%), 270 (M^+, 100), 255 (16), 239 (18), 167 (77) and 165 (22).

3-(2,5-Dimethoxyphenyl)-7-isopropyldihydrobenzofuran **9c**, $\delta_H(CCl_4)$ 1.26 (6 H, d, *J* 7 Hz, $CHMe_2$), 3.10 (1 H, sep, *J* 7 Hz, $CHMe_2$), 3.59 (3 H, s, OMe), 3.76 (3 H, s, OMe), 4.14–4.30 (1 H, m, $CHCH_2$), 4.70–5.02 (2 H, m, $CHCH_2$) and 6.46–6.96 (6 H, m, ArH); *m/z* 299 (M + 1, 21%), 298 (M^+, 100), 283 (14), 255 (98), 142 (17) and 91 (37).

7-t-Butyl-3-(2,5-dimethoxyphenyl)dihydrobenzofuran **9d**, $\delta_H(CCl_4)$ 1.36 (9 H, s, CMe_3), 3.59 (3 H, s, OMe), 3.76 (3 H, s, OMe), 4.16–4.34 (1 H, m, $CHCH_2$), 4.72–4.98 (2 H, m, $CHCH_2$) and 6.46–7.01 (6 H, m, ArH); *m/z* 313 (M + 1, 22%), 312 (M^+, 100), 297 (74), 255 (84), 159 (32), 151 (27), 149 (27), 135 (33) and 127 (40).

Irradiation of Diazo Compounds **1** *and* **6** *in Diethyl Ether at* −196 °C.—Irradiation was carried out as described in the preceding paper[5] and the following ether adducts were isolated by PLC.

Ethyl 2-(2-methoxyphenyl)-1-methyl-2-phenylethyl ether **4a**, $\delta_H(CCl_4)$ 1.19 (3 H, t, *J* 7 Hz, CH_2Me), 1.33 (3 H, d, *J* 6 Hz, CHMe), 3.30 (2 H, q, *J* 7 Hz, CH_2Me), 3.60 (3 H, s, OMe), 3.50–3.82 (2 H, m, CHCH) and 6.83–7.30 (9 H, m, ArH); *m/z* 270 (M^+, 20%), 198 (24) and 73 (100).

2-(2,5-Dimethylphenyl)-2-(2-methylphenyl)-1-methylethyl ethyl ether **10a**, $\delta_H(CCl_4)$ 1.23 (3 H, t, *J* 7 Hz, CH_2Me), 1.32 (3 H, d, *J* 6 Hz, CHMe), 3.28 (2 H, m, CH_2Me), 3.52–3.88 (9 H, 6 s, OMe) and 6.60–7.20 (7 H. m, ArH); *m/z* 330 (M^+, 12%), 257 (31) and 121 (100).

Irradiation of Diazo Compounds **1** *and* **6** *in Methanol at* 10 °C.—Irradiation was carried out as described in the preceding paper[5] and the following methyl ethers were isolated almost quantitatively by PLC.

2-Methoxy-3-methylphenyl(phenyl)methyl methyl ether **5b**, $\delta_H(CCl_4)$ 2.22 (3 H, s, MeAr), 3.28 (3 H, s, OMe), 3.56 (3 H, s, OMe), 5.48 (1 H, br s, C*H*OMe) and 6.67–7.20 (8 H, m, ArH); *m/z* 242 (M^+, 22%), 227 (67), 210 (17), 209 (22), 195 (32), 165 (27), 149 (15), 121 (31), 105 (35) and 91 (100).

3-Isopropyl-2-methoxyphenyl(phenyl)methyl methyl ether **5c**, $\delta_H(CCl_4)$ 1.25 (6 H, d, *J* Hz, $CHMe_2$), 3.30 (1 H, sep, *J* 7 Hz, $CHMe_2$), 3.37 (3 H, s, OMe), 3.64 (3 H, s, OMe), 5.60 (1 H, br s, C*H*OMe) and 6.81–7.42 (8 H, m, ArH); *m/z* 270 (M^+, 20%), 255 (76), 223 (49), 121 (31), 105 (30), 91 (100) and 77 (28).

3-t-Butyl-2-methoxyphenyl(phenyl)methyl methyl ether **5d**, $\delta_H(CCl_4)$ 1.39 (9 H, s, CMe_3), 3.31 (3 H, s, OMe), 3.62 (3 H, s, OMe), 3.72 (3 H, s, OMe), 3.76 (3 H, s, OMe), 5.82 (1 H, 6 s, C*H*OMe) and 6.60–7.16 (6 H, m, ArH); *m/z* 284 (M^+, 47%), 269 (43), 253 (36), 252 (35), 239 (23), 237 (60), 227 (100), 195 (45), 177 (27) and 147 (55).

2,5-Dimethylphenyl(2-methylphenyl)methyl methyl ether **11a**, $\delta_H(CCl_4)$ 3.28 (3 H, s, CHOMe), 3.66 (3 H, s, OMe), 3.68 (3 H, s, OMe), 3.76 (3 H, s, OMe), 5.84 (1 H, s, C*H*OMe) and 6.60–7.20 (7 H, m, ArH); *m/z* 288 (M^+, 82%), 257 (29), 165 (18), 151 (51), 135 (26), 121 (100) and 91 (24).

2,5-Dimethylphenyl(2-methoxy-3-methylphenyl)methyl methyl ether **11b**, $\delta_H(CCl_4)$ 2.26 (3 H, s, MeAr), 3.30 (3 H, s, OMe), 3.66 (6 H, s, OMe), 3.72 (3 H, s, OMe), 5.80 (1 H, s, C*H*OMe) and 6.60–6.92 (6 H, m, ArH); *m/z* 302 (M^+, 87%), 287 (13), 271 (36), 181 (19), 165 (39), 151 (100), 149 (34), 135 (37), 121 (29) and 105 (25).

2,5-Dimethylphenyl(3-isopropyl-2-methoxyphenyl)methyl methyl ether **11c**, $\delta_H(CCl_4)$ 1.23 (6 H, d, *J* 7 Hz, $CHMe_2$), 3.23 (1 H, sep, *J* 7 Hz, $CHMe_2$), 3.30 (3 H, s, OMe), 3.64 (3 H, s, OMe), 3.67 (3 H, s, OMe), 3.70 (3 H, s, OMe), 5.84 (1 H, br s, C*H*OMe$_3$) and 6.48–7.10 (6 H, m, ArH); *m/z* 330 (M^+, 80%), 315 (14), 299 (44), 283 (10), 255 (39), 181 (19), 177 (20), 165 (39), 151 (100), 121 (31) and 91 (30).

3-t-Butyl-2-methoxyphenyl(2,5-dimethoxyphenyl)methyl methyl ether **11d**, $\delta_H(CCl_4)$ 1.39 (9 H, s, CMe_3), 3.31 (3 H, s, OMe), 3.62 (3 H, s, OMe), 3.72 (3 H, s, OMe), 3.76 (3 H, s, OMe), 5.82 (1 H, br s, C*H*OMe) and 6.60–7.16 (6 H, m, ArH); *m*/*z* 344 (M^+, 63%), 329 (12), 313 (37), 297 (18), 255 (17), 191 (10), 181 (19), 165 (26), 151 (100), 121 (28), 105 (13) and 91 (17).

Irradiation for Analytical Purposes.—All irradiations outlined in Tables 1–4 were carried out in a Pyrex tube of 5.0 cm^3 capacity as described in the preceding paper.[5]

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