

Formation of Heptafulvene in Reactions of [(Methoxycarbonyl)methyl]phenylcarbene in the Gas Phases

Hideo Tomioka* and Kohji Taketsuji

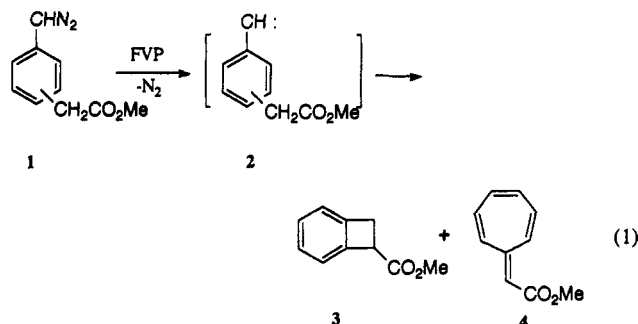
Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan

Received April 30, 1993

Summary: Flash vacuum pyrolysis of [(methoxycarbonyl)methyl]phenyl]diazomethanes produced 1-(methoxycarbonyl)benzocyclobutene, as a result of intramolecular C-H insertion in the ortho isomer of [(methoxycarbonyl)methyl]phenyl]carbene generated by carbene-carbene rearrangement, and 8-(methoxycarbonyl)heptafulvene, presumably formed by intramolecular H migration in the seven-membered ring intermediates involved in the rearrangement.

Much attention has been paid to the interconversion of aromatic carbenes (e.g. cycloheptatrienyldiene) and arylcarbenes (e.g., phenylcarbene) since its discovery not only from the synthetic viewpoint but also from the standpoint of mechanism.¹ The rearrangement has permitted the straightforward synthesis of organic compounds which are mostly otherwise not readily obtained, and the mechanism of rearrangement still continues to plague organic chemists. Although the rearrangement can serve as means of delivering a divalent carbon from one site to another through a benzene ring, its potential has not yet been fully exploited. For example, most substituents employed for such studies have been alkyl groups, and therefore the carbene is trapped mostly by intramolecular C-H bonds. Carbenes can interact more effectively with other functional groups, especially those bearing such heteroatoms as oxygen and nitrogen.² In this light, we generated a phenylcarbene bearing an alkoxy carbonyl group in the gas phase at high temperature and found that the alkoxy carbonyl group not only survived intact during the course of the phenylcarbene rearrangement, but also interacted with the carbenic center to generate carbonyl as well as oxonium ylides which ultimately produced 3-alkylphthalide and 2-alkoxy-1(2*H*)-benzocyclobutene.³ As an extension of such studies, we generated a phenylcarbene containing a (methoxycarbonyl)methyl group under the same conditions and found in this case that the (methoxycarbonyl)methyl group not only trapped the carbenic center at the ortho position but also quenched the seven-membered ring intermediates involved in the rearrangement.

Flash vacuum pyrolysis (350 °C/10⁻⁵ Torr) of [*o*-(methoxycarbonyl)methyl]phenyl]diazomethane (*o*-1)⁴ afforded 1-(methoxycarbonyl)benzocyclobutene (3)⁵ as a sole isol-



able volatile product in 25% yield. Similar pyrolysis of the para isomer of 1,⁴ on the other hand, produced, in addition to 3 (8%), a new product (17%), which was assigned as 8-(methoxycarbonyl)heptafulvene (4).⁶ FVP of *m*-1⁴ also produced the same two products (3, 4% and 4, 5%) although the ratio was different from that obtained from the para isomer. The product identities were unambiguously proved by direct comparison with the authentic samples^{5,6} prepared independently.

The mechanism of the formation of 3 and 4 from 1 is an interesting question. The formation of the benzocyclobutene (3) as a common product from all the isomers suggested that the phenylcarbenes with a (methoxycarbonyl)methyl (MCM) group (2) generated by FVP of 1 undergo carbene-carbene rearrangement from the para to meta to ortho isomers of the carbenes, where the carbenic center is trapped by the proximate MCM group to produce 3. A mechanism for the formation of the benzocyclobutene (3) is either direct insertion of the carbene into the methylene C-H bonds of MCM or by way of 1,4 H migration followed by cyclization of the resulting *o*-quin-

(1) For reviews, see: (a) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* 1985, 41, 1479. (b) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980; Chapter 5, pp 115-163. (c) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. I, pp 263-320. (d) Jones, W. M. *Acc. Chem. Res.* 1977, 10, 353. (e) Jones, W. M. *Rearrangement in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, pp 95-160.

(2) For reviews, see: (a) Moss, R. A.; Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols 1 and 2. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (c) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; Chapter 4. (d) Regitz, M., Ed. *Methoden der Organischen Chemie* (Houben-Weyl); Thieme: Stuttgart, 1989; Vol. E19b.

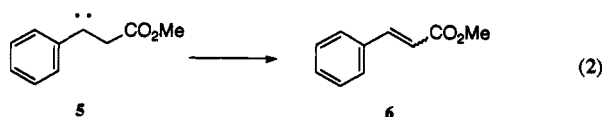
(3) Tomioka, H.; Kobayashi, N.; Murata, S.; Ohtawa, Y. *J. Am. Chem. Soc.* 1991, 113, 8771.

(4) All the diazomethanes (1) used in this study were prepared by following the essentially similar procedure of Creary (Creary, X. *Org. Synth.* 1985, 69, 207.) starting from methyl (formylphenyl)acetates. These diazomethanes were usually rather unstable and therefore generated *in situ* by pyrolysis of the sodium salt of (formylphenyl)acetate tosylhydrazide. The (formylphenyl)acetates were prepared as follows. Methyl (*p*-formylphenyl)acetate was prepared by the treatment of methyl phenylacetate with ClCH₂OMe/SnCl₄ to produce [*p*-(chloromethyl)phenyl]acetate which was then refluxed with hexamethylenetetramine in 5% AcOH-H₂O. (*m*-Formylphenyl)acetate was obtained by cyanation of methyl (*m*-bromophenyl)acetate with CuCN to afford (*m*-cyanophenyl)acetate which was then reacted with SnCl₄/HCl, followed by refluxing H₂O. (*o*-Formylphenyl)acetate was prepared according to the procedure of Jung by ozonization of 2-(trimethylsilyloxy)indene (Jung, M. E.; Brown, R. W.; Hagenah, J. A.; Strouse, C. E. *Tetrahedron Lett.* 1984, 25, 3659).

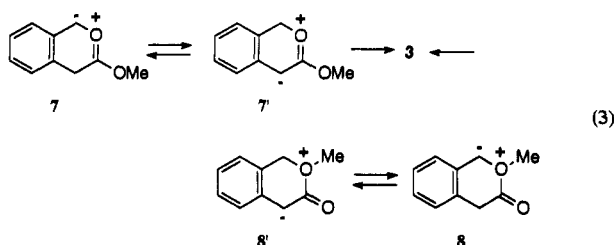
(5) The authentic benzocyclobutene (3) was prepared by photolysis of 2-diazo-1-indanone in benzene containing 5% MeOH: ¹H NMR (250MHz, CDCl₃) δ 3.47 (d, *J* = 4.2Hz, 2H), 3.74 (s, 3H), 4.31 (dd, *J* = 4.2, 3.9Hz, 1H); MS *m/e* (rel intensity) 162 (M⁺, 64.0), 131 (91.1), 103 (100), 91 (31.7), 77 (57.9). See: Kirmse, W.; Horner, L.; Muth, K. *Chem. Ber.* 1958, 91, 430.

(6) The authentic heptafulvene (4) was prepared according to the reported procedure by the treatment of methyl propylacetate with Ph₃C⁺BF₄⁻ followed by deprotonation with NEt₃; Oda, M.; Kitabara, Y. *Chem. Ind.* 1989, 920. The propylacetate was obtained from cycloheptatriene by way of tropylium tetrafluoroborate; Conrow, K. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 1138. Conrow, K. *J. Am. Chem. Soc.* 1959, 81, 5461. ¹H NMR (250 MHz, CDCl₃) 3.67 (s, 3H), 5.26 (s, 1H), 6.14-6.57 (m, 5H), 7.95 (d, *J* = 11.5Hz, 1H); MS *m/e* (rel. intensity) 162 (M⁺, 44.3), 131 (100), 105 (62.1), 77 (84.9).

odimethane.⁷ It is important to note here that no products expected to be formed from α -isomer of the carbene, i.e., phenyl[(methoxycarbonyl)methyl]carbene (5), such as



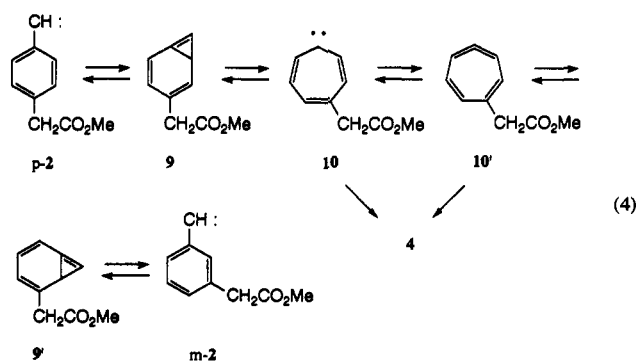
methyl cinnamates (6) were detected in the mixture. This implies that the ortho carbene is trapped by the MCM before it undergoes rearrangement to the α isomer. This is in sharp contrast with that observed with *o*-tolylmethylene which rearranges to phenylmethylcarbene in competition with benzocyclobutene formation¹ and is rather surprising since the C-H bonds of MCM must be less reactive toward carbene than methyl C-H bonds in the light of the electron-withdrawing nature of the CO₂Me group. It is also important to note here, in this connection, that no products apparently produced from the ylidic intermediates expected to be generated as a result of the interaction of the carbene with the MCM were also detected, while only ylidic products were obtained in the FVP reactions of [(methoxycarbonyl)phenyl]carbenes.³ It is very tempting then to propose that the benzocyclobutene (3) is formed via ylidic intermediates. There are two possible ylides, the carbonyl (7) and oxonium ylides (8). Conceptionally, it is possible to draw a



reasonable pathway to 3 starting from either of the ylides. Thus, proton migration to form a zwitterion (7' or 8') followed by the Stevens-type benzyl migration results in the formation of 3. A strong preference for benzyl over alkyl migration which is known to be characteristic of Stevens rearrangement⁸ can explain the proton migration of the initially formed ylides, followed by benzyl migration to 3.

The formation of the heptafulvene (4) is even more intriguing. The fact that 4 is not produced in the FVP of *o*-1 clearly indicates the ortho isomer of the carbene is not the precursor. This is rather unusual in the carbene-carbene rearrangements including arylcarbenes having functional groups since in most of these carbenes the carbene centers undergo repeated rearrangement through a benzene ring until the ortho and/or α isomers where the functional groups are ready to interact with the carbenic center leading to the final stable products are produced.¹ The formation of 4 cannot be explicable without invoking other intermediates involved in the rearrangement. Intermediates according to "the Baron mechanism"^{1a} are shown for the conversion of the para to meta isomers of

the phenylcarbenes. Among those intermediates, ones with a seven-membered ring are the most probable precursors leading to 4. Thus, either 1,5 H migration in the cycloheptatriene (10') or 1,6 H shift in the cyclo-



heptatrienyliene (10) will result in the formation of 4. The mechanism of rearrangement is still controversial, and other mechanisms^{1a} are also proposed to explain some peculiar observations such as dependence of the product ratios on the precursor structures, which cannot be explicable in terms of the Baron mechanism. However, control experiments including the trapping of possible intermediates provide evidence for the intervention of those seven-membered intermediates in the rearrangement.

The formation of products derived from seven-membered ring intermediates during the rearrangement is not unprecedented. Thus, Wentrup and his associates obtained benz[*a*]azulene and 1-azaazulene in the FVP reactions of fluorenylcarbene and indolylcarbene, respectively, which must be most reasonably produced by intramolecular trapping of the methylcycloheptatrienyliene/methylcycloheptatetraene.⁹ Present results indicate that the products derived from the seven-membered intermediates are possible even in a monocyclic system without extra stabilization by benzo or analogous conjugation and suggest that the intramolecular trapping of the methylcycloheptatrienyliene/methylcycloheptatetraene is not exceptional. A presumable possibility is that this H migration might occur even in the phenylcarbenes with simpler substituents, e.g., tolylmethylene, but is masked owing to the inherent instability of the product which must lead to the decomposition products, often observed as "tar" in the pyrolysis tube.¹⁰

Thus, the present investigation indicating that the heptafulvene formation from the seven-membered ring intermediates involved in the gas phase rearrangement of arylcarbenes is a typical is very important since it suggests not only that it serves as another evidence for the intermediate structure but also that the carbene rearrangement can be used in the synthesis of seven-membered ring compounds.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan. The authors also wish to thank Professor T. Machiguchi of Saitama University and Professor M. E. Jung of the University of California at Los Angeles for helpful advice in preparing 4 and (*o*-formylphenyl)acetate, respectively.

(9) Wentrup, C.; Becker, J. *J. Am. Chem. Soc.* 1984, 106, 3705.

(7) (1) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* 1987, 109, 683. (b) Chapman, O. L.; Tsou, U.-P. E.; Johnson, J. W. *Ibid.* 1987, 109, 553.

(8) For reviews, see: (a) Johnson, A. W. *Ylide Chemistry*; Academic Press: New York, 1966. (b) Stevens, T. S. *Prog. Org. Chem.* 1968, 7, 48. (c) Lepley, A. R.; Giumanini, A. G. In *Mechanism of Molecular Migrations*; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 3, p 297.

(10) Heptafulvene itself is known to be very unstable: Doering, W. von E.; Wiley, D. W. *Tetrahedron* 1960, 11, 183. See also, Shimanouchi, H.; Ashida, T.; Sasada, Y.; Kakudo, M.; Murata, I.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* 1966, 39, 2322. Oda, M.; Kitahara, Y. *Ibid.* 1969, 42, 2386.