Triradicals

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Reactivity of the 3,4,5-Tridehydropyridinium Cation—An Aromatic σ,σ,σ-Triradical**

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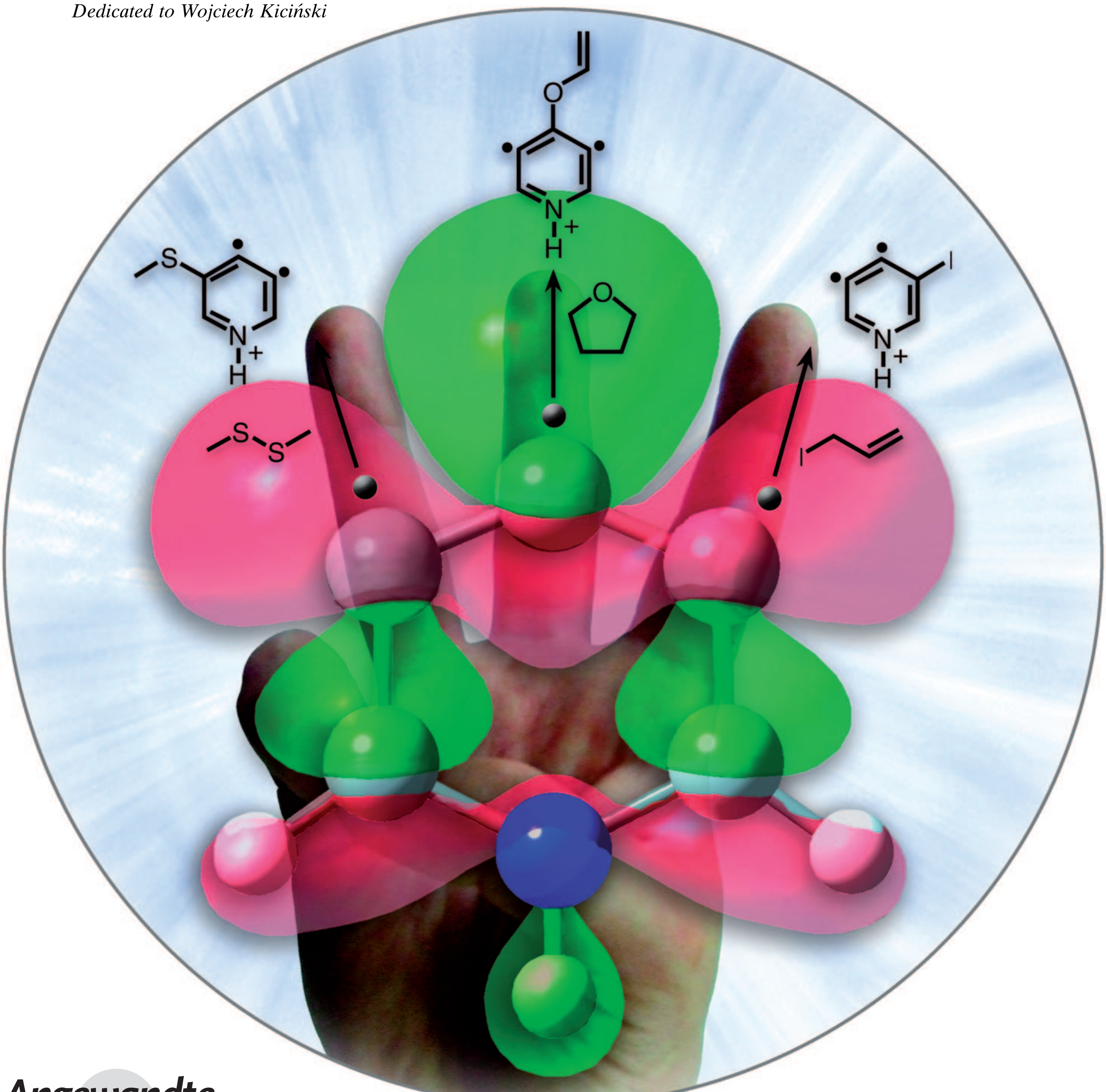
Dedicated to Wojciech Kiciński



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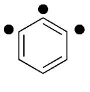
Aromatic carbon-centered σ,σ,σ-triradicals (**1**–**3**) have been the subject of several recent studies.[1–8] Theoretical studies[1–4] have predicted that the ${}^2A_1$ state is the ground state for 1,3,5-tridehydrobenzene (**3**). The ground state of 1,2,3-tridehydrobenzene (**1**) was initially assigned[2b,c] to be ${}^2B_2$, but later experimental and theoretical studies[6,7] showed that the ground state is actually ${}^2A_1$, with the ${}^2B_2$ state lying about 1–2 kcal mol^{-1} higher in energy. The least studied isomer, 1,2,4-tridehydrobenzene (**2**), has been predicted[2c] to have a ${}^2A'$ ground state.



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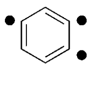

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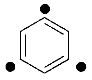

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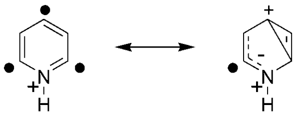
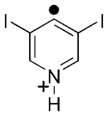
Experimental data for the tridehydrobenzenes are limited. The few studies that have been reported include thermochemical measurements on 1,3,5-tridehydrobenzene (**3**)[1] and matrix isolation with IR detection of 1,2,3-tridehydrobenzene (**1**)[6] and perfluoro-1,3,5-tridehydrobenzene.[5] Recently, we reported[8] the first reactivity study on a related σ,σ,σ-triradical, the 2,4,6-tridehydropyridinium cation (**4**). Triradical **4** abstracts, for example, three SCH_3 groups from dimethyl disulfide molecules, which reveals the presence of three reactive radical sites. However, the three radical sites are not equally reactive. The chemical properties of **4** suggest that this triradical contains a relatively unreactive *meta*-benzyne group (which is stabilized by the ionic resonance structure **5**) and a highly reactive radical site.



4 **5**

We report here a kinetic reactivity study on an isomer of triradical **4**, namely, the 3,4,5-tridehydropyridinium cation (**6**), carried out in a Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer. The gas-phase reactions of this triradical are compared to those of triradical **4**, as well as to those of two related σ,σ-biradicals—the previously unreported 3,4-didehydropyridinium cation (**7**) and the previously reported 3,5-didehydropyridinium cation (**8**)[9]—and two previously reported σ-monoradicals—3-dehydropyridinium cation (**9**)[10] and 4-dehydropyridinium cation (**10**; Table 1).[8]

Upon collisional activation, the protonated triradical precursor, 3,4,5-triiodopyridinium cation, loses first the I atom at C4. This was verified by isolating the resulting monoradical **11** and examining its reactivity toward tetrahydrofuran. The observed reactions—H atom abstraction (92 %) and CH_2 abstraction (8 %)—as well as the reaction efficiency (24 %), closely resemble those of monoradical **10** (Table 1). The second activation step yields the 5-iodo-3,4-didehydropyridinium cation (**12**), as evidenced by its reactivity toward tetrahydrofuran (CH_2O abstraction: 58 %; two H-atom abstractions: 36 %; C_2H_4 abstraction: 6 %; reaction efficiency: 31 %), which is nearly identical to that observed for biradical **7** (Table 1). The third activation step produces triradical **6**.



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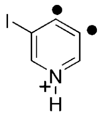

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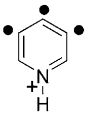

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Triradical **6** was isolated and allowed to react with several reagents for various periods of time. Like triradical **4**, triradical **6** is highly reactive and generally reacts by a greater number of different pathways than related mono- and biradicals (Table 1). However, the reactivity of **6** differs from that of **4** in several ways. For example, **4** is a relatively strong Brønsted acid, but **6** is not (which is due to the proximity of two of the (electron-withdrawing) radical sites to the protonated nitrogen atom in **4**).[11] Furthermore, while **4** undergoes three consecutive atom or group abstraction reactions with several reagents, **6** undergoes one, two, or three such reactions, depending on the reagent. It is also noteworthy that all of the radical sites in **6** are often quenched in the primary reaction whereas **4** typically undergoes secondary reactions to quench unreacted radical sites. Hence, the different locations of the three radical sites in **4** and **6** have a major influence on their chemical properties. The reactivities of **4**, **6**, and **7**–**10** are compared and discussed in detail below.

Monoradicals **9** and **10** both rapidly abstract a H atom from tetrahydrofuran and cyclohexane, HCN and CN groups from *tert*-butyl isocyanide, an I atom from allyl iodide, and a SCH_3 group from dimethyl disulfide (Table 1). Monoradical **9** is slightly more reactive than **10** due to its higher electrophilicity, as quantified here by the vertical electron affinity (vEA; **9**: 6.08 eV; **10**: 5.84 eV; (U)BLYP/aug-cc-pVDZ//(U)BLYP//cc-pVDZ).[12] For an electrophilic monoradical an increase in the vEA leads to a more polar, and hence lower-energy, transition state, which increases its reactivity.[13]

The reactivity of the singlet biradical **8** is similar to that of the monoradicals. For example, it abstracts two H atoms from tetrahydrofuran (Table 1). However, compared to the monoradicals, **8** is much less reactive. This is not surprising since the stabilizing through-space interaction between the two

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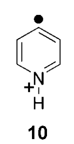
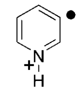
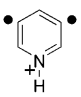
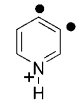
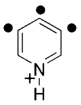
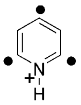
Table 1: Reaction efficiencies[a] and branching ratios[b] for reactions of mono-, bi-, and tridehydropyridinium cations with neutral reagents.

			Reagent		
radical	tetrahydrofuran	cyclohexane	allyl iodide	dimethyl disulfide	*tert*-butyl isocyanide
 **10**	H abs **81%** CH_2 abs **8%** C_2H_3 abs **6%** CHO abs **3%** C_2H_3O abs **2%** **efficiency = 28%**	H abs **100%** **efficiency = 14%**	I abs **92%** C_3H_5 abs **8%** **efficiency = 53%**	SCH_3 abs **100%** **efficiency = 75%**	HCN abs **64%** (2°) HCN abs *7%* (2°) C_4H_8 abs *93%* CN abs **36%** **efficiency = 90%**
 **9**	H abs **100%** **efficiency = 38%**	H abs **100%** **efficiency = 21%**	I abs **90%** C_3H_5 abs **10%** **efficiency = 57%**	SCH_3 abs **100%** **efficiency = 77%**	CN abs **96%** (2°) C_4H_8 abs HCN abs **4%** (2°) C_4H_8 abs **efficiency = 87%**
 **8**	2 H abs **72%** C_2H_4 abs **20%** C_3H_3 abs **8%** **efficiency = 1%**	2 H abs **100%** **efficiency = 0.1%**	I abs **72%** (2°) I abs *87%* (2°) C_3H_5 abs *13%* C_3H_5 abs **26%** (2°) I abs *91%* (2°) C_3H_5 abs *9%* C_3H_4 abs **2%** **efficiency = 15%**	SCH_3 abs **82%** (2°) SCH_3 abs $SSCH_3$ abs **12%** (2°) SCH_3 abs $HSCH_3$ abs **3%** SCH_2 + CH_3 abs **3%** **efficiency = 58%**	HCN abs **79%** (2°) C_4H_8 abs H^+ trns + diss **21%** **efficiency = 68%**
 **7**	CH_2O abs **66%** 2 H abs **31%** C_2H_4 abs **3%** **efficiency = 33%**	2 H abs **100%** **efficiency = 2%**	C_3H_4 abs **85%** HI abs **9%** C_3H_5 abs **6%** **efficiency = 31%**	$HSCH_3$ abs **47%** SCH_3 abs **46%** H_2S abs **7%** **efficiency = 84%**	HCN abs **100%** (2°) C_4H_8 abs **efficiency = 100%**
 **6**	C_2H_3O abs **42%** 2 H abs **22%** (2°) H abs C_2H_5 abs **15%** CH_4 abs **14%** CH_3O abs **5%** C_2H_5O abs **2%** **efficiency = 69%**	2 H abs **40%** (2°) H abs H abs **31%** (2°) 2 H abs C_2H_5 abs **16%** C_4H_7 abs **7%** C_3H_7 abs **4%** C_6H_{11} abs **3%** **efficiency = 53%**	I abs **68%** (2°) C_3H_4 abs *87%* (3°) HI abs (2°) C_3H_5 abs *8%* (2°) HI abs *6%* CH_2 abs **15%** C_3H_4 abs **12%** (2°) CH_2 abs C_3H_5 abs **5%** **efficiency = 71%**	SCH_3 abs **94%** (2°) SCH_3 abs *18%* (2°) $HSCH_3$ abs*82%* $SSCH_3$ abs **6%** **efficiency = 73%**	HCN abs **74%** (2°) CN abs *37%* (2°) HCN abs *63%* (3°) addition H^+ trns + diss **19%** Add - CH_3 **7%** **efficiency = 92%**
 **4**	H^+ trns **39%** 2 H abs **25%** (2°) H abs *51%* (2°) CH_2 abs *30%* (2°) C_2H_3 abs *19%* H^- abs **17%** H_2O abs **16%** (2°) H abs H abs **3%** **efficiency = 74%**	H abs **39%** 2 H abs **22%** (2°) H abs H^- abs **12%** C_3H_5 abs **10%** C_4H_7 abs **8%** C_2H_5 abs **4%** CH_4 abs **3%** C_2H_6 abs. **2%** **UI[c] = 4%** **efficiency = 44%**	I abs **76%** (2°) C_3H_4 abs *12%* (2°) C_3H_5 abs *28%* (3°) I abs (2°) I abs *60%* (3°) C_3H_5 abs (3°) I abs CH_2 abs **13%** C_3H_5 abs **6%** C_3H_4 abs **5%** **efficiency = 58%**	SCH_3 abs **89%** (2°) SCH_3 abs *71%* (3°) SCH_3 abs (2°) $HSCH_3$ abs*11%* (2°) $SSCH_3$ abs*18%* H^+ trns **11%** **efficiency = 76%**	H^+ trns + diss **95%** HCN abs **5%** **efficiency = 98%**

[a] Reaction efficiencies[16,21,22] are reported as $k_{\text{reaction}}/k_{\text{collision}} \times 100\%$. The reaction efficiency is the percentage of collisions leading to a reaction. The precision for the efficiencies is estimated to be 10%. [b] abs = abstraction; trns = transfer; diss = dissociation; add = addition; secondary and tertiary products are indicated as (2°) and (3°), respectively, and are listed under the primary and secondary products that produce them; branching ratios for primary and secondary products are given in bold and italics, respectively. The precision is estimated to be 10%. [c] UI = unreactive isomer.

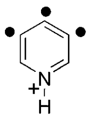
unpaired electrons (as evidenced by the large singlet–triplet (S-T) splitting of $-21.7\ \mathrm{kcal\,mol^{-1}}$; BD(T)/cc-pVTZ//UBPW91/cc-pVDZ) is partially lost in the transition states of radical reactions.[14,15] In contrast, singlet biradical **7** reacts substantially faster than **8** with all reagents, and some of its products are different from those observed for **8**. For **7**, the much stronger (compared to **8**) through-space interaction between the two unpaired electrons (S-T splitting: $-36.2\ \mathrm{kcal\,mol^{-1}}$; BD(T)/cc-pVTZ//UBPW91/cc-pVDZ) prevents all radical reactions.[16,17] As a consequence, **7** behaves like an activated electrophilic alkyne and readily undergoes nonradical reactions with nucleophiles, such as the abstraction of CH_2O from tetrahydrofuran (Table 1). These reactions do not require the uncoupling of the radical sites in the transition state, and therefore are not dependent on the magnitude of the S-T splitting. Finally, cyclohexane was the only reagent studied that is not a nucleophile. Not surprisingly, **7** reacts very slowly with this reagent (by two H-atom abstractions), whereas the monoradicals undergo facile H-atom abstraction reactions (Table 1).

Interestingly, the data for **7**–**10** indicate that some of the reactions can occur by either a radical or a nonradical mechanism. Reactions that may occur by either mechanism (i.e., are observed for **7**–**10**) are abstraction of C_3H_5 from allyl iodide, SCH_3 from dimethyl disulfide, and HCN from *tert*-butyl isocyanide. Reactions that appear to occur by a radical mechanism only (i.e., are not observed for **7**) are abstraction of a single H atom from tetrahydrofuran and cyclohexane, an I atom from allyl iodide, and a CN group from *tert*-butyl isocyanide. Finally, reactions that appear to occur by a nonradical mechanism only (i.e., are only observed for **7**) are abstraction of CH_2O from tetrahydrofuran, HI from allyl iodide, and H_2S from dimethyl disulfide.

Before considering the reactivity of triradical **6**, it should be noted that its (ground) $^2B_2$ state and the (excited) $^2A_1$ state differ in energy by only 2.6 kcal mol^{-1} (BD(T)/cc-pVTZ//UBPW91/cc-pVDZ).[18,19] Because solvation energies for gas-phase complexes are typically 5–20 kcal mol^{-1},[20] it is likely that both doublet states are populated to some extent in these experiments. It is possible that the $^2B_2$ and $^2A_1$ states react differently, but the nature of the experiments does not permit identification of reactivity associated with one state or the other. This may also be the case for triradical **4**, which is predicted[18] to have a $^2B_2$ ground state and a $^2A_1$ (excited) state that lies 11.1 kcal mol^{-1} higher in energy (BD(T)/cc-pVTZ//UBPW91/cc-pVDZ).

The reactivity of triradical **6** more closely resembles that of biradical **8** than biradical **7** (i.e., radical reactions dominate; Table 1), but **6** reacts much faster than **8**. Triradical **6** also reacts faster than the monoradicals with most reagents. The high reactivity of **6** can be attributed to its very high vEA (7.20 and 6.70 eV for the $^2B_2$ and $^2A_1$ states, respectively; (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ) compared to those of **7**, **8**, **9**, and **10** (5.64, 6.30, 6.08, and 5.84 eV, respectively).[12] Thus, it appears that the very high electron affinity of **6** counterbalances the reduction in the radical reactivity caused by the coupling of the three unpaired electrons. This is also likely to be the case for triradical **4** (vEAs for the (ground) $^2B_2$ and (excited) $^2A_1$ states: 7.01 and 7.18 eV, respectively; (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ).

In principle, any one of the three radical sites in **6** may be involved in the first radical reaction. The biradical formed from the abstraction of an I atom from allyl iodide by **6** reacts with allyl iodide by abstraction of C_3H_4, C_3H_5, and HI (i.e., secondary products of the I atom abstraction product; Table 1). The branching ratios for these three secondary products are nearly identical to those observed for the reaction of **7** with allyl iodide (Table 1). Moreover, abstraction of an I atom, a reaction characteristic of *meta*-benzyne analogues such as **8**, was not observed. Hence, the biradical formed from **6** upon the first I-atom abstraction is likely to be **13**, rather than **14**.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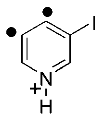
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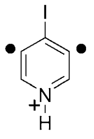
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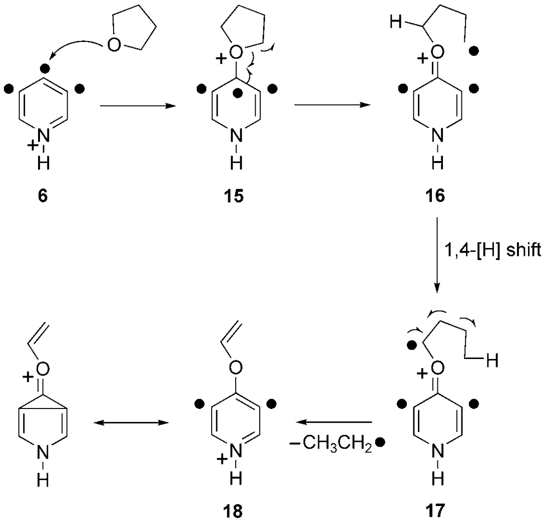
To provide additional evidence for the regioselectivity of these radical reactions, the primary products formed from abstraction of one, and two, H atoms from cyclohexane by **6** were isolated and allowed to react with cyclohexane. The product formed upon abstraction of one H atom reacts with cyclohexane by abstraction of two H atoms with an efficiency of 2%. This reaction efficiency is closer to that observed for **7** (2%) than for **8** (0.1%; Table 1). Thus, the first H-atom abstraction by **6** appears to occur at C3, which is in agreement with the results obtained for allyl iodide. The product formed upon abstraction of two H atoms reacts with cyclohexane by one H-atom abstraction with an efficiency of 20%. This reaction efficiency is closer to that observed for monoradical **9** (21%) than for monoradical **10** (14%; Table 1), which suggests that the first two H atoms are abstracted by the radical sites at C3 (first) and C4 (second), leaving the radical site at C5 as the last to react.

Triradical **6** reacts with *tert*-butyl isocyanide mainly by HCN abstraction (74%; Table 1), and this reaction could involve either one or two of the three radical sites. The isolated HCN-abstraction product reacts with *tert*-butyl isocyanide by CN (37%) and HCN (63%; Table 1) abstraction. Since neither biradical **7** nor **8** reacts by CN abstraction, while the two monoradicals **9** and **10** react by both CN and HCN abstraction, the HCN abstraction product is likely to be a monoradical. The CN/HCN abstraction branching ratio (i.e., 37/63) is nearly identical to that observed for **10** (36/64), but not for **9** (96/4; Table 1). These observations suggest that not only are two of the radical sites involved in the reaction but also that the remaining radical site in the HCN abstraction product is at C4. The involvement of the second radical site at C5 is different from what was observed for allyl iodide and cyclohexane. However, it should be noted that whereas abstraction of two I or H atoms from allyl iodide and cyclohexane, respectively, most likely occurs by a radical mechanism, HCN abstraction can occur by a nonradical mechanism.[21]

Triradical **6** reacts with tetrahydrofuran mainly by C_2H_3O abstraction (42%; Table 1). This particular reaction was also observed for monoradical **10** (Table 1). A possible mechanism for this reaction is shown in Scheme 1. Nucleophilic attack of the oxygen atom in tetrahydrofuran at the most electron-deficient carbon atom in **6** (C4; which is due, in part, to an ionized carbene-type resonance structure that permits greater charge delocalization away from the nitrogen atom[18]) yields **15.** This step is expected to occur much faster for triradical **6** than for monoradical **10** because the presence of two adjacent radical sites in **6** increases the electrophilicity of C4. Subsequent ring opening of **15** to form **16**, followed by a 1,4-[H] shift, produces **17**, which then loses an ethyl radical. The isolated C_2H_3O abstraction product was found to be unreactive toward tetrahydrofuran. This observation lends support to the assigned structure, since the vinyloxy group is expected to stabilize the ionic bicyclic resonance structure of



Scheme 1. Possible mechanism for the major reaction of triradical **6** with tetrahydrofuran.

18 (analogous to **5**) and thus hinder radical reactions.[23] This proposal is further supported by the finding that the 4-hydroxy-3,5-didehydropyridinium cation is unreactive toward tetrahydrofuran.

In summary, the results obtained for triradical **6** indicate that for reactions that occur by a radical mechanism, the first bond formation occurs at the C3 radical site. The second bond formation then occurs at the C4 radical site. However, for reactions that occur by nonradical mechanisms, the first bond formation may occur at either C3 or C4. The chemical properties of the isomeric triradicals **4** and **6** are similar but not identical. The differences between these two triradicals appear to arise primarily from the much higher reactivity of the *ortho*-benzyne group(s) in **6** than the *meta*-benzyne group(s) in **4**, as well as the greater Brønsted acidity of **4**.

Experimental Section

The precursor for biradical **7**, 3,4-pyridinedicarboxylic anhydride, was obtained from Sigma–Aldrich and used as received. The precursor for triradical **6**, namely 3,4,5-triiodopyridine, was synthesized by using literature methods.[24,25] The bi- and triradicals were generated in an FT-ICR mass spectrometer by using previously reported methods.[16,21] SORI-CAD[26] was used to cleave either C–C (**7**) or C–I (**6**) bonds in the protonated precursors. After isolation, **6** and **7** were allowed to react with reagents for varying periods of time as described previously.[9,16,21,22,27] The structures of all radical species were confirmed by using structurally diagnostic reactions.[16,21] All molecular orbital calculations were carried out with the Gaussian 98[28] electronic structure program suite.

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