Photochemical Reactions of 1,3-Bis(diazo)indan-2-one in an Argon Matrix at 10 K

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Irradiation of 1,3-bis(diazo)indan-2-one (**3**) in an argon matrix at 10 K afforded the diazo ketene (**7**) *via* the photolabile diazo ketocarbene (**5**), and further irradiation caused the decomposition of the second diazo group to give strained carbonyl compounds as final photoproducts.

Bis(diazo) ketones have been of interest as intermediates for the synthesis of cyclopropenones and strained alkynes.[1] Chapman and his co-workers attempted to synthesize the unsubstituted cyclopentyne (**1**) by the photolysis of 2,6-bis(diazo)cyclohexanone in an argon matrix at 8 K, but could not observe the IR spectrum of (**1**) because of its rapid isomerization to vinylidenecyclopropane.[2] They succeeded, however, in the synthesis and spectroscopic characterization of acenaphthyne by the irradiation of 1,3-bis(diazo)-1,2-dihydrophenalen-2-one. In spite of the theoretical prediction of the vibrational frequencies of cyclobutyne (**2**),[3] no attempt has been made to synthesise (**2**) in frozen matrices; attempts to generate it in solution were unsuccessful.[4] We report here the photochemical reactions of 1,3-bis(diazo)indan-2-one (**3**), which is a potential precursor of benzocyclobutenyne (**4**), in an Ar matrix at 10 K.

Irradiation (350 ± 20 nm; 2 h) of (**3**)[†] matrix isolated in Ar at 10 K resulted in the appearance of two kinds of new carbonyl stretching bands with a decrease in the intensities of the peaks assigned to the diazo and carbonyl stretch of (**3**). One of the first-formed carbonyl compounds with the C=O stretch at 1647 cm^{-1} was assigned the diazo ketocarbene structure (**5**) for the following reasons. First, the carbonyl absorption of this species shifted to a lower frequency than that of the bis(diazo) ketone (**3**) in analogy with the ketocarbenes reported by Chapman and his co-workers.[5] Secondly, when the Ar matrix was doped with 1% O_2, warming the matrix containing (**5**) to 35 K resulted in the complete disappearance of (**5**) and generation of a new species with IR bands at 970 and 945 cm^{-1}, which was reasonably assigned to the corresponding carbonyl oxide (**6**).[6] Finally, as observed by EPR spectroscopy, irradiation of (**3**) in a 2-methyltetrahydrofuran glass at 18 K produced triplet signals due to the diazo ketocarbene (**5**), $D = 0.3631$ cm^{-1} and $E = 0.0225$ cm^{-1}.[7] The other carbonyl absorptions appeared at 1728 and 1718 cm^{-1}. These peaks were tentatively assigned to the carbonyl stretch in a ketodiazirine structure, since the carbonyl absorptions of ketodiazirines were reported to shift to higher frequencies than in the corresponding diazo compounds.[8]

Further irradiation (350 ± 20 nm; 17 h) resulted in the total disappearance of the IR absorptions of (**3**) and the first-formed carbonyl compounds, and produced an intense peak at 2106 cm^{-1} and weak peaks at 1569, 1066, and 542 cm^{-1}. The

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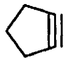
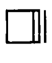
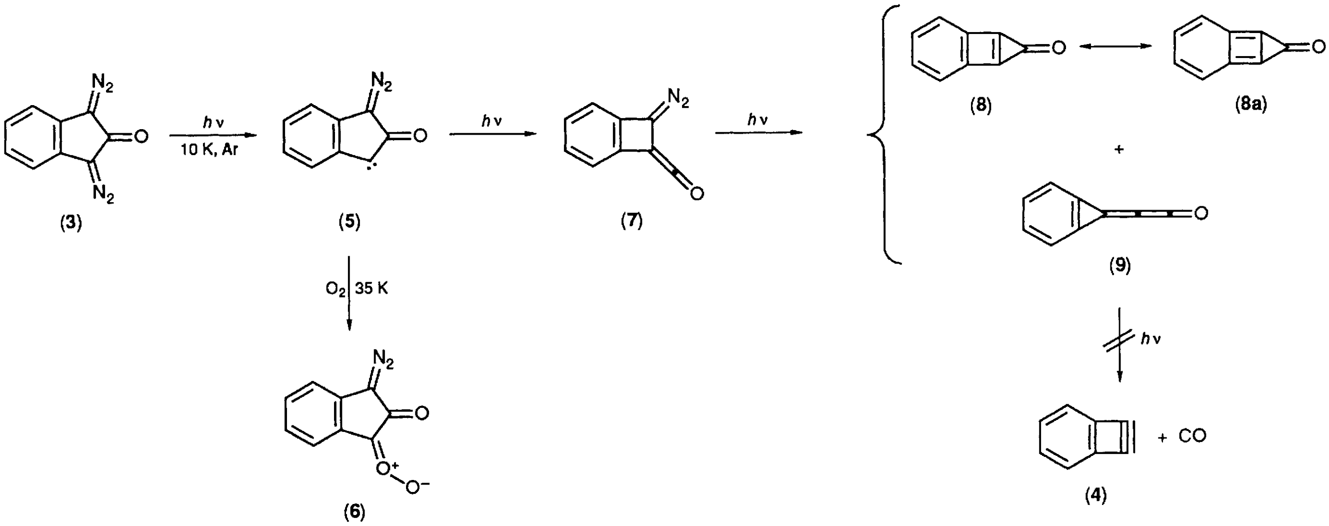
[†] Compound (**3**) was prepared in 47% yield by acid-catalysed reaction of indan-2-one with isopentyl nitrite, followed by treatment of the resulting bisoximino ketone with an alkaline chloramine solution: orange granules; m.p. 127 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 7.10 (br. s, 4H); IR $\nu_{max.}$ (Ar; 10 K) 2096m, 2084vs, 1692m, 1370s, 1183s, 1096w, 746w cm^{-1}; UV (Ar; 10 K) $\lambda_{max.}$ 289, 301sh, 349, 368, and 374sh nm.



(1)



(2)



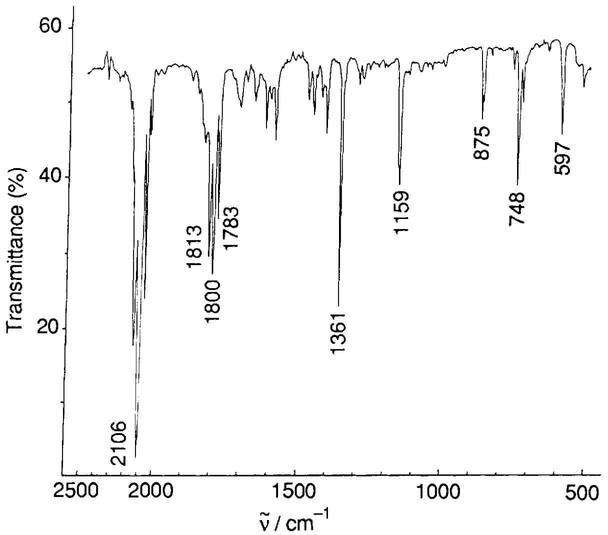


Figure 1. IR spectrum obtained by irradiation (λ >350 nm; 34 h) of (3) matrix isolated in Ar at 10 K.

resulting species was assigned the diazo ketene structure (7) on the basis of the intense diazo-ketene stretching vibration at 2106 cm^{-1} and the disappearance of the carbonyl moiety.‡ The matrix containing (7) had a red colour, and its UV-VIS spectrum showed a broad band with a maximum at 507 nm.

Continued irradiation (λ >350 nm; 24 h) of (7) at 10 K resulted in a decrease in intensities of the IR peaks due to (7). Simultaneously, characteristic bands at 1813, 1800, and 1783 cm^{-1} and an intense peak at 1361 cm^{-1} appeared. However, the 2106 cm^{-1} band ceased to decrease at 80% of the maximum intensity, and increased slightly on further irradiation (Figure 1). In the UV–VIS spectrum, irradiation (λ >350 nm) of the red matrix containing the diazo ketene (7) caused the appearance of very intense UV absorptions with fine vibrational structures in the region 320—370 nm.

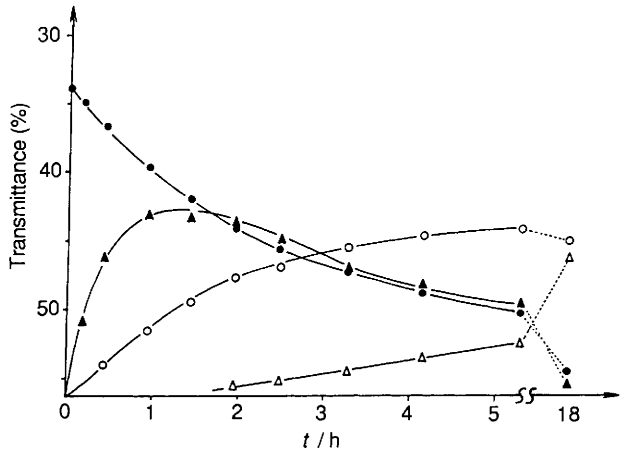


Figure 2. Change in intensity of the characteristic peaks with irradiation time (350 ± 20 nm): (3) (●) 1467; (5) (▲) 1647; (7) (○) 1569; (8) (△) 1800 cm^{-1}.

Irradiation of the diazo ketene (7) in an Ar matrix gave a mixture of a ketone with a strained carbonyl function and a compound with a cumulenic structure. The ketone may have the cyclopropenone structure (8). However, (8) is better described as having the dimethylenecyclopropanone structure (8a), since the centre of the carbonyl stretching bands is much lower than that of known cyclopropenones,[2,9] and the observed UV absorptions could be assigned to the $\pi \rightarrow \pi^*$ transitions of the *o*-xylylene structure of (8a); the fine vibrational structure of *o*-xylylene has been reported.[10] It is difficult to identify the photoproduct with the 2106 cm^{-1} IR band, although the propadienone (9) is a possible candidate, since the cumulenic stretching band of matrix-isolated propadienone appears at 2125 cm^{-1}.[11] This compound would be formed by a Wolff-type rearrangement of the carbenic ketene generated from (7).[12]

The photoproducts (8) and (9) were stable under short-wavelength irradiation (λ >200 nm; 37 h), though it has been reported that the photolyses of cyclopropenones produce the corresponding alkynes with extrusion of carbon monoxide.[2,10,13] Thus we could not characterize benzocyclobutenyne

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‡ The diazoketene generated by the photolysis of 2,6-bis(diazo)-cyclohexanone was reported[2] to show IR peaks at 2120 and 2118 cm^{-1}.

(**4**) in an approach starting with 1,3-bis(diazo)indan-2-one (**3**).§

Figure 2 shows the change in intensity of the characteristic peaks with irradiation time (350 ± 20 nm). The curves indicate clearly that the species are formed sequentially. Thus, it is concluded that the two diazo groups of the bis(diazo) ketone (**3**) decompose stepwise to give the diazo ketene (**7**) as a transient intermediate. Moreover, the diazo ketocarbene (**5**), the precursor of (**7**), has been characterized by IR and EPR spectroscopy. This affords a new class of spectroscopically characterized nonconcerted Wolff rearrangements, since a partial double bonding character of the CO–CN_2 bond is thought to be responsible for the retardation of the rearrangement in this case.¶

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§ Recently Sander and Chapman reported the photochemical addition of carbon monoxide to 3,3,6,6-tetramethylcyclohexyne.[14] The failed photochemical decarbonylation of the cyclopropenone (**8**) might be attributed to the fact that the photostationary state between (**4**) and (**8**) largely favours the latter.

¶ Chapman and his co-workers have reported the IR spectroscopic characterization of ketocarbenes, in which the strain in the transition state suppressed the Wolff rearrangement.[5] The suppression of the Wolff rearrangement due to a partial double bonding character has been reported in the photochemistry of α-diazoamides in solutions.[8b,15]

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