Benzoxetene. Direct Observation and Theoretical Studies

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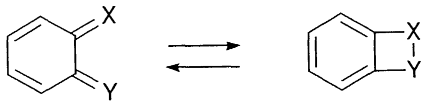
Irradiation of either o-hydroxphenyldiazomethane or benzofuranone in argon matrix at 10 K generates benzoxetene which is in photoequilibrium with o-quinone methide.

A relatively variety of o-quinoid compounds (**A**) have been generated and employed as intermediates in organic synthesis. Some of them have been even observed and characterized by spectroscopic means. [1] Another interesting aspect of these molecules lies in their isomerization between benzo-condensed four-membered heterocyclic ring systems (**B**). Thus, little is known concerning the strained benzenoid form, which can be formed from **A** principally either thermally or photochemically. Recent attempts to characterize these species by direct spectroscopic observation coupled with theoretical calculation have begun to unfold their nature.[1-4] The stability of the closed isomer very much depends on the nature of X and Y, and, so far, only derivatives with at least one substituent being CH_2 have been either isolated or detected.[2~5] For instance,



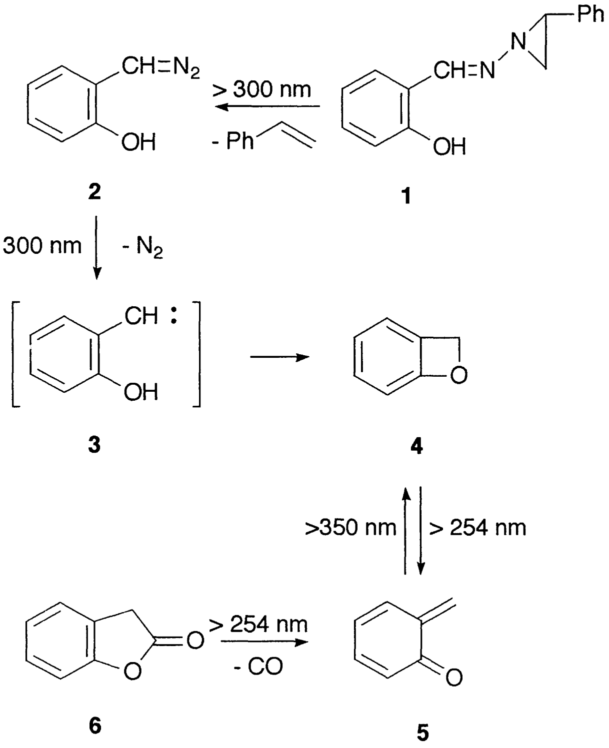
A **B**

benzocyclobutene ($X=Y=CH_2$)[1] and benzothiet ($X=CH_2$, $Y=S$)[2] are isolated while benzoazetine ($X=CH_2$, $Y=NH$)[5] is detected. In this light, it is rather surprising to note here that almost no efforts have been made to detect benzoxetene ($X=CH_2$, $Y=O$) although the corresponding quinoid form has been generated and characterized from several precursors.[3] In this paper, we wish to publish the first direct observation of the title compound by matrix isolation techniques.

Most promising precursor for oxetene is o-hydroxyphenylcarbene (**3**) which is expected to give the oxetene as a result of O-H insertion.[6] As the preparation of diazo precursor (**2**) was rather difficult, we used "masked" diazo compound (**1**) developed by Eschenmoser.[7] Irradiation (λ>300 nm) of **1** matrix-isolated in argon at 10 K gave strong absorption due to styrene, suggesting that the desired decomposition took place even at this low temperature. We also observed a sharp band at 2115 cm^{-1} presumably ascribable to the diazo groups of **2**, which grew to some extent but started to decompose upon prolonged irradiation under the same conditions. The absorption bands ascribable to hydroxy group also started to decrease. On the other hand, new bands showing maxima at 1600, 1453 and 790 cm^{-1} appeared.[8] After all the starting compound was decomposed, the spectra mainly consisted of the bands due to styrene and the photoproduct, and changed very little upon further irradiation. However, upon irradiation with shorter-wavelength light (λ>254 nm), the photoproduct started to decompose to afford a secondary photoproduct exhibiting maxima at 1688 and 1616 cm^{-1}.[7] This secondary product reproduced the initial product upon irradiation with light of λ>300 nm.

What are those photoproducts? Analysis of the major IR bands provided some insights into their structures. First, the presence of the band at 1688 cm^{-1} of the secondary product indicated the presence of a carbonyl group. This, coupled with the band at 1568 cm^{-1} ascribable to combination of $C=CH_2$ and C=O stretching modes, points to o-quinone methide (**5**) as the most plausible structure for the product. Unambiguous evidence is lent to this assignment by direct comparison of the spectra of **5** obtained by the irradiation of benzofuranone (**6**).[3] Thus, all the product bands ascribable to **5** completely coincided with each other. Not surprisingly, the quinone (**5**) from **6** also produced the initial product from **2** upon irradiation with longer wavelength light (λ>350 nm).

A priori, there are several possible structures for the compound which can be in photoequilibrium with **5**.



However, benzoxetene (**4**) can be proposed as the most probable isomer based on the valence isomerization observed with analogous systems.[2] Moreover, the observed IR bands fit quite well with those expected for **4**.

In order to gain more support for these assignments, *ab initio* calculations[9] were carried out for **4** and **5**. The calculations at the HF/6-31G** level of theory revealed that both

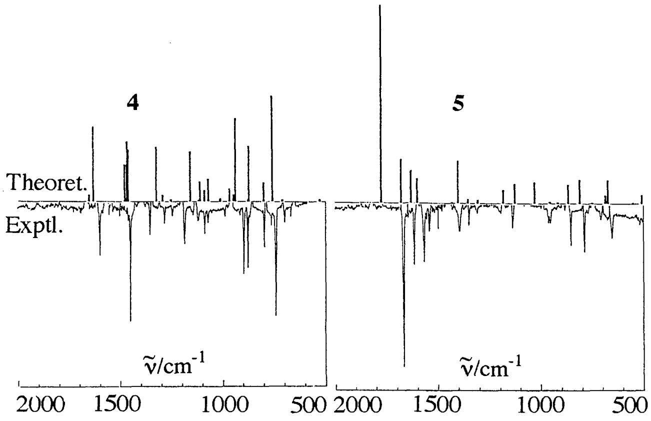


Figure 1. Experimental (Ar, 10 K) and theoretical (HF/6-31G**) IR spectra for **4** and **5**.

of the molecules have true energy minima on the corresponding potential energy surfaces and that the quinoid form (**5**) is more stable than the oxetene (**4**) by 5.1 kcal/mol. The vibrational frequencies were calculated for those compounds and were compared with the experimental vibrational frequencies observed with **4** and **5**, which indicated that the calculated frequencies[10] match the experimental data quite well, not only for **5** but also for **4** (Figure 1). Thus, the predicted relative energies as well as the calculated frequencies of the proposed intermediates in the tautomerization of C_7H_6O molecules fully support the assignments of the hitherto unknown oxetene (**4**).

Two points should be noted here. First, the optimized structures of both **4** and **5** are planar, and while **5** has an o-quinoid structure, with alternating single and double bond, **4** has a benzenoid structure with the four-membered ring only slightly twisted. Second, it is very interesting to compare thermodynamic properties of the present system with those reported earlier. Thus, we calculated the relative stabilities of the quinoid and closed forms as well as the transition state (TS) energies of the interconversion for benzocyclobutene, benzothiet and benzoazetine with the same level of the theory (MP2/6-31G**//HF/6-31G**). The results summarized in Table 1 indicate that the predicted relative energies are in good agreement with the experimental observations. Thus, benzocyclobutene and benzothiet which are isolated under normal conditions are calculated to be more stable than the corresponding quinoid forms by some 20 kcal/mol and kinetically also fairly stable with respect to ring-opening. The corresponding quinoid forms are expected to be kinetically less stable with respect to ring-closure. This is exactly what is observed with benzocyclobutene and benzothiet. From these considerations, it can be predicted that the equilibrium must shift to the quinoid side as Y substituents are changed from S to NH to O. Rather large TS energy between **4** and **5** would predict that **4** is kinetically stable at least with respect to the ring opening.

Table 1. Thermodynamic data of o-quinoid and benzenoid forms from *ab initio* calculations

			(kcal/mol)	
X	Y	**A**	TS	**B**
CH_2	O	0	40.3	5.05
CH_2	NH	0	31.0	- 5.80
CH_2	S	0	16.1	- 19.7
CH_2	CH_2	0	22.3	- 22.9

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8 **4**: IR (Ar, 10 K) 1600 (s), 1462 (w), 1453 (vs), 1356 (w), 1284 (w), 1180 (m), 1120 (w), 1088 (w), 988 (w), 896 (m), 874 (m), 796 (m), 740 (vs), 700 (w), cm^{-1}.
5: IR(Ar, 10 K) 1668 (vs), 1616 (m), 1568 (m), 1540 (m), 1396 (w), 1348 (w), 1136 (w), 960 (w), 952 (w), 852 (m), 788 (m), 652 (w) cm^{-1}.

9 The *ab initio* calculations were carried out using the program packages Gaussian 92 and/or SPARTAN on SGI workstation computer and standard basis sets.

10 The theoretical frequencies were scaled by 0.91, as recommended by Grev; R. S. Grev, C. L. Janssen, and H. F. Schaefer, *J. Chem. Phys.*, **95**, 5128 (1991).