

## LOW TEMPERATURE PHOTOLYSIS OF BENZOCYCLOBUTANONE AND 2,2-DIHYDROCYCLOBUTA[1]PHENANTHRENONE: EVIDENCE FOR PHOTOCHROMIC BEHAVIOR

NIGEL P. HACKER and NICHOLAS J. TURRO

*Department of Chemistry, Columbia University, New York, NY 10027 (U.S.A.)*

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### Summary

Direct photolysis of benzocyclobutanone and 2,2-dihydrocyclobuta[1]-phenanthrenone at 77 K results in the formation of ketenes which are characterized by UV and IR spectroscopy.

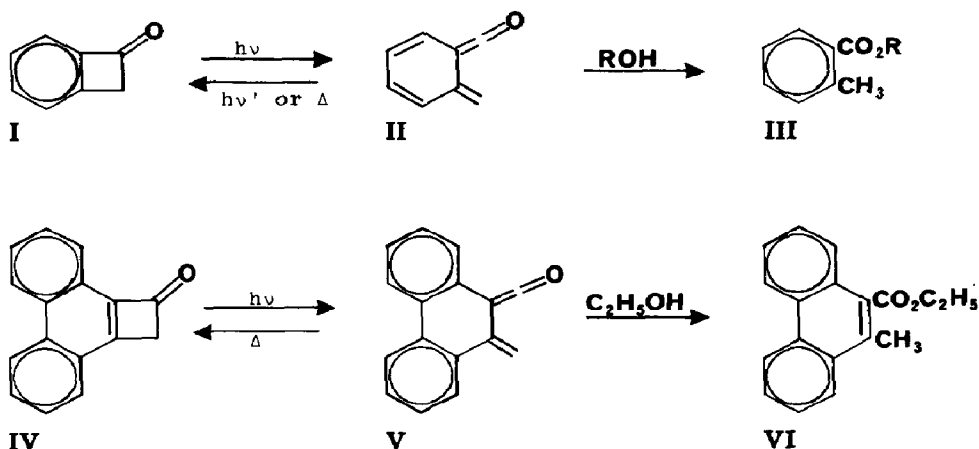
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### 1. Introduction

The chemistry of benzocyclobutanes is dominated by the ability of the cyclobutane ring to cleave and yield an *o*-xylyene intermediate [1]. This intermediate may be generated photochemically or thermally from a benzocyclobutane and has been intercepted by olefins to yield [4+2] cycloadducts. This reaction is particularly useful in the synthesis of benzannulated products [2] and has also found wide use in steroid synthesis [3]. The photochemical cleavage of benzocyclobutanone (BCB) is particularly interesting in that ring cleavage will produce an *o*-xylyene intermediate which is also a ketene. We are interested in the generation of ketenes from direct irradiation of suitable precursors (*e.g.* BCB) as models for the photoactive compounds used in polymer matrices of photoresists [4 - 6].

The photolysis of BCB in alcoholic solutions yields ester derivatives of *o*-toluic acid, a result that is consistent with the premise that the reaction proceeds predominantly via a ketene intermediate [7]. Further evidence for the ketene is available from the observation of an intermediate which absorbs at  $2120\text{ cm}^{-1}$  in argon at 20 K [8].

We report here a UV and IR absorption spectroscopy study of the photolysis of BCB and 2,2-dihydrocyclobuta[1]phenanthrenone (DCP) at 77 K as potential ketene precursors:



## 2. Experimental details

BCB and DCP were prepared by literature methods [9, 10]. The UV absorption spectrum of BCB at 77 K (Fig. 1) in 3-methylpentane exhibited two sets of absorption bands centered at 290 nm ( $\epsilon = 3.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and at 250 nm ( $\epsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). Irradiation of BCB at 77 K at 300, 290 or 250 nm caused the matrix to turn yellow and resulted in a new absorption at 400 nm ( $\epsilon = 3.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) accompanied by simultaneous loss of absorption at 290 and 250 nm with isosbestic points at 301, 278, 254 and 226 nm. Irradiation of this species at 350 or 400 nm or warming the matrix to its melting point results in a loss of the yellow color and the 400 nm absorption and regeneration (above 80%) of the BCB absorptions. This photochromic behavior is compatible with the ketene structure (II) which may photochemically or thermally ring close to BCB. The IR spectrum of a thin film of BCB or a 10% BCB frozen solution in 3-methylpentane at 77 K (Fig. 2) exhibited absorptions at 1790 and 1770  $\text{cm}^{-1}$  (C=O stretch) and at 1570  $\text{cm}^{-1}$  (cyclobutene C=C stretch). Irradiation of BCB at 77 K at 300, 290 or 250 nm also caused the sample to turn yellow and resulted in a new absorption at 2110  $\text{cm}^{-1}$  (C=C=O stretch), which is typical for a ketene [4, 5, 11], and loss of the absorptions due to BCB. Furthermore, irradiation of this intermediate at 350 nm results in loss of the 2110  $\text{cm}^{-1}$  absorption and regeneration of the characteristic BCB frequencies. Attempts to regenerate BCB from the ketene intermediate by warming the 3-methylpentane sample to 130 K resulted in loss of the 2110  $\text{cm}^{-1}$  frequency but no increase in the BCB frequencies. This result may have been due to loss of some of the sample into the vacuum system. From the identical photochromic behavior of the yellow intermediate produced in the IR and UV absorption experiments, we conclude that both sets of experiments produced the ketene II which is characterized by a UV absorption at 400 nm and an IR absorption at 2110  $\text{cm}^{-1}$ .

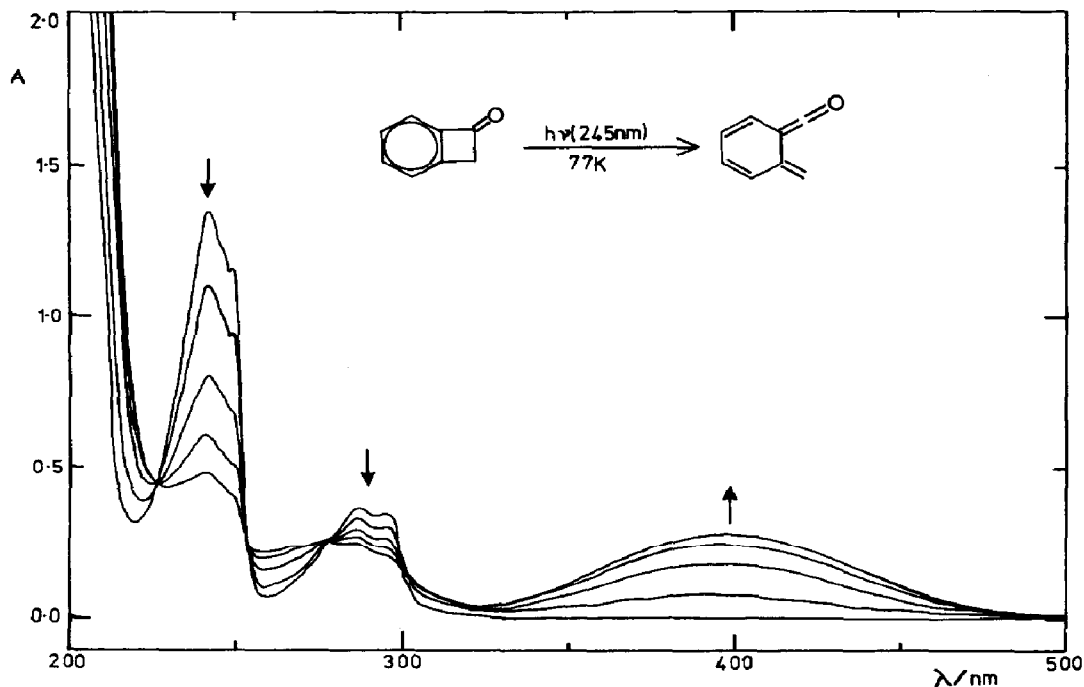


Fig. 1. UV spectra of BCB in 3-methylpentane ( $1.15 \times 10^{-4}$  M) at 77 K and 0, 10, 20, 30 and 45 s.

### 3. Results and discussion

It has been demonstrated previously that the photoactive compound in photoresists is thermally stable when warmed to 273 K *in vacuo* [4, 5]. The thermal instability of the ketene II may be attributable to the loss of aromaticity upon formation from BCB. However, if we examine the same reaction for the phenanthrene analogue IV, the resultant ketene V has two aromatic rings intact and may have increased stability relative to its precursor. The irradiation ( $\lambda = 300$  nm) of DCP in 3-methylpentane at 77 K (Fig. 3) resulted in the generation of a new species with absorption bands at 262 nm ( $\epsilon = 1.6 \times 10^4$  M $^{-1}$  cm $^{-1}$ ) and 247 nm ( $\epsilon = 1.8 \times 10^4$  M $^{-1}$  cm $^{-1}$ ). While further irradiation of this new species did not regenerate DCP, warming the sample to 293 K and recooling to 77 K resulted in the return of the DCP absorption bands (above 95% yield). The IR spectrum of a thin film of DCP cast by evaporation from dichloromethane solution at room temperature and then cooled to 77 K exhibits the characteristic carbonyl absorptions of a cyclobutanone at 1770 and 1740 cm $^{-1}$ . Irradiation of this sample results in a new species with an IR absorption at 2090 cm $^{-1}$  (C=C=O stretch) which is accompanied by a decrease in the intensity of the peaks due to DCP. Unfortunately, a high concentration of the 2090 cm $^{-1}$  species was stable even after warming the sample to 273 K, but a further increase in the temperature to 298 K caused the disappearance of the absorption at 2090 cm $^{-1}$ .

and the regeneration of the DCP absorption frequencies. The similarity in behavior of the species produced in the IR and UV experiments (2090  $\text{cm}^{-1}$ ; 280 and 255 nm) suggests that they are due to the same intermediate, the ketene **V**. Furthermore, irradiation of a solution of DCP in ethanol at room temperature results in a high yield (above 80%) of ethyl-9,10-methylphenanthrene carboxylate, suggesting that the reaction proceeds predominantly through the ketene intermediate **V**.

From these experiments, we conclude that direct irradiation of BCB and DCP produces the ketene intermediates **II** and **V** respectively which are stable indefinitely at 77 K. The same ketenes are also produced in solution at 298 K and may be trapped by alcohols to give the ester derivatives **III** and **VI** respectively. Finally, the ketene **V** is more thermally stable than its analogue **II**, probably because of the increased aromatic stabilization of **V** relative to its ketene precursor.

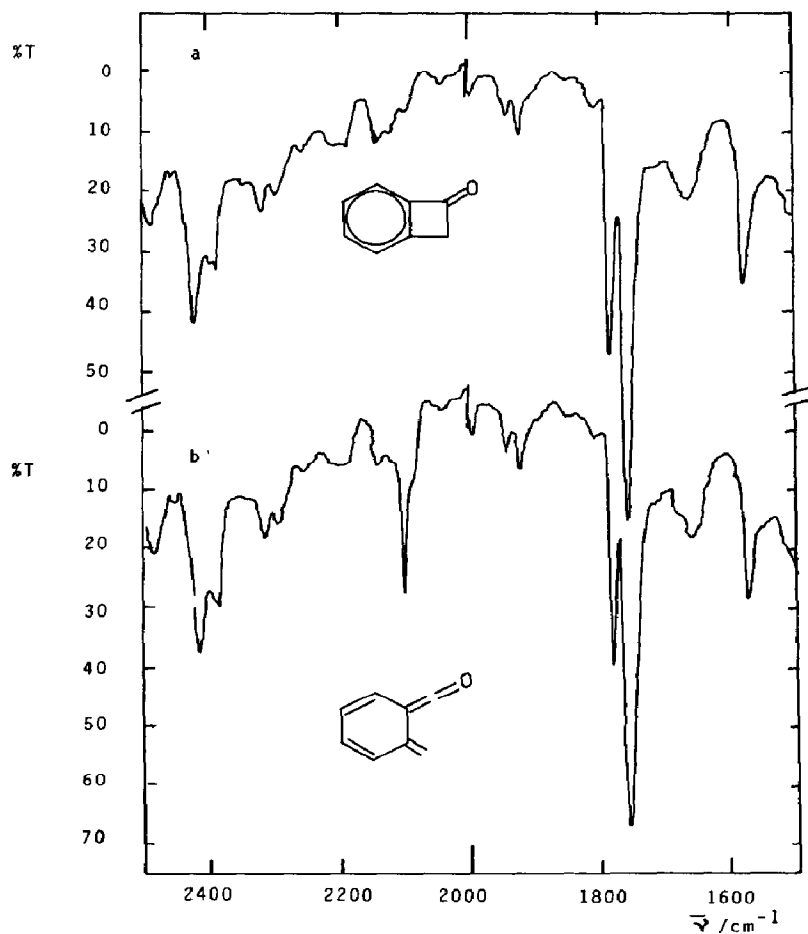


Fig. 2. IR spectra at 77 K: curve a, 10% mixture of BCB in 3-methylpentane; curve b, after photolysis at 250 nm for 60 s.

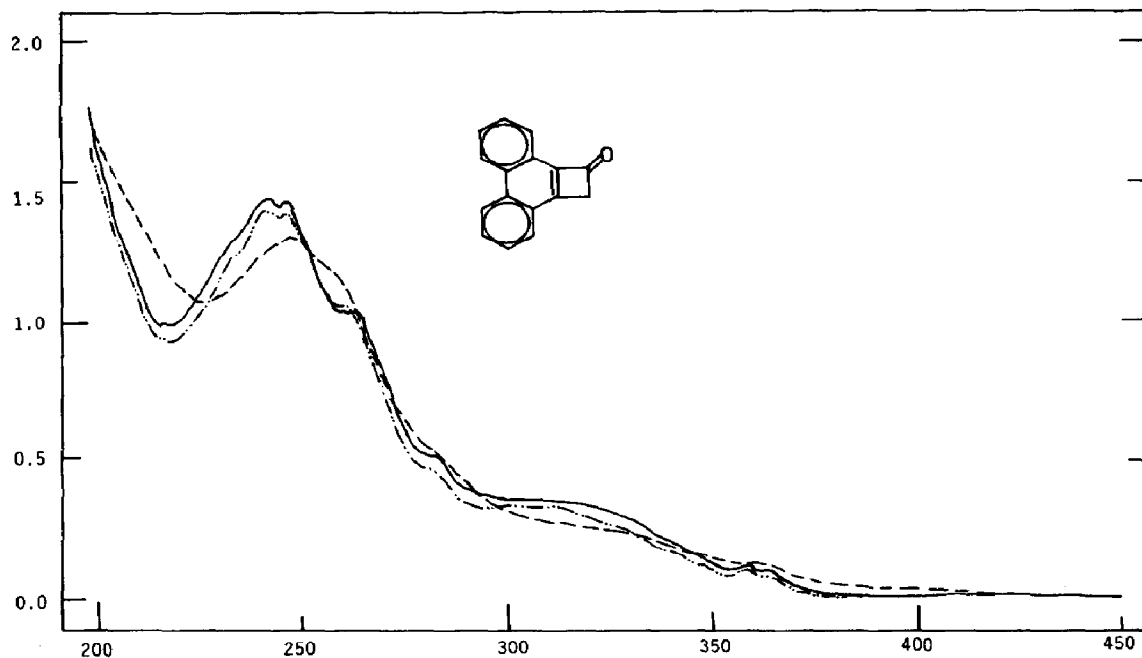


Fig. 3. UV spectra of DCP at 77 K: —, before photolysis; ---,  $h\nu = 1000$  s ( $\lambda = 300$  nm); - · - · -, warmed to room temperature and cooled to 77 K.

## Acknowledgments

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