
Reactivities of Methoxycarbonylphenylcarbenes Generated by Flash Vacuum Pyrolysis

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Whilst flash vacuum pyrolysis of *p*-, *m*-, and *o*-methoxycarbonylphenyldiazomethanes gave 3-methylphthalide and 2-methoxybenzocyclobutenone, neither product could be detected in the pyrolysis of methyl α -diazophenylacetate.

Much attention has been paid to the interconversion of substituted phenylcarbenes in which a divalent carbon is transmitted to the position where intramolecular reactions are accessible.¹ Thus, the isomeric tolylmethylenes interconvert by a carbene-to-carbene rearrangement mechanism, and they react with the methyl substituent *via* a hydrogen shift to produce, ultimately, benzocyclobutene and styrene.² Although the rearrangement can serve as a way of delivering a divalent carbon from one site to another through a benzene ring, it has not yet been exploited. For example, most substituents employed for such studies have been alkyl groups and therefore carbene is trapped by intramolecular C-H bonds. Moreover the mechanism of the interconversion still continues to plague organic chemists.^{3,4} We report here that a divalent carbon can be delivered through a conduit of benzene rings bearing methoxycarbonyl groups

which not only traps carbene quite efficiently to afford the products derived from the intramolecular carbonyl ylide intermediate, but also sheds some light on the long-standing question^{3,4} of whether a common intermediate is involved in the interconversion.

o-Methoxycarbonylphenyldiazomethane (**1a**) was pyrolyzed at 350–450 °C, and chromatographic separation of the pyrolysate on silica gel afforded 3-methylphthalide (**2**)⁵ and 2-methoxybenzocyclobutenone (**3**). The structure of the new ketone (**3**) was determined on the basis of i.r. and ¹³C n.m.r. spectroscopic evidence.† In addition, the benzocyclobutenone framework

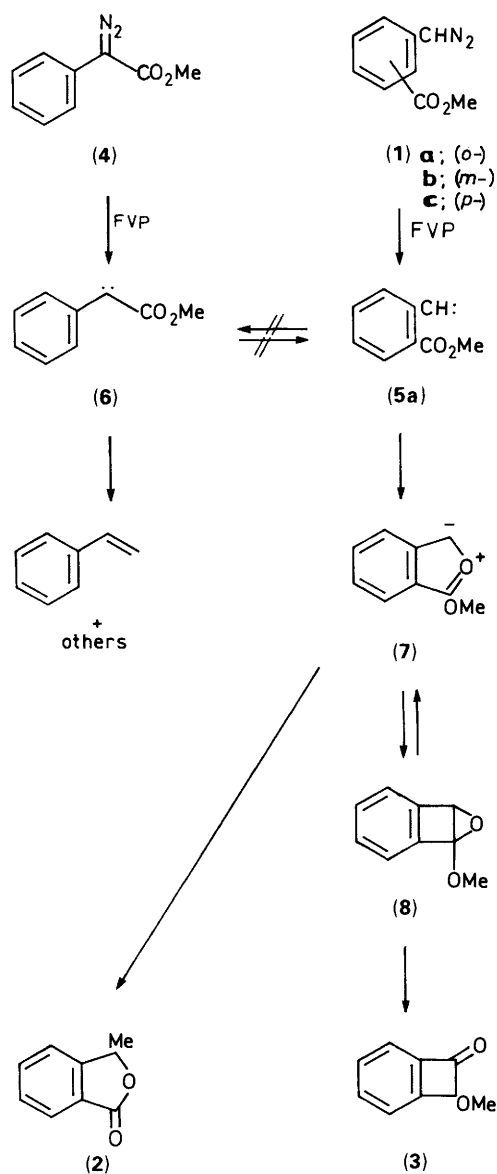
† 2-Hydroxybenzocyclobutenone and its trimethylsilyl derivative have been reported.⁶

was confirmed by the irradiation of (3) in methanol to give methyl (*o*-methoxymethyl)benzoate.* Similar pyrolysis of the *meta*-(1b) and *para*-(1c) isomers of the diazomethane also afforded the products (2) and (3) although the ratio changed significantly (*vide infra*).

In contrast, neither of the two products (2) and (3) could be detected in the pyrolysis of methyl α -diazophenylacetate (4) at 300–450 °C. The chromatographic analysis revealed that the pyrolysate comprised of styrene, benzaldehyde, acetophenone, and methyl phenylacetate, though the overall yield of these products was not 20%.† Not all the products formed by the pyrolysis of (4) could be detected in the reaction of the methoxycarbonylphenyldiazomethanes (1). The results show that interconversion between (5a) and (6) is not attained in both directions.

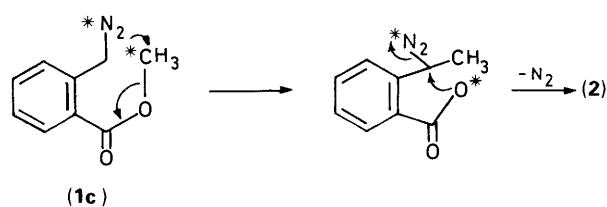
The formation of (2) and (3) is rationalized by the transient formation of the carbonyl ylide (7) derived from the intramolecular reaction of the carbene with the carbonyl oxygen. Hamaguchi and Iyata confirmed the intermediacy of (7) in the Cu-catalyzed decomposition of (1a),⁹ though the formation of (2) or (3) has never been reported in the thermolysis or the photolysis of (1a) in solution.‡ The migration of the methyl group in the ylide (7) would lead to 3-methylphthalide (2), and the isomerization of (7) to the oxirane (8)§ followed by the hydrogen migration would afford benzocyclobutenone (3). The formation of the same products from *m*- (1b) and *p*-methoxycarbonylphenyldiazomethane (1c) suggests that the methoxycarbonyl group is intact in the course of the phenylcarbene rearrangement.

The results summarized in the Table clearly indicate that the total yield as well as the ratio of the two products vary significantly with the reaction temperature and the precursor. Thus, the ratio of (2) to (3) tends to increase at higher reaction temperature. This is apparently attributable to the thermal lability of (3). Control experiments showed that (3) was less stable than (2) but that (2) and (3) did not interconvert under the reaction conditions. More importantly, the thermolysis of *o*-methoxycarbonylphenyldiazomethane (1a) produces a higher fraction of (2) over (3) than the *meta*- and *para*-isomers. Such anomalous product ratios from the *ortho*-isomer has been also noted in the thermolysis of the isomeric tolyldiazomethanes; the *ortho*-isomer gives nearly three times as much benzocyclobutene as styrene, while from *meta*- and *para*-isomers the ratio is *ca.* 0.8.¹⁰ Admitting that benzocyclobutene is derived from *o*-tolylmethylene while styrene from α -methylphenylmethylene, several mechanisms in which *p*- and *m*-tolylmethylenes rearrange to α -methylphenylmethylene without recourse to the *ortho*-isomer have been proposed³ to accommodate the experimental observation. The present results cannot be



Scheme.

explained by any of these mechanisms since both (2) and (3) are apparently derived from the *ortho*-isomer, but can be best explained by that of Chapman⁴ who proposed that *o*-tolylidiazomethane can 'leak away' to benzocyclobutene without passing through *o*-tolylmethylene as a result of facile hydrogen atom transfer in the diazomethane. A mechanism which can explain the formation of (2) from (1c) is shown in equation (1). Thus, a diazo carbon atom of (1c) attacks the neighbouring methyl group to expel the carboxylate group which, in turn, attacks the resulting diazo carbon to form (2). It



* The photochemical cleavage of benzocyclobutenone has been observed.⁷

† The dimeric compounds such as biphenyl, diphenylmethane, and 1,2-diphenylethane were also detected in the pyrolysate. The reaction pathway for the carbene (6) to give a number of products has not been thoroughly revealed, though the formation of styrene and acetophenone are explicable according to the mechanism described for biscarbomethoxy-carbene.⁸

‡ For example, the photolysis of (1a) in cyclohexane produces phthalide (63%) and methyl *o*-methylbenzoate (18%).

§ (a) Recently we have characterized the carbonyl ylide (7) and its photoisomerization to the oxirane (8) by the use of matrix isolation techniques: S. Murata, Y. Ohtawa, and H. Tomioka, *Chem. Lett.*, 1989, 853. (b) Since there are two oxygens on the ester and either might participate in the ylide formation, compounds (2) and (3) can be produced with economy and without the long-range migration of the methyl group, if the other ylide is formed. We are not able to eliminate this possibility since the less stable intermediate may be generated at a high temperature.

Table. Yield of products of methoxycarbonylphenyldiazomethane pyrolysis^a

Substrate	Temp. (°C)	Yield (%) ^b		Ratio (2):(3)
		(2)	(3)	
(1a)	350	45	21	2.1
	400	38	10	3.8
	450	41	8	5.1
(1b)	350	4	5	0.8
	400	7	4	1.8
	450	19	12	1.6
(1c)	350	5	7	0.7
	400	11	6	1.8
	450	19	13	1.5

^a Pyrolysis was carried out by passage through a 350–450 °C quartz tube at 10⁻⁵ Torr. ^b Determined by g.c. The averages of triplicate runs; reproducibility was <5%.

should be noted here that the thermal decomposition of the diazo compounds is greatly enhanced by adding electrophile, e.g., alcohol,¹¹ azodicarboxylate,¹² and nitrosobenzene¹² presumably due to the formation of diazonium ion as a result of electrophilic attack on the diazo carbon. This means that electrophilic attack by the methyl group on the diazo carbon followed by the attack of carboxylate group and elimination of nitrogen occurring simultaneously in the resulting diazonium ion would be an attractive pathway. However, other pathways involving a neutral intermediate, e.g., radical, are equally reasonable since a zwitterionic form of the diazo group may be less likely in the gas phase than in the liquid phase.

Experimental

Flash Vacuum Pyrolysis of Methoxycarbonylphenyldiazomethane (1).—The sodium salt of methoxycarbonylbenzaldehyde tosylhydrazone (30 mg) (prepared by the reaction of the tosylhydrazone and sodium hydride in dry THF) was heated at 80 °C. The resulting diazomethane was directly passed through a 350–450 °C quartz tube packed with glass wool (25 cm × int. diam. 28 mm) at 10⁻⁵ Torr, and the volatile products were collected in a receiver cooled with liquid nitrogen. The products on the receiver were washed off with acetone. The

yields shown in the Table were obtained by the use of gas chromatography. The pyrolysis of (1a) (200 mg) at 350 °C, followed by preparative t.l.c. separation [silica, light petroleum–ether (19:1)], afforded 3-methylphthalide (2) (40%)⁵ and 2-methoxybenzocyclobutenone (3) (16%) as a colourless oil; *m/z* (%) 148 (*M*⁺, 5), 133 (*M*⁺ – CH₃, 100), 119 (32), and 105 (27); *v*_{max.} (neat) 1 770 cm⁻¹ (CO); δ(CDCl₃) 3.55 (3 H, s), 5.59 (1 H, s), and 7.4–7.6 (4 H, m); δ_C(CDCl₃) 57.0, 93.2, 121.5, 124.3, 131.4, 135.5, 147.7, 156.0, and 190.2 p.p.m.

Acknowledgements

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