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The 1,2,4-Triazolyl Cation: Thermolytic and Photolytic Studies

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The generation of the 1,2,4-triazolyl cation (**1**) has been attempted by the thermolysis and photolysis of 1-(1,2,4-triazol-4-yl)-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) and the thermolysis of 1- and 4-diazonium-1,2,4-triazoles, using mainly mesitylene as the trapping agent. Thermolysis of **2** gave mostly 1,2,4-triazole, together with 3-(1,2,4-triazol-4-yl)-2,4,6-trimethylpyridine, 4-(1,2,4-triazol-4-ylmethyl)-2,6-dimethylpyridine, and 4-(2,4,6-trimethylbenzyl)-2,6-dimethylpyridine. Thermolysis of each of the diazonium salts in the presence of mesitylene again gave mainly triazole together with very low yields of 1-(1,2,4-triazol-1-yl)-2,4,6-trimethylbenzene and the corresponding -4-yl isomer in about the same ratio. On the other hand, photolysis of **2** in mesitylene gave mainly 1-(1,2,4-triazol-1-yl)-2,4,6-trimethylbenzene. A photoinduced electron transfer from mesitylene to **2** has been observed and preliminary laser flash photolyses of **2** and the corresponding 2,4,6-triphenylpyridinium salt have been carried out. The observed transients are explained as arising from the first excited states of the pyridinium salts rather than from **1**. Ab initio MO calculations are reported and indicate that the predicted electronic ground-state of the triazolyl cation is a triplet state of B_1 symmetry with five π electrons, which corresponds to a diradical cation (**1c**). Possible mechanisms for the formation of the various products are proposed.

Introduction

Nitrenium ions have received much attention in recent years:[1] synthesis and synthetic applications,[2] and their implication as "ultimate carcinogens" from aromatic amines.[3] Alkyl-,[2e] aryl-,[1,2a,c] acyl-,[4] and methoxynitrenium ions [5] have all been generated, but there was no reference to the production of five-membered heteroaromatic σ-nitrenium ions until 1991, when we published a preliminary communication on the subject.[6a] The only relevant papers published until then dealt with the calculations of the orbital energy levels of the π-cations of the 1*H*-imidazol-1-ylium, -pyrazolylium and -pyrrolylium,[7] and the generation of such π-cations stabilized by two or more electron-donor dimethylamino groups.[8]

We initiated a study of the possible thermolytic generation and reaction of the 4-(1,2,4-triazolyl) cation **1** from readily available and inexpensive 4-amino-1,2,4-triazole[6a,9] and have extended it to the photolysis of suitable nitrenium ion precursors. We now describe these studies in full.

The original conception was that should a nitrenium ion **1a** be formed by cleavage of a σ-bond to N-4, it could possibly undergo electronic reorganization to the 5π diradical cation (**1b**), to an isomeric 5π diradical cation (**1c**), to the 4π cation (**1d**) (antiaromatic if fully conjugated), and to the σ-cation (**1e**), isomeric with **1a** (Scheme 1). In addition, singlet and triplet multiplicities would be possible.[10]

We have shown[4a,6a] that *N*-amino- and *N*-acylaminopyridiniums produce nitrenium ions on thermolysis. Thus, heating 1-(*N*-phthalimido)-2,4,6-triphenylpyridinium tet-

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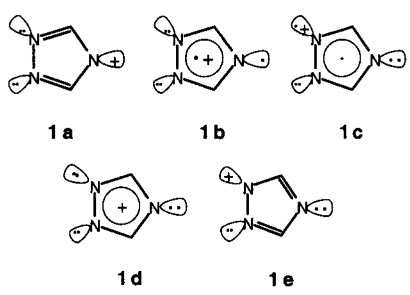
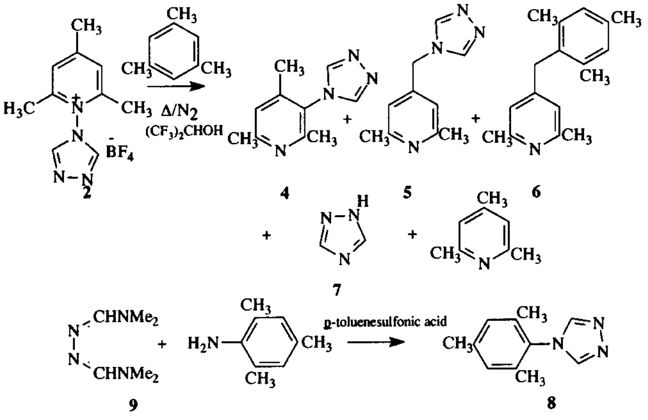
Scheme 1



Scheme 2



rafluoroborate in mesitylene/$(CF_3)_2CHOH$ at 180 °C gave *N*-mesitylphthalimide, while thermolysis or photolysis in anisole gave phthalimidoanisoles in 71.6% yield. Photolysis of 1-(*N*-phthalimido)-2,4,6-trimethylpyridinium tetrafluoroborate in anisole containing $(CF_3)_2CHOH$ and CF_3CO_2H gave, following hydrazinolysis, the anisidines (94.5%) (*o*-:*m*-:*p*-, 66.4:8.3:20.3), clearly suggesting that an electrophilic reactive intermediate (the diacylnitrenium ion) was generated.

Results

The 1-(1,2,4-triazol-4-yl)-2,4,6-trimethylpyridinium tetrafluoroborate (**2**) was readily prepared in 68% yield from 2,4,6-trimethylpyrilium tetrafluoroborate and 4-amino-1,2,4-triazole (**3**). Thermolysis of **2** under N_2 in degassed mesitylene (containing sufficient hexafluoro-2-propanol to bring **2** into solution at room temperature) at 208 °C for 7 h gave a mixture of at least eight compounds, from which could be isolated 3-(1,2,4-triazol-4-yl)-2,4,6-trimethylpyridine (**4**) (3.9%), 4-(1,2,4-triazol-4-ylmethyl)-2,6-dimethylpyridine (**5**) (4.7%), 4-(2,4,6-trimethylbenzyl)-2,6-dimethylpyridine (**6**) (20.9%), 1,2,4-triazole (**7**) (60.5%), and 2,4,6-collidine (Scheme 2). No 2-(1,2,4-triazol-4-yl)-mesitylene (**8**) was detected. An authentic sample of the latter was synthesized (44% yield) from *N*,*N*-dimethylformamide azine (**9**) and 2-aminomesitylene in the presence of *p*-toluenesulfonic acid.[6b]

Compound **4** exhibited three different methyl singlets (δ 2.56, 2.24, 2.03) expected for an unsymmmetrically substituted pyridine, and a single proton peak at δ 7.03, expected for a pyridine β-proton. The two protons of the triazole ring resonated at δ 8.19 (s, 2H). The mass spectrum had the molecular ion peak at *m*/*z* 188 ($C_{10}H_{12}N_4$). The structure was established unambiguously by single-crystal X-ray diffraction (see Figure 1, and Tables S1−S5, of the Supporting Information for the crystal data). Compound **5** also exhibited a molecular ion peak at *m*/*z* 188, which fragmented in a manner similar to the way **4** did. The NMR spectrum showed the presence of the two symmetrically placed methyl groups (δ 2.51, s, 6H), two pyridine β-protons at δ 6.71 (s, 2H), the triazole protons at δ 8.15 (s, 2H), and a singlet for the methylene group (δ 5.15, s, 2H). A crystal structure could not be determined owing to the poor quality of the crystals, but a high resolution mass spectrum confirmed the molecular formula as being $C_{10}H_{12}N_4$. The structure of **6** was confirmed by its IR, NMR, and mass spectral data (see Experimental Section) and by microanalysis. Triazole (**7**) was characterized unambiguously in a similar manner and, in a possible “overkill”, by comparing its single-crystal X-ray data with those published in the literature.[11]

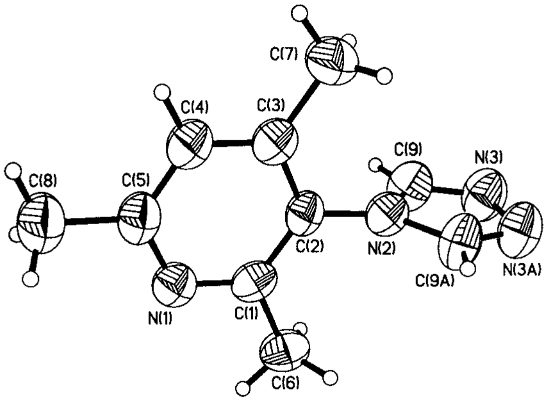


Figure 1. Thermal ellipsoid plot (50% probability) of **4** showing the atom numbering scheme.

An alternate route to the 4-(1,2,4-triazoyl) cation was explored, namely the diazotization of 4-aminotriazole.[9] Treatment of **3** with nitrosonium tetrafluoroborate in dry acetonitrile gave only **7** (hydrogen abstraction from acetonitrile, the only available hydrogen source), and no Ritter reaction-type products were detected. When the same reaction was carried out in the presence of mesitylene at room temperature, **7** was again isolated (77%), and nitrogen and nitrous oxide (the latter detected by infrared spectroscopy) were evolved. Remarkably, 1-(1,2,4-triazol-1-yl)-2,4,6-trimethylbenzene (**10**) was also isolated (1%), as were traces of 1-(1,2,4-triazol-4-yl)-2,4,6-trimethylbenzene (**8**) and the unsymmetrical mesitylene dimer (**12**). The latter were detected by GC/MS and **8** was also identified by comparison with the sample prepared as above. An authentic sample of **10** was synthesized from 2,4,6-trimethylphenylhydrazine hydrochloride and *s*-triazine using the general procedure of Grundmann and Ratz.[12] The same products, in approximately the same ratio, were obtained when **3** was treated with isoamyl nitrite in the presence of acetic acid and excess mesitylene, or when 1-amino-1,2,4-triazole (**11**) was treated as above with $NO^+BF_4^-$ (Scheme 3). No **10** was detected in the thermolysis of **2** in mesitylene.

We now turned to an exploration of the photolytic decomposition of the *N*-triazolopyridinium salts. Not unexpectedly, the results are quite different from the thermolytic ones. Thus, when **2** in acetonitrile and mesitylene was photolyzed (300 nm) for 30 h, the major

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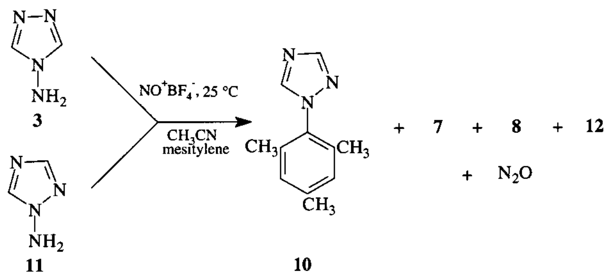
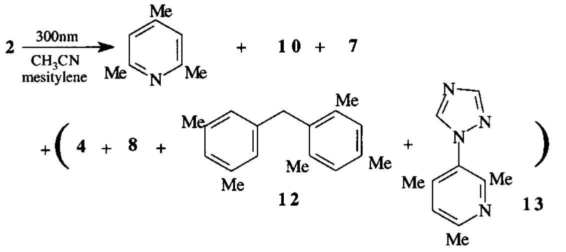
(11) Deuschl, H. *Ber. Bunsen-Ges. Physik. Chem.* **1965**, *69*, 550.
(12) Grundmann, C.; Ratz, R. *J. Org. Chem.* **1956**, *21*, 1037.

Scheme 3



Scheme 4



Scheme 5

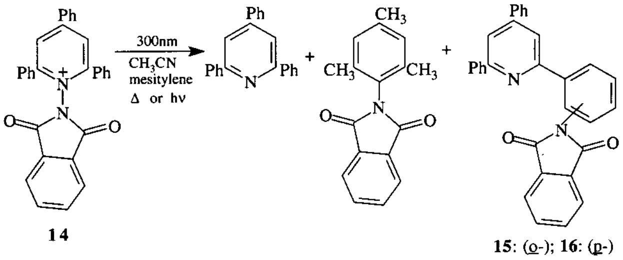


Table 1. % Yields of Products Formed from the Photolysis of 2 in Various Solvents[a]

solvent	7	2,4,6-collidine	13	10
CD_3CN	6	12	20[b]	_
CD_3CN/MES[c]	18	81	trace[d]	48[e]
CD_3CN/CD_3OD[f]	24	38	9.1	_
CD_3OD	42	38	trace[d]	_

[a] Using 300 nm lamps in a Rayonet reactor at 5 °C. % Yields based on amount of decomposed pyridinium salt (in almost all cases >90%). [b] Together with a trace of its isomer, **4**. [c] MES = mesitylene. [d] Less than 1%; undetectable by NMR, observed by GC/MS. [e] Together with a trace of **8**. [f] 90:10 (v/v).

products observed were **10** (48%), **7** (18%), and 2,4,6-collidine (81%). Trace amounts of the 4-triazolylmesitylene **8** (the isomer of **10**) were detected by GC/MS. Under some conditions, small amounts of the mesitylene dimer **12** (comparison with know authentic sample),[4a,13] as well as 3-(1,2,4-triazol-4-yl)-2,4,6-trimethylpyridine (**4**) and its isomer **13**, were also observed by GC/MS (Scheme 4).

Mesityltriazole **10** is also produced (15−20%), albeit less cleanly (the GC/MS spectrum is much more complex), by the photolysis of 1-(1,2,4-triazol-4-yl)-2,4,6-triphenylpyridinium tetrafluoroborate under the same conditions as were used for **2**. The more complex reaction mixture may be partly owing to intramolecular attack on the 2-phenyl group, but other processes may well be involved. It has been observed[6a] that in the thermolysis of 1-(*N*-phthalimido)-2,4,6-triphenylpyridinium tetrafluoroborate (**14**) in toluene/$(CF_3)_2CHOH$, some 2-(*o*-aminophenyl)-4,6-diphenylpyridine was formed, as was a small amount of a mixture of *o*- and *p*-methyldiphenylmethane (cf. **12** above) (Scheme 5). The same reaction, but carried out in mesitylene in the presence of CF_3CO_2H gave, among other products, 2,4-diphenyl-6-(*o*-phthalimidophenyl)pyridine (8.5%) (**15**) (whose structure was confirmed by single-crystal X-ray analysis) and the corresponding *para* derivative (**16**) (trace).[4b] Photolysis of **14** in mesitylene/CF_3CO_2H gave **15** (25.7%) and **16** (12.6%) among others.[4b]

The formation of the 1-yl isomer (**10**) in reasonable amounts in the photolysis of **2** is noteworthy, compared with the formation of the 4-yl products **4** and **5** in the thermolysis (no **10** detected). This suggested the possibility that, in the photolysis, a concerted heterolysis of the pyridinium salt was assisted by the nucleophile mesitylene attacking the triazole at N-1. To test this possibility, an isomer of **2**, 1-(1,2,4-triazol-1-yl)-2,4,6-trimethylpyridinium tetrafluoroborate (**17**), was synthesized from **11** and 2,4,6-trimethylpyrilium tetrafluoroborate. Its photolysis in mesitylene/actonitrile gave **10** (45%) and traces of **8** and **12** (detected by GC/MS), in addition to **7** (19%), thus negating this possibility.

The photolysis was carried out using a variety of solvent combinations (acetonitrile, hexafluoro-2-propanol, mesitylene) and reaction conditions (degassed, in the presence of air, at various temperatures) and using either 254, 300, or 350 nm lamps. The reaction occurred the fastest when the 254 nm lamps were used, ca. 6 times more slowly with 300 nm lamps and the slowest with the 350 nm lamps. Most of the runs were carried out using the 300 nm lamps to minimize the absorption of light by mesitylene while still allowing for a reasonable rate of decomposition of the pyridiniums (greater than 90% decomposition after 20 h). The highest yield of **10** (48%) was obtained from **2**, using mesitylene in anhydrous degassed acetonitrile at 0−5 °C and 300 nm lamps.

When **2** was photolyzed in pure acetonitrile, the major products were **7** (6%), 2,4,6-collidine (12%), and **13** (20%), with traces of **4** (GC/MS) (Table 1). To determine whether the formation of **13** involved an intra- or intermolecular process, the 1-(1,2,4-triazol-4-yl)-2,4,6-triphenyltriphenylpyridinium salt was photolyzed in acetonitrile containing 2,4,6-collidine in excess and gave mainly **13**. The corresponding photolysis of **2** in acetonitrile/2,6-lutidine gave a mixture of two isomers of **18**, in addition to some **7** and **13**. Thus, the formation of **13** is clearly an intermolecular process in the case of the above photolysis of the triphenylpyridinium, as is the formation of **18** from **2**, suggesting that the formation of **13** from the trimethylpyridinium (**2**) in mesitylene is also an intermolecular process. The 4-yl isomers **4** and **8** are not photoisomerized to the corresponding 1-yl compounds **13** and **10**, though **4** and **8** are slightly decomposed after irradiation with 300 nm light in degassed acetonitrile for 20 h.

We attempted to trap cation **1** with a variety of nucleophiles (Scheme 6). Photolysis of **2** in methanol-d_4/

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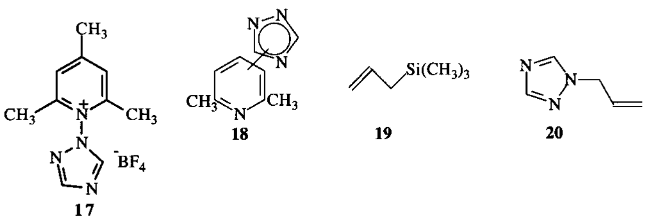
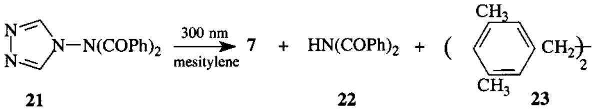
(13) (a) Wen, L.-S.; Kovacic, P. *Tetrahedron* **1978**, *34*, 2723. Kovacic, P.; Wu, C. *J. Org. Chem.* **1961**, *26*, 749. (b) See, however, Takeuchi, H. *J. Chem. Soc., Chem. Commun.* **1987**, 961, and discussion in footnote to ref 4a above. (c) The notion of "tight pairs" (or their equivalent), formed as intermediates in the heterolysis of *N*-substituted pyridinium salts, is not novel: it has been proposed many times; see, for example, Takeuchi, H.; Hayakawa, S.; Koyama, K. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2277. Takeuchi, H.; Higuchi, D.; Adachi, T. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1525. Katritzky, A. R.; Musumara, G. *Chem. Soc. Rev.* **1984**, 56−58. Fishbein, J. C.; McClelland, R. A. *J. Chem. Soc, Perkin Trans. 2* **1995**, 663. Novak., M.; Kahley, M. J.; Li Jung; Kennedy, S. A.; James, T. G. *J. Org. Chem.* **1995**, *60*, 8294, among others.

Scheme 6



Scheme 7



acetonitrile (10:90 v/v) gave no methoxytriazole, but the yield of triazole itself increased from 6% (acetonitrile) to 24% (methanol-d_4/acetonitrile). Photolysis of **2** in the presence of α-methylstyrene, 1-trimethylsilyloxycyclohexene, 1-methoxy-1-trimethylsilyloxy-2-methylpropene,[14a] and vinyltrimethylsilane gave rather complex reaction mixtures containing triazole but none of the expected addition or substitution products.[14b] On the other hand, photolysis of **2** in the presence of allyltrimethylsilane (**19**) gave a very low yield ($\ll$5%) of 1-allyl-1,2,4-triazole (**20**).

Allyltrimethylsilane and related silyl alkenes are quite reactive toward electrophiles, including carbocations, giving substitution products such as **20** with the loss of the trisubstituted silane.[15] Allyltrimethylsilane also undergoes electron-transfer-initiated photoaddition to iminium salts via radical cation intermediates.[16] The half-life of **2** in the presence of allyltrimethylsilane (**19**) depends on the concentration of the latter, which is compatible with either an SET process or with an assisted S_N2' type reaction.[17]

We also carried out experiments to see whether a 1,2,4-triazolyl free radical would react with mesitylene or with 2,4,6-collidine to form **8**, **10**, **4**, or **13**.

Photolysis of **21** in mesitylene using 300 nm lamps[18] proved to be a clean source of the desired radical, producing the products expected from homolysis: 1,2,4-triazole (**7**), dibenzoylimide (**22**), and the symmetrical 3,5-dimethylbenzyl radical coupling product **23** (Scheme 7). No **10** was detected.[19]

Results of Theoretical Calculations

Selected geometrical parameters (bond lengths in angstroms and bond angles in degrees) of the CASSCF(10,8)/6-31G(d)-optimized structures for the most relevant low-lying electronic states of **1** are shown in Figure 2. The harmonic vibrational analysis proved each of these structures to be a true potential energy minimum.[20] Simple qualitative pictorial descriptions of the four highest occupied MOs of the calculated electronic states are shown in Figure 2. It is worth noting that the $6b_2$ MO is an out-phase combination of the nonbonding σ orbitals associated to the N_1 and N_2 atoms. The total and relative energies calculated at various levels of theory are shown in Table 2, along with the computed ZPVE.

Both the CASSCF(10,8) and CASPT2-g1 methods predict the electronic ground-state to be a triplet state of B_1 symmetry with five π electrons, which corresponds to diradical cation **1c**, the lowest energy electronic singlet state being a closed-shell singlet of A_1 symmetry with four π electrons, denoted $^1A_1(4\pi)$, which corresponds to π-cation **1d**. Furthermore, the two methods agree in predicting the six π electron singlet state corresponding to σ-cation **1a**, denoted $^1A_1(6\pi)$ to lie high in energy above the ground state. The remarkable geometrical differences found between the $^3B_1$, $^1A_1(4\pi)$, and $^1A_1(6\pi)$ states (see Figure 2) can be easily rationalized on the grounds of the different nodal planes of the higher occupied MOs (see Figure 3). Thus, the shortening of the N_1C_5 and N_2C_3 bond distances in the $^3B_1$ state, as compared with those calculated for the $^1A_1(4\pi)$ state, is a consequence of the promotion (relative to the electronic configuration of $^1A_1(4\pi)$) of a $6b_2$ electron to the $1a_2$ MO, which is N_1C_5 and N_2C_3 bonding. Analogously, the promotion (relative to the electronic configuration of $^1A_1(4\pi)$) of two $9a_1$ electrons to the $1a_2$ MO causes a remarkable shortening of the N_1C_5 and N_2C_3 bonds in the $^1A_1(6\pi)$ state. Moreover, the extremely long N_1N_2 bond distance in the latter state is traced back to the N_1N_2 antibonding character of the $1a_2$ MO. On the basis of the calculated bond lengths, the electronic structure of $^3B_1$, $^1A_1(4\pi)$, $^1A_1(6\pi)$ can be qualitatively represented by the structures shown at the bottom of Figure 3. The π electron system of the $^3B_1$ and $^1A_1(4\pi)$ states can be formally regarded as formed by two ($^3B_1$) or two ($^1A_1(4\pi)$) π electrons and a localized $N_1{=}N_2$ double bond. In contrast, the π electron system of the $^1A_1(6\pi)$ state can be described as two localized (nonconjugated) C=N double bonds plus a π nonbonding lone pair localized on N_4, rather than as an aromatic 6π electron system. This feature is attributed to the fact that in the $^1A_1(6\pi)$ state the positive charge of the cation resides on the latter nitrogen atom.

At the CASPT2/cc-pVTZ level of theory, the $^1A_1(4\pi)-{}^3B_1$ energy separation is calculated to be 10.1 kcal/mol. Inclusion of the ZPVE correction (1.1 kcal/mol) to the latter value yields a singlet−triplet energy separation of 11.1 kcal/mol. To assess the reliability of our theoretical results, we note that for the parent nitrenium ion NH_2^+ the $^1A_1-{}^3B_1$ energy gap calculated at the CASPT2-g1/cc-pVTZ//CASSCF(2,2)/6-31G(d) + ZPVE level (31.8 kcal/mol)[21] differs by less than 2 kcal/mol from the experimental value (30.1 ± 0.2 kcal/mol).[22]

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[14] (a) Moran, R. J.; Cramer, C.; Falvey, D. E. *J. Org. Chem.* **1997**, *62*, 2742. (b) The known reactivity of acetonitrile towards cations, radicals, and radical cations may explain, in part, the low material balance in some of our reactions, although we did not detect *any* Ritter reaction products or stable solvent-derived products. See Lisjer, H. J. P.; Arnold, D. R. *J. Phys. Chem. A* **1998**, *102*, 5592.

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[16] Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.

[17] The low yield of **19** may also be owing to the reported desilylation of the allylsilane-derived radical cation by the weakly nucleophilic acetonitrile. Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617.

[18] See the similar generation of the 1,2,3-triazolyl radical. Kalambokis, E. A.; Maroulis, A. J.; Alexandrou, N. E. *J. Heterocycl. Chem.* **1993**, *30*, 1301.

[19] *tert*-Butyl 1-(1,2,4-triazolepercarboxylate), synthesized from *tert*-butyl hydroperoxide and 1,1′-carbonylbis(1,2,4-triazole), underwent nucleophilic attack at the carbonyl group on thermolysis, as does *tert*-butyl 1-imidazole percarboxylate. Bourgeois, M. J.; Filliatre, C.; Lalandem R.; Maillard, B.; Villenave, J. J. *Tetrahedron Lett.* **1978**, *36*, 3355.

[20] In a previous study[4] of the low-lying electronic states of **1**, it was found that the optimum $C_{2\_}$ structure calculated at the CASSCF-(10, 8)/6-31G(d) level for the six-electron singlet state $^1A_1$ showed one negative vibrational frequency of b_2 symmetry. This spurious result was a consequence of the fact that the force constant matrix was calculated numerically by finite differences of analytical gradients rather than from the analytical second derivatives of the energy.

[21] Olivella, S.; Solé, A., unpublished results.

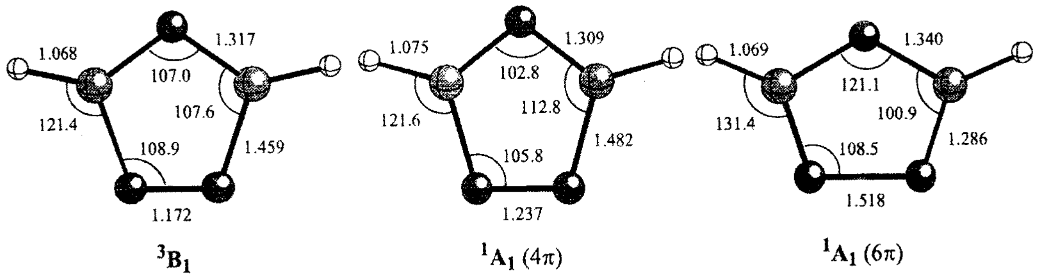

Figure 2. Selected geometrical parameters of the CASSCF(10,8)/6-31G(d) optimized structures for the most relevant low-lying electronic states of the 1,2,4-triazolyl cation. Distances are given in angstroms and angles in degrees.

Table 2. Total Energies (*E*, Hartrees) Calculated at Different Levels of Theory and Zero-Point Vibrational Energies (ZPVE, kcal/mol) for Low-Lying Electronic States of 4-(1,2,4-Triazolyl) Cation

	E^a			
state	CASSCF(10,8) 6-31G(d)	CASSCF(10,8)^b cc-pVTZ	CASPT2^b cc-pVTZ	ZPVE^{c,d}
$^3B_1$	−239.88678 (0.0)	−239.97255 (0.0)	−240.75356 (0.0)	28.2
$^1A_1(4\pi)$	−239.87949 (4.6)	−239.96756 (3.1)	−240.73749 (10.1)	29.3
$^1A_1(6\pi)$	−239.84228 (27.9)	−239.92813 (27.9)	−240.71352 (25.2)	29.8

[a] Relative energies in kcal/mol are shown in parentheses. [b] Calculated at the CASSCF(10,8)/6-31G(d) optimized geometries. [c] Calculated from the unscaled CASSCF(10,8)/6-31G(d) harmonic vibrational frequencies. [d] A referee has suggested the possibility that the results could be explained by *triplet* **1d.** This is not possible since such a molecule is calculated not to be a true minimum ($^3B_2$ (4π)) and is predicted to lie at least 30.2 kcal/mol above the $^3B_1$ ground state.

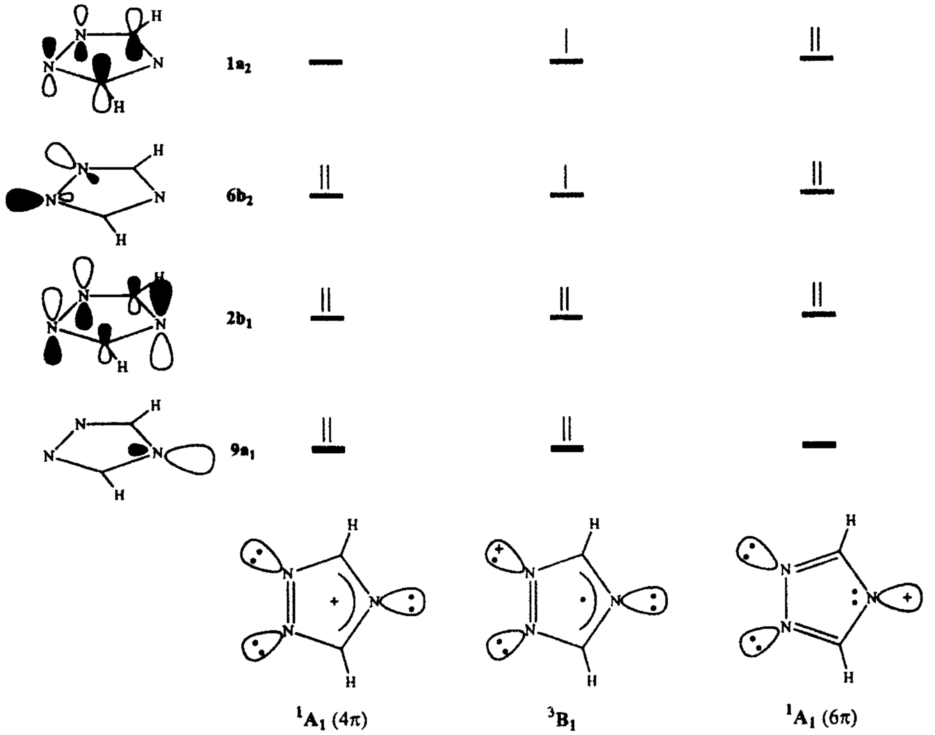

Figure 3. Simple qualitative pictorial descriptions of the four highest occupied MOs of the most relevant low-lying electronic states of the 1,2,4-triazolyl cation.

General Discussion

Thermolyses. The most obvious difference between the thermolyses and photolyses of the *N*-triazolopyridiniums is that the triazole moiety does not lead to a triazolomesitylene in the former, but does in the latter. The absence of **8** in the thermolysis mandates the absence of cation **1** as a *free* entity under these conditions. The most likely route to **5** would go via the anhydro-base **24**: a 1,5-sigmatropic shift (thermally allowed) would lead to **5**. A similar 1,5-shift (also thermally allowed since the positive charge is not involved in the reorganization of the electrons) would lead to **4**. We suggest that **6** may be formed from **24** by an attack of mesitylene at the methene carbon concerted with the departure of the triazole anion (Scheme 8).

To explain the formation of **7** as the main product (60% yield) from **24** requires a competing process, since the maximum amount of triazole anion formed in the concerted process would be 20.9% (**24** to **6**). One possibility

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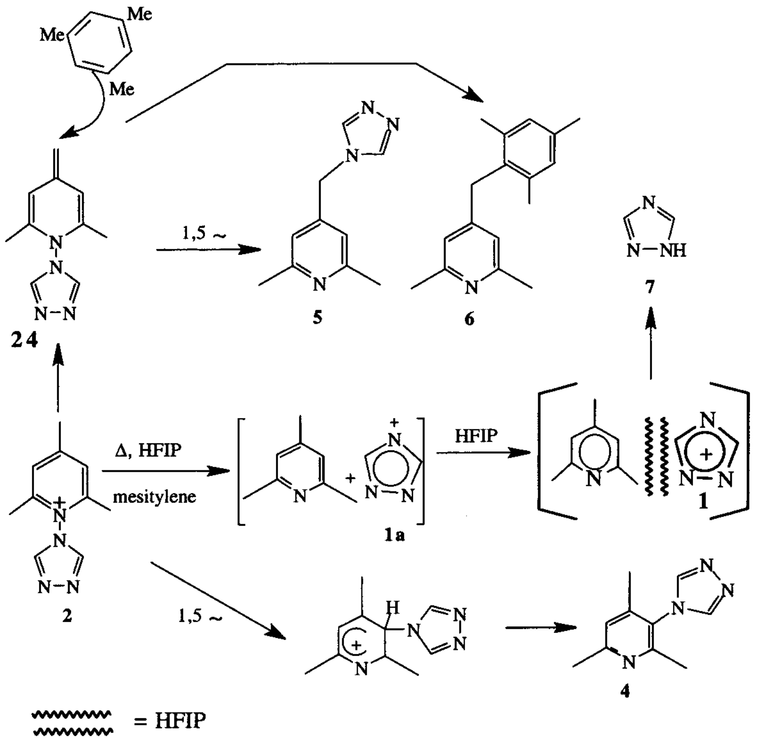
(22) Gibson, S. T.; Greene, P. J.; Berkowitz, J. *J. Chem. Phys.* **1985**, *83*, 4329.

Scheme 8



considered was that **2** underwent N−N bond homolysis giving the triazolyl free radical (see later), which abstracted a benzylic hydrogen to give the observed **7** and a benzyl-type radical. Arguing against this proposal is the fact that there seems to be no precedent for such a homolysis taking place with the pyridiniums.[1] Takeuchi and co-workers[13c] and we[4a] have observed only heterolysis on thermolysis of *N*-aminopyridiniums, while Falvey,[14a] Takeuchi,[13c] and we[4c] have shown that heterolysis occurs during photolysis as well. Furthermore, the generation of a triazole free radical in the presence of mesitylene would lead to a benzyl type radical known to dimerize to the corresponding dibenzyl rather than give the diphenylmethane derivative which is formed from diradical cations.[4a,13b] Hydrogen-abstraction by triplet nitrenium ions is a well-documented reaction.[1,12c,d,18]

Had *free* **1c** been formed by N−N heterolysis,[23] one would have expected at least *some* electrophilic attack on mesitylene to give a 1-triazolyl substitution product (as was observed in the diazonium ion decompositions). Since no such product was formed in the thermolyses of the pyridiniums, we suggest that some triazolyl cation could form via N−N heterolysis, leading to a tight pair[13c] (as shown in Scheme 8, or possibly as a σ-complex with the pyridine N-atom) with collidine[24a] in HFIP/mesitylene; the more polar HFIP could leak into the cage to give a solvent-separated pair. As HFIP is relatively acidic (for example, it protonates an electronically excited aromatic nucleus in the absence of a protic acid[24c]), it should, at least, hydrogen-bond,[24b] if not actually protonate, the N of collidine to a small extent (an equilibrium process) within the solvent-separated pair cage, to give collidinium and the trifluoroisopropoxide anion. A vicinal *diradical* cation such as **1c** could then abstract a *hydride* ion from the isopropoxide to give **7** and hexafluoroacetone which would escape (bp −26 °C) under our reaction conditions. While aromatic radical cations are stabilized by HFIP[24b,c] because hydrogen-atom abstraction would lead to the production of the corresponding cation and the unstable radical $(CF_3)_2C{-}OH$ (in which the single electron would be delocalized onto the oxygen),[25c] diradical cations on the other hand would abstract hydride from the alkoxide and lead to two stable neutral species. Supporting this proposal is the fact that collidine was isolated as one of the products of the thermolysis, and that similar hydride ion abstractions by NH_2^+ have been reported.[26c]

Photolyses. In contrast, the results from the photochemical reactions indicate that the products are probably formed by intermolecular stepwise processes. Some nitrenium ions have recently been detected using laser flash photolysis.[26] We have carried out very preliminary experiments on the laser flash photolysis (355 nm, 6 mJ, 30 ps pulse) of **2** and the corresponding 2,4,6-triphenylpyridinium salt. Both salts visibly fluoresce and show transients upon direct excitation. The absorbance maximum of the transient from **2** is at 485 nm (Figure 4), and those from the triphenyl compound are at 450 and 630

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(23) For a possible model of how a π-cation could be produced by the heterolytic cleavage of a σ-bond, see Abramovitch, R. A.; Qing, S.; Olivella, S. *Heterocycles* **1992**, *33*, 483.

(24) (a) This could be a weak π-type complex of the collidine with the nitrenium ion of the type that are known to be formed between pyridines and metals (Tomasik, P.; Ratajewicz, Z. Pyridine-metal Complexes. In *The Chemistry of Heterocyclic Compounds*; Newkome, Strekowski, Eds.; **1985**; Ch. 5, and Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 501), or a σ-type complex with the N-atom of collidine.[13c] (b) For H-bonding ability of HFIP, see Eberson, L.; Hartshorn, M. P.; Persson, O.; Radner, F. *J. Chem. Soc., Chem. Commun.* **1996**, 2105. (c) For protonating ability of HFIP, see Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 9648.

(25) Kozhevnikov, I. V.; Kim, V. I.; Talzi, E. P.; Sidelnikov, V. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1392. Eberson, L.; Nyberg, K. *Acc. Chem. Res.* **1973**, *6*, 106. Abramovitch, R. A.; Roy, J.; Uma, V. *Can. J. Chem.* **1965**, *43*, 3407.

(26) (a) Moran, R. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1996**, *118*, 8965. (b) Chiapprino, D.; Falvey, D. E. *J. Phys. Org. Chem.* **1997**, *10*, 917. (c) Srivastava, S.; Kercher, M.; Falvey, D. E. *J. Org. Chem.* **1999**, *64*, 5853.

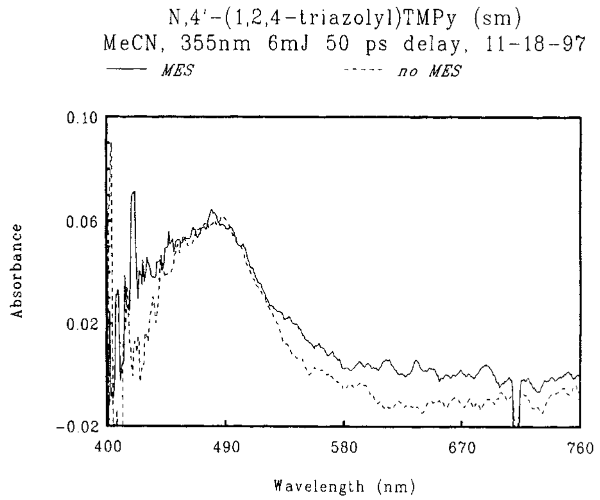

Figure 4. Transient absorptions of **2** in the presence and absence of mesitylene.

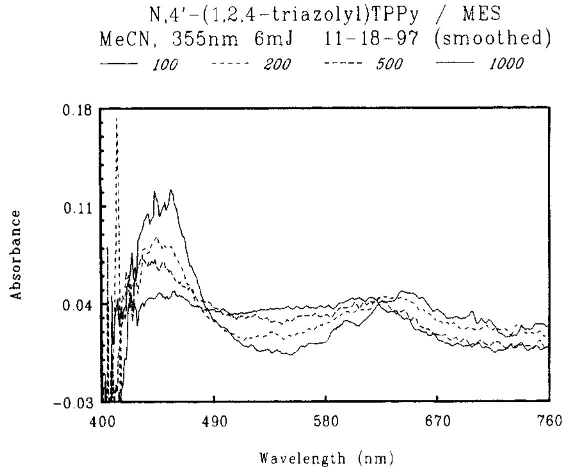

Figure 5. Decay of transient absorptions of 1-(1,2,4-triazol-4-yl)-2,4,6-triphenylpyridinium tetrafluoroborate in mesitylene/acetonitrile (100 to 1000 ps).

nm (Figure 5). The transient from **2** decays on the time scale of a few nanoseconds, which decay is somewhat accelerated by the addition of mesitylene. The position and shape of the spectral band, shown in Figure 4, is not altered by the presence of mesitylene. The spectrum arising from the triphenyl compound changes between 50 and 500 ps following the laser pulse, with the 450 nm peak decaying and producing a new absorption between 490 and 600 nm.

Owing to the observed lifetimes, the visible fluorescence, and the fact that the two salts give different transients, we suggest that the bands at 485 and 450 nm could arise from the first excited singlet states of each of the pyridinium salts, rather than from an intermediate triazolyl cation. Indeed, triazole itself does not absorb to any appreciable extent above 200 nm. Falvey and Cramer[14a] subjected *N*-(diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate to LFP (308 nm) and observed two transients at 425 and 660 nm which they attributed to $Ph_2NH^{+\cdot}$.[14a] The latter species was generated by 266 nm LFP of *N*-nitrosodiphenylamine in the presence of malonic acid in acetonitrile solution and monitored at 690 nm—the aminyl radical was formed first[27] which then underwent protonation. The fact that only one major transient was observed for the trimethylpyridinium and two for the triphenylpyridinium could be interpreted speculatively as follows: the transients in the 450−485 nm range are owing to the singlet excitation; the one at 630 nm, observed only with the triphenylpyridinium, could be owing to the formation of an intermediate in the *intra*molecular attack of the 2-phenyl group by the triazolyl ring to give a diradical cation σ-complex (**28**) as sketched in Scheme 9. Some credibility is lent to this hypothesis by the finding by Katritzky and co-workers that 1,2-diphenylpyridinium perchlorates undergo intramolecular ring-closure on irradiation with 300 nm light,[28] and 2-phenyl-1-(1,2,3-triazol-4-yl)pyridinium salts undergo similar intramolecular cyclizations.[28] We hope to report more detailed studies of the LFP of these pyridiniums, as well as EPR spectral studies from steady-state irradiations in the future. The above results, along with the reported photochemical properties of pyridinium compounds in the presence of electron donors,[29] led us to examine the possibility of a photoinduced electron transfer (PET) from mesitylene to salt **2**. The intensity of fluorescence of **2** as a function of mesitylene concentration was measured, and no change was observed in the shape of the spectral band, but a change was observed in the intensity of the fluorescence leading to the Stern−Volmer relationship[30] displayed in Figure 6a,b. The quenching rate constant, k_q ($= K_q\tau^{-1}$), in acetonitrile, obtained from the slope (K_q) of the Stern−Volmer plot and the fluorescence lifetime τ (ca. 2 ns, from the LFP studies), is 1.4×10^{10} M^{-1} s^{-1}. A similar value (1.3×10^{10} M^{-1} s^{-1}) has been reported for electron transfer from mesitylene to 10-methylacridinium ion.[30]Such an electron transfer would produce the mesitylene radical cation **29** and the pyridinyl radical **30**, which could fragment to the triazolyl radical **26** and coupling could then lead to **10**, while hydrogen-abstraction would yield **7** and **10** (Scheme 10).

Pyridinyl radicals, which are accessible by electrochemical reduction, photolysis,[31a] or by chemical means,[31b] are isolable in some cases,[31c] but usually dimerize or fragment. The latter is the predominant reaction observed in cases in which a heteroatom is bound to the pyridinyl nitrogen,[31c] such as is **30**. To test if **30** could be a possible intermediate in our reactions, **2** was reduced with Na/Hg under nitrogen in acetonitrile solution.[32] 2,4,6-Collidine and triazole (**7**) were the major products, together with lesser amounts of collidine dimers. No detectable amounts of the dimer of radical **30** were detectable (NMR, GC/MS). This fragmentation of **30**, together with the LFP spectroscopic data, strongly suggests that **10** is not formed via the intermediacy of free **1** in the photolyses. These results also argue against the possibility that **2** undergoes direct homolysis of the N−N bond (as discussed previously).

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(27) Wagner, B. D.; Ruel, G.; Lusztyk, J. *J. Am. Chem. Soc.* **1996**, *118*, 13.

(28) (a) Katritzky, A. R.; Zakaria, Z.; Lunt, E. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1879. (b) Katritzky, A. R.; Agha, B.; deVille, G. Z. *Org. Magn. Reson.* **1983**, *21*, 649.

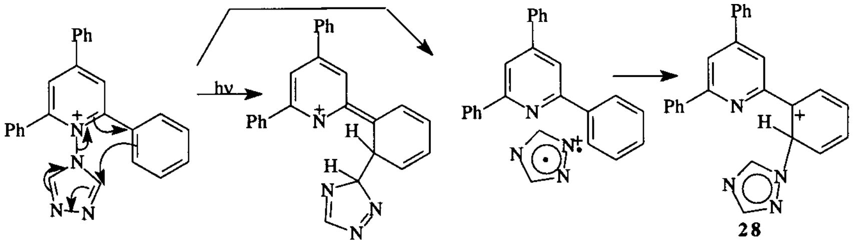
(29) (a) Mariano, P. *Acc. Chem. Res.* **1983**, *16*, 130. (b) See also: Bockman, T. M.; Lee, K. Y.; Kochi, J.; *J. Chem. Soc., Perkin Trans. 2* **1992**, 1581.

(30) Fujita, M.; Ishida, A.; Takamuku, S.; Fukuzumi, S. *J. Am. Chem. Soc.* **1996**, *118*, 8566.

(31) (a)Kosower, E. M.; Schwager, I. *J. Am. Chem. Soc.* **1964**, *86*, 4493. (b) Kosower, E. M. *Molecular Biochemistry*; McGraw-Hill: New York, 1962. (c) Kosower, E. M. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic Press: New York, 1976; Vol. II, Ch. 1.

(32) Kosower, E. M.; Ikegami, J. R. *J. Chem. Soc. (C)* **1967**, 1664.

Scheme 9



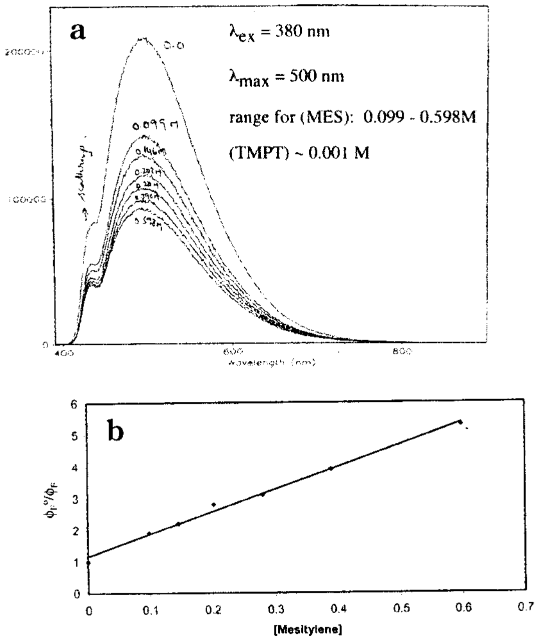


Figure 6. (a) Fluorescence intensity of **2** as a function of the mesitylene concentration. (b) Stern–Volmer plot of fluorescence of **2** in mesitylene/acetonitrile.

On the other hand, the formation of **1c** as an intimate pair with either 2,4,6-collidine or 2,4,6-triphenylpyridine may be required to account for the formation of **13** (with traces of **4**) from **2** in the absence of mesitylene (Scheme 11). In the presence of added 2,6-dimethylpyridine, this tight pair may be solvent-separated leading to the formation of triazololutidine**18** and triazole (**7**) (triazolocollidine **13** could still arise from the intimate pair—a 3,3-sigmatropic shift is not allowed photochemically). A similar separation of the pair from the photolysis of the triphenylpyridinium salt in the presence of external collidine would explain the formation of **13**, which would necessarily arise from the solvent separated pair.

That no product resulting from hydrogen-abstraction from the pyridine side-chains was observed may be due to the fact that, if this abstraction did occur, it would produce a picolyl cation in which the positive charge would be delocalized over the nitrogen atom (i.e., a nitrenium ion); see argument above in the discussion of the thermal formation of **6**.

The thermolysis of the diazonium salts from **3** and from **11** produces 77% of the parent triazole **7**, as well as a very low yield of the electrophilic substitution products, the triazololmesitylenes **10** and **8** from *both* **3** and **11** in about the same ratio. This suggests the formation of a common intermediate, **1c**. If the mesitylene were reacting directly with the diazonium salts **3** and **11** via an S_N2' process, different ratios of **10** to **8** would be expected to have resulted from the two aminotriazoles. Also formed was N_2O, which is consistent with either the formation of a hydroxyazo intermediate,[33] or a labile *N*-nitrosoamine.[34] The main product observed, **7**, could be formed by a SET from mesitylene to **1c** leading to the triazolyl free radical and the mesitylene radical cation. The radical could abstract a H-atom efficiently from the acetonitrile cosolvent to form **7** and much less efficiently from the mesitylene radical cation to give **7** and the substituted benzyl cation leading to **12.** Clearly, the electrophilic substitution of mesitylene by **1c** is a very inefficient process (see related discussion in ref 13c).

That the reactive intermediate from the thermolysis of the diazonium salts is not a free radical[35] was established by the photolysis of **21** (which gives rise to the radical) in the presence of mesitylene, but no **10** was formed in this way.

Unlike other nitrenium ions (singlets) generated photolytically from the corresponding pyridiniums,[2e,14a] the triplet diradical cation **1c** does not react in the same way with electron rich donors, but gives mainly the hydrogen abstraction product from suitable donors, as is typical of triplet nitrenium ions. Note in Table 1 the increase in yield of triazole **7** from 6% to 42% as the methanol-d_4:acetonitrile ratio increases.[1,36] In conclusion, therefore, it appears that the thermolysis of the pyridinium salt **2** does not generate free **1**, and the products (with the possible exception of triazole itself) result mostly from concerted processes. Thermolysis of the *N*-diazonium salts produces **1**, while photolysis of the pyridiniums in the presence of mesitylene gives products whose formation is best accounted by single electron transfer from the substrate to the pyridinum, whereas photolysis in methanol and acetonitrile is best explained by involving the intermediacy of **1**. Finally, the triazolium's behavior (when it is formed) is well-accounted for by its predicted diradical cation structure **1c**.

Experimental Section

Details of Computational Methods. Calculations described in this work were performed on an HP9000 J280/2 workstation at the University of Barcelona and on the IBM SP2 at the Centre de Supercomputació de Catalunya (CESCA).

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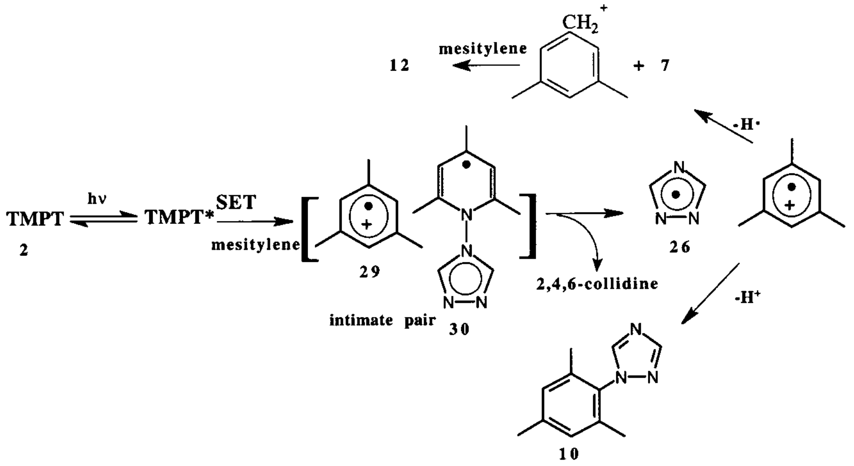
[33] Kreher, R.; Bergmann, V. Z. *Naturforsch., Anorg. Chem., Org. Chem.* **1992**, *37b*, 881. DeRosa, M.; Haberfield, P. *J. Org. Chem.* **1981**, *46*, 2639, and references therein.

[34] Kuzmenko, V. V.; Pozharskii, A. F. *Adv. Heterocycl. Chem.* **1992**, *53*, 85.

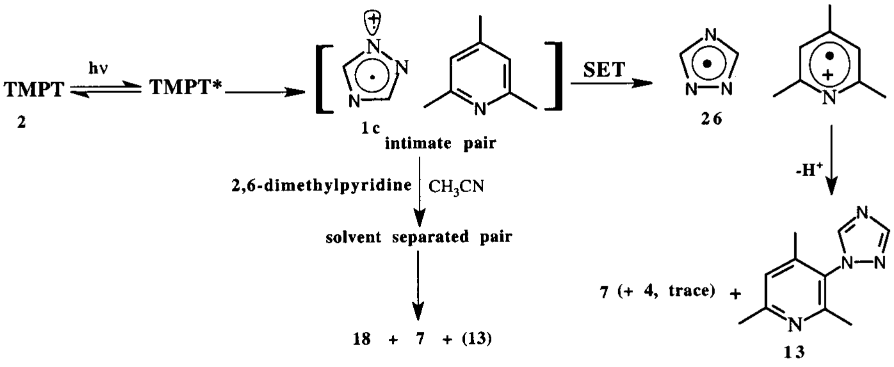
[35] March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*, 4th ed.; John Wiley & Sons: New York, 1992; Ch. 14, Sec. 4–18,

[36] For free radical and triplet nitrenium ions abstracting the α-hydrogen from ethanol, see Canning, P. J. S.; McCrudden, K.; Maskill, H. Sexton, B. *J. Chem. Soc., Chem. Commun.* **1998**, 197. Bunnett, J. F.; Yijima, C. *J. Org. Chem.* **1977**, *42*, 639. Gassman, P. G.; Fox, B. L. *J. Am. Chem. Soc.* **1967**, *89*, 338.

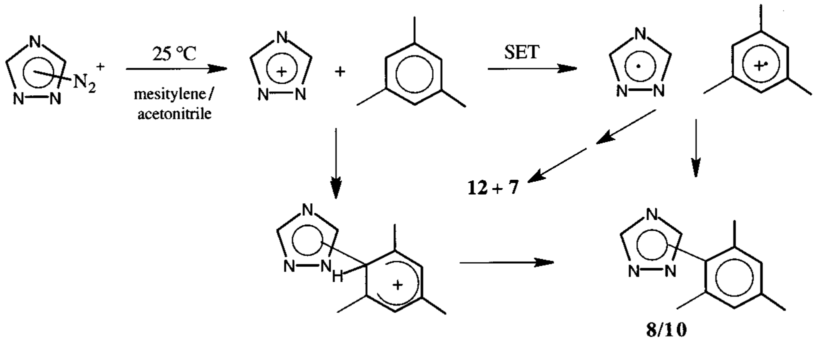
Scheme 10



Scheme 11



Scheme 12



The equilibrium geometries of the most relevant low-lying electronic states of the 4-(1,2,4-triazolyl) cation (**1**) were initially optimized, within appropriate molecular symmetry constraints, with the d-polarized split-valence 6-31G(d) basis set[37] employing analytical gradient procedures.[38,39] The closed-shell singlet states were calculated with the self-consistent field (SCF) molecular orbital (MO) method using a spin-restricted Hartree–Fock (RHF)[40] wave function, while the lowest triplet state was calculated at the SCF level of theory with a restricted open-shell (ROHF) function.[41] All these ab initio calculations were performed with the GAMESS[42] program package. The equilibrium geometries were further optimized by use of a multiconfiguration SCF (MCSCF) wave function of the complete active space (CASSCF) class[43] with the 6-31G(d) basis set. The CASSCF calculations were performed by adopting an eight-orbital ten-electron valence space, hereafter designated (10,8). The valence orbitals included the five π MOs of the triazolyl ring plus the three σ-type orbitals associated with the in-plane nonbonding lone pairs of the nitrogen atoms. Distribution of 10 *active* electrons among these eight *active* orbitals leads to CASSCF(10,8) wave functions formed as a linear combination of 318 and 384 spin-adapted configuration state functions (CSFs) for the $^3B_1$ and $^1A_1$ electronic states, respectively. All CASSCF optimizations were carried out by using GAMESS program. The normal modes and harmonic vibrational frequencies of the structures optimized at the CASSCF(10,8) level of theory were obtained by diagonalizing the mass-weighted Cartesian force constant matrix calculated from analytical second derivatives of the total energy by using GAUSSIAN 94 program package.[44] The

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(37) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(38) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(39) Bofill, J. M. *J. Comput. Chem.* **1994**, *15*, 1.

(40) Roothaan, C. C. J. *Rev. Mod. Phys.* **1973**, *23*, 69.

(41) Davidson, E. R. *Chem. Phys. Lett.* **1973**, *21*, 565.

(42) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(43) For a review, see: Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.

unscaled CASSCF(10,8) frequencies were used to compute the zero-point vibrational energy (ZPVE) corrections to the energies.

To incorporate the effect of dynamical valence-electron correlation on the relative energy ordering of the low-lying electronic states of **1**, second-order multiconfigurational perturbation theory calculations based on the CASSCF(10,8) reference function (CASPT2)[45] were carried out. CASPT2 single point energies were calculated at the CASSCF(10,8)/6-31G(d) optimized geometries, using the Dunning correlation-consistent polarized valence triple-ζ [10s5p2d1f/4s3p2d1f] basis set for carbon and nitrogen, and [5s2p1d/3s2p1d] for hydrogen, designated cc-pVTZ,[46] and all valence electrons were correlated. Since the "normal" CASPT2 method, sometimes denoted CASPT2-0, is known to underestimate the energy of some open-shell relative to closed-shell electronic states, the CASPT2-g1 procedure with the full Hartree−Fock matrix was used in the construction of the zeroth-order Hamiltonian.[47] The CASPT2 calculations were performed with the MOLCAS 4 program package.[48]

Laser Flash Photolysis. A mixture of pyridinium salt and mesitylene was dissolved in acetonitrile (distilled from P_2O_5, stored under argon, and delivered with the aid of a syringe into a 10 mm quartz fluorimeter cell equipped with a Teflon stopcock. The UV−vis spectrum of the mixture was recorded before laser photolysis to ensure purity prior to laser photolysis.

Time-resolved difference absorption spectra on the picosecond time-scale were obtained by utilizing the 355 nm (third harmonic) pulse from a Quantel YG 501-C mode-locked Nd^{3+}:YAG laser as the excitation source. The analyzing light was generated by focusing the residual fundamental (1064 nm) on a mixture of H_2O and D_2O (1:1 v:v) contained in a 10 cm cuvette. The emergent white light was focused on a bifurcated fiber-bundle (Dolan-Jenner) which directed the two analyzing beams through the excited and unexcited volumes of the sample at a 90° angle to the excitation beam. The two analyzing beams were collected by a fiber-optic cable and passed through a monochromator (ISA model HR-320) to a dual diode array (Princeton Instruments model DD-512) to record the signal. The monochromator was calibrated with the 436 and 542 nm lines from a mercury lamp. Time resolution was achieved by passing the fundamental (1064 nm) along a variable-delay stage (Velmex model B4036Q13). Before each spectral acquisition, a background data set was collected without exciting the sample. Absorbances were calculated using the relationship: $\Delta A = I_o I^b / I_o^b I$, where I_o represents the intensity of the analyzing beam passing through the unexcited column of the sample and I_o^b and I^b represent the intensities of the background. Spectra were acquired at a uniform excitation energy of 6 mJ per pulse, and they represented the average of 300 transients.

Time-resolved spectra on the nanosecond/microsecond time scale were obtained using the third harmonic (355 nm) of a Quantel YG 580-10 Q-switched Nd^{3+}:YAG laser with a 10 ns pulse width as the excitation source. The output of a 150 W xenon arc lamp focused on the sample at a 90° angle to the excitation beam served as the probe light. The probe beam emerging from the sample was focused on the entrance slit of an Oriel model 772.50 monochromator equipped with a model 77298 (500 nm blaze) grating in the spectral range between 300 and 800 nm. The monochromatic light was detected by a Hamamatsu model R-928 photomultiplier tube. The timing sequence of the excitation and probing of the sample was controlled by a Kinetics Instruments sequence generator and laser controller. Data acquisition and digitization were performed with a Tektronix model 7104 oscilloscope in conjunction with a Tektronix model C101 video camera and DCS-01 software. The ns/us spectral decays were processed with the ASYST (2.0) scientific software package.[26b]

Fluorescence Experiments. Steady-state luminescence measurements were performed on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450-W xenon source and an R928 photomultiplier tube as detector.

X-ray Crystallographic Analysis. Intensity data were measured at 22 ± 1 °C by using $\omega/2\theta$ scans ($2\theta_{max} = 45°$) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nicolet *R*3*m*V diffractometer. Periodic measurement of three intensity standards indicated no need for a decay correction, and analysis of azimuthal scans of several moderately intense reflections verified that an absorption correction was not required. Lorentz and polarization corrections were applied to the data. The structure was solved by using direct methods and refined by using full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in optimized positions ($d_{C-H} = 0.96$ Å) and were allowed to ride on the atom to which they were bonded; isotropic group thermal parameters were refined for all of the hydrogen atoms (U_{iso}(H): 0.103(7) Å^2). Structure solution, refinement and the calculation of derived results were performed with the SHELXTL-Plus[49] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber,[50] and the real and imaginary anomalous dispersion corrections were those of Cromer.[51]

Crystal data: $C_{10}H_{12}N_4$, fw 188.23 u, orthorhombic space group, *Pnma* (No. 62), $a = 15.780(6)$, $b = 7.375(3)$, $c = 8.806(3)$ Å, $V = 1024.8(6)$ Å^2, $Z = 4$, $\rho_{calcd} = 1.22$ g cm^{-3}. The trimethylpyridinium ring sits on a crystallographic mirror (*x*, _, *z*) which bisects the triazole ring. Final residual values of $R = 0.046$ and $R_w = 0.059$ for 438 observed data ($I > 3\sigma(I)$).

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Supporting Information Available: Complete listings of crystallographic data, atomic coordinates, bonding distances and angles, anisotropic thermal parameters, packing diagrams, and observed and calculated structure factors. Experimental procedures and full characterization for all new compounds (^{1}H and ^{13}C NMR, IR, MS, elemental analyses, mp). This material is available free of charge via the Internet at http://pubs.acs.org.

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