

m-Benzyne and *p*-Benzyne

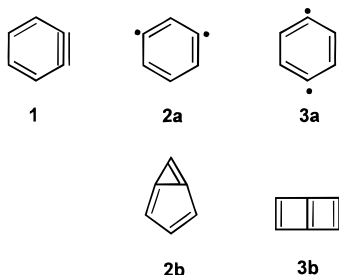
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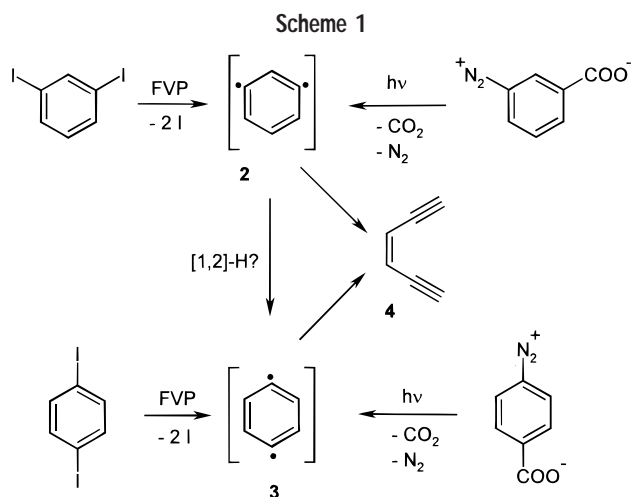
Introduction

For more than half a century the three isomeric benzyne have been a challenge to synthetic and mechanistic organic chemistry. In 1942 Wittig proposed *o*-dehydrobenzene **1** as a reactive intermediate in the decomposition of lithiated halobenzenes,^{1a} and in 1956 Roberts et al. used ¹⁴C isotopic labeling to demonstrate that **1** is formed during the reaction of chlorobenzene and sodium amide.^{1b} Since then **1** and its derivatives have emerged as important synthetic reagents.¹ The ultimate goal of synthetic chemistry is to isolate compounds, and indeed **1** could be generated and isolated in low-temperature matrixes by Chapman and co-workers² more than 25 years ago, and meanwhile this benzyne is thoroughly characterized by IR and UV-vis spectroscopy.^{2–5}



The chemistry and physical properties of *m*-benzyne **2** and *p*-benzyne **3** are much less well understood, although these benzyne, and in particular **3** and its derivatives, have been targets of a renewed interest during the last few years. Much of the motivation to investigate these species stems from the discovery that nature uses benzyne as “warheads” in biologically highly active compounds.⁶ The biological activity of calicheamicin and related antibiotics is triggered by the cyclization of an enediyne moiety to form a *p*-benzyne derivative. Subsequent hydrogen abstraction from double-stranded DNA results in irreversible DNA damage. The concerted re-

search in the synthesis of precursors on one hand and physical and theoretical description on the other hand not only helps to understand this complicated process, but also allows rational design of aromatic diradicals with tailored properties. One approach to this is the introduction of heteroatoms into the benzyne ring.⁷ Early experimental and theoretical studies gave rise to some controversy in the literature since they provided evidence for both the diradical structures **2a** and **3a** and their bicyclic isomers **2b** and **3b**. In 1963 Fisher and Lossing investigated the flash vacuum pyrolysis (FVP; 960 °C, 10^{−3} mbar) of 1,2-, 1,3-, and 1,4-diiodobenzene with mass spectroscopic detection.⁸ On the basis of the measured ionization potential, the C₆H₄ species produced in the FVP of 1,2-diiodobenzene was assigned to the expected *o*-benzyne **1**. However, the two other isomeric diiodobenzenes gave hex-3-ene-1,5-diyne **4** as the principal product, indicating that the dehydrobenzenes **2** and **3** (if formed at all) are not stable under these conditions (Scheme 1). The **3** → **4**



rearrangement is a simple CC cleavage reaction which does not change the CH connectivity, while the formation of **4** from **2** in addition requires the migration of a hydrogen atom. One mechanism that was discussed was the [1,2]-H migration in **2** to give **3**, which then rapidly opens to **4**.

Berry and co-workers studied the gaseous products from the photoinitiated decomposition of the isomeric *o*-, *m*-, and *p*-benzenediazonium carboxylates (Scheme 1) using UV and mass spectroscopy, and claimed that the benzyne **1**, **2**, and **3**, respectively, were formed.⁹ While the formation of **1** from the ortho derivative could be clearly demonstrated in these experiments,^{9a} the structure of the C₆H₄ species observed in the decomposition of *m*- and *p*-benzenediazonium carboxylate^{9b,c} is less clear. In particular, for **3** the lifetime in the gas phase was determined to be more than 2 min,^{9b} which does not correspond to the expectation for a reactive diradical,¹⁰ while under similar conditions the lifetimes of **1** and **2** were in the microsecond to millisecond regime.

The reverse reaction, the cycloaromatization of strained diynes, was shown by Masamune and co-workers in

Wolfram Sander was born in Heidelberg, Germany, in 1954. He received his Diploma degree in chemistry with Hans Plieninger in 1979 and his Ph.D. with Rolf Gleiter at the University of Heidelberg in 1982. He was introduced to the matrix isolation technique as a Postdoctoral Fellow with Orville L. Chapman at the University of California, Los Angeles, and returned to the University of Heidelberg in 1984. After completing his Habilitation in 1989, he joined the Institute of Organic Chemistry at the University of Braunschweig as Associate Professor, and since 1993 he has been Full Professor of Chemistry at the University of Bochum. His research interest in the field of physical organic chemistry is the characterization of reactive intermediates using matrix isolation spectroscopy and time-resolved techniques.

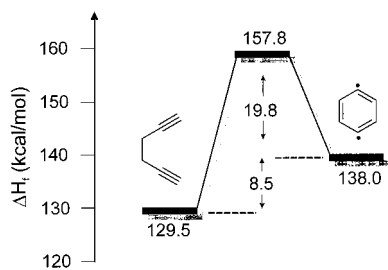
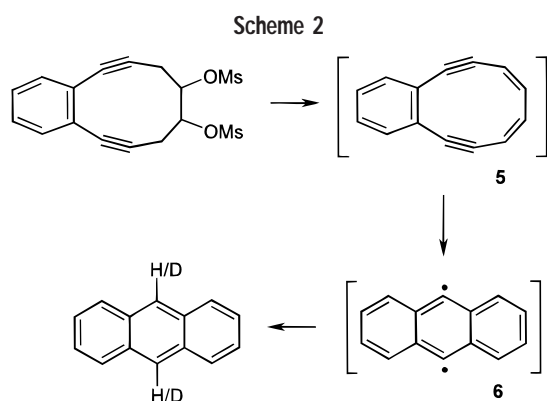


FIGURE 1. Thermochemical data for the reversible **4** → **3** rearrangement. Experimental enthalpies (kcal/mol) published by Roth et al. (ref 14) and Squires et al. (ref 22e).

1971.¹¹ Attempts to synthesize the [10]annulene **5** resulted in the formation of anthracene, which in deuterated solvents was labeled at the 9 and 10 positions, indicating the formation of 9,10-didehydroanthracene **6** as a short-lived intermediate (Scheme 2).



In 1972 Jones and Bergman reported that the thermal ring-opening of *p*-benzyne **3** is reversible, and that the cycloaromatization of enediynes **4** produces **3** as a trapable reaction intermediate.^{12,13} The reversible **4** → **3** isomerization was used by Roth et al. to determine the heat of formation of **3** to 138.0 ± 1 kcal/mol, just 8.5 kcal/mol above that of **4** (Figure 1).¹⁴ The activation barrier for the ring-opening of **3** was measured to be 19.8 ± 1 kcal/mol.

Numerous trapping experiments in solution provided evidence for both the diradicals **2a** and **3a** and the bicyclic structures **2b** and **3b**. Diradical **2a** was obtained from the thermal decomposition of 1,3-benzenediazonium carboxylate¹⁵ and diaryliodonium 3-carboxylates.^{16,17} The dehydrobromination of an indene derivative produced 1,3-didehydronaphthalene with a diradical structure,¹⁸ while on the other hand evidence for the existence of bicyclo[3.1.0]hexatriene **2b** was derived from the dehydrobromination of dibromobicyclo[3.1.0]hexene.^{19,20} The trapping experiments of Bergman and co-workers on the cycloaromatization of **4** clearly demonstrate the diradical character of *p*-benzyne represented by structure **3a**,^{12,13} while elimination of HCl from 3-chloro[2.2.0]bicyclohexadiene in the presence of a reactive diene produced the Diels–Alder trapping product of butalene **3b**.²¹ Thus, the trapping experiments are inconclusive with respect to determining the structure of the trapped species, and in most cases do not even allow differentiation between

trapping of two sequentially formed monoradicals or a diradical.

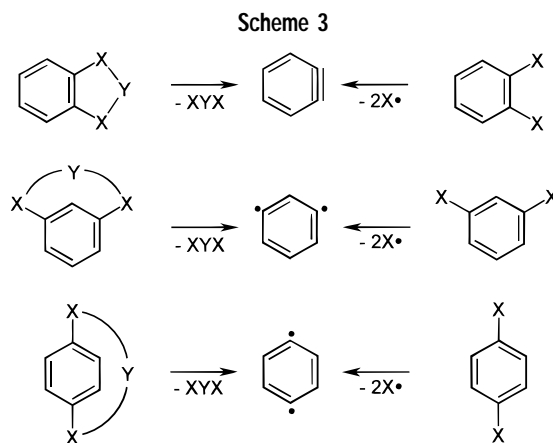
During the last few years very detailed thermochemical data on *m*- and *p*-benzyne obtained from negative ion photoelectron spectroscopy were published by Wenthold, Squires, and co-workers.²² The heats of formation $\Delta H_{f,298}^{\circ}$ of **1**, **2**, and **3** were determined to be 105.1 ± 3.2, 121.9 ± 3.1, and 137.8 ± 2.9 kcal/mol, the latter value in excellent agreement with the measurement of Roth and co-workers,¹⁴ and the singlet–triplet splittings ΔE_{ST} to be 37.5 ± 0.3, 21.0 ± 0.3, and 3.8 ± 0.4 kcal/mol, respectively.^{22e} Thus, both **1** and **2** are thermodynamically more stable than enediyne **4** ($\Delta H_{f,298}^{\circ} = 129.5$ kcal/mol),²³ and the **2** → **4** ring-opening under FVP conditions⁸ is a high-temperature process governed by the entropy term.

The benzyne have been targets of a number of high-level ab initio and DFT calculations which agree with the experimental data in predicting increasing thermodynamic stability in the order **3** < **2** < **1** and a singlet ground state for all three isomers.^{24–29} The experimental values are reproduced best, almost within the error limits, at the CCSD(T) level of theory.^{26–28}

Thus, reliable thermodynamic data on the benzyne are now available, which suggest that all three isomers are kinetically stable at low temperature and in principle should be isolable under suitable conditions, as long as intermolecular reactions are suppressed. While this was demonstrated for **1** many years ago,^{2–5} the matrix isolation of **2** and **3** was only recently achieved in our laboratory.^{30–32,38,39} The recent progress in the isolation and spectroscopic characterization of *m*- and *p*-benzyne **2** and **3** is the topic of this Account.

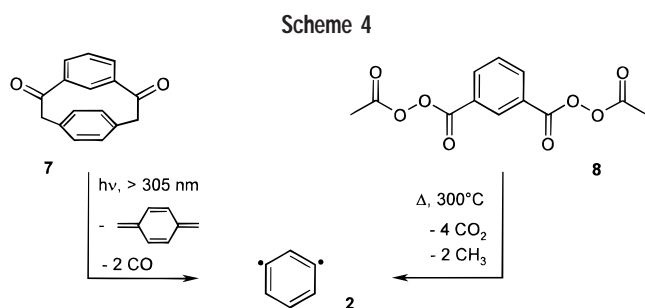
The Parent Benzyne

The major problem in the matrix isolation of benzyne **2** and **3** is to design suitable precursors which allow the synthesis of the benzyne either in the gas phase with subsequent trapping in an inert matrix at low temperature or directly by photolysis of the matrix-isolated precursor. *o*-Benzyne **1** can easily be generated from a variety of benzene derivatives bridged in the ortho position, one of the simplest and most efficient precursors being phthalic anhydride (Scheme 3).⁵ Cleavage of unbridged disubstituted benzenes yields free radicals as byproducts, which



might cause unwanted secondary reactions. Photolysis of matrix-isolated precursors of this type leads to benzyne and radicals in the same matrix cage, which rapidly recombine even at low temperature if the reactive molecules are not separated by inert molecules, such as CO₂. Radical pairs separated by two CO₂ molecules produced by irradiation of matrix-isolated diacyl peroxides were studied by Pacansky and co-workers^{33–36} and recently by Radziszewski et al.³⁷ We therefore investigated the thermo- and photochemistry of isophthaloyl and terephthaloyl bis-(diacylperoxides), which should yield free radicals, two molecules of CO₂, and benzyne **2** and **3**, respectively. Cyclic precursors for the benzyne which avoid the formation of free radicals are meta- and paracyclophanediketones. These cyclophanes are expected to be photolytically cleaved (α -cleavage) to give CO, *p*-xylylene, and the benzyne.

***m*-Benzyne 2.** The UV photolysis of [2.2]metaparacyclophanediketone **7** in solid argon at 10 K indeed produced the expected fragments CO and *p*-xylylene (Scheme 4) and a novel compound with a very strong IR absorption



at 547 cm⁻¹.^{31,38} The comparison of the experimental IR spectrum with that calculated at the CCSD(T) level of theory revealed a very high agreement of experiment and theory; in particular the 547 cm⁻¹ vibration was assigned to a b₁ symmetrical ring deformation mode calculated (unscaled) at 545 cm⁻¹ (strongest absorption in the calculated spectrum). This vibration changes the hybridization of the radical centers and therefore sensitively depends on the accurate description of the electronic structure of **2**. GVB theory, for example, seriously overestimates the frequency and underestimates the intensity of this mode.³⁸ Obviously, CCSD(T) theory reliably reproduces not only the thermodynamic properties of **2**, but also the vibrational spectrum.³⁹

The identification of **2** was confirmed by the independent synthesis from bis(diacylperoxide) **8**, which at 300 °C in the gas phase smoothly decomposes to CO₂, methyl radicals, and **2** (Scheme 4). Under these conditions—FVP with subsequent trapping of products in argon at 10 K—benzyne **2** and the methyl radicals are statistically distributed in the matrix and isolated in separate matrix cages. Annealing of the matrix at 35 K allows for the diffusion of trapped species and bimolecular reactions. Both **2** and CH₃ rapidly disappear, which is easily monitored by IR spectroscopy. Photolysis of matrix-isolated **8** also produces **2**; however, it is now formed in the same matrix cage as the methyl radicals, separated only by two

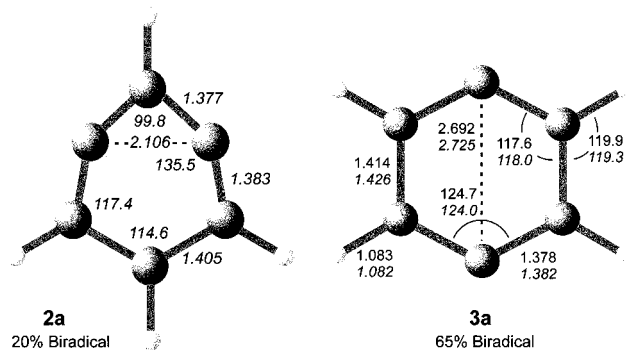
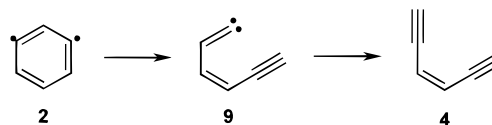


FIGURE 2. Geometrical data of *m*-benzyne **2a** and *p*-benzyne **3a** from CCSD(T) calculations (refs 26, 27, and 38).

molecules of CO₂. Consequently, due to unwanted thermal reactions, the yield of **2** is now much lower.

An interesting aspect of the thermolysis of **8** and other precursors such as isophthaloyl diiodide is the formation of enediyne **4** at higher temperatures (>600 °C),³⁰ in agreement with the observation of Fisher and Lossing on the FVP of 1,3-diiodobenzene.⁸ Since, according to all experimental and theoretical evidence, **3** is about 16 kcal/mol less stable than **2**, a thermal **2** → **3** isomerization followed by the ring-opening of **3** is mechanistically not plausible. More likely is the ring-opening of **2** to give vinylidene **9**, which rapidly⁴⁰ rearranges to **4**.³⁰ The barrier



of the ring-opening of **2** is estimated to be much higher than that of **3**, and thus this process limits the lifetime of **2** only at very high temperatures. An alternative route is a concerted H-migration and ring-opening with a calculated barrier (B3LYP/6-31G(d,p)) of about 50 kcal/mol.⁴¹ The IR spectrum of **2** allows us to distinguish between the diradicaloid and the bicyclic structures **2a** and **2b** (Figure 2). Structure **2b** is a minimum at the RB3LYP but not at the CCSD(T) level of theory, and therefore the CCSD(T) spectrum of **2a** and the RB3LYP spectrum of **2b** are compared to the experimental spectrum of **2**. According to these calculations, the C1–C3 bond length of the highly strained bicyclic structure **2b** is 1.6 Å, and the C1–C2–C3 angle is 72.6° (Figure 2). Characteristic of the calculated spectrum of **2b** is the intense a₁ symmetrical C1–C3 stretching vibration at 411 cm⁻¹, which is not found in our experimental spectrum.

In diradical **2a** the a₁ symmetrical mode, with a large contribution of the C1–C3 stretching, is calculated to be of low intensity at 386 cm⁻¹.³⁸ The red shift of this mode compared to that in **2b** reflects the weaker C1C3 bond in **2a**. Overall, band positions and relative intensities in the IR spectra calculated for **2a** and **2b** differ enough for a definitive assignment of the observed spectrum to the diradicaloid structure **2a**. The same conclusion was drawn by Squires and co-workers from the negative ion photoelectron spectroscopy of **2**.^{22e} For the singlet state an

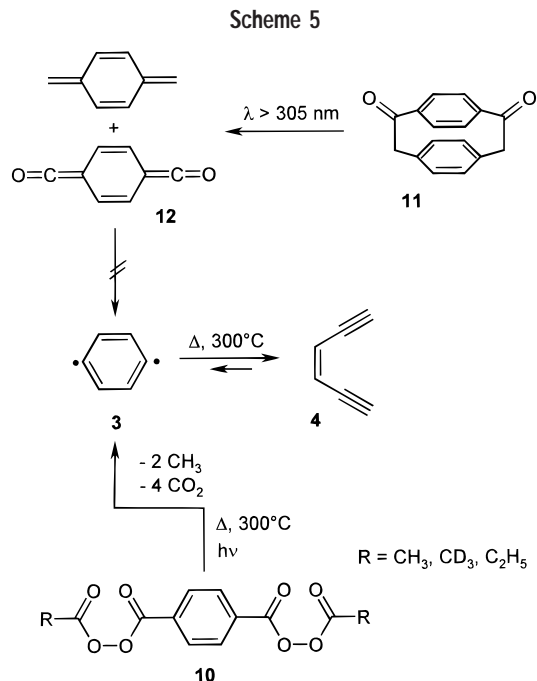
extended progression with irregular peak spacings of ca. 300 cm⁻¹ was observed, which rules out the bicyclic structure **2b** with a short C1–C3 bond.

Compared to benzene, the diradicaloid structure **2a** is strongly distorted, with the C1–C3 distance (distance between the radical centers) reduced from 2.4 Å (in benzene) to 2.1 Å and the C1–C2–C3 angle reduced from 120° to 102°, while the angles at the radical centers (C2–C1–C6 and C2–C3–C4) increase to 136°. The ring strain introduced by this distortion is balanced by the stabilizing through-bond interaction between the radical centers C1 and C3. This stabilization profits both from a smaller C1–C3 distance and therefore larger overlap of the singly occupied orbitals and from the rehybridization at the radical centers (due to the increase of the bond angle from 120° to 136°), which increases the p character of these orbitals. In addition, the radical centers are stabilized by through-bond interactions involving σ* orbitals of the vicinal CC bonds. This partial delocalization of the single electrons reduces the diradical character of **2a** to just 20%, which is reflected by the comparatively large singlet–triplet splitting of 21 kcal/mol. Neither **2a** nor **2b** is therefore accurate a description of the structure and bonding of **2**.

***p*-Benzyne 3.** In principle the same type of precursors—cyclophanes and bis(diacyl peroxides)—should also be suitable for the synthesis of **3** in low-temperature matrixes. A problem arises from the low barrier for the ring-opening of **3** of only 20 kcal/mol,¹⁴ which leads to very small equilibrium concentrations of **3** and mainly enediyne **4** during gas-phase pyrolyses. Indeed, repeating Bergman's original experiment^{12a}—the deuterium scrambling in 1,6-*d*₂-**4**—under FVP conditions revealed that the exchange of deuterium, and thus the cycloaromatization, is very rapid at temperatures around 500 °C.⁴² As expected, the pyrolysis of peroxide **10** produced **4** as the main product while **3** was not observed in the IR spectra. These experiments demonstrate that FVP with subsequent trapping of the products in solid argon is not suitable to obtain concentrations of **3** high enough for IR detection.

UV photolysis of matrix-isolated cyclophane **11** gave *p*-xylylene and diketene **12** in a clean reaction (Scheme 5).⁴³ Ketenes can be used as thermal or photochemical precursors of carbenes in the gas phase and in solution,^{44,45} although the fragmentation to CO and carbenes is an endothermic reaction. We therefore hoped that further irradiation of **12** would result in the subsequent loss of two molecules of CO and formation of **3**. Unfortunately, matrix-isolated **12** proved to be stable toward prolonged UV irradiation, presumably because of a rapid in-cage recombination of CO and the ketocarbene formed as the primary intermediate. This is consistent with many observations of the photostability of matrix-isolated ketenes, while the reverse reaction, trapping of carbenes with CO to give ketenes, is frequently used to identify carbenes in matrixes.^{46–48} Thus, this route to *p*-benzyne **3** had to be dropped.

Finally, we investigated the matrix photolysis of peroxides **10** (Scheme 5), which on irradiation in solid argon



gave large amounts of CO₂, methyl (R = CH₃, CD₃) or ethyl (R = C₂H₅) radicals, and several other products.³² A novel compound obtained in low yields exhibited a strong IR absorption at 724.8 cm⁻¹, exactly where DFT calculations (UB3LYP/6-311G+G(p,d)) predict the strongest absorption of **3** (b_{3u} symmetrical mode at 758 cm⁻¹, 728 cm⁻¹ after the usual scaling). A second vibration at 980.0 cm⁻¹ was assigned to the b_{1u} symmetrical mode calculated at 1005 cm⁻¹ (scaled). There are only two further vibrations predicted to be of similar intensity: one at 427 cm⁻¹, which could not be observed due to the low signal-to-noise ratio in this region of the spectrum, and one at 886 cm⁻¹, which strongly overlaps with absorptions of other matrix constituents. On annealing the matrix at 40 K, the free radicals and **3** rapidly disappeared. The assignment of two IR absorptions of **3** was confirmed by Radziszewski's investigations of the 248 nm photochemistry of 1,4-diodobenzene in neon matrixes at 6 K.³² Although the yield of **3** was extremely low, the same two IR bands were clearly observed in this experiment. In addition, all IR active absorptions below 2000 cm⁻¹ predicted in the calculations were found experimentally, thus confirming the assignment of **3**.

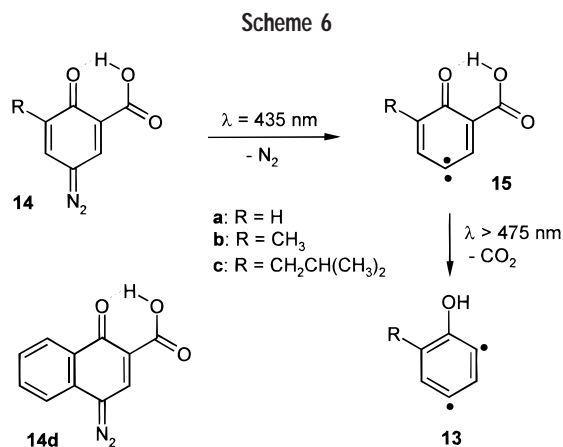
The vibrational data of singlet **3** extracted from the negative ion photoelectron spectrum^{22e} nicely complement our matrix data. Two totally symmetric, and thus IR inactive, vibrations at ca. 600 and 1000 cm⁻¹ were reported,^{22e} corresponding to a_g symmetrical modes predicted at 600 and 980 cm⁻¹ (UB3LYP, scaled).³² This also demonstrates the reliability of DFT calculations in reproducing IR spectra of singlet diradicals of type **3a**.

The diradical character of *p*-benzyne **3** is calculated to be about 65%, much larger than that of *m*-benzyne **2**.²⁶ This results from the larger distance of the radical centers of 2.7 Å in **3a** (CCDS(T), Figure 2), and therefore through-space interactions are less important. The interaction, however, is still large enough to slightly stabilize the lowest

singlet compared to the triplet state. The butalene structure **3b** is much higher in energy than the diradical structure **3a**, and the calculated IR spectrum of **3b** does not match the experimental data. We therefore conclude that *p*-benzyne is described best as diradical **3a**.

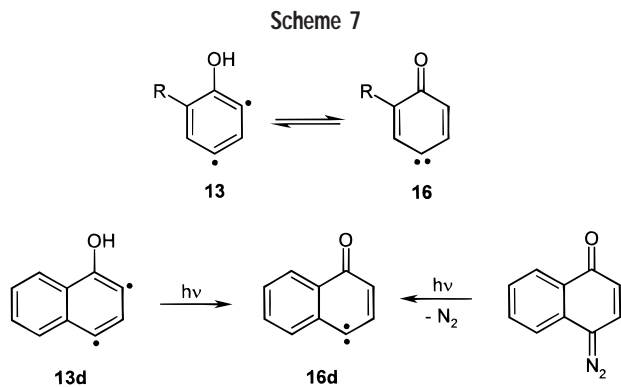
Derivatives of *m*- and *p*-Benzyne

***m*-Dehydrophenols 13.** A completely different route to derivatives of *m*-benzyne starts from *p*-benzoquinone diazide carboxylic acids **14** (Scheme 6),^{38,49} which yield



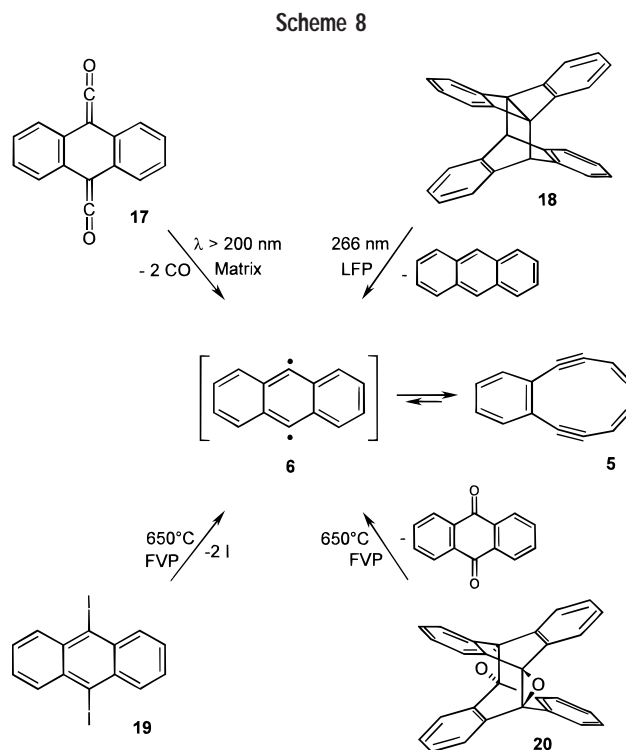
carbenes **15** on irradiation with monochromatic blue light ($\lambda = 435 \text{ nm}$). The crystal structures of diazides **14a** and **14c** reveal very strong intramolecular hydrogen bonds with distances of the two hydrogen-bridged oxygen atoms of only 2.475 Å⁵⁰ and 2.442 Å,³⁸ respectively. The IR spectra indicate that these hydrogen bonds are present in the carbenes **15** as well, and it is thus not surprising that on photodecarboxylation (irradiation with $\lambda > 475 \text{ nm}$) the carboxyl hydrogen atom is transferred to the ketone oxygen atom to give dehydrophenols **13**. Again, CCSD(T) calculations helped in assigning the IR spectra of the benzyne.^{38,39} The parent diazide **14a** can be easily modified by introducing side chains (e.g., **14b** and **14c**) or by benzo-annelation (**14d**), which makes substituted dehydrophenols **13** easily available. This synthesis is not limited to matrix isolation but could also be shown to be an efficient source of *m*-benzynes in solution.³⁸

Benzyne **13** are tautomers of carbenes **16**, and we were interested in whether there was a benzyne to carbene rearrangement. Indeed, **13a** (R = H) shows UV photo-



chemistry, but instead of the well-known 4-oxo-2,5-cyclohexadienylidene **16a**,⁵¹ ring-opened ketenes of unknown constitution are formed.³⁸ Only the benzo-annelated **13d** rearranged to the corresponding carbene **16d** (Scheme 7), which provided an independent proof for the constitution of **13d**.

9,10-Didehydroanthracene 6. Dehydroanthracene **6** was postulated by Masamune and co-workers as a reactive intermediate during the attempted synthesis of diyne **5** (Scheme 2),¹¹ and the matrix isolation of **6** was reported in 1976 by Chapman and Kolc.⁵² Irradiation ($\lambda > 200 \text{ nm}$) of bisketene **17** in organic glasses (3-methylpentane, 77 K) yielded a species with a series of UV-vis absorptions in the range 256–449 nm. Warming the photolyzed mixture to room temperature produced anthracene, and in CCl₄ solution 9,10-dichloroanthracene, both the expected trapping products of diradical **6**. In solid argon at 10 K the new compound showed IR absorptions at 710 and 760 cm⁻¹. On the basis of the trapping experiments and the spectroscopic data, the new compound was assigned as dehydroanthracene **6** (Scheme 8).



Recently Schottelius and Chen investigated the photochemistry of **18**, a formal adduct of **6** and anthracene, using laser flash photolysis (LFP; Scheme 1).⁵³ 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 a 500 μs lifetime and an absorption maximum at 335 nm. The fast transient was assigned as **6**, while the slow transient was assigned the structure of the ring-opened 3,4-benzocyclodeca-3,7,9-triene-1,5-diyne **5** (Scheme 8). Since the UV data of **6** from the LFP experiments⁵³ were in disagreement with the earlier matrix spectra,⁵² the alternative thermal precursors **19** and **20**

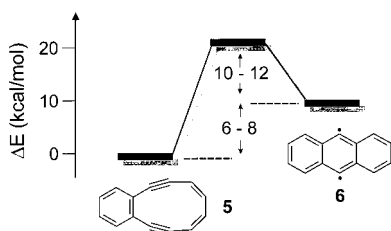


FIGURE 3. Thermochemical data for the reversible **5** → **6** rearrangement. Estimated energies (kcal/mol) based on DFT calculations from ref 54.

were studied in our laboratory,⁵⁴ and in addition the matrix photochemistry of bisketene **17** was reinvestigated.⁵⁵

FVP of both precursors with subsequent trapping of the products in argon at 10 K produced the ring-opened diene **5**, identified by comparison of experimental and calculated IR spectra. No evidence for dehydroanthracene **6** was obtained from these experiments, which suggests that **6** does not survive the gas-phase pyrolyses. This is in agreement with estimations from LFP experiments⁵³ and DFT calculations⁵⁴ of a barrier for the ring-opening of about 12 kcal/mol, even less than that of *p*-benzynes **3** (Figure 3). Since the ring-opening is predicted to be slightly exothermic, the chance of generating **6** via gas-phase pyrolysis is very low.

Matrix-isolated **19** is photochemically stable, and **20** decomposes only at very short wavelength UV irradiation slowly to compounds of unknown constitution. These precursors are thus not suitable for the photochemical generation of aryne **6**. Bisketene **17**, on the other hand, is easily decarbonylated by UV irradiation, as was observed by Chapman and Kolc.⁵² Due to the advances in computational chemistry during the last few years, IR spectra of molecules as large as **17** and its possible photoproducts can now be reliably calculated. Broad band UV irradiation of **17** exactly reproduced the IR and UV–vis spectra described previously by Chapman and Kolc,⁵² which could now, by comparison with the products from the pyrolyses of **19** and **20**,⁵⁴ be assigned to diene **5**. Monochromatic UV irradiation (254 nm) of **17**, however, produced CO and the novel ketocarbene **21** (Scheme 9).⁵⁵ Carbene **21** proved

to be photolabile, and visible light irradiation resulted in the loss of the second molecule of CO followed by the ring-opening to diene **5**.

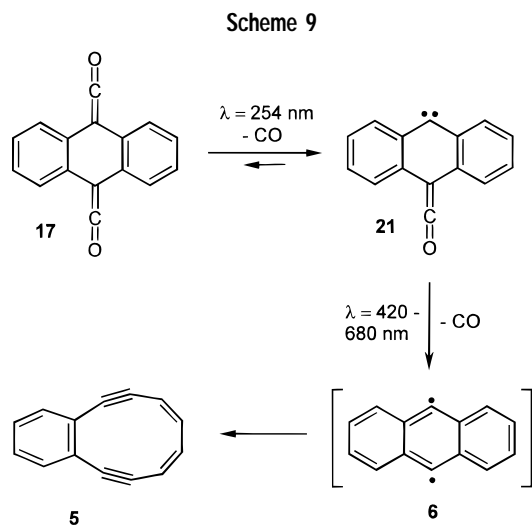
Concluding Remarks

Although the physical characterization of the benzenes **2** and **3** made progress during the last few years, the chemistry of these unusual compounds is still largely unknown. Atom abstractions have been described, but in several instances it is not clear whether indeed the free benzenes were trapped or rather monoradicals were trapped in two consecutive steps. Matrix isolation in combination with kinetic studies in solution can help in developing new and efficient synthetic routes to the benzenes and in unraveling the chemistry of these diradicals. While methods for the synthesis and isolation of *m*-benzynes **2** and several of its derivatives are described in this Account, *p*-benzynes **3** still remains a challenge. An interesting chemical application of the benzenes that has not yet been explored is their use as building blocks in cycloaddition reactions. Another field for future research is the fine-tuning of the singlet–triplet splitting, and thus of the chemical reactivity and biological activity of the benzenes. Benzenes **2** and **3** are prototypes of meta- and para-coupled aromatic diradicals with low-lying high-spin states. In this field the isolation and characterization of benzenes and related aromatic polyradicals could help in calibrating and improving theoretical methods and in designing novel organic high-spin systems. Thus, exploring the structure and reactivity of the benzenes and related species will remain a challenge to synthetic, mechanistic, and computational chemistry.

*This Account is dedicated to the memory of Robert Squires, who contributed much to the knowledge of the benzenes. His data on the thermochemistry of the benzenes are landmarks in the field of reactive intermediates, and in numerous discussions he inspired the work done in Bochum. I am indebted to Andreas Balster, Dr. Götz Bucher, Carsten Kötting, Dr. Ralph Marquardt, Dr. Holger Wandel, Hans Henning Wenk, and other co-workers cited in the references for hundreds of time-consuming matrix experiments which were finally rewarded by the matrix isolation and spectroscopic characterization of *m*- and *p*-benzynes. Without the intense and fruitful interplay of experiment and theory, our work in this field would not have been successful. I am grateful to Professor Elfi Kraka and Professor Dieter Cremer of the University of Göteborg for many discussions, advice in all questions of theory, and a large number of time-consuming calculations. I also thank Professor Paul Wenthold for preprints of his recent papers and discussions on the thermochemistry of the benzenes. The work from our laboratory was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.*

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