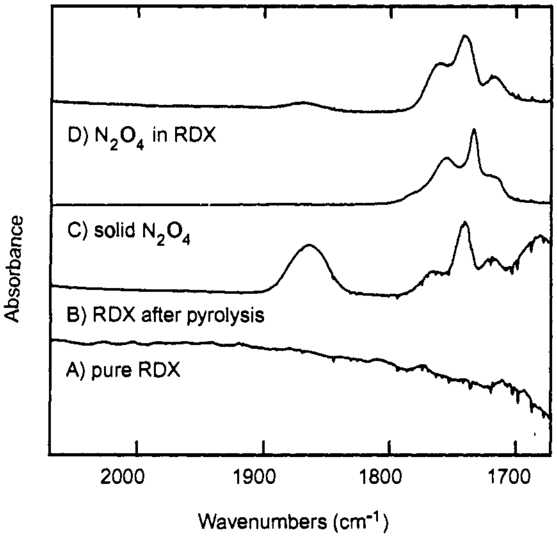

Figure 1. (A) Portion of the infrared spectrum of RDX following deposition from a Knudsen oven onto a 77 CsI optical window. The sample was warmed to room temperature and covered with a second CsI window, and the assembly was recooled to 77 K in high vacuum prior to obtaining the spectrum. (B) Infrared spectrum of the same sample as in trace A following CO_2 laser pyrolysis. The beam was rastered over the sample such that each region was subjected to a single laser pulse (4.7 J/cm^2 at 944 cm^{-1}). (C) Infrared spectrum of a thin film of N_2O_4 deposited from the vapor (NO_2/N_2O_4) onto a 77 K CsI window in vacuum. (D) Infrared spectrum of a thin film sample of NO_2/N_2O_4 codeposited with RDX onto a 77 K CsI window.

to an estimated 500 K in 35 μs (the nominal laser pulse width). Because the films are in contact with a relatively massive substrate, they rapidly cool back to 77 K with a characteristic time scale estimated to be 2 ms based on the thermal conductivity of RDX.[2,15] The extent of heating and decomposition can be controlled by changing the laser fluence (energy per unit area per pulse). A complete description of the experimental technique and results for RDX pyrolysis will be presented in a forthcoming paper.

The formation of initial pyrolysis products is detected by obtaining transmission FTIR spectra of the thin films before and after CO_2 laser irradiation. A representative spectrum is shown in Figure 1. Trace A shows a portion of the infrared spectrum of an RDX film prior to photolysis. Although no RDX absorptions are apparent here, other regions of the spectrum show a complicated series of intense absorption bands. The spectrum obtained after laser pyrolysis at high fluence (4.7 J cm^{-2}) shows the appearance of new absorption features centered at 1864 and 1735 cm^{-1} (trace B). The 1864-cm^{-1} band is attributable to nitric oxide on the basis of good agreement with the gas-phase vibrational frequency of NO (1876 cm^{-1}). The triplet of bands centered at 1735 cm^{-1} is similar to an absorption band identified as CH_2O in a previous study of UV photolysis of matrix-isolated RDX by Alix and Collins.[16,17] However, we believe it is actually due to N_2O_4, the dimer of NO_2, which exhibits a strong absorption in this region.[18] Our assignment was easily confirmed by obtaining the FTIR spectrum of a thin solid film of N_2O_4 deposited directly from the vapor (an equilibrium mixture of NO_2 and N_2O_4) onto the IR window at 77 K (shown in trace C). The spectrum of a mixed sample of N_2O_4 in RDX was also obtained (trace D). In each case, the position and shape of the N_2O_4 absorption band closely match those of the photolysis product shown in trace B. In addition to NO and N_2O_4, the IR spectra following high-fluence pyrolysis show evidence for formation of HCN (2086 cm^{-1}), N_2O (2236 cm^{-1}), and CO_2 (2343 cm^{-1}).

The N_2O_4 absorption band was also observed in experiments conducted at lower laser fluence (about 2.4 J/cm^2 per pulse). Under these conditions, only a small fraction of the RDX molecules are dissociated. The absorption bands of N_2O, HCN, and CO_2 were absent, and only a trace of NO was observed. *These experiments provide convincing evidence that N–N bond scission is the first step in the thermal decomposition mechanism of RDX.*

The only other reasonable decomposition channel is the concerted depolymerization observed by Zhao et al.[11] which forms methylenenitramine, CH_2NNO_2. Although the infrared spectrum of this molecule is not known, its vibrational frequencies have been calculated by Mowry et al.[19] Most of the calculated frequencies lie close to absorption bands of RDX and would be difficult to observe in this type of pyrolysis experiment. However, the bands expected at 1220, 896, and 621 cm^{-1} lie in regions of the IR spectrum which are relatively free of interference from RDX and should have been detected using spectral subtraction methods if CH_2NNO_2 were produced by pyrolysis. There is no evidence for any of these bands in the pyrolysis experiments carried out in this study.

Finally, we note that our conclusion that solid RDX dissociates via N–N bond scission is not necessarily in conflict with the conclusion of Zhao et al. that depolymerization dominates in the gas-phase decomposition mechanism. We speculate that the presence of neighboring molecules in the condensed phase strongly inhibits the depolymerization mechanism due to the large positive volume of activation expected for this three-body channel. In contrast, the product molecules separate freely in the analogous gas-phase process. Therefore, both our results and those of Zhao et al. may be correct and compatible with each other. They simply correspond to very different experimental conditions.

Acknowledgment. This research is supported by the U.S. Army Research Office under Contract No. DAAL03-90-G-0043.

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Iron-Mediated [4 + 2] Cycloaddition of 1,3-Butadiene with Ethyne and Propyne in the Gas Phase

R. Bakhtiar, J. J. Drader,† and D. B. Jacobson*

Department of Chemistry
North Dakota State University
Fargo, North Dakota 58105-5516

Received February 25, 1992

The Diels–Alder reaction is a versatile and convenient route to stereospecific synthesis of six-membered rings.[1] The low reactivity of unactivated alkynes and alkenes as dienophilic reagents, however, is a major limitation of this [4 + 2] cycloaddition process.[2] Transition metal complexes have been found to facilitate intermolecular[3-5] and intramolecular[6] dienyne cycloadditions, presumably via η^3-complex formation and reductive

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* Author to whom correspondence should be addressed.

† Ronald E. McNair Scholar.

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elimination.[7] In this report we describe [4 + 2] cycloaddition of 1,3-butadiene with ethyne and propyne mediated by bare Fe^+ in the gas phase.

Experiments were performed on a Nicolet FTMS-1000 Fourier transform mass spectrometer.[8-10] Fe^+ was generated by laser desorption/ionization from a high-purity iron foil[11] with Fe(1,3-butadiene)$^+$ formed by dehydrogenation of 1-butene (reaction 1).[12]

$$Fe^+ + CH_2{=}CHCH_2CH_3 \rightarrow FeC_4H_6^+ + H_2 \qquad (1)$$

1-Butene was introduced into the vacuum chamber via a pulsed solenoid inlet valve[13] in order to prevent complicating side reactions with background 1-butene.[12] A static argon pressure of 1×10^{-5} Torr was maintained throughout these experiments and serves to facilitate ion thermalization prior to reaction and serves as the target for collision-activated dissociation (CAD).[14,15] Neutral reactant pressures were on the order of $(2\text{–}4) \times 10^{-8}$ Torr.[16]

Both ethyne and propyne react rapidly with Fe(1,3-butadiene)$^+$ by reactions 2 and 3 with rate constants (k) of $(8.7 \pm 2.6) \times 10^{-10}$ and $(1.4 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, respectively.[16,17] The structures of **1** and **2** were probed by CAD and specific ion/molecule reactions.

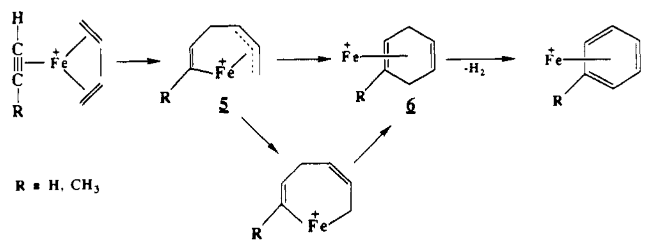
$$FeC_4H_6^+ + C_2H_2 \longrightarrow \begin{cases} \xrightarrow{0.92} \underset{\mathbf{1}}{FeC_6H_6^+} + H_2 & (2a) \\ \xrightarrow{0.08} Fe^+ + (C_6H_8) & (2b) \end{cases}$$

$$Fe(C_4H_6)^+ + HCCCH_3 \longrightarrow \begin{cases} \xrightarrow{0.97} \underset{\mathbf{2}}{FeC_7H_8^+} + H_2 & (3a) \\ \xrightarrow{0.03} Fe^+ + (C_7H_{10}) & (3b) \end{cases}$$

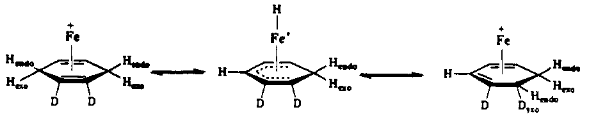
CAD of both **1** and **2** yields exclusive formation of Fe^+, indicating C–C bond formation between diene and dienophile. CAD breakdown curves (fragment ion abundances vs kinetic energy) for **1** and authentic Fe(benzene)$^+$ (**3**) as well as for **2** and authentic Fe(toluene)$^+$ (**4**) are identical (same products and energy dependency). In contrast, CAD of isomeric $FeC_7H_8^+$ ions, Fe(cycloheptatriene)$^+$ and Fe(bicyclo[2.2.1]hepta-2,5-diene)$^+$, yields significant C–C bond cleavage products.

Additional structural information for **1** and **2** was obtained by specific ion/molecule reactions. Both **1** and **3** undergo *exclusive*, rapid adduct formation with C_2H_2 ($k = 3.0 \pm 0.9$) $\times 10^{-10}$ and $(2.8 \pm 0.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively). Rapid alkyne adduct formation is characteristic of Fe(arene)$^+$ species,[18] with stabilization presumably involving infrared radiative emission.[19] Benzene-d_6 reacts similarly with both **1** and **3** to yield primarily adduct formation (ca. 90%) and some C_6H_6 displacement (ca. 10%) ($k = (1.4 \pm 0.4) \times 10^{-9}$ and $(1.2 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, respectively, for **1** and **3**). CAD of each of these $Fe(C_6H_6)(C_6D_6)^+$ adducts yields competitive C_6H_6 (52%) and C_6D_6 (48%) eliminations. $FeC_7H_8^+$ ions, **2** and **4**, also yield exclusive, rapid adduct formation with propyne ($k = (9.1 \pm 2.7) \times 10^{-10}$ and $(1.0 \pm 0.3) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, respectively). The structural studies above (CAD combined with ion/molecule reactions) strongly support formation of Fe(benzene)$^+$ and Fe(toluene)$^+$ in reactions 2a and 3a.

Scheme I



A proposed mechanism for formation of Fe(benzene)$^+$ and Fe(toluene)$^+$ in reactions 2 and 3 involves initial formation of an η^3-complex, **5**, followed by reductive elimination, yielding a coordinated nascent 1,4-cyclohexadiene ([4 + 2] cycloaddition) complex, **6** (Scheme I).[3-7] The high efficiency[20] of reactions 2 and 3 suggests no significant barriers for these processes.[21] Formation of Fe(1,4-cyclohexadiene)$^+$ and Fe(1-methyl-1,4-cyclohexadiene)$^+$ from ethyne and propyne, respectively, is highly exothermic.[22] Subsequent dehydrogenation yields the corresponding Fe(benzene)$^+$ and Fe(toluene)$^+$ complexes.[24] Ethyne-d_2[25] reacts with Fe(1,3-butadiene)$^+$, yielding H_2 (97%), HD (3%), and D_2 (≪1%) eliminations. [4 + 2] cycloaddition initially forms species **7** with Fe^+ bridging the ring where only the endo ring hydrogens are available for abstraction by iron.[26] Reversible hydrogen abstractions result in migration of the double bonds around the ring (reaction 4), however; only the two original endo ring hydrogen atoms are available for elimination. The small amount of HD and D_2 eliminations (ca. 3%) with ethyne-d_2 may be due to 1,5-sigmatropic shifts (exofacial migration) for **8**, which would yield an endo deuterium species.[27] Absence of methane elimination with propyne, reaction 3, is consistent with Scheme I where initial cycloaddition yields **6**, which can only undergo dehydrogenation (reversible hydrogen abstraction yields an *exo*-methyl species, e.g., reaction 4).



(4)

7 **8**

Reaction of Fe(1,3-butadiene)$^+$ with both alkenes (ethene, propene, 1,1-difluoroethene) and nitriles (hydrogen cyanide, acetonitrile) was studied. *Slow* adduct formation was the exclusive process with *no* cycloaddition observed. CAD of these adducts yields initial formation of $FeC_4H_6^+$ exclusively (i.e., simple loss of alkene or nitrile).

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The above results provide evidence for facile [4 + 2] cycloaddition of 1,3-butadiene with ethyne and propyne mediated by atomic Fe^+ in the gas phase. We are exploring the scope of this novel cycloaddition process by varying the diene, dienophile, and the ligand environment on Fe^+ as well as studying other transition metals. In particular, the electronic structure of both diene and dienophile will be varied in order to address the electronic requirements for cycloaddition.

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Rosarin: A New, Easily Prepared Hexapyrrolic Expanded Porphyrin

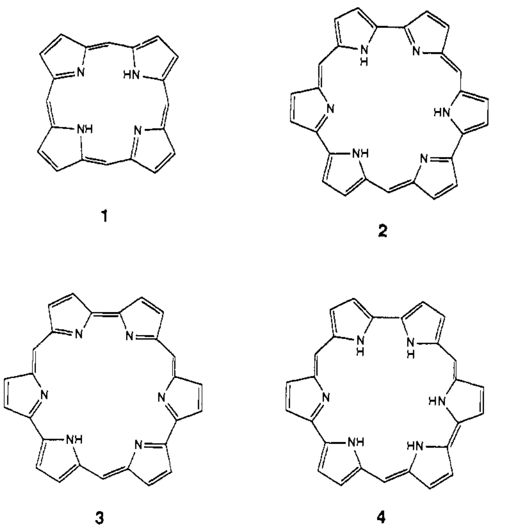
Jonathan L. Sessler,[*,†] Steven J. Weghorn,[†]
Takashi Morishima,[†] Miguel Rosingana,[†] Vincent Lynch,[†]
and Virgil Lee[‡]

Department of Chemistry and Biochemistry
University of Texas at Austin, Austin, Texas 78712
Department of Chemistry, Stanford University
Stanford, California 94305

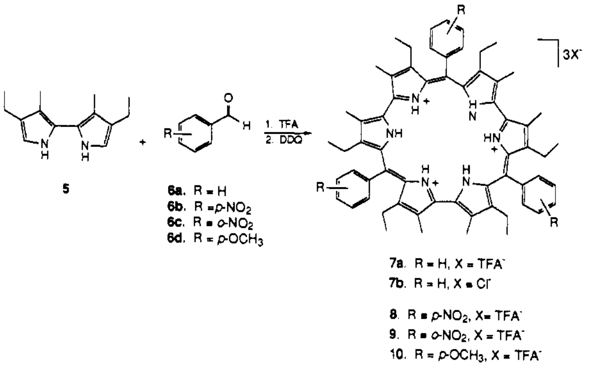
Received June 25, 1992

The porphyrins (e.g., porphine, **1**) are of ubiquitous biological importance and remain among the most widely studied of all known macrocycles. Increasingly, however, attention is being devoted to the study of larger pyrrole-containing macrocycles. Such larger systems, the so-called "expanded porphyrins",[1] appear attractive with regard to a variety of biomedical applications ranging from magnetic resonance imaging (MRI)[1-3] and photodynamic therapy (PDT)[1,4,5] to anion chelation and drug delivery.[1,6] While there are now a number of expanded porphyrins known,[1] including penta- and hexapyrrolic macrocycles such as sapphyrin,[7] pentaphyrin,[8] hexaphyrin,[9] and rubyrin,[10] none is easy to prepare. Thus, there remains a need for a general and facile synthesis of expanded porphyrins. We now wish to report such a synthesis and, also, present the first member of a new class of alkyltris(bipyrrole)trimethine-derived expanded porphyrins of generalized structure **2**.[11] On the basis of the bright-red-to-purple color of the triprotonated derivatives, we have assigned the trivial name rosarin (from the Latin *rosa*) to this new class of molecules (Chart I).

Chart I. Porphine and Generalized 22π-, 24π-, and 26π-Electron Rosarins



Scheme I. Synthesis of Protonated Rosarins **7a,b–10**



The synthesis of the protonated form of the title molecule, 4,9,13,18,22,27-hexaethyl-5,8,14,17,23,26-hexamethyl-2,11,20-triphenylrosarin (**7**), is shown in Scheme I. The reaction is based on a general synthesis of tetra-meso-substituted porphyrins first reported by Rothemund in 1936[12] and subsequently optimized by others.[13-16] In this approach, a 2,5-unsubstituted pyrrole is condensed with an aromatic aldehyde under acidic, oxidative conditions. In the present synthesis, the pyrrolic starting material is replaced by an alkyl-substituted bipyrrole subunit, such as **5**[7c] (Scheme I). Thus, the preparation of triphenylrosarin **7** bears a formal resemblance to recent syntheses of highly strained tet-

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[†] University of Texas at Austin.

[‡] Stanford University.

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