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Matrix Studies of the Photolysis of o-Carbomethoxyphenyldiazomethane. Direct Observation of Carbonyl Ylide and Its Photoinduced Valence Tautomerization

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Photoreactions of o-carbomethoxyphenyldiazomethane (**1**), in Ar matrix at 10 K are studied by means of infrared spectroscopy. Irradiation (>350 nm) of **1** generates the carbonyl ylide, which undergoes the reversible photo-isomerization to the corresponding oxirane.

It is generally accepted that carbonyl ylides can be formed in thermolysis or photolysis of oxiranes$^{1)}$ or oxadiazolines,$^{2)}$ and the chemistry of these intermediates have been investigated extensively. The general reaction pathways of carbonyl ylides are ring closure to give oxiranes, fragmentation to carbenes and ketones, and cycloaddition with various multiple bonds. A facile light-induced equilibrium between the ylide and the oxirane was also reported.$^{3)}$ Moreover carbonyl ylides have been reported to be generated by the reaction of carbenes with carbonyl compounds.$^{4)}$ In recent years carbonyl ylides formed from these reactions have been detected spectroscopically by laser flash technique, and the rate constants for the ring closure and the reaction with various olefins have been measured.$^{4b,4d)}$

In this paper we wish to report the infrared spectrum of the carbonyl ylide, generated by the intramolecular reaction of the carbene with carbonyl moiety in Ar matrix. In addition we present the infrared observation of the reversible valence tautomerization of the carbonyl ylide to the benzocyclobutadiene oxide derivative.

o-Carbomethoxyphenyldiazomethane (**1**)$^{5)}$ was sublimed under 10^{-6} Torr at 0 °C and codeposited with Ar onto a 20 K CsI window. On the irradiation (>350 nm) of the diazo ester **1** at 10 K, the intense bands at 1717, and 1248 cm^{-1} assigned to the ester moiety stretching vibrations began to disappear, as well as the intense peak at 2066 cm^{-1} due to the diazo stretch. This observation clearly demonstrated that the photochemically generated carbene **2** would react rapidly with the adjacent carbonyl moiety. As the intensities of the peaks due to the material **1** decreased, a primary photoproduct **3** with infrared bands at 1653, 1590, and 1096 cm^{-1} appeared. After irradiation for 6 h , however, these new peaks ceased to grow, and continued irradiation resulted in the complete disappearance of **3** and the simultaneous formation of the final photoproduct **4** with the intense peaks of 1475, and 1397 cm^{-1}.

On further irradiation with shorter wavelength light (>254 nm), however, the intensities of the peaks of **4** decreased significantly and the peaks due to the primary product **3** appeared again. A photostationary state is attained between **3** and **4** under these conditions. Since upon long wavelength irradiation (>350 nm) the product **3** was completely converted into **4** again, the transformation of **4** to **3** was revealed to be reversible. Difference spectrum before and after irradiation with shorter wavelength light is shown in Fig. 1. The negative and positive peaks in the figure are attributable to the primary **3** and the final photoproduct **4**, respectively.

On the basis of the spectroscopic evidence that the carbene **2** interacted with the adjacent carbonyl group, we assign the carbonyl ylide structure to the primary photoproduct **3**. Since the reversible photoisomerization of carbonyl ylides to the corresponding oxiranes was already reported,[3)] the final product **4** is possible to be assigned to 1-methoxybenzocyclobutadiene oxide. The infrared spectra appear to

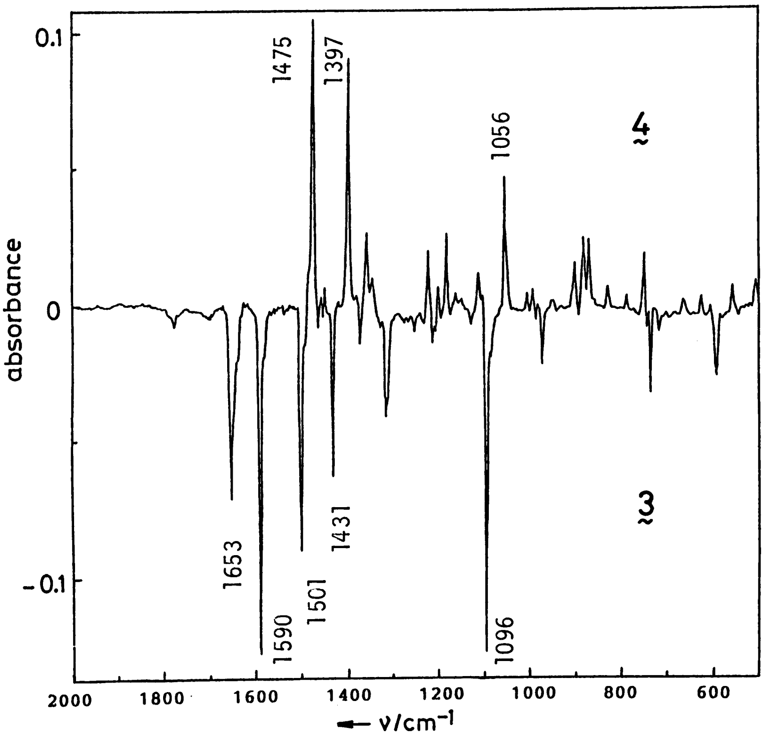
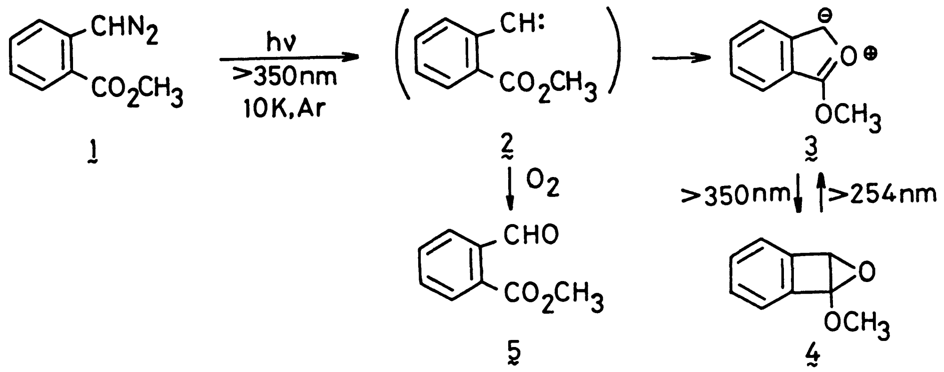


Fig. 1. Difference IR spectrum of the photochemistry of **4**.



support these structures. The unaltered bands at around 740 cm^{-1},6) and the two peaks in the 1390 - 1500 cm^{-1} region, where two peaks at 1501 and 1431 cm^{-1} due to **3** seem to shift to 1475 and 1397 cm^{-1} in **4**, show that the ortho-fused benzene skeleton is intact in the course of photo-isomerization. The intense peaks at 1653, and 1590 cm^{-1} in **3** seem to be assigned to the stretching vibrations of the methoxy-substituted carbonyl ylide moiety.7,8) The infrared absorptions characteristic of the epoxy framework are observed at around 1200, and 800 cm^{-1} in the spectrum of **4**.9)

When the Ar matrix was doped with 5-20% O_2, we could observe no infrared peaks assigned to **3** and **4**. The major photoproduct in O_2-containing matrix was identified as o-carbomethoxybenzaldehyde (**5**) by comparison with an authentic sample.10) These results clearly prove that the carbonyl ylide **3** is formed via the carbene **2**, not directly from the diazo compound **1**.

In contrast to o-isomer **1**, irradiation of m- or p-carbomethoxyphenyldiazomethane in Ar matrix at 10 K showed that the ester group remained intact in the course of photoreactions. The spectral changes in m- or p-isomer were explained in terms of the generation of the corresponding carbene, followed by the photochemical isomerization to the cycloheptatetraene derivative. This reaction scheme is in agreement with that of the photochemistry of m- or p-tolyldiazomethanes in Ar matrices.11)

In conclusion, we have directly observed by means of infrared spectroscopy that the carbonyl ylide is formed by the intramolecular interaction of the carbene center with the adjacent carbonyl group, and that this intermediate photoisomerizes reversibly to the oxirane in Ar matrix at 10 K.12)

References

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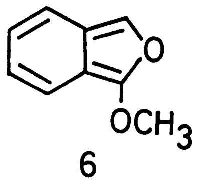
5) A. Oppe, Chem. Ber., 46, 1095 (1913).

6) Since the intense bands at 747 and 740 cm^{-1} were almost intact after short wavelength irradiation, in the difference spectrum no significant bands appeared in this region.

7) Ullman and Henderson, Jr. reported that 1,3-diphenyl-2-benzopyrylium 4-oxide showed a strong C-O stretching peak at 1520 cm^{-1}, and that its bisulfate salt showed distinctive peaks at 1616 and 1541 cm^{-1}; E. F. Ullman and W. A. Henderson, Jr., J. Am. Chem. Soc., 88, 4942 (1966).

8) It is noted that one of the canonical forms of **3** is drawn as 1-methoxyisobenzofuran (**6**), which has been reported as a transient intermediate but never isolated; M. Hamaguchi and T. Ibata, Chem. Lett., 1976, 287; M. A. Makhlouf and B. Rickborn, J. Org. Chem., 46, 2734 (1981). In spite of the peaks at 1653 and 1590 cm^{-1}, however, we cannot conclude that the carbonyl ylide structure **3** contributes predominantly to this intermediate, because the model compounds of **6**, e.g., 2-methoxyfuran and diphenylisobenzofuran, have intense peaks at around 1620cm^{-1}.



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9) Infrared spectrum of 1-cyanocyclobutene oxide (1-cyano-5-oxabicyclo-[2.1.0]pentane) was reported; 2250, 1245, 1145, and 850 cm^{-1}: D. M. Gale, S. S. Cherkofsky, J. Org. Chem., 38, 475 (1973). Arnold and Kornischky reported that 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene oxide showed infrared bands at 1250, 850, and 763 cm^{-1}: Ref. 3c.

10) The generation of ozone (1036cm^{-1}) was also observed. The oxidation of phenylcarbene in O_2-doped matrices was already reported; W. Sander, Angew. Chem., Int. Ed. Engl., 24, 988 (1985).

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12) We could not observe this reversible photo-isomerization process by means of UV-vis spectroscopy at 10 K. This is partly because the ylide **3** has no intense absorption in the visible region.

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