Matrix Isolation of a Reactive o-Quinoid Compound - 6-Methylene-2,4-cyclohexadien-1-imine

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Abstract: Photolysis of (*o*-aminophenyl)diazomethane (5) in argon at 10 K or flash vacuum pyrolysis of *o*-aminobenzylalcohol (2) with subsequent trapping in solid argon produces mixtures of 6-methylene-2,4-cyclohexadien-1-imine (1) and benzazetine (3) in ratios depending on the experimental conditions.

o-Quinoid compounds are reactive intermediates of importance in organic chemistry. While *o*-quinone is isolable at room temperature, other members of this family are rather instable and have to be characterized using low temperature techniques. Recently Ripoll et al.¹ reported on the generation of 6-methylene-2,4-cyclohexadien-1-imine (1) by flash vacuum pyrolysis (FVP) of tetrahydroquinoline or *o*-aminobenzylalcohol (2). The isomeric ring-closed product benzazetine (3) was not detected under these experimental conditions. An alternative route to 1 is the [1,4]-H shift of *o*-aminophenylcarbene (4). Here we report on the synthesis of imine 1 and benzazetine 3 from both (*o*-aminophenyl)diazomethane (5) (via carbene 4) and aminoalcohol 2, and show that FVP of 2 produces a mixture of 1 and 3.



Photochemistry of o-Aminophenyldiazomethane (5). *o*-Aminophenyldiazomethane (5) was synthesized by warming the lithium salt of *o*-aminobenzaldehyde tosylhydrazone to 90 - 100°C and depositing the volatile diazo compound with a large excess of argon directly on top of a cold (20 K) window.² Irradiation of 5 with visible light (λ = 544 nm, Ar, 11 K) produced iminoquinone 1, which

was characterized by its IR- (Table 1, Figure 1) and UV/vis-spectra (λ_{max} = 350, 282, 234 nm). The assignment of the observed IR spectrum to 1 was supported by ab initio calculations using the HF/6-31G(+sd+sp) basis implemented in the Turbomole³ set of programs (Table 1). These calculations reproduce both the band positions (assuming the usual 10% blue-shift) and relative band intensities reasonably well.



Figure 1. Difference IR spectrum showing the photochemistry of imine 1 in Ar at 10 K. Bottom: bands disappearing on irradiation at 444 nm, assigned to 1. Top: bands appearing on irradiation, assigned to 3.

A comparison of IR spectroscopic data of 1, *o*-xylylene,⁴ and *o*-benzoquinone methide⁵ reveals the similarity of these compounds. In the IR spectrum of 1, a medium intensity band at 1642.6 cm⁻¹ is assigned to the C=N str. vibration, the carbonyl absorption in *o*-benzoquinone methide is found at 1657 cm⁻¹, while, as expected, in *o*-xylylene no absorption is found within this range.



All three *o*-quinoid compounds exhibit UV maxima in the 350 - 400 nm range. Imine 1 is photolabile and on irradiation at $\lambda = 444$ nm readily rearranges to give solely benzazetine 3 (Figure 1).⁶ Irradiation at shorter wavelength ($\lambda = 308$ nm, XeCI Excimer-Laser) yield both 1 and 3 in a photostationary equilibrium.

Nr.	v [cm ⁻¹]a	l [%]þ	v [cm ⁻¹] ^c I [%] ^b		
38	1642.6	34	1680	95	
37	1542.8	39	1611	38	
36			1607	7	
35	1537.5	49	1576	23	
34	1428.0	sh	1423	2	
33	1406.3	42	1403	38	
32	1361.0	25	1350	18	
31	1327.2	sh	1324	11	
30	1280.5	31	1259	6	
	(1276.6	28)			
28	1177.3	14	1154	5	
27	1089.1	.59	1066	100	
	(927.6	36)			
26	924.2	38	1020	28	
	(872.6	37)			
	(866.4	97)			
21	864.9	100	897	93	
18	765.1	25	791	8	
15	651.8	16	668	14	

Table 1. IR spectroscopic data of o-iminobenzoquinone methide 1

Table :	2.	IR	spectroscop	xic dat	a of	benzazetine
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Nr.	v [cm ⁻¹] ^a	⁰ [%] ا	v [cm ⁻¹] ^c I [%] ^b		
38	1548.6	28	1613	8	
37	1529.8	75	1604	47	
	(1424.7	35)			
35	1358.6	sh	1447	17	
34	1330.2	51	1441	18	
33	1264.6	40	1331	49	
31	1171.5	50	125 9	· 7	
	(1168.7	41)			
27	1077.5	86	1105	10	
25	978.2	24	1074	14	
24	944.0	9	1014	3	
22	900.6	49	965	10	
20	860.1	sh	895	15	
19	835.5	27	885	7	
16	770.9	100	763	75	
	(719.3	45)			
14	715.9	48	648	28	
	(707.7	13)			
13	644.1	30	598	100	

^aMeasured in Ar at 10 K. ^bRelative Intensities. ^cHF/6-31G(+sd+sp) calculations, scaled by 0.9. ^aMeasured in Ar at 10 K. ^bRelative Intensities. ^cHF/6-31G(+sd+sp) calculations, scaled by 0.9.

FVP of o-Aminobenzylaicohol (2) and Photolysis of 2-Indolinone (6). FVP of alcohol 2 at 850°C and 10⁻⁵ mbar with subsequent trapping in Ar at 20 K produced a mixture of **1** and **3** in an approximate ratio of 4:3. This is in contrast to the report of Ripoll et al.,¹ who observed **1** as the major product. A comparison of the reported IR data with ours suggests that these authors also produced a mixture of **1** and **3**. According to semiempirical AM1 calculations⁷ the ring-opening of **1** to give **3** is endothermic by 11.2 kcal/mol, in contrast to benzocyclobutene, which was calculated⁸ to be 4.9 kcal/mol more stable than *o*-xylylene.

The thermal fragmentation of 1 was additionally monitored by using a quadrupole mass spectrometer, directly coupled to the pyrolysis oven. The decomposition of 2 (m/z = 129) to yield 1 and/or 3 (m/z = 105, 15 eV ionisation energy) and water began at 600°C and was almost complete at 850°C.

Short-wavelength irradiation ($\lambda > 254$ nm) of 2-indolinone (6) produced iminoquinone 1 in a very slow reaction. Due to the slow conversion and low product yields only UV/vis spectra could be recorded. The UV/vis spectra of 1 generated from all precursors are in reasonable agreement with each other and the results of Ripoll et al.¹

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References and Notes

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- 2. Matrix-isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. IR spectra were recorded with a Bruker IFS 66 FT-IR spectrometer between 4000 and 400 cm⁻¹ with a resolution of 1 cm⁻¹, UV/vis spectra with an HP 8452A diode array spectrometer with a resolution of 2 nm. Irradiations were carried out with Hg high-pressure arc lamps in combination with cut-off and interference filters or an XeCI Excimer-Laser (308 nm).
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- 6. UV Irradiation (λ = 308 or >385 nm) produced a mixture of 1, 3, and a third compound X, which has not been identified, so far. On further irradiation X does not produce 1 or 3, neither does 1 or 3 produce X under any irradiation conditions. From that we conclude that X is a photoproduct of carbene 4.
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