Photochemistry of 9,10-Dicarbonyl-9,10-dihydroanthracene – A Source of 9,10-Dehydroanthracene?

Hans Henning Wenk[a] **and Wolfram Sander***[a]

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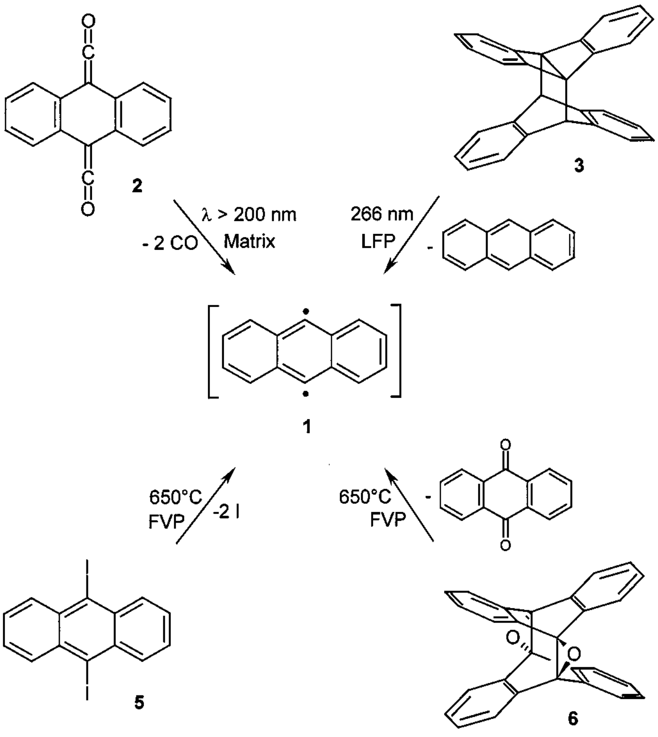
9,10-Didehydroanthracene (**1**) is an interesting derivative of *p*-benzyne that has been subject of several studies. In contrast to an earlier report, the photochemical decarbonylation of 9,10-dicarbonyl-9,10-dihydroanthracene (**2**) does not lead to **1** but rather to the ring-opened ene-diyne **4**. The key intermediate for this reaction is keto carbene **7** which is formed by monodecarbonylation of **2**. Carbene **7** is labile towards visible-light irradiation and easily looses the second CO molecule to give **4**. Carbene **7** and diyne **4** are characterized by IR and UV/Vis spectra, the IR spectra are compared to calculations at the B3LYP/6-31G(d,p) level of theory.

Introduction

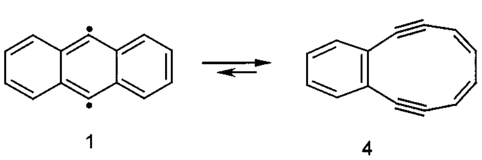
p-Benzyne and its derivatives are reactive intermediates in cycloaromatization reactions[1,2] and the theoretical description[3–5] as well as the physical characterization[6,7] and synthetic applications[8,9] have been of interest to many research groups. In 1976 Chapman and Kolc reported on the matrix isolation of 9,10-dehydroanthracene (**1**), generated by the photolytic decarbonylation of 9,10-dicarbonyl-9,10-dihydroanthracene (**2**) (Scheme 1).[10] A series of UV/Vis absorptions in the range 256–449 nm and IR bands at 710 and 760 cm^{-1} were attributed to **1**. Irradiation of bisketene **2** in solid 3-methylpentane at 77 K and subsequent warming to room temperature resulted in the formation of anthracene, the trapping product of **1**. In the presence of CCl_4 9,10-dichloroanthracene was formed, again suggesting that **1** was trapped.

Schottelius and Chen investigated the photochemistry of **3**, a formal adduct of **1** and anthracene, using laser flash photolysis (LFP, Scheme 1).[3] Two transients were observed, a "fast" transient with a lifetime of 2.1 μs and an absorption maximum at 295 nm, and a "slow" transient with 500 μs lifetime and an absorption maximum at 335 nm. The "fast" transient was assigned to **1**, while the "slow" transient was assigned the structure of the ring-opened 3,4-benzocyclodeca-3,7,9-triene-1,5-diyne (**4**).

Recently, we described the flash vacuum pyrolysis (FVP) with subsequent trapping of the products in argon at 10 K of 9,10-diiodoanthracene (**5**) and the diepoxide **6**.[11] Both precursors produced diyne **4**, which was identified by comparison of the experimental and calculated IR spectra. Thus, the **1** → **4** rearrangement is rapid under FVP conditions and significant amounts of **1** are not formed. This is in agreement with estimations of a barrier of around 12 kcal/mol and an exothermicity of several kcal/mol.[3,11]



Scheme 1. Synthesis of dehydroanthracene **1** from various precursors



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Since the products of the photolysis of bisketene **2** had only been partially characterized (only two IR absorptions reported),[10] and since IR spectra of diradicals of the size of **1** can now be reliably characterized with DFT methods, we reinvestigated the matrix photochemistry of **2**.

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[a] Lehrstuhl für Organische Chemie II der Ruhr-Universität,
D-44780 Bochum, Germany
Fax: (internat.) + 49(0)234/709-4353
E-mail: sander@neon.orch.ruhr-uni-bochum.de

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Results and Discussion

Irradiation of bisketene **2**, matrix-isolated in argon at 10 K, with $\lambda = 254$ nm results in the decrease of the very strong ketene absorption at 2093.4 cm^{-1} and formation of CO (2136.6 cm^{-1}) and a second ketene **A** with a strong absorption at 2105.8 cm^{-1} and medium intensity absorptions at 1604.1, 1466.8, and 1272.3 cm^{-1} (Figure 1, Table 1). The conversion of **2** is only partial even on prolonged UV irradiation, which indicates an internal filtering effect of the photoproducts. The new ketene **A** is stable towards UV irradiation, but completely disappears on broad-band visible-light (420−680 nm) irradiation. The major photoproduct of **A** is diyne **4**, which is easily identified by comparison of the IR spectrum with that obtained from the pyrolyses of **5** or **6**.[11] The minor photoproduct is bisketene **2**, which demonstrates that the **2** → **A** photochemistry is partially reversible.

The same sequence of photoproducts starting from matrix-isolated **2** was also observed using UV/Vis spectroscopy: 254-nm irradiation of **2** leads to the novel product **A** which is highly labile toward broad-band visible-light irradiation. **A** exhibits two band systems in the visible region: weak absorptions in the red with maxima at 558 and 572 nm, and a broad absorption with a vibrational fine structure corresponding to 1000 cm^{-1} in the blue between 396 and 456 nm ($\lambda_{max} = 436$ nm), which explains the long-wavelength photochemistry of **A**. In the UV region maxima at 340, 264, and 236 nm are found, which account for the internal filtering effect (Figure 2). Broad-band visible-light irradiation rapidly leads to the disappearance of all absorptions of **A** and formation of new UV bands (one set of weak bands at 396, 357, 339, 323 and strong bands at 270, 262, 250 nm) assigned to diyne **4**.

The most reasonable structure for ketene **A**, which accounts for the spectroscopic data as well as for its photochemistry, is that of keto carbene **7** (Scheme 2). Thus, the decarbonylation of **2** proceeds stepwise, and if the wavelength of the irradiation is carefully controlled, carbene **7** builds up as the primary intermediate in appreciable amounts. Broad-band UV/Vis irradiation of **2** directly leads to diyne **4** as the main product. Dehydroanthracene **1** is not observed under any conditions, although we can not completely exclude the formation of trace amounts not identified in the spectra.

The assignment of **7** is confirmed by comparison of the experimental IR spectrum with that calculated for **7** at the UB3LYP/6-31G(d,p) level of theory (Table 1). According to these calculations the singlet and triplet states, S-**7** and T-**7**, are almost degenerate ($\Delta E_{ST} = 0.2$ kcal/mol, B3LYP + ZPE). At this level of theory ΔE_{ST} of diphenylcarbene is calculated to 6.4 kcal/mol, more than 2 kcal/mol higher than the experimental value (4 kcal/mol in isooctane, in more polar solvents even smaller),[12] and that of methylene to 11 kcal/mol, again about 2 kcal/mol higher than the experimental value.[13] It is thus reasonable to assume that S-**7** is about 2 kcal/mol more stable than T-**7**. In agreement with this prediction the calculated spectrum of S-**7** matches the experimental spectrum (band positions and relative intensities, Table 1) much better than that of T-**7** (Table 2). A singlet ground state of **7** also explains why this carbene could not be trapped with molecular oxygen in the matrix (0.5% O_2-doped argon matrix, annealing at 35−40 K). This reaction is very fast and highly characteristic for triplet

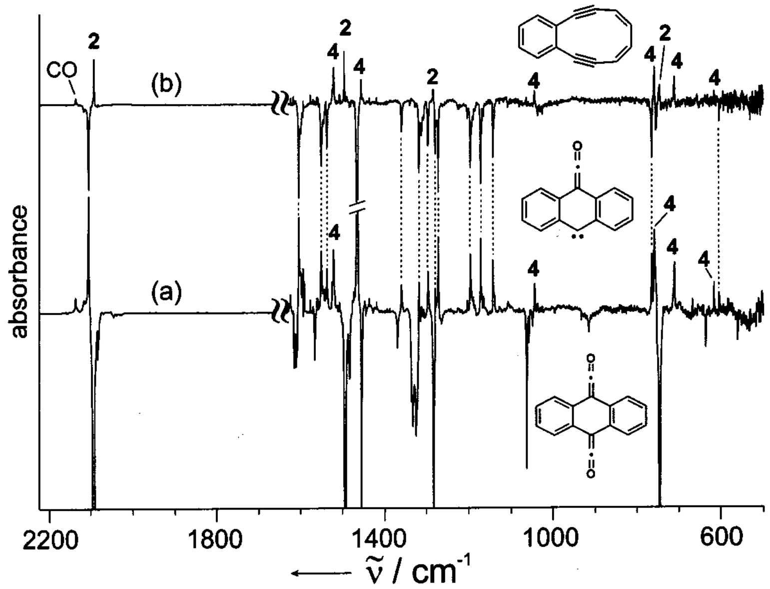


Figure 1. (a) IR difference spectrum showing the photochemistry of bisketene **2** (Ar, 10 K); bottom part, bands disappearing; top part, bands appearing on irradiation with 254 nm; (b) IR difference spectrum showing the photochemistry of **A** (Ar, 10 K); bottom part, bands disappearing; top part, bands appearing on irradiation with 420−680 nm; bands marked **4** are unambiguously assigned to enediyne **4** by comparison with experimental (ref.[11]) and calculated data, bands marked **2** are those of newly formed diketene

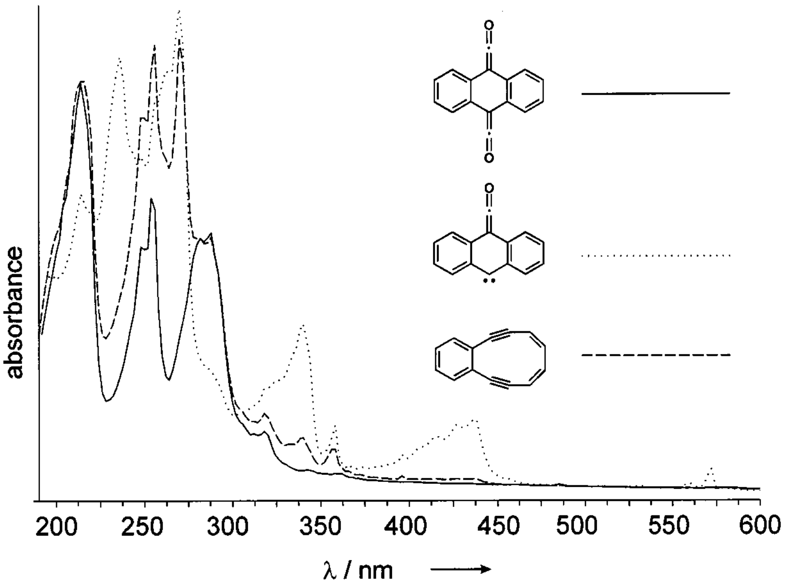
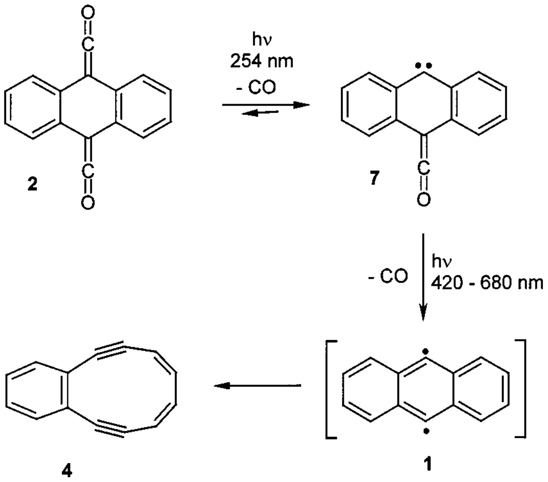


Figure 2. UV/Vis spectra (Ar, 12 K) of bisketene **2** after deposition (————), irradiation with 254 nm (······) and subsequent irradiation with 420–680 nm (------)



Scheme 2.

carbenes, while singlet carbenes react, if at all, only slowly.[14,15]

Conclusion

Oxo carbene **7** is the key intermediate in the photochemistry of bisketene **2**. The DFT calculations [B3LYP/6-31G(d,p)+ZPE] predict the monodecarbonylation of **2** to give S-**7** to be endothermic by 54.4 kcal/mol, which is less than the experimental value of 78 kcal/mol for the decarbonylation of ketene, and thus easily accessible photochemically. On the other hand, photolysis of many simple ketenes in solid matrices does not lead to an efficient decarbonylation, since the carbene and CO formed in the same matrix rapidly recombine to the ketene. Obviously, a thermal barrier prevents the recombination of **7** and CO, and photochemical activation preferentially results in the loss of the second CO molecule, while the carbonylation back to **2** is a minor path only. The decarbonylation of **7** to give T-**1** is calculated to be endothermic by 35.5 kcal/mol and thus requires photochemical activation. In our experiments we do not obtain any direct spectroscopic evidence for dehydroanthracene **1**, and it is not clear whether the **1** → **4** ring opening is a photochemical or a hot ground state reaction.

These findings also explain the spectra previously described by Chapman and Kolc.[10] Since broad-band UV/Vis irradiation (λ > 200 nm) was used in that study, bisketene **2** was directly transformed to diyne **4**. The two IR ab-

Table 1. IR-spectroscopic data of singlet carbene S-**7**

Mode	$\tilde{\nu}_{exp}$ [cm^{-1}][a]	$I_{rel,exp.}$[b]	$\tilde{\nu}_{calcd.}$ [cm^{-1}][c]	$I_{rel,calcd.}$[b]	Sym.
16	532.7	0.7	527.1	1.1	B_1
18	603.8	1.0	616.5	0.5	B_2
25	764.5	3.0	781.6	9.1	B_1
39	1142.6	2.7	1162.5	1.0	A_1
40	1164.8	0.8	1184.1	0.4	B_2
41	1171.4	3.8	1196.8	1.8	A_1
42	1195.4	3.0	1210.9	3.4	A_1
43	1202.9	0.6	1245.0	1.0	B_2
44	1272.3	4.1	1296.6	3.4	A_1
45	1296.3	2.3	1299.1	7.6	B_2
46	1311.9	0.4	1334.7	2.1	B_2
47	1317.7	1.7	1335.7	3.8	A_1
48	1360.0	1.4	1373.0	4.8	B_2
50	1419.5	0.3	1477.0	0.6	B_2
52	1436.8	0.6	1491.1	5.2	B_2
53	1466.8	10.1	1504.2	9.8	A_1
54	1536.4	2.7	1586.1	1.1	B_2
55	1549.4	3.6	1594.2	4.3	A_1
56	1604.1	4.8	1644.3	8.1	B_2
58	2105.8	100.0	2193.2	100.0	A_1

[a] Argon, 10 K. – [b] Relative intensities (based on the strongest absorption). – [c] Calculated at the B3LYP/6-31G(d,p) level of theory. The assignment is tentative and is based on band positions and intensities.

Table 2. IR-spectroscopic data of triplet carbene T-**7** calculated at the B3LYP/6-31G(d,p) level of theory.

Mode[a]	$\tilde{\nu}_{calcd.}$ [cm^{-1}]	$I_{rel,calcd.}$[b]	Sym.
11	429.6	1.0	B_1
18	611.3	0.5	B_2
23	756.4	1.7	B_1
25	761.1	8.2	B_1
36	1064.2	0.5	B_2
37	1088.5	1.0	A_1
42	1241.4	1.3	B_2
43	1253.1	0.8	A_1
45	1311.8	1.0	A_1
46	1318.7	2.7	B_2
47	1335.3	1.9	B_2
49	1419.4	1.0	B_2
50	1466.9	3.3	B_2
51	1485.0	0.9	A_1
52	1494.7	0.6	A_1
54	1590.0	1.1	B_2
58	2178.3	100.0	A_1

[a] Vibrational modes with I_{rel} > 0.5% are listed. – [b] Relative intensities (based on the strongest absorption).

sorptions at 710 and 760 cm^{-1} observed by these authors correspond to the two strongest absorptions of **4** at 710.7 and 758.4 cm^{-1}, and the UV/Vis spectrum is also in excellent agreement with that of **4**. Although benzyne **1** is estimated to be less stable than **4** by 6–8 kcal/mol, the equilibrium concentrations of the highly reactive diradical **1** at room temperature are high enough to account for the formation of anthracene and dichloroanthracene as the trapping products of **1**.[3][11]

The broad UV absorption at 335 nm in the transient spectrum of **4** observed by Schottelius and Chen[3] most closely matches a set of weak bands with maxima at 339 and 358 nm in the matrix spectrum. The strong absorption at 270 nm in the matrix spectrum with an approximately ten times higher extinction coefficient was not reported in the transient spectrum, presumably because this region of the spectrum was masked by other products. Unfortunately, in our experiments the bisketene **2** strongly absorbs at 295 nm, the only transition found in the transient spectrum of **1**[3] and thus it would be hardly possible to detect trace amounts of **1** in the matrix spectra.

In summary, although the matrix isolation of low yields of *p*-benzyne was recently achieved in our laboratory,[16] the synthesis and isolation of derivatives in yields high enough to examine its chemistry still remains a challenge. The barrier for the ring opening of **1** is even lower than that of *p*-benzyne, and so far neither gas-phase pyrolysis nor low-temperature photolysis of a variety of precursors was successful in the isolation of diradical **1**.

Experimental Section

Matrix-isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by co-deposition of a large excess of argon (Messer-Griesheim, 99.9999%, approximately 0.15 mmol/min) and the trapped species on a cold CsI window. To obtain optically clear matrices, the cold window was retained at 30 K during deposition, and the matrix was subsequently cooled to 10 K.

Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range of 400–4000 cm^{-1}. Irradiations were carried out with use of Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics or a Gräntzel mercury low-pressure lamp (254 nm). IR irradiation from the arc lamp was absorbed by a 10-cm path of water. Schott cut-off filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

9,10-Dihydro-9,10-dicarbonylanthracene was synthesized according to a literature procedure described by Blomquist and Meinwald.[17]

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