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Trifluoromethyl substitution on the pyrazole ring was found to enhance photoreactivity *via* the P_4 pathway which involves interchange of the N2-C3 ring atoms. Thus, 1-methyl-3-(trifluoromethyl)pyrazole (**1**) and 1-methyl-5-(trifluoromethyl)pyrazole (**3**) transposed with a P_4/P_6 or P_4/P_6+P_7 ratio of 2.1:1. 1-Methyl-4-(trifluoromethyl)pyrazole (**2**) transposed regiospecifically by the P_4 transposition pathway. Compounds **2** and **3** were also observed to undergo photocleavage to yield enaminonitrile and enaminoisocyanide products.

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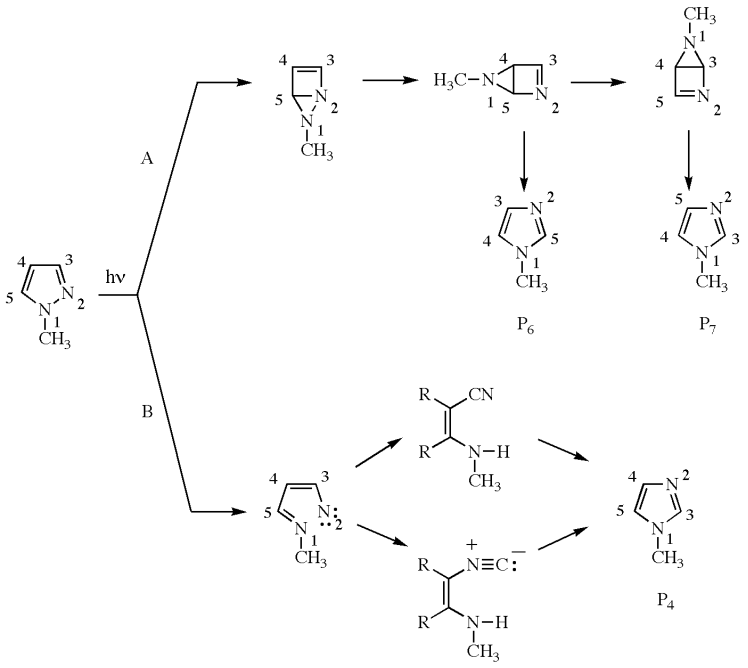
Previous work in this [1-3] and other laboratories [4-6] indicates that the photochemistry of 1-methylpyrazoles involves competition between electrocyclic ring closure (Path A, Scheme 1) and cleavage of the N1-N2 bond (Path B, Scheme 1). Path A results in the formation of a 1,5-diazabicyclo[2.1.0]pentene intermediate which undergoes one or two sigmatropic shifts of nitrogen followed by rearomatization of the two resulting isomeric 2,5-diazabicyclo[2.1.0]pentene species to yield 1-methylimidazoles with two different scrambling patterns identified as P_6 and P_7 respectively [7]. Alternatively, Path B leads to a species that can be viewed as a vinyl nitrene that rearranges to a 1-methylimidazole with a P_4 scrambling pattern. If the initial pyrazole bears a hydrogen atom at ring position 3, this rearrangement occurs *via* detectable enaminonitrile and enaminoisocyanide photocleavage products as shown in Scheme 1. This P_4 scrambling pattern involves only interchange of the N2 and C3 ring atoms.

Scheme 1

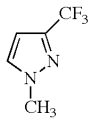


Deuterium labeling studies have revealed that the phototransposition of 1-methylpyrazole occurs about 60% by way of Path A while 40% of the transposition product is formed *via* Path B [1]. Interestingly, although methyl or fluoro substitution in the pyrazole ring substantially enhances reactivity *via* Path B [1], it has been suggested that trifluoromethyl substitution greatly increases reactivity *via* Path A [6]. In order to more thoroughly explore the effect of trifluoromethyl substitution on the regiochemistry of the 1-methylpyrazole-to-1-methylimidazole phototransposition, the three isomeric trifluoromethyl substituted 1-methylpyrazoles **1-3** have been synthesized and their photochemistry studied.

Results and Discussion.

Synthesis of Reactants and Expected Phototransposition Products.

3-and 5-(Trifluoromethyl)pyrazoles (**1**) and (**3**) were synthesized by allowing methylhydrazine to react with



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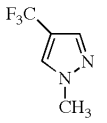

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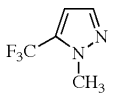
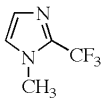


3

4-ethoxy-1,1,1-trifluoro-3-buten-2-one as previously described [8]. 1-Methyl-4-(trifluoromethyl)pyrazole (**2**) was prepared by condensation of 2-trifluoro-1,3-bis(dimethylamino)trimethinium hexafluorophosphate and methylhydrazine in a modification of the published procedure [9].

The expected phototransposition products, 2-, 4-, and 5-(trifluoromethyl)imidazoles **4**, **5**, and **6**, were prepared by photo-trifluromethylation of 1-methylimidazole carried



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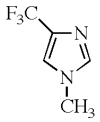

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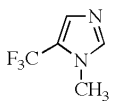


6

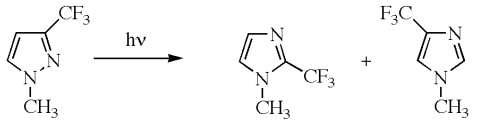
out by irradiation of a mixture of trifluoromethyl iodide and 1-methylimidazole in methanol solution [10].

Photochemistry of Trifluoromethyl Substituted 1-Methylpyrazoles.

A solution of 1-methyl-3-(trifluoromethyl)pyrazole (**1**) in acetonitrile was irradiated at ambient temperature with the quartz-filtered light of a 450-W Hg arc. The reaction was monitored by uv-absorption spectroscopy, quantitative gas-liquid chromatography (GLC), and ^{1}H-NMR spectroscopy.

Aliquots were periodically removed, diluted, and analyzed by uv-absorption spectroscopy. This showed that irradiation was accompanied by a shift in the absorption maximum from λ 215 (ε = 3267-M^{-1}) to 212 nm. This suggested the conversion of **1** to a mixture of **4**, **5**, and/or **6**, which absorb in the uv at 221 nm (ε = 4200 M^{-1}), 203 nm (ε = 6080 M^{-1}), and 200 nm (ε = 5120 M^{-1}) respectively.

GLC analysis as a function of irradiation time showed the gradual consumption of **1** and the formation of two GLC-volatile primary products identified as 1-methyl-2-(trifluoromethyl)imidazole (**4**) and 1-methyl-4-(trifluoromethyl)imidazole (**5**) by direct chromatographic and

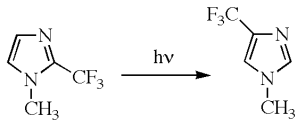


1 **4** **5**

spectroscopic comparison with authentic samples of these compounds. No 1-methyl-5-(trifluoromethyl)imidazole (**6**) could be detected by GLC as a photoproduct in this reaction. Quantitative GLC showed that after 10 minutes of irradiation 15% of **1** was consumed whereas the yields of **4** and **5** were 64% and 31% respectively [11].

The resulting solution was concentrated under reduced pressure and the residue was dissolved in deuteriochloroform and analyzed by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectrum exhibited a singlet at δ 3.90 due to the 1-methyl group of the unconsumed reactant and signals at δ 3.72 and 3.67 for the 1-methyl groups of **4** and **5** respectively, but no signal at δ 3.70 where the 1-methyl protons of 1-methyl-5-(trifluoromethyl)imidazole (**6**) are known to absorb. The spectrum also showed signals at δ 6.46 and 7.34 due to the protons at C4 and C5 respectively of the reactant **1**, signals at δ 7.01 and 6.92 due to the protons at C4 and C5 respectively of 1-methyl-2-(trifluoromethyl)-imidazole (**4**) and signals at δ 7.42 and 7.17 due to protons at C2 and C5 respectively of 1-methyl-4-(trifluoromethyl)imidazole (**5**), but no signals at δ 7.46 and 7.36 where the protons at C2 and C4 respectively of 1-methyl-5-(trifluromethyl)imidazole (**6**) are known to absorb. The ^{1}H-NMR spectrum of the crude photoproduct mixture was very clean and did not exhibit any other significant signals.

Although more prolonged irradiation was accompanied by the continued consumption of **1**, the yield of **4** began to decrease while the yield of **5** continued to increase. This concentration vs. irradiation time profile suggested that although **5** is a primary product from **1**, **5** is also formed from **4** in a secondary phototransposition process. As required by this suggestion, direct irradiation of an acetonitrile solution of **4** resulted in the formation of **5**. This 1-methylimidazole-to-1-methylimidazole phototransposition, which has also

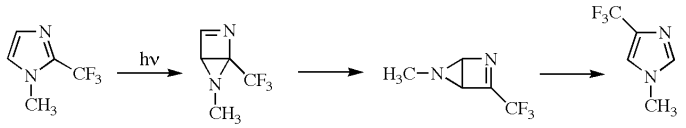


4 **5**

been observed in dimethyl substituted imidazoles [1], is consistent with the electrocyclic ring closure –heteroatom migration mechanism shown in Scheme 2.

According to the scrambling pattern shown in Scheme 1, 1-methyl-4-(trifluoromethyl)imidazole (**5**) is the expected P_6 phototransposition product from **1**.

Scheme 2

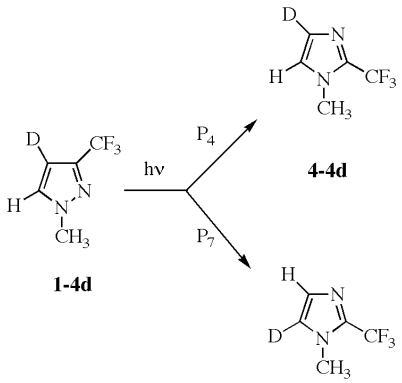


4 **4a** **5a** **5**

The mechanistic route for the formation of 1-methyl-2-trifluoromethylimidazole (**4**) is less certain. Thus, despite the significantly different bond-breaking and bond-forming requirements of the P_4 and P_7 pathways (Scheme 1), by coincidence, in this case both pathways lead to the same product, 1-methyl-2-trifluoromethylimidazole (**4**).

In order to resolve this ambiguity, the photochemistry of 4-deuterio-1-methyl-3-(trifluoromethyl)pyrazole (**1-4d**) was studied. Inspection of Scheme 1 shows that while the

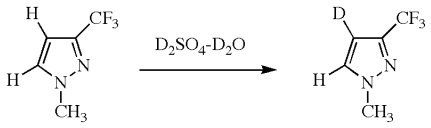
Scheme 3



1-4d **4-4d** **4-5d**

C5 proton of **1-4d** is expected to transpose to the C5 ring position in **4** by the P_4 pathway, transposition *via* the P_7 pathway places this proton at the C4 ring position as shown in Scheme 3.

4-Deuterio-1-methyl-3-(trifluoromethyl)pyrazole (**1-4d**) was prepared by treatment of **1** with 70% sulfuric acid-d_2 in deuterium oxide. The mass spectrum of the deuterated

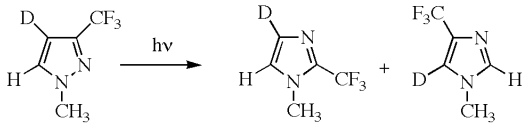


1 **1-4d**

product exhibited a base peak for the molecular ion at m/z 151, indicating that one proton had been exchanged by one deuterium atom. The spectrum also exhibited a prominent signal at m/z 150 that was 50% of the intensity of the M^+ peak. This is due either to a M^+-1 peak formed by loss of one H-atom from the molecular ion or from a large amount of undeuterated 1-methyl-3-(trifluoromethyl)pyrazole (**1**) in the sample. The mass spectrum of undeuterated **1** also exhibited a base peak for the molecular ion at m/z 150 and a prominent signal at 149 which was also 50% of the intensity of the M^+ peak. This must be due to a M^+-1 peak formed by loss of one H-atom from the molecular ion. These results show that the prominent signal at m/z 150 in the mass spectrum of **1-4d** is also due to an M^+-1 peak formed by loss of one H-atom from the molecular ion and is not due to undeuterated **1** in the sample. The ^{1}H-NMR spectrum of the deuterated product exhibited signals at δ 3.90 (s, 3H) and 7.34 (s, 1H) which are due to the protons of the 1-methyl group and the proton at C5 but only a very small signal at δ 6.46 due to residual protons at C4 of the pyrazole ring.

A solution of 4-deuterio-1-methyl-3-(trifluoromethyl)-pyrazole (**1-4d**) in acetonitrile was irradiated for 10 minutes in order to minimize secondary photochemical reactions. After removal of the solvent the residue was dissolved in deuteriochloroform and analyzed by ^{1} H-NMR spectroscopy. In addition to singlets at δ 3.83, 3.66, and 3.59, due to the protons of the 1-methyl groups of the reactant and products, the spectrum also exhibited a signal at δ 7.26 due to the C5 proton of **1-4d**, and signals at δ 7.33 and 6.84 due to the protons at C2 and C5 of 5-deuterio-1-methyl-4-(trifluoromethyl)imidazole (**5-5d**) and 4-deuterio-1-methyl-2-(trifluoromethylimidazole (**4-4d**)respectively.

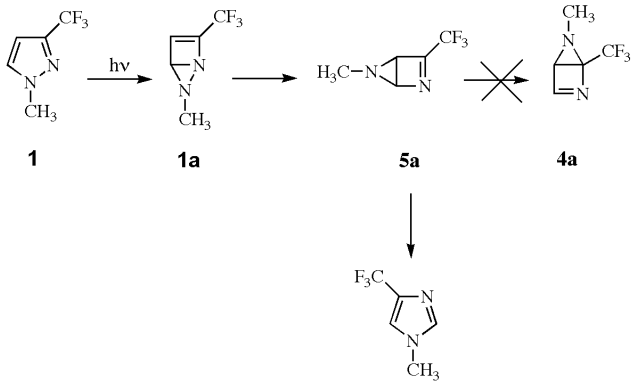
These results show that **1-4d** has phototransposed to **4-4d** and **5-5d** as demanded by the P_4 and P_6 pathways respectively.



1-4d **4-4d** (P_4) **5-5d** (P_6)

These deuterium labeling studies show that 1-methyl-3-(trifluoromethyl)pyrazole (**1**) phototransposes to 1-methyl-2-(trifluoromethyl)imidazole (**4**) *via* pathway B, which involves interchange of the N2 and C3 ring atoms in **3**, and to 1-methyl-4-(trifluoromethyl)imidazole (**5**) by pathway A involving electrocyclic ring closure of **1** to **1a** and one

Scheme 4



1 **1a** **5a** **4a** **5**

nitrogen migration leading to the P_6 phototransposition product, but not by the double-walk process that would lead to the P_7 product. Thus, although the first nitrogen walk (Scheme 4) converts **1a** to the more stable **5a**, the second nitrogen walk (**5a** → **4a**) would not be expected to occur since it would result in the conversion of **5a**, stabilized by substitution at the polar C-N double bond, to a less stable isomer **4a** with the substituent at the bridgehead position. Accordingly, aromatization of **5a** to **5**, the observed P_6 product, would be expected to occur faster than the second nitrogen walk to yield **4a**. Absence of a P_7 product in this reaction is consistent with this reasoning.

A solution of 1-methyl-4-(trifluoromethyl)pyrazole (**2**) in acetonitrile was also irradiated. The uv-absorption spectrum as a function of irradiation time showed a shift in the absorption maximum from λ 210 to 200 nm. In this case, however, irradiation was also accompanied by an increase in absorbance at 260 nm from 0 before irradiation to 1.7 after 30 minutes of irradiation.

Although the new absorption maximum at 200 nm suggests the formation of 1-methyl-4-(trifluoromethyl)imidazole (**5**) in this reaction, this latter compound does not absorb at 260 nm. Both enaminonitrile and enaminoisocyanide photocleavage products (Scheme 1) are known to absorb in the 260 nm region of the spectrum [2]. These two types of compounds have previously been distinguished on the basis of their stability in acidic medium [2]. Thus, although enaminonitriles are generally stable upon addition of a small quantity of acid, enaminoisocyanides are immediately destroyed.

In order to determine the effect of added acid on the compound or compounds that absorb at 260 nm, the irradiated solution of (**2**) that exhibited an absorbance at 260 nm of 1.7 was treated with one microdrop of concentrated hydrochloric acid. The absorbance at 260 nm immediately decreased to 1.1. Interestingly, addition of a second microdrop of acid caused no further change in the absorbance at 260 nm. These results indicate that the absorbance at 260 nm is due to one compound that is very sensitive to acid and another that is not. This suggests that the absorption at 260 nm is due to the formation of the two photocleavage products, 3-(*N*-methylamino)-2-(trifluoromethyl)propenenitrile (**7**) and 2-(*N*-methylamino)-1-(trifluoromethyl)-ethenylisocyanide (**8**).

7 **8**

Analysis by infrared absorption spectroscopy provided further evidence for the formation of photocleavage products **7** and **8**. A solution of **2** in methanol solvent was irradiated until the absorbance at 260 nm was maximized at 1.7. Infrared analysis of the residue remaining after evaporation of the solvent showed absorptions at 2210 and 2306 cm^{-1} characteristic of nitrile and isocyanide functional groups respectively. Neither the pyrazole reactant nor any of the imidazole phototransposition products exhibit similar absorptions.

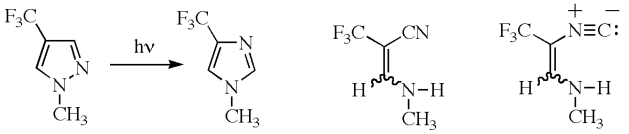
The photoreaction of 1-methyl-4-(trifluoromethyl)pyrazole (**2**) in acetonitrile was also monitored by GLC and ^{1}H-NMR spectroscopy. After 5 minutes of irradiation quantitative GLC showed that 11% of reactant **2** has been consumed and that 1-methyl-4-(trifluoromethyl)imidazole (**5**) was formed in 83% yield. After a total of 30 minutes of irradiation the solution was concentrated. The residue was dissolved in deuteriochloroform, and analyzed by ^{1}H-NMR spectroscopy.

The ^{1}H-NMR spectrum exhibited clear evidence for the presence of (*Z*)- and (*E*)- 3-(*N*-methylamino)-2-(trifluoromethyl)propenenitrile (*Z*)/(*E*)-(**7**), and (*Z*)- and (*E*)-2-(*N*-methylamino)-1-(trifluoromethyl)ethenylisocyanide (*Z*)/(*E*)-(**8**). Accordingly, the spectrum exhibited a pair of doublets at δ 2.98 (J = 4.6 Hz) and 3.18 (J = 5.3 Hz) and a second pair at δ 2.72 (J = 5.0 Hz) and 2.60 (J = 5.2 Hz) due to the *N*-methylprotons of (*Z*)- and (*E*)-**7** and (*Z*)- and (*E*)-**8** respectively. In addition, the spectrum exhibited a pair of doublets at δ 7.14 (J= 14.4 Hz) and ~7.46 (partially overlapping with the signal for the C2 proton of **5**) due to the C3 protons of (*Z*)- and (*E*)-**7**, and another pair at δ 6.87 (J = 14.9 Hz) and 6.69 (J = 13.6 Hz) due to the C2 protons of (*Z*)- and (*E*)-**8**.

The ^{1}H-NMR spectrum also confirmed the presence of unreacted **2** and the phototransposition product **5** in the reaction mixture. Thus, the spectrum exhibited singlets at δ 3.87 and 3.67 due to the *N*-methyl protons of **2** and **5** respectively, but no signals at δ 3.70 or 3.72 where the *N*-methyl protons of 1-methyl-2-(trifluoromethyl)imidazole (**4**) or 1-methyl-5-(trifluoromethyl)imidazole (**6**) respectively are

known to absorb. The spectrum also exhibited singlets at δ 7.58 and 7.61 due to the C5 and C3 protons respectively of the reactant **2**, signals at δ 7.42 and 7.16 due to the C2 and C5 protons respectively of the transposition product **5**, but no signals at δ 6.99 and 6.91 or at δ 7.46 and 7.36 where the ring protons of **4** and **6** are known to absorb.

These chromatographic and spectroscopic data confirm that 1-methyl-4-(trifluoromethyl)pyrazole (**2**) has undergone



2 **5** **7** **8**

photocleavage to (*Z*)-and (*E*)-3-(*N*-methylamino)-2-(trifluromethyl)propenenitrile (*Z*)/(*E*)-(**7**) and (*Z*)- and (*E*)-2-(*N*-methylamino)-1-trifluoromethyl)ethenylisocyanide (*Z*)/(*E*)-(**8**) and phototransposition to 1-methyl-4-(trifluoromethyl)imidazole (**5**). Thus, the transposition of **2** to **5** has occurred by interchange of the N2 and C3 atoms of the pyrazole ring while C4 of the reactant has transposed to C4 of the imidazole product as required by the P_4 pathway. Accordingly, **2** has transposed regiospecifically by the P_4 transposition pathway.

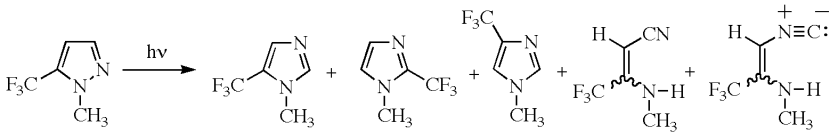
Irradiation of 1-methyl-5-(trifluoromethyl)pyrazole (**3**) also led to photocleavage and phototransposition. Thus, irradiation was accompanied by a decrease in the absorption maximum of **3** at 220 nm and an increase in the absorbance at 260 nm from 0 to 1.2 due to the formation of nitrile and isocyanide photocleavage products. Infrared analysis of a sample after irradiation and concentration revealed sharp absorptions at 2306 and 2211 cm^{-1} characteristic of cyano and isocyano functional groups respectively.

GLC analysis as a function of irradiation time showed a decrease in the concentration of **3** and the formation of three new peaks with retention times identical to 1-methyl-2-(trifluoromethyl)imidazole (**4**),1-methyl-4-(trifluoromethyl)imidazole (**5**), and 1-methyl-5-(trifluoromethyl)imidazole (**6**). After 5 minutes of irradiation quantitative GLC showed that 19% of the reactant **3** had been consumed and that **4**, **5**, **6**, had been formed in yields of 19%, 12% and 65% respectively.

After a total of 30 minutes of irradiation the solvent was evaporated, the residue was dissolved in deuteriochloroform, and analyzed by 'H-NMR spectroscopy. The spectrum clearly revealed the presence of both (*E*) and (*Z*) isomers of both photocleavage products **9** and **10**. Thus, the spectrum exhibited a pair of doublets at δ 3.01 (J = 5.4 Hz) and 2.74 (J = 5.1 Hz) and a second pair at δ 3.20 (J = 5.4 Hz) and 2.62 (J = 5.2 Hz) for the *N*-methyl protons of (*E*) and (*Z*) –**9** and (*E*) and (*Z*)-**10** respectively. Furthermore, the spectrum showed singlets at δ 3.56 and 4.80 and at δ 3.67 and 4.90 due to the C2 protons of (*E*) and (*Z*)-**9** and the C1 protons of (*E*) and (*Z*)-**10**.

The ^{1}H-NMR spectrum also confirmed the formation of the phototransposition products **4**, **5**, and **6**. Thus, the spectrum exhibited signals at δ 3.75 and at δ 7.01 and 6.93 for the *N*-methyl and C4 and C5 protons of **4**, at δ 3.68 and at δ 7.42 and 7.17 for the *N*-methyl and C2 and C5 protons of **5**, and at δ 3.70 and at δ 7.46 and 7.35 for the *N*-methyl and C2 and C4 protons of **6**.

These chromatographic and spectroscopic data confirm that 1-methyl-5-(trifluoromethyl)pyrazole **3** has undergone phototransposition to yield 1-methyl-5-(trifluoromethyl)-imidazole (**6**), 1-methyl-2-(trifluormethyl)imidazole (**4**),

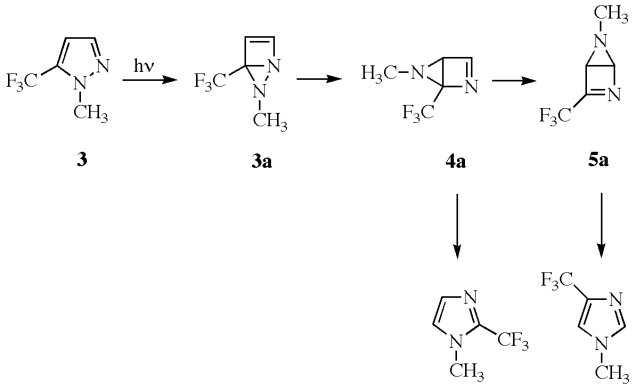


3 **6 (P_4)** **4 (P_6)** **5 (P_7)** **9** **10**

and 1-methyl-4-(trifluoromethyl)imidazole (**5**), and photocleavage to yield (*E*) and (*Z*)-3-(*N*-methylamino)-3-(trifluoromethyl)propenenitrile (*E*)/(*Z*)-**9** and (*E*) and (*Z*)-2-(*N*-methylamino-2-(trifluoromethyl)ethenylisocyanide (*E*)/(*Z*)-**10**.

These results show that the trifluoromethyl group at C5 of the pyrazole reactant has transposed to ring positions 5, 2 or 4 in photoproducts **6**, **4**, and **5**, respectively. According to the scrambling patterns shown in Scheme 1, these are the products expected by the P_4, P_6 and P_7 transposition pathways respectively.

Scheme 5



3 **3a** **4a** **5a**

Thus, both 1-methyl-3-(trifluoromethyl)pyrazole (**1**) and 1-methyl-5-(trifluoromethyl)pyrazole (**3**) phototranspose by pathway B involving only interchange of the N2 and C3 ring atoms, and by pathway A involving electrocyclic ring closure and heteroatom migration. In the case of the 5-substituted isomer **3** (Scheme 5), in addition to the first nitrogen walk converting **3a** to **4a**, a second [1,3]-shift also occurs leading to **5a**, the more stable isomer. Thus, in addition to aromatization of **4a** to the observed P_6 product **4**, aromatization of **5a** would provide **5**, the P_7 product.

Conclusion.

Although trifluoromethyl substitution on the pyrazole ring has been reported to enhance reactivity *via* the P_6 transposition pathway [6], these results are not consistent with that suggestion. Thus, whereas 1,3-dimethylpyrazole has previously been shown to transpose with a P_4/P_6 ratio of 1.6, these current results show that 1-methyl-3-(trifluoromethyl)pyrazole (**1**) transposes with a P_4/P_6 ratio of 2.1. Thus, replacement of the methyl group at C3 with a trifluoromethyl group has enhanced reactivity by the P_4 transposition pathway. Similarly, although 1,5-dimethylpyrazole transposes with a $P_4/(P_6+P_7)$ ratio of 1.26, 1-methyl-5-(trifluoromethyl)pyrazole (**3**) transposes with a $P_4/(P_6+P_7)$ ratio of 2.1. Finally, both 1,4-dimethylpyrazole and 1-methyl-4-(trifluoromethyl)pyrazole (**2**) transpose regiospecifically *via* the P_4 pathway.

EXPERIMENTAL

^{1}H-NMR spectra were recorded at 400.1 MHz in deuteriochloroform on a Bruker FT-NMR system. Infrared and ultraviolet absorption spectra were recorded using a Perkin Elmer Spectrum One FT-IR spectrometer or a Hitachi U-2000 spectrophometer respectively. Gas chromatographic analyses were performed on a Perkin Elmer-8500 FID instrument equipped with a 30m x 0.25 mm i.d. fused silica column coated with 0.25μ Supelcowax 10 bonded phase.

Synthesis of Reactants and Transposition Products.

Pyrazoles **1** and **3** [8] and imidazoles **4**-**6** [10] were prepared by literature procedures.

Pyrazole **2** was prepared by the reaction of methylhydrazine with 2-trifluoromethyl-1,3-bis(dimethylamino)trimethinium hexafluorophosphate using the published procedure for the reaction of methylhydrazine with the corresponding chloride salt [9]. The hexafluorophosphate salt was prepared from the chloride salt as previously described [12].

4-Deuterio-1-methyl-3-(trifluoromethyl)pyrazole(**1-4d**).

1-Methyl-3-(trifluoromethyl)pyrazole (**1**), (0.42 g, 2.8 mmol) was dissolved in sulfuric acid-d_2 (4.6 ml, 70% in deuterium oxide), protected from the atmosphere, and maintained at 70 °C in the dark for 12 days. The solution was neutralized (sodium bicarbonate) and extracted with dichloromethane (5x5ml). The organic extract was dried (sodium sulfate) and concentrated by distillation through a vigreux column leaving 4-deuterio-1-methyl-3-(trifluoromethyl)pyrazole (**1-4d**) as a colorless oil (0.068 g, 0.45 mmol, 16%):^{1}H-nmr (deuteriochloroform):δ 3.89 (s, 3H), 7.34 (s,1H); ms: m/z 151(M^+).

Irradiation and Analysis Procedures.

A solution of the appropriate reactant (3.0 ml, 1.5 X 10^{-2} *M*) in acetonitrile or methanol was placed in a quartz tube (1.0 cm inside diameter X 12.0 cm long). The tube was sealed with a rubber septum and purged with argon for 10 minutes prior to irradiation. The tube was suspended in an ambient temperature water bath adjacent to a water-cooled Quartz immersion well containing a 450W medium pressure Hg lamp.

Reaction progress was monitored by removing aliquots periodically during the irradiation for analysis by GLC or by UV after dilution. GLC retentions of all products are given relative to the appropriate reactant. Quantitative GLC analysis of reactant consumption and product formation was accomplished by using calibration curves constructed for the reactants and products by plotting detector responses versus concentration for five standards of known concentration. Correlation coefficients ranged from 0.994 tp 0.998. After the appropriate irradiation time the solution was concentrated at room temperature under reduced pressure. The residue was either dissolved in deuteriochloroform (0.55 ml) for ^{1}H-NMR analysis or in dichloromethane (0.100 ml). In the latter case the dichloromethane was allowed to evaporate on a sodium chloride plate which was analyzed by IR spectroscopy.

1-Methyl-3-(trifluoromethypyrazole (**1**).

Aliquots were removed and analyzed after irradiation times of 5,10,15, and 30 minutes. UV analysis (1:30 dilution) showed a shift in the absorption maximum from 215 to 212 mm. After 10 minutes of irradiation GLC analysis showed the consumption of **1** (15%) and the formation of 1-methyl-2-(trifluoromethyl)imidazole (**4**) (64%) and 1-methyl-4-(trifluoromethyl)imidazole (**5**) (31%) with relative retentions of 1.34 and 2.59 respectively. ^{1}H-NMR analysis after 30 minutes of irradiation showed the formation of 1-methyl-2-(trifluoromethyl)imidazole (**4**): δ 3.72 (s, 3H), 6.92 (s, 1H),7.01 (s, 1H) and 1-methyl-4-(trifluoromethyl)imidazole (**5**): δ 3.67 (s, 3H), 7.17 (s, 1H), 7.42 (s, 1H).

4-Deuterio-3-(trifluoromethyl)pyrazole (**1-4d**).

After 10 minutes of irradiation ^{1}H-NMR analysis showed the formation of 4-deuterio-2-(trifluoromethyl)imidazole (**4-4d**): δ 3.72 (s, 3H), 6.92 (s, 1H) and 5-deuterio-1-methyl-4-(trifluoromethyl)imidazole (**5-5d**): δ 3.67 (s, 3H), 7.42 (s, 1H).

1-Methyl-4-(trifluoromethyl)pyrazole (**2**).

Aliquots were removed and analyzed after irradiation times of 5, 10, 15, 20 and 30 minutes. UV analysis (1:30 dilution) showed a shift in the absorption maximum from 210 to 200 nm and the formation of a new absorption band at 260 nm (OD=1.70). After 5 minutes of irradiation GLC analysis showed the consumption of **2** (11%) and the formation of 1-methyl-4-(trifluoromethyl)imidazole (**5**) (83%) with a relative retention of 3.5.

^{1}H NMR analysis after 30 minutes of irradiation showed the formation of 1-methyl-4-(trifluoromethyl)imidazole (**5**): δ 3.67(s, 3H), 7.17 (s, 1H), 7.42 (s, 1H); (*E*) -(N-methylamino)-2-(trifluoromethyl)propenenitrile (*E*)-(**7**); δ 3.18 (3H, d, J = 5.3 Hz), 7.46 (d, overlapping with signal for H2 of **5**), (*Z*)-(*N*-methylamino)-2-trifluoromethyl)propenenitrile (*Z*)-(**7**); δ 2.98 (3H, d, J= 4.6 Hz), 7.14 (1H, d, J=14.4 Hz), (*E*)-2-(N-methylamino)-1-(trifluoro-

methyl)ethenylisocyanide (*E*)-(**8**); δ 2.60 (3H, d, J = 5.2 Hz), 6.69 (1H, d, J = 13.6 Hz), (*Z*)-2-*N*-methylamino)-1-trifluoromethyl)ethenylisocyanide (*E*)-(**8**); δ 2.72 (3H, d, J = 5.0 Hz), 6.87 (1H, d, J = 14.9 Hz), (*Z*) –2-(*N*-methylamino)-1-trifluoromethyl)ethenylisocyanide (*Z*)-(**8**); δ 2.72 (3H, d, J = 5.0 Hz), 6.87 (1H, d, J = 14.9 Hz), IR; 2210 and 2306 cm^{-1}.

1-Methyl-5-(trifluoromethyl)pyrazole (**3**).

Aliquots were removed and analyzed after irradiation times of 5, 10, 15 and 30 minutes. UV analysis (1:75 dilution) showed the formation of a new absorption band at 261 nm (OD = 1.1). After 5 minutes of irradiation GLC analysis showed the consumption of **3** (19%) and the formation of 1-methyl-2-(trifluoromethyl)imidazole (**4**) (19%) and 1-methyl-4-(trifluoromethyl)imidazole (**5**) (12%) and 1-methyl-4-(trifluoromethyl)imidazole (**6**) (65%) with relative retentions of 5.9, 10, and 5.8 respectively.

^{1}H-NMR analysis after 30 minutes of irradiation showed the formation of 1-methyl-2-(trifluoromethyl)imidazole (**4**): δ 3.72 (s, 3H), 6.92 (s, IH), 7.01 (s, 1H),1-methyl-4-(trifluoromethyl)-imidazole (**5**): δ 3.67 (s, 3H), 7.17 (s, 1H), 7.42 (s, 1H), 1-methyl-5-(trifluoromethyl)imidazole(**6**): δ 3.70 (s, 3H), 7.35 (s, 1H), 7.46 (s, 1H), (*E*)-(*N*-methylamino)-3-trifluoromethyl)propenenitrile (*E*)-(**9**): δ 3.01 (d, 3H, J = 5.4 Hz), 3.56 (s, 1H), (*Z*)–3-(*N*-methylamino)-3-trifluoromethyl)propenenitrile (*Z*)-(**9**): δ 2.74 (d, 3H, J = 5.1 Hz), 4.08 (s, 1H), (*E*)-2-(*N*-methylamino)-2-(trifluoromethyl)ethenylisocyanide (*E*) –(**9**): δ 3.20 (d, 3H,J = 5.4Hz), 3.67 (s, 1H), (*Z*)-2-(*N*-methylamino)-2-(trifluoromethyl)-ethenylisocyanide (*Z*)-(**9**): δ 2.62 (d, 3H, J = 5.2 Hz), 4.90 (s, 1H), IR; 2211 and 2306 cm^{-1}.

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