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PHOTOCHEMISTRY OF MATRIX-ISOLATED NORBORNADIENE

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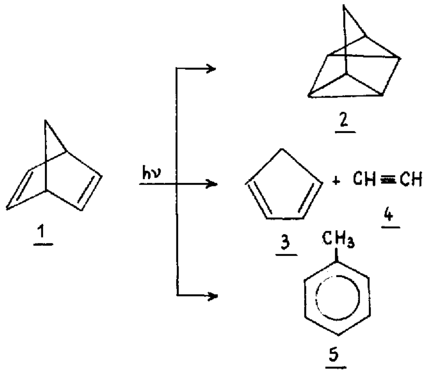
ABSTRACT

Norbornadiene, isolated in argon, xenon and nitrogen matrices at 20 K, was irradiated with UV light. Characterized by UV–VIS–IR absorption spectroscopy the photoproduct, representing a single species, was assigned to quadricyclane. This result is compared with the literature data on photochemistry of norbornadiene in the gas and liquid phase. The role of the rigid matrix environment on selectivity of the photochemical reaction is discussed.

INTRODUCTION

The valence isomerization between norbornadiene (NBD) **1** and quadricyclane (Q) **2** has attracted much attention as a chemical energy storage system.[1–4] Light-induced isomerization of NBD has been extensively studied in the liquid phase both under direct and sensitized excitation.[5–7] Q has been characterized as a major photoproduct however cyclopentadiene **3**, acetylene **4** and toluene **5** have been detected also. In contrast to the observation in the liquid phase the photoreaction in the gas phase leads mostly to **3** and **4**.[8,9] Small amounts of **5** and **2** have been recovered also. An explanation offered assumes participation of vibrationally excited states in the photoreaction of NBD in the gas phase.[8,9] It has also been proposed that formation of **3**, **4** and **5** involves biradicals **6** and **7** as intermediates. Recent studies on the



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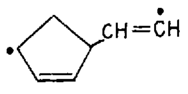
overtone vibrational photochemistry of Q indicated the importance of the hot NBD intermediate in controlling the overall gas phase reaction.[10]



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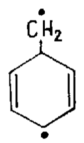

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The aim of this work is to present the studies of photochemical transformation of NBD in the solid phase. The matrix-isolation technique has been used for that purpose.[11–14] Since vibrational excitation plays an important role in the phototransformation of NBD we expected that this reaction will be useful for testing the excited guest–host interactions in rigid matrices. On the other hand the cryogenic conditions should facilitate interception of unstable intermediates.

EXPERIMENTAL SECTION

Materials

NBD and Q purchased from Aldrich was used as received. Argon, xenon and nitrogen supplied by Gazy Techniczne (Poland) was purified by passing the gas through low temperature traps.

Sample preparation

A gas mixture of known amounts of the substrate vapor and matrix gas was deposited from a vacuum line (background pressure of 5×10^{-6} torr) onto a cesium iodide or sapphire window mounted on the expander stage of a Spectrim (Cryogenic Technology) cryostat. The gas mixture was deposited at a flow rate 50–70 μmol/min and the total amount deposited varied from 3 to 7 mmol. The irradiation and measurements were performed at 20 K.

Irradiation and measurements

Photochemical reactions were carried out with a high pressure mercury lamp HBO-200 (Narva, GDR). Interference filter UV-KSIF (Carl Zeiss Jena, GDR) at maximum transmittance at 254 nm was used. IR spectra of matrix-isolated species were obtained with a Specord M-80 (Carl Zeiss Jena, GDR) spectrophotometer working at a resolution of $2\,cm^{-1}$. UV–VIS spectra were measured with a Carry 2300 (Varian) spectrophotometer and the baseline correction due to light scattering caused by a matrix was made.

RESULTS AND DISCUSSION

UV and IR spectra of NBD isolated in Ar-matrix are shown in Figures 1 and 2. Irradiation with UV light caused profound changes in the spectra. As is shown in Figure 1 a gradual

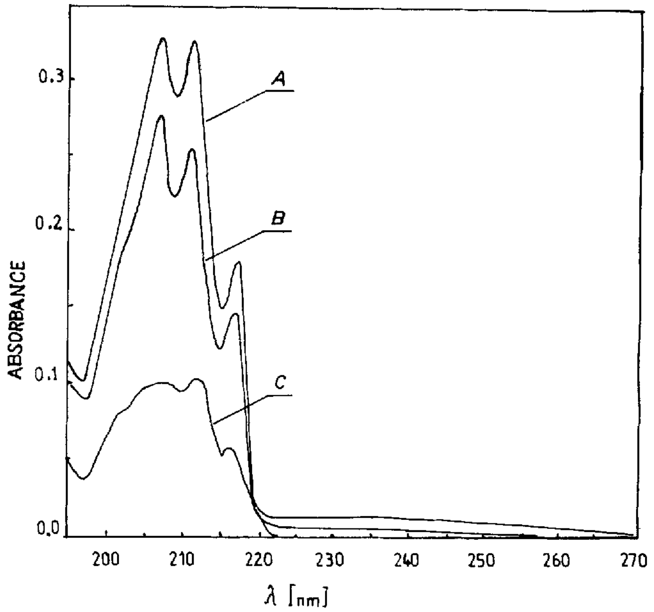

Figure 1. UV spectrum of argon matrix-isolated NBD (NBD: Ar = 1:400): A—before irradiation, B—after irradiation for 10 min, C—after irradiation for 45 min

decrease in NBD absorption is observed upon photolysis and the only observable distinct change in the spectrum is manifested by appearance of a shoulder at 202 nm. Prolonged irradiation (2 h) also caused formation of two tiny bands at 256 nm (A = 0·007) and 266 nm (A = 0·01). The IR spectrum of the irradiated sample of NBD (Figure 2B) shows a set of newly formed bands. Observed vibrational frequencies of NBD and its photoproduct are presented in Tables 1 and 2.

Figure 3 shows the IR spectrum of matrix-isolated Q. Some bands presented in this spectrum are characteristic for NBD. During sample preparation Q isomerized to NBD to the extent of a few percent every time. No traces of NBD were seen in the sample of Q prior to sample preparation. Even very careful sample preparation, repeated for many times, never allowed isolation of Q without a noticeable amount of NBD. This fact was also manifested in the UV spectrum of matrix-isolated Q. Most probably Q isomerized to NBD during sample preparation when the gas mixture was exposed to a surface of the metal parts in the deposition line.

We omit in the present discussion vibrational assignment of the bands observed in the IR spectra, simply because this is not directly relevant to the problem presented and one can find such discussion elsewhere.[5]

Careful analysis of the spectra allows for unambiguous assignment of Q to a major product of NBD photolysis. All bands assigned to the photoproduct in the IR spectrum of photolyzed NBD have the same positions and relative intensities (Table 2) as the bands of matrix-isolated Q (Table 3). Also the picture presented in Figure 1 is consistent with the fact that Q absorbs below 205 nm[5] and the only observable change in the spectra is seen in that region. Photochemical reaction of NBD was very selective in Ar, Xe and N_2 matrices and only prolonged irradiation produced a trace of the side product, observed only in the UV spectra,

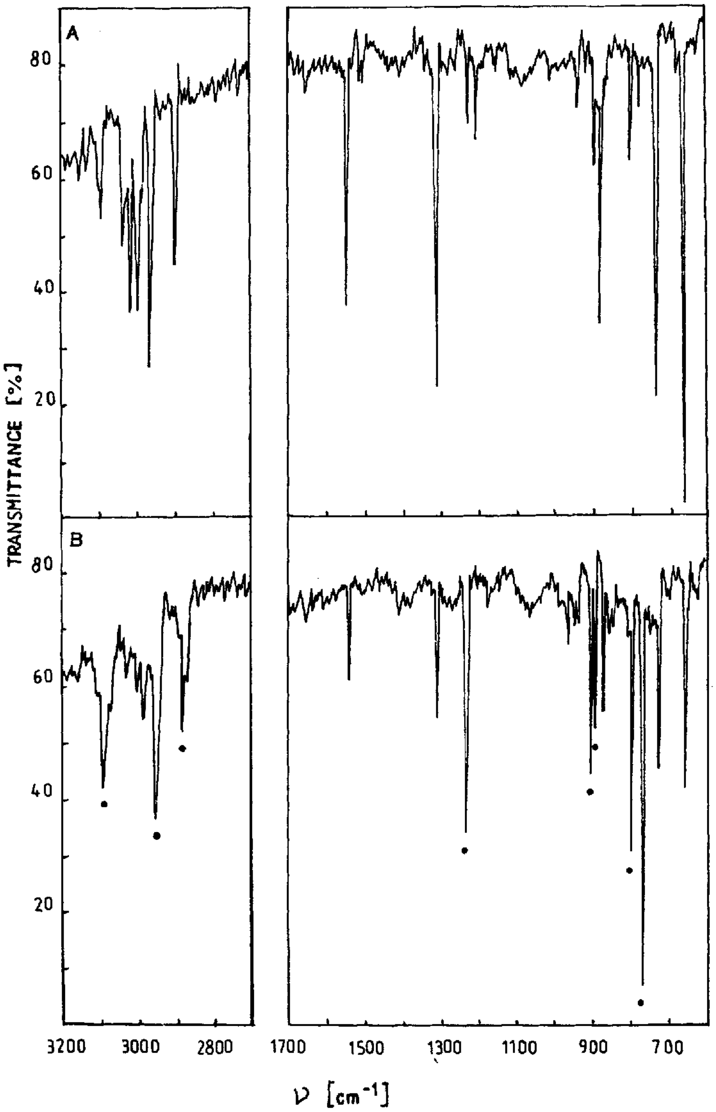

Figure 2. IR spectrum of argon matrix-isolated NBD (NBD : Ar = 1 : 400): A–before irradiation, B–after irradiation for 90 min. Dots indicate newly observed bands. In the region of 2800–3200 cm^{-1} the spectrum was taken with ordinate expansion 1·25

Table 1. Observed vibrational frequencies (cm^{-1}) of argon matrix-isolated NBD

3142 vw	2885 m	901 w
3121 vw	1552 s	881 s
3082 w	1316 s	805 m
3028 w	1232 m	736 vs
3005 m	1212 m	665 vs
2987 m	1158 vw	
2955 m	945 w	

Table 2. Observed vibrational frequencies (cm^{-1}) assigned to the photoproduct of argon matrix-isolated NBD

3085 m	1246 s	806 s
2948 m	915 m	778 vs
2884 m	902 m	

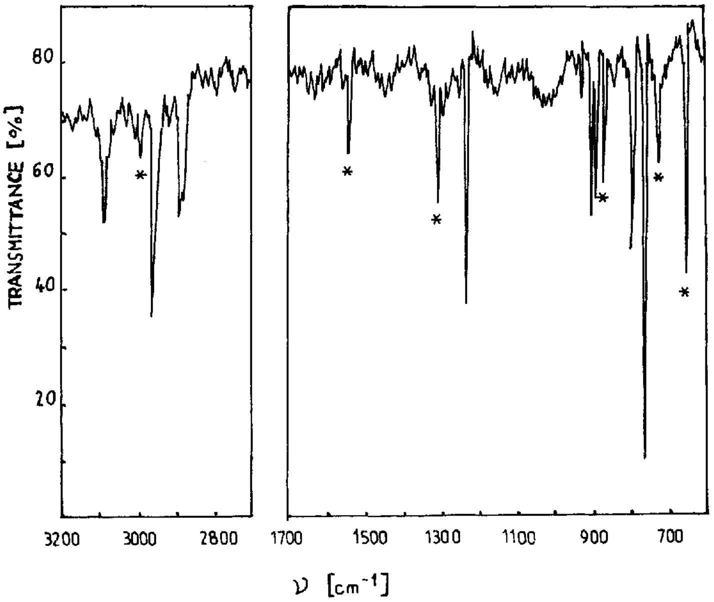

Figure 3. IR spectrum of argon matrix-isolated Q (Q : Ar= 1 : 400): The bands of NBD are marked with an asterisk. In the region of 2800–3200 cm^{-1} the spectrum was taken with ordinate expansion 1·25

Table 3. Observed vibational frequencies (cm^{-1}) of argon matrix-isolated Q[a]

3085 m	1316 m*	881 m*
2987 w*	1246 s	806 s
2948 m	946 w	778 vs
2884 m	915 m	736 m*
1552 m*	902 m	665 s *

[a] Asterisks indicate the bands of NBD

in amount estimated as less than 1%. We tentatively assigned this product to cycloheptatriene (266 nm) and its open ring isomer, i.e. 3,5-heptadien-1-yne (256 nm). Photochemical isomerization NBD → Q was almost equally effective in all matrices studied.

Since vibrational relaxation of matrix-isolated species in rare gas matrices is often relatively slow[15–17] it seemed that behavior of excited NBD may parallel the gas phase observation. Under such expectation the studies might be primarily aimed at stabilization of biradicals **6** and **7**, proposed as reactive intermediates. Surprisingly the photolysis of NBD in matrices almost exclusively produced Q in a very high yield. The selectivity of photochemical reaction of NBD can be rationalized in terms of matrix rigidity. One may expect that a rigid matrix environment exerts constraint on the transition state and the preference is given to the reaction leading to the product of a shape which best fits the matrix site occupied by reacting molecule. Obviously it is easy to imagine that Q well satisfies such a requirement. On the other hand the amount of energy introduced to molecule by electronic excitation well exceeds the energy of the matrix crystal lattice.[11,12] So, this excess energy should be sufficient even to melt the matrix locally and then to satisfy every steric demand. This may not be the case when the energy transfer to the crystal lattice is relatively slow. There are known examples of sterically demanding photochemical reactions which effectively proceed in rare gas matrices.[13–14] However, there are also reports suggesting a crucial role of the rigid matrix environment on the photochemical processes.[18–20] At present it is difficult to specify exactly how the matrix perturbs the photochemical reaction, nevertheless the reported observation seems to contribute to further understanding of this problem.

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