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Characterization of the Bisketene Photoisomer of Benzocyclobutenedione

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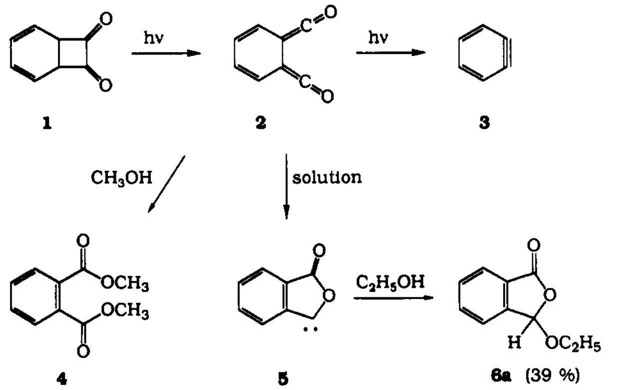
The photochemistry of benzocyclobutenedione (1) has been the subject of several detailed investigations under solution conditions,[1,2] as a thin film[3] and in glassy matrices[4] at −196 °C, in Ar matrices,[5,6] and under laser flash conditions at room temperature.[7] Nevertheless, there are still problems with the primary photochemistry.

It has been reported that the photolysis of 1 produces two intermediates, assigned as bisketene 2 and carbene 5,[1,2,5-7] and that under matrix conditions benzyne (3) is ultimately produced.[4-6]



After direct observation of bisketene 2 in an Ar/methanol matrix, it has been trapped with methanol to give dimethyl phthalate 4.[5] This is somewhat surprising since the reaction 2 → 4 constitutes an oxidation reaction with formal loss of H_2. One may understand such oxidations taking place in solution photochemistry,[8] but it is not obvious that 4 should be the only product under matrix conditions. Bisketene 2 has been observed directly by IR spectroscopy and was first reported to absorb at 2091 cm^{-1} in an Ar matrix;[5] more recently, it was claimed not to absorb at 2091 but instead at 2064 and 2125 cm^{-1}.[6]

The bisketene 2 has also been trapped in [2 + 4] cycloaddition reactions in solution, and carbene 5 has been trapped in [2 + 2] cycloadditions to alkenes and alkynes under such conditions.[2] A mixture of dimers derived from both 2 and 5 also results from solution photolysis of 1.[1,2] In the laser flash photolysis study,[7] 2 was identified as a long-lived intermediate ($\tau > 100$ μs). Carbene 5 has not been observed directly, but its existence was inferred from ylide formation with pyridine and adamantanethione and trapping with methanol.[7] It should be noted that there are several examples of rapid reaction between ketenes and pyridine or other tertiary amines, giving zwitterionic intermediates at room temperature.[9]

Experimental Section

Benzocyclobutenedione (1),[10a] methyl 2-formylbenzoate (8),[10b] and 3-methoxyphthalide (6b)[7] were prepared according to literature methods. Dimethyl phthalate (4) was obtained from Aldrich Chemical Co.

Ar matrix isolation was performed on a Leybold-Heraeus closed-cycle liquid He cryostat at 11-25 K (2×10^{-5} mbar).[11] Photolyses were carried out using a Hanovia high-pressure Xe-Hg lamp (1000 W) equipped with a monochromator. FT-IR spectra were recorded on a Perkin-Elmer 1720X spectrometer.

GC-MS was recorded on a Hewlett-Packard Model 5970 MSD/5890 GC using a 25-m (i.d. 0.22 mm) BP5 capillary column at an initial temperature of 100 °C, programmed to 270 °C at a rate of 16 °C/min; injector temperature 200 °C; column head pressure 135 kPa. Retention times: 1, 5.292 min; 8, 5.763 min; 6b, 6.240 min; 4, 6.658 min (base-line resolution; mean half height peak width 0.03-0.04 min).

Trapping of Ketene 2 with Methanol. Ketene 2 was generated by photolysis of 1 at λ = 290 nm at 11 K in an Ar-MeOH (~100:1) matrix. After ca. 75% conversion of 1 to 2 (followed by IR spectroscopy), the Ar was removed by gentle warming to 80 K. The system was then flushed with Ar gas and allowed to warm to room temperature. The material on the sample target was examined by GC-MS as detailed above. Only four compounds were detected. They were identified by direct GC-MS comparison with the authentic materials and found to be (with relative peak areas) the following: 1 (1.16), 8 (2.30), 6b (2.71), and 4 (1.00).

Results and Discussion

Photolysis of 1, isolated in Ar matrix at 11 K, at λ = 290 nm produced ketene 2 on the basis of the evidence presented below. The new species absorbed at 2138, 2077, 1595, 1346, 1080, and 965 cm^{-1} and thus had no frequencies in common with those reported earlier.[5,6] The intensity ratio of the two bands at 2138 and 2077 cm^{-1} is ca. 1:1, and they are by far the strongest bands in the spectrum (Figure 1). They are ascribed to the coupled vibrations of the two ketene functions in 2. The reaction 1 → 2 is photoreversible, as previously stated by Chapman[5] without any details. Thus, photolysis of 2 at $\lambda > 320$ nm regenerates 1. One cycle (1 → 2 → 1) is illustrated in Figure 1. It can be repeated several times before 2 is finally converted to benzyne (3).

At 290 nm there was ca. 80% conversion of 1 to 2 in 1 h, and no benzyne was detectable. After 2 h, there was 100% conversion, and traces of benzyne were now detectable (vide infra). Using λ = 280 nm, the rate of formation of 2 was about the same, but benzyne formation

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(1) Brown, R. F. C.; Solly, R. K. *Tetrahedron Lett.* **1966**, 169-174.

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(5) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134-6135.

(6) Simon, J. G. G.; Münzel, N.; Schweig, A. *Chem. Phys. Lett.* **1990**, *170*, 187-192.

(7) Boate, D. R.; Johnston, L. J.; Kwong, P. C.; Lee-Ruff, E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 8858-8863.

(8) Small amounts of phthalaldehyde and phthalic acid were obtained on the photolysis of ninhydrin in aqueous solution: Matsuura, T.; Sugae, R.; Nakashima, R.; Omura, K. *Tetrahedron* **1968**, *24*, 6149-6156.

(9) (a) Moore, H. W.; Duncan, W. G. *J. Org. Chem.* **1973**, *38*, 156. (b) Satchell, D. P. N.; Satchell, R. S. *Chem. Soc. Rev.* **1975**, *4*, 231. (c) Seikaly, H. R.; Tidwell, T. T. *Tetrahedron* **1986**, *42*, 2587. (d) Wynberg, H.; Staring, E. G. J. *J. Am. Chem. Soc.* **1982**, *104*. 166. (e) Barra, M.; Fisher, T. A.; Cernigliaro, G. J.; Sinta, R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2630. (f) Kappe, C. O.; Färber, G.; Wentrup, C.; Kollenz, G. *J. Org. Chem.*, in press. It is shown in this paper that other dipoplar species such as dimethyl sulfoxide and triphenylphosphine oxide act in a way similar to pyridine, catalyzing ketene dimerization, presumably via intermediate zwitterion formation.

(10) (a) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, 3606-3607. (b) Brown, C.; Sargent, M. V. *J. Chem. Soc. C* **1969**, 1818-1820. Eliel, E. L.; Burgstahler, A. W. *J. Am. Chem. Soc.* **1949**, *71*, 2251.

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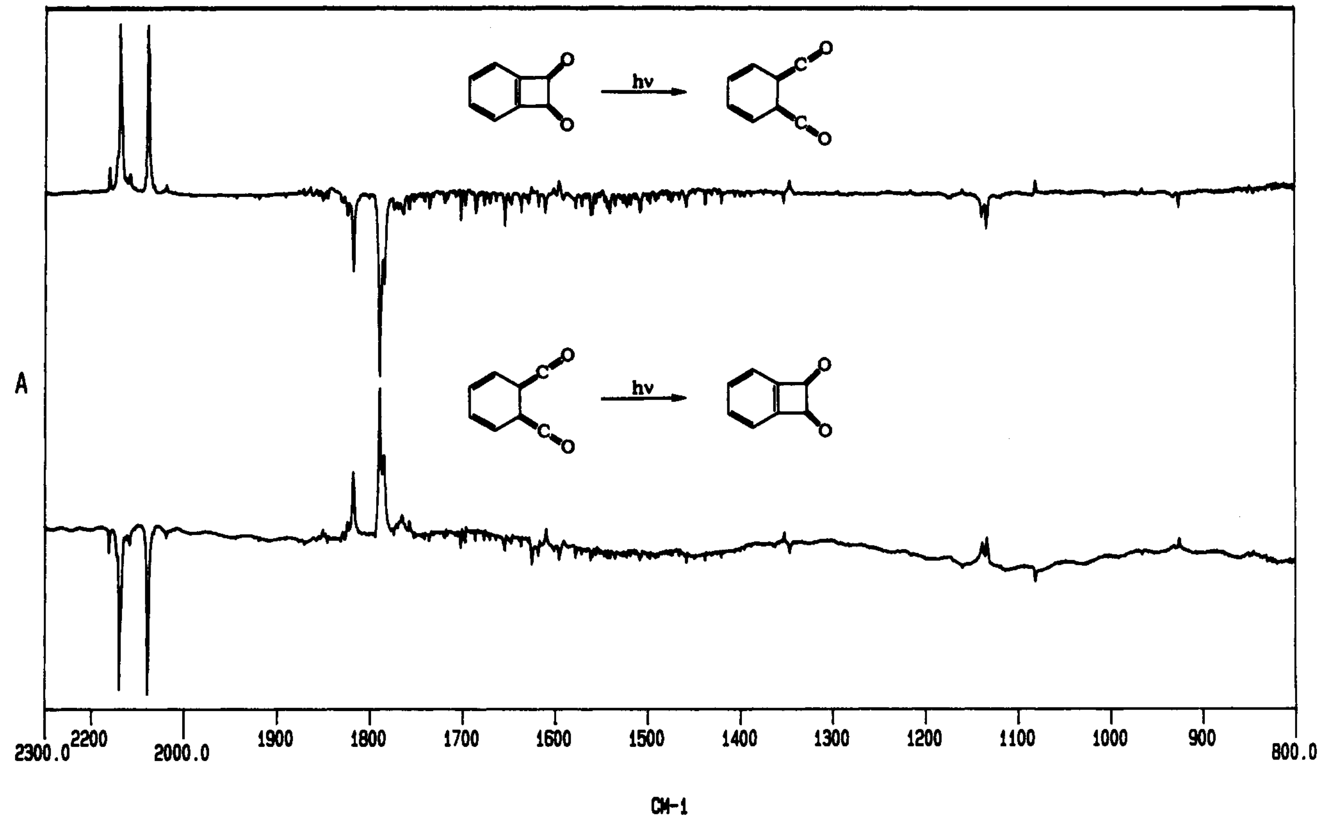
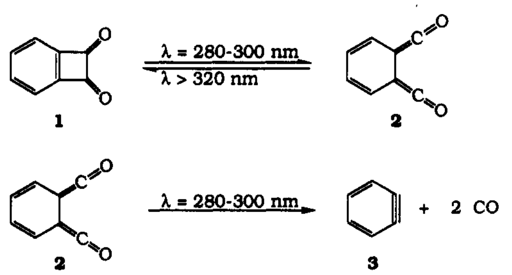
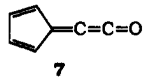


Figure 1. Difference-FTIR spectra of the photolyses of 1 and 2. Upper trace: conversion of 1 (negative peaks) to 2 (positive peaks) at λ = 290 nm. Lower trace: conversion of 2 (negative peaks) to 1 (positive peaks) at λ > 320 nm. Both spectra in Ar matrix at 11 K. Bands due to 2 are at 2138, 2077, 1595, 1346, 1080, and 965 cm^{-1}.



was now much faster; it was complete in 4 h. The production of 2 was slower at λ = 300 nm (full conversion of 1 to 2 in 5 h). Prolonged irradiation at λ = 300 nm (5–7 h) afforded new species absorbing at 2086 and 2066 cm^{-1}, together with benzyne. The species absorbing at 2086 cm^{-1} is presumably cyclopentadienylideneketene (7), observed by Brown et al.[12] at 2089 cm^{-1}, by Schweig et al.[6] at 2087 cm^{-1}, by Radziszewski et al.[13] at 2085 cm^{-1} (Ne matrix), and by us at 2090 cm^{-1} (Ar, 12 K) or 2080 cm^{-1} (neat).[11]



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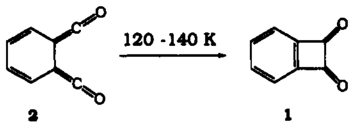
Prolonged irradiation of 2 leads to benzyne (3) (complete in 10 h at 290 nm) and CO. No other products or intermediates were observed at this wavelength. In agreement with literature data[5,13] benzyne absorbed at 1054, 1038, 848, 736, and 469 cm^{-1}. The very weak triple bond stretching vibration near 1846 cm^{-1} was not observed.[13] Difference spectroscopy clearly demonstrated that the IR bands due to 2 disappeared as those of 3 and CO (2140 cm^{-1}) formed (290 nm; 10 h).[14]

We have also found that the bisketene 2 thermally reverts to 1:



It was possible to generate neat 2 by photolysis of a thin

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(12) Brown, R. F. C.; Browne, N. R.; Coulston, K. J.; Eastward, F. W.; Irvine, M. J.; Pullin, A. D. E.; Wiersum, U. E. *Aust. J. Chem.* **1989**, *42*, 1321–1344.

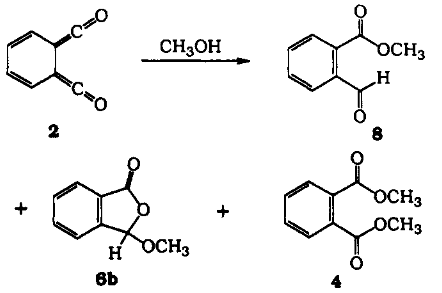
(13) Radziszewski, J. G.; Hess, A. B.; Zahradnik, R. *J. Am. Chem. Soc.* **1992**, *114*, 52–57.

(14) (a) There has been some confusion in the literature over the C≡C stretching vibration of benzyne, which was originally reported at 2085 cm^{-1} (Ar matrix),[14b] a value that has been repeatedly stated by others.[14c] However, it is now known that the C≡C stretch appears at 1846 cm^{-1} (Ne matrix)[13] in agreement with the gas-phase value of 1860 cm^{-1} derived from the photoelectron spectrum of $C_6H_4^{-}$.[15] We first suggested that a weak band at 2080 cm^{-1} (neat in phthalic anhydride) in the product of flash vacuum pyrolysis (FVP) of phthalic anhydride could be due to cyclopentadienylideneketene (7), and we were able to show that this species persisted at temperatures where benzyne has disappeared, even though we were unable at that time to exclude that benzyne, too, had an absorption near 2080 cm^{-1}.[11] We have repeated and confirmed these observations regarding the FVP of phthalic anhydride. We also agree with other authors[6,13,15] that benzyne does not possess a band near 2080–2090 cm^{-1} in the IR since we can easily generate 3 without any 7 being present. (b) Chapman, O. L.; Chang, C.-C.; Kolc, J.; Rosenquist, N. R.; Tomioka, H. *J. Am. Chem. Soc.* **1975**, *97*, 6586–6588. (c) Dunkin, I. R.; MacDonald, J. G. *J. Chem. Soc., Chem. Commun.* **1979**, 772. Nam, H.-H.; Leroi, G. E. *J. Mol. Struct.* **1987**, *157*, 301–304. Laing, J. W.; Berry, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 660. Nam, H.-H.; Leroi, G. E. *Spectrochim. Acta, Part A* **1985**, *41*, 67–73. Nam, H.-H.; Leroy, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 4096–4097. Schweig, A., Münzel, N.; Meyer, H.; Heidenreich, A. *Struct. Chem.* **1989**, *1*, 89–100.

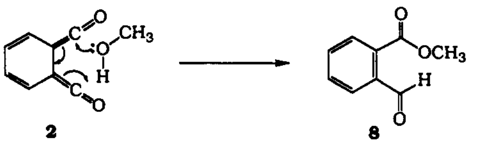
(15) Leopold, D. G.; Miller, A. E. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1379–1384.

film of 1 at 11 K. Under these conditions, 1 absorbs at 1768, 1787, and 1816 cm^{-1} in the IR and 2 at 2076 and 2135 cm^{-1}. Warming of the film containing 2 to 120–140 K caused conversion of 2 to 1, as seen by difference spectroscopy.

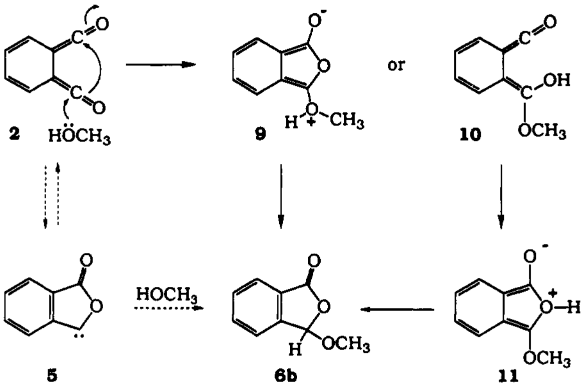
For further proof of the identity of ketene 2, it was generated, observed, and trapped in an argon–methanol matrix (ca. 100:1) by photolysis of 1 at 290 nm. After ca. 75% conversion of 1, the system was warmed, allowing Ar to evaporate, and then flushed with Ar until room temperature was reached. The products isolated at room temperature were examined by GC–MS, which revealed only three compounds, 8, 6b, and 4, apart from residual starting material (1) (See Experimental Section for details).



Dimethyl phthalate (4) is indeed a minor product. It corresponds to oxidation of a nonobserved dihydrophthalate. The important product 8 corresponds to addition of methanol to 2:



The other major product, 3-methoxyphthalide (6b), could conceivably be formed from carbene 5 by insertion into the O–H bond of methanol. However, under our reaction conditions, a direct addition of methanol to bisketene 2 is more likely, taking place via intermediates 9 or 10 and 11:



The hydration of ketenes to give enediols (enols of carboxylic acids) has been thoroughly studied in recent years and provides a good analogy for the enol intermediate 10.[16]

We have no direct evidence for the presence of 5 in our matrices where it would be expected to exhibit a strong C=O band above 1750 cm^{-1}. (There were weak bands near 1850 cm^{-1} in several matrices, in particular in the Ar–MeOH matrix, but this is not an ideal medium for IR spectroscopy; the 1850 cm^{-1} species may be due to benzocyclopropenone.[13]) Therefore, we prefer to rationalize the formation of the products (8, 6b, and 4) in terms of the observable intermediate 2.[17]

In conclusion, 5,6-dicarbonylcyclohexa-1,3-diene (2), formed by photolysis of benzocyclobutenedione (1), absorbs in an Ar matrix at 2077 and 2138 cm^{-1}. 2 thermally reverts to 1 at 120–140 K and photochemically at $\lambda > 320$ nm. The reaction $1 \rightleftarrows 2$ can be driven in both directions several times before significant decarbonylation to benzyne occurs. In agreement with the observations of others, benzyne does not absorb in the IR near 2080–2090 cm^{-1}. Trapping of bisketene 2 in an Ar–MeOH matrix leads to methyl 2-formylbenzoate (8), 3-methoxyphthalide (6b), and dimethyl phthalate (4) (2.3:2.7:1 by GC–MS). The carbene 5 was not directly observable in this work, and the isolation of 3-alkoxyphthalides (6) from the photolysis of 1 in alcohols should not be taken as unequivocal evidence for the formation of 5 in these reactions.

Acknowledgment. This work was supported by the Australian Research Council. T.M. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship.

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(17) (a) It may be of interest to note that the thermal chemistry of 1 and other precursors of benzyne (*3*) is in need of revison as regards the claimed observation of PE spectra of 3.[17b,c] We show elsewhere that the ionization potential claimed[17b,c] for benzyne near 9.23 (9.24) eV is *not* due to benzyne. It is, in fact, due to the stable compound benzene![17d] (b) Dewar, M. J. S.; Tien, T.-P. *J. Chem. Soc., Chem. Commun.* **1985**, 1243–1244. (c) Schulz, R.; Schweig, A. In *Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988; pp 289–367 (in particular pp 334–336). (d) Senio, A.; Gracian, F.; Pfister-Guillouzo, G.; Mosandl, T.; Wentrup, C. Unpublished results.