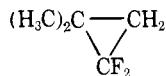


Attempts to verify the HCF_2Br isotopic composition by examining the HCF_2Br^+ ions at m/e 132, 133 have given inconclusive results owing to limited sample size and the sensitivity and resolution limitations of the mass spectrometer.

It is interesting to note that the average photon consumption per molecule of halomethane reacted (2100–8000) is far in excess of the 25–35 photons per molecule required for dissociation on thermochemical grounds. This disparity may be explained through the absorption of photons by many molecules in the focal region with only a few of these achieving sufficient energy to dissociate.

Summary and Conclusions

In the course of these studies it has been possible to prepare macroscopic quantities of fluorocarbon compounds with measurable carbon isotopic enrichments even though the reaction systems in which this is accomplished are quite complex. The reactions may involve both the difluorocarbene diradical and the halodifluoromethyl radical. Other investigators have reported that halodifluoromethyl radicals such as $\cdot\text{BrCF}_2$ form straight-chain adducts with olefins rather than cyclopropyl compounds, and tend to dimerize to form $(\text{CF}_2\text{Br})_2$ rather than form C_2F_4 through some bromine elimination process.^{19,21–24} Thus, in the present study, the fluorinated reaction products C_2F_4 and



are best explained by the formation of a $:\text{CF}_2$ species which then either dimerizes or adds across the unsaturated portion of the olefin. The origin of the products HCF_2Cl , HCF_2Br , and $\text{H}_2\text{C}=\text{CF}_2$ is less clearly defined and these could arise from both $:\text{CF}_2^-$ and $\cdot\text{CF}_2\text{X}$ -hydrocarbon interactions. The general concept of using tuned laser radiation to produce an isotopically specific, reactive intermediate, such as $:\text{CF}_2$ or $\cdot\text{CF}_2\text{X}$, and then utilizing this intermediate in the direct synthesis of labeled compounds appears to be worthy of intensified further investigation.

In addition it has been shown how information obtained from isotopically selective reactions can be utilized in the assignment of infrared absorption bands to specific isotopic species and how the laser-induced chemical approach may offer a convenient method for producing enriched materials for spectroscopic studies.

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Reactivities of Amino and Aminium Radicals: Oxidative Photoaddition of Tetramethyl-2-tetrazene to Olefins

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Abstract: In the presence of oxygen, tetramethyl-2-tetrazene photolytically added to cyclohexene, norbornene, and 1,5-cyclooctadiene under acidic conditions yielding 1-amino-2-hydroperoxides that are reduced to the corresponding amino alcohols. Neither photolysis of the tetrazene under neutral condition nor thermolysis under acidic conditions produced the similar addition compounds. It is concluded that the monoprotonated tetrazene photolytically dissociated to form two dimethylaminium radicals which initiate the attack on carbon-carbon double bonds.

The thermal decomposition of tetraalkyl-2-tetrazenes in dilute acidic conditions, initially reported by Renouf¹ and Fischer and Troschke,² has been sporadically reinvestigated mostly using tetramethyl-2-tetrazene (TMT) as a model compound, and has been confirmed to give the alkylidene imines, e.g., $\text{CH}_2=\text{NCH}_3$, as the primary product.^{3–6} This thermal reaction is generally interpreted with an ionic pathway

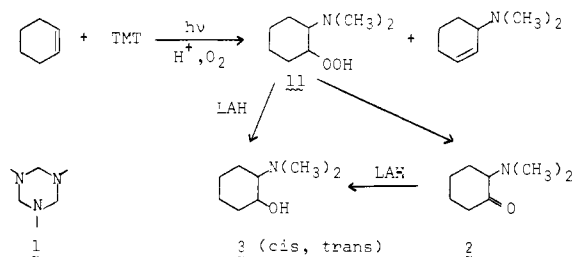
by postulating a dialkylamino diazonium ion⁵ or a dialkylnitrenium ion⁴ (or its ion pair with a counteranion) as the reactive intermediate.^{6–10} On the basis of evidence for the homolytic cleavage of tetraphenyltetrazene in concentrated sulfuric acid, Hammond, Seidel, and Pincock⁸ have proposed the aminium radical, the protonated amino radical arising from the bis-protonated tetrazene, as the reactive intermediate. Radical

mechanisms for TMT decomposition appear to be supported by the observation that reasonably "persistent" ESR signals of the tetrazene cation radical ($\text{TMT}^{\cdot+}$) and tetramethylhydrazine cation radical ($\text{TMH}^{\cdot+}$) are generated when the tetrazene is treated with an acid anhydride,⁵ an alkylating agent,¹¹ or a strong acid^{5,12} in various solvents. Complex radical mechanisms have been proposed for the generation of $\text{TMT}^{\cdot+}$, $\text{TMH}^{\cdot+}$, and others.^{5,11} However, in dilute aqueous hydrochloric acid solutions, decomposition of tetrazenes gives clean first-order kinetics indicating a simple reaction mechanism.⁶ In addition, it is also suggested that in acidic solutions the TMT-H^+ undergoes intramolecular rearrangement to form the observed products, dimethylamine, *N*-methylformylideneimine, and nitrogen.¹⁰

Thermolysis and photolysis of TMT have been shown to generate the dimethylamino radical¹³⁻¹⁵ which does not abstract hydrogen atom unless the temperature is higher^{13,16-19} than 134 °C and does not add to olefins^{20,21} or aromatic systems,¹⁷ but primarily undergoes bimolecular self-reaction.²² Michejda and Campbell have reported that the thermal decomposition of the TMT-ZnCl_2 complex in the presence of styrene (or aromatic ring-conjugated and terminal olefins) yields the bis(dimethylamino) adducts under nitrogen and 1-dimethylamino-2-hydroxy-2-phenylethane under oxygen in which $\text{ZnCl}_2\text{-}[(\text{CH}_3)_2\text{N}\cdot]_2$ and $\text{ZnCl}_2\text{-}(\text{CH}_3)_2\text{NO}_2$ complexes have been proposed as the reactive intermediate,²³ respectively. Mechanistically it is noteworthy that the latter complex stereospecifically epoxidizes the olefins; the nucleophilic attack of dimethylamine on these epoxides is the major pathway that lead to the amino alcohols. Our interests in the reactivities of aminium and amino radicals^{24,25} had led us to study TMT decompositions which resulted in the discovery of an aminium radical initiated oxidative addition of TMT to olefins. The results are reported in this paper.

Results

In aqueous solution, TMT showed UV absorption at 246 and 277 nm;⁷ protonated TMT, however, exhibited only an absorption peak at 236 nm ($\log \epsilon$ 3.95)⁹ which was used to monitor the disappearance of TMT. Acid decomposition of TMT in the dark was very slow in the vicinity of 0 °C but became reasonably fast around room temperature. The decomposition in hydrochloric acid-methanol solution in the presence of cyclohexene produced a quantitative yield of *N,N,N'*-trimethylhexahydro-*s*-triazine (**1**), the trimer of *N*-methyl-



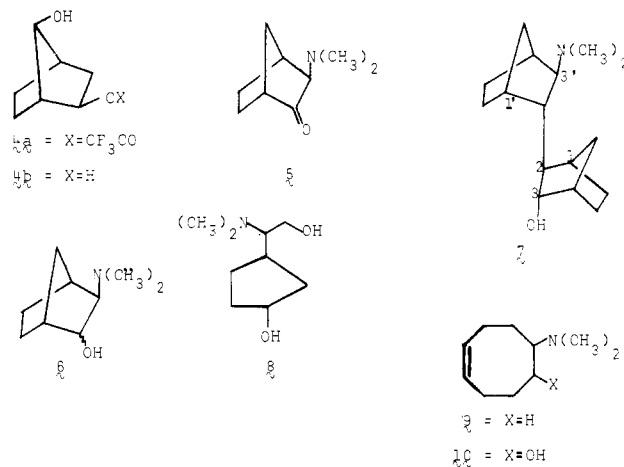
formylideneimine. Since the NMR monitor of the decomposition indicated the appearance of the signals of protonated dimethylamine and imine trimer **1** in 1:1 ratio, all the percentage yields in this investigation were calculated on the base of yielding 1 mol equiv of products from 1 mol of TMT. Similarly, in acetonitrile-trifluoroacetic acid solution the imine trimer **1** was obtained as the major product regardless of the presence or absence of olefins. In all of these thermal decompositions, a basic product incorporating an olefin moiety was not detected.

Photolysis of TMT was first studied in acetonitrile solution containing 0.5-1 M trifluoroacetic acid (TFA) under a nitrogen atmosphere in the presence of cyclohexene. As the

product patterns exhibited typical radical type addition and were very complex, TMT photolysis was carried out under oxygen, a radical trapper. All photolysis reactions were run at 0 °C and supplemented with the necessary control experiments in the dark showing that the extent of thermal decomposition was insignificant.

Photolysis of TMT in the presence of oxygen and an olefin resulted in formation of oxidizing species as demonstrated by iodimetry. In every case, a deep yellow color developed immediately on irradiation and faded slowly as the reaction approached the completion. The crude products were therefore reduced with sodium borohydride or lithium aluminum hydride before the work up. The crude products from the oxidative photoaddition of TMT to cyclohexene, before hydride reduction, contained 2-dimethylaminocyclohexanone (**2**, IR absorption 1710 cm^{-1}), 3-dimethylaminocyclohexene, and a mixture of *cis*- and *trans*-2-dimethylaminocyclohexanols (**3**) in a ratio of 15:2:80 as determined by comparisons with authentic samples²⁶ using VPC. The reduced material showed only the VPC peaks corresponding to the last two fractions in a ratio of 1:20.

TMT photolysis under oxygen in the presence of norbornene gave a small amount of the neutral fraction showing their absorptions at 1779, 1219, and 1170 cm^{-1} typical of a trifluoroacetate, the VPC analysis of which indicated the presence of many components. The major peak corresponded to that of 7-hydroxybicyclo[2.2.1]hept-2-yl trifluoroacetate (**4a**, <3%), an authentic sample of which was prepared by solvolysis of 2,3-*exo*-epoxynorbornane (**13**)^{27,28} in the presence of trifluoroacetic acid. The basic fraction was shown to contain 3-dimethylaminonorbornan-2-one (**5**, 40%) and *exo*- and *endo*-amino alcohols **6** (10 and 7%, respectively) in addition to the imine trimer **1** (55%). When the photolysis product was carefully worked up and reduced at 0 °C, it gave, in the neutral fraction, a small amount of 2,7-dihydroxybicyclo[2.2.1]heptane (**4b**),²⁸ obviously derived from the trifluoroacetate **4b**. The basic fraction contained seven minor components (<5% each) in addition to the *endo* alcohol **6** (57% by VPC analysis) which was isolated in pure state and was characterized. One of the minor VPC peaks (4% yield) matched with that of the *exo* alcohol²⁹ **6**.



By column chromatography dimeric amino alcohol **7**, as well as the *exo* and *endo* alcohols **6**, was isolated; the latter were unambiguously characterized. The unusually low-field proton at the C-3 position of **7** shows a similar coupling pattern to that of *endo* alcohol **6** indicating a 2-*exo*,3-*endo* configuration for this portion. The ¹³C NMR exhibits the low chemical shifts at 22.70 ppm for the C-6' and at 20.52 ppm for the C-5; the former was due to the shielding of the 2-*endo* C-C bond and the latter due to that of the *endo*-OH group. If radical attacks from the *exo* side of a norbornene ring, as generally happens

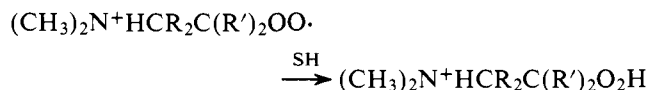
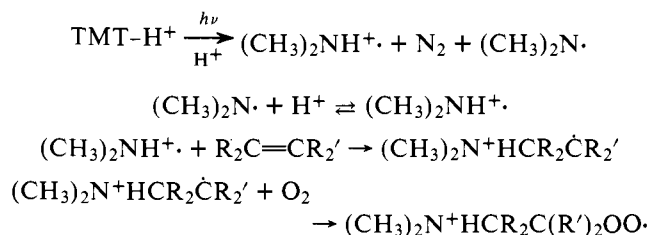
in other cases,^{29,31} and the subsequent C radical reacts from the endo side, 2-*exo*-(3'-*exo*-dimethylaminobicyclo[2.2.1]-hept-2'-*endo*-yl)bicyclo[2.2.1]heptan-3-*endo*-ol as shown in 7 would be expected. In the chromatography, another compound having the molecular formula of C₉H₁₉NO₂ was also isolated. The presence of two OH groups and an N(CH₃)₂ group was indicated by the NMR spectrum. On the basis of mass spectroscopic fragmentation pattern and the IR and NMR data, the structure of *cis*-3-(1'-dimethylamino-2'-hydroxyethyl-1')cyclopentanol (**8**) was tentatively assigned to this compound.

In contrast to the facile photoaddition described above, TMT photolysis under oxygen in the absence of an acid gave no addition products to norbornene, but the imine trimer **1** was obtained as the major product (45%). The neutral fraction after a TFA treatment gave eight major and a number of minor VPC peaks; one of the major peaks was identified as that of **4a** (<3%) and one of the minors as norbornene 2,3-epoxide.

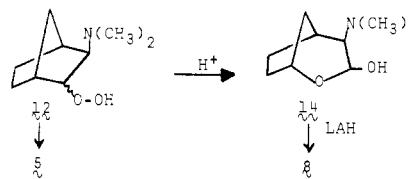
TMT photolysis in the presence of 1,5-cyclooctadiene and oxygen gave a small amount of compound **9** (<1%) and *trans*- and *cis*-amino alcohols **10** as the major product in the ratio of 1:1.7. The *trans*-amino alcohol **10** (27%) was identical in all respects with the sample obtained in the oxidative photoaddition of *N*-nitrosodimethylamine to 1,5-cyclooctadiene.³² *cis*-**10** (46%), which had not been obtained previously, showed a very similar mass spectral pattern with that of the *trans*-**10** and nicely resolved NMR signals for the methine and olefinic protons suggesting the presence of a preferential conformation. From the decoupling experiment, the two methine protons were shown to be weakly coupled (1 Hz). On the basis of the coupling patterns of these two methine protons (*J* = 4 Hz for -CHOH- and *J* = 10.7 and 4.2 Hz for -CHN), the (CH₃)₂N group might preferentially orient pseudoequatorial and the OH group pseudoaxial.³³

Discussion

The photolabile species in the above photoreaction is the monoprotonated TMT which obviously dissociates after excitation to form two aminium radicals and nitrogen. That the dimethylaminium radical is formed during the photolysis in acidic solution is indicated by the formation of copious amounts of the addition products to various olefins in contrast to the failure to form such products when TMT is decomposed by thermolysis in acidic conditions and by photolysis under neutral conditions in the presence of the olefins. This is another independent proof of the previous proposal derived from photolysis of *N*-nitroamines that, while aminium radicals add to a carbon-carbon double bond, neutral amino radicals do not add. Failure of amino radicals to add to cyclohexene has been mentioned and the activation energy of the radical attack on a double bond is calculated to be as high as 35–40 kcal/mol by ab initio SCF and CI methods.²⁰ On the other hand efficient attack of aminium radicals on a double bond has been demonstrated in photolysis of nitrosamines,²⁴ chloramines,³⁴ and nitroamines²⁵ in which the existence of a C-radical intermediate and its scavenging by a radical trapper, such as oxygen, have been shown.^{29,32} These processes should lead to the formation of hydroperoxides such as **11** and **12** via a peroxy radical as the primary product as outlined on the following reaction mechanism



although it is not clear what is the hydrogen atom donor (SH) in the last step. As the zero hour solution exhibits three singlets in the 1:2:1 ratio, TMT must be monoprotonated under the conditions. It is assumed that protonation of amino radical, (CH₃)₂N[·], occurs much faster than other reactions in view of generally accepted fast acid-base equilibria. The oxidizing species detected at the end of the photolysis are not determined but are assumed to be the hydroperoxides, the decomposition of which, to the corresponding ketones, such as **2** and **5**, are known.³⁵ In view of the facile decomposition of these hydroperoxides, the stereoselectivity of the oxidative photoadditions of TMT to these olefins could not be determined. However, in the addition to norbornene, the approach of the dimethylaminium radical appears to be exclusively from the *exo* side as has been observed in other cases.^{29,31} It is assumed that an acid catalyzed rearrangement³⁵ of hydroperoxide **12** may lead to



14 which is reduced to **8** as the final product. Stereochemical requirements for such rearrangements are generally stringent. The radical addition to norbornene gives both the *endo* and *exo* hydroperoxide, but which one undergoes the rearrangement cannot be determined. It is pertinent to point out that cleavage products such as 1,3-bisformylpentane observed in oxidative photoaddition of *N*-nitrosamines to norbornene²⁹ are not among the products obtained. In the photoaddition to 1,5-cyclooctadiene, the *cis* hydroperoxide fails to undergo a transannular ring closure in contrast to the facile oxa ring formations observed in the oxidative photoaddition of nitrosamines to the diene.³²

During the oxidative photoaddition to norbornene, 2,3-*exo*-epoxynorbornane **13** is generated in a small amount as shown by the isolation of the diol **4b** and its trifluoroacetate **4a**, both of which are solvolysis products of **13** under the reaction conditions. Treatment of **4a** with aqueous dimethylamine solution gives, among the complex products, a small amount of *exo* alcohol **6**; the amount is too small to be taken as a significant pathway to the formation of *exo*-**6**. It is concluded that epoxide **13** is formed only in small amounts under the present conditions and can not be the precursor to the amino alcohols. The difference between the present oxidative TMT photoaddition and the thermal decomposition of TMT-ZnCl₂-O₂ system²³ appears to be the reactive intermediates involved in the two systems. The former involves aminium radical initiated attacks on an olefinic bond and follows a stepwise radical addition mechanism. The latter has been proposed to involve a stereospecific epoxidation of an olefin by ZnCl₂-(CH₃)₂NO₂[·] complex followed by epoxide ring opening; this process appears to work efficiently with conjugated olefins.

Both photolyses of TMT under neutral conditions and TMT-H⁺ under acidic conditions are not quenched by oxygen, which finds similarity in photolysis of *N*-nitroso-²⁹ and *N*-nitroamines.²⁵ This suggests that the dissociations of photoexcited TMT or TMT-H⁺ are very fast and probably faster than bimolecular collisions with oxygen molecules in the solution. All of these photolyses are excellent methods to generate aminium radicals and good synthetic methods for β -amino alcohols. However, the mechanism of, in particular the reactive

intermediate involved in, the thermal decomposition of TMT-H⁺ in dilute acidic conditions remains to be clarified.

Experimental Section

General Conditions and Materials. Unless specified otherwise the following conditions were used. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer using liquid films or Nujol mulls. Ultraviolet spectra were taken with either a Cary 14 or a Unicam SP8000 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-56/60 or a XL-100 equipped with a Nicolet 1080 computer in CCl₄ or CDCl₃ with Me₄Si as the internal standard. The chemical shifts of protons were reported in τ values and those of ¹³C in parts per million from Me₄Si and coupling constants in hertz (Hz). The decoupling experiments were performed with the XL-100 spectrometer. Mass spectra were recorded with Hitachi Perkin-Elmer RMU-6E mass spectrometer. High resolution mass spectra were performed at the University of British Columbia, Mass Spectrometric Services. Elemental analyses were carried out by Mr. M. K. Yang using a Perkin-Elmer 240 microanalyzer. Gas chromatographic analyses were performed on an F & M Model 810-19 dual flame analytical machine using a Varian Aerograph Model 20 recorder equipped with a Model 224 Disc chart integrator. Analyses by gas chromatography-mass spectrometry were performed by Mr. G. Owen to whom we are much indebted.

Column chromatography used neutral or basic alumina (Brockman activity I, 80–200 mesh) or silicic acid (Mallinkrodt, 100 mesh). Acetonitrile (Fisher Scientific) was passed through alumina immediately before use. The commercially available olefins were used as supplied. Nitrogen supplied in compressed cylinder (Union Carbide of Canada) was purified by passing through a train of a Fieser's solution, concentrated sulfuric acid, and KOH pellets.

TMT was prepared by HgO oxidation of 1,1-dimethylhydrazine according to the procedure of Watson.¹⁴ The oil was distilled at 42–46 °C (30 mmHg): IR 3000, 2962 (s), 2858 (s), 1469 (s), 1276, 1002 (s), 897, and 822 cm⁻¹; UV in ethanol $\lambda_{\text{max}}^{\text{EtOH}}$ 277 nm (ϵ 8.0 × 10³) (reported⁶ λ_{max} 277 (ϵ 8.3 × 10³); NMR τ 7.19 (s).

Photolysis. General. A solution of TMT, the substrate, and other components placed in a photolysis apparatus was purged with oxygen for 10 min and was irradiated at 0 °C with a 200-W Hanovia mercury lamp through a Vycor filter. At proper intervals, an aliquot was pipetted out and was exactly diluted to record the UV absorption of the solution; the maximum at 239 nm decreased as photolysis proceeded. The zero hour sample was kept at 0–5 °C in a dark place to serve as the control. The decrease of the 239-nm peak in this sample was insignificant. During photolysis, when the oxygen stream was interrupted, evolution of bubbles due to generated nitrogen was observed.

The photolysate turned to a bright yellow color immediately on irradiation and the color faded at the end of the photolysis. The photolysate was generally evaporated under reduced pressure at the running water temperature. The residue was made basic with 40% KOH solution and reduced with NaBH₄ in aqueous ethanol solution. Alternatively the basic aqueous solution was extracted with ether; the solution was dried and reduced with LiAlH₄.

Photolysis of TMT under Oxygen. 1. In the Presence of Cyclohexene. A solution of TMT (2 g), cyclohexene (2 g), trifluoroacetic acid (10 g), and acetonitrile (100 mL) was photolyzed under oxygen at 0 °C for 90 min. The resulting photolysate was shown to contain 0.0048 equiv of oxidizing agents by iodimetry. The basic fraction was extracted with ether and one-half of the dried ether solution was treated with lithium aluminum hydride. The other half was evaporated to afford an oil (677 mg) which was analyzed by VPC (20% Dowfax GNA, 10% TEP on Chromosorb P 60/80, 8 ft. × 1/4 in. copper tube) to give the peaks corresponding to ketone **2** (3.7 min), 3-dimethylaminocyclohexene (5.4 min), and a mixture of *cis*-**3** and *trans*-**3** (9.4 min) in a ratio of 15:2:80. 3-Dimethylaminocyclohexene was synthesized from 3-bromocyclohexene and dimethylamine; other compounds were available from the previous investigation.²⁶

The oil recovered from the reduction (700 mg) was analyzed by VPC with the same Dowfax column in which, by peak matching method with authentic samples,²⁶ 3-dimethylaminocyclohexene (5.3 min, 3.5%) and a mixture of *cis*- and *trans*-2-dimethylaminocyclohexanols (**3**, 9.5 min, 55%) were identified.

2. In the Presence of Norbornene. A solution of TMT (3 g), nor-

bornene (7.5 g), trifluoroacetic acid (23 g), and acetonitrile (200 mL) was photolyzed under oxygen at 0 °C for 2 h. The photolysate was evaporated and made basic with 40% KOH solution and was extracted with ether at 0 °C. The solution was evaporated to give a residue. The residue was immediately taken up in ethanol (50 mL), added with sodium borohydride (2 g) in water (50 mL), and stirred for 24 h.

The reduced products were separated to the acid (71 mg) and the basic (2.91 g) fractions. The acid fraction was treated with *p*-nitrobenzoyl chloride in pyridine to give the bis-*p*-nitrobenzoate of 2,7-dihydroxynorbornane (**4b**) which had identical spectra and mp 164–165 °C with those of the synthetic sample.^{27,28} No bis-*p*-nitrobenzoate of bis(1,3-hydroxymethyl)cyclopentane²⁹ was found in the products. The basic fraction (2.91 g) was analyzed by VPC with a 10% SE-30 column to give the following peaks: 5.2 min (3%), 5.6 (57), 6.5 (4), 7.8 (6), 11.1 (6), and 13.2 (5). By the peak matching method with authentic samples, the major 5.6-min peak was identified as endo alcohol **6** and the minor 6.5-min peak as exo alcohol **6**.

The basic fraction (2.2 g) was chromatographed on a neutral alumina column to give, on elution with 1% MeOH in ether, a yellow liquid (114 mg) which was sublimed to give a dimeric alcohol **7**: mp 73–75 °C; IR 3400, 2780, 1650 (w), 1380, 1042, 1016, 993 (s), 972 (s), and 919 cm⁻¹; ¹H NMR τ 5.54 (ddd, *J* = 4.5, 1.5, 0.5 Hz, 1 H), 7.35 (m, *W*_{1/2} = 7 Hz, 1 H), 7.50 (m, 1 H), 7.56 (s, D₂O exchangeable, 1 H), 7.76 (s, 6 H), 7.65–7.95 (m, 3 H), and 8.00–9.25 (m, 14 H); ¹³C NMR 82.72 (d), 77.05 (d), 5296 (d), 47.59 (d), 44.00 (q, N-CH₃), 39.93 (d), 37.35 (d), 34.41 (2t), 33.41 (2d), 29.20 (t), 27.13 (t), 22.70 (t), and 20.52 (t); mass spectrum *m/e* (rel intensity) 249 (M⁺, 1), 248 (18), 247 (71), 218 (18), 206 (62), 202 (13), 192 (13), 180 (10), 152 (16), 150 (15), 136 (16), 124 (66), 98 (70), and 84 (100). Anal. Calcd for C₁₆H₂₇NO: C, 77.06; H, 10.91; N, 5.62. Found: 76.72; H, 10.36; N, 5.78.

The solid material (712 mg) eluted with 3% methanol in ether was sublimed to give translucent prisms of endo alcohol **6**: mp 67–68 °C; IR 3360 (br), 2956 (s), 2878, 2832, 1660 (w), 1464 (s), 1156 (s), 1078, 1051 (s), 1020, 869 (s), and 739 cm⁻¹; ¹H NMR τ 5.85 (D₂O exchangeable, 1 H), 6.13 (ddd, *J* = 4.0, 2.9, 0.8 Hz, 1 H), 7.74 (s, 6 H), 7.66–7.82 (m, 5 H), 8.10–8.92 (m, 7 H); ¹³C NMR 78.6 (d), 78.2 (d), 43.6 (q, NCH₃), 42.5 (d), 39.0 (d), 34.3 (t), 29.4 (t), 19.4 (t); mass spectrum *m/e* (rel intensity) 155 (M⁺, 65), 140 (14), 138 (14), 126 (12), 124 (12), 112 (14), 110 (17), 98 (100), and 84 (72). Irradiation at τ 7.75 collapsed the ddd signal at τ 6.13 to a doublet (*J* = 2.9 and 0.8 Hz) and irradiation at τ 8.45 simplified the same signal to a doublet (*J* = 4.0 Hz).³³ Anal. Calcd for C₉H₁₇NO: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.90, H, 11.10; N, 9.00.

Further elution with increasing methanol percentages gave mixtures of the endo alcohols **6** and other minor components. Rechromatography of this mixture and sublimation gave an oil which was 95% pure **8**: IR 3340, 2950, 2868, 2834, 2786, 1640 (w), 1458 (s), 1340, 1262, 1035 (s), and 858 cm⁻¹; NMR τ 6.00 (m, 1 H), 6.20–6.50 (m, 2 H), 6.30 (br s, D₂O exchangeable, 2 H), 7.70 (s, 6 H); high resolution mass spectrum *m/e* (rel intensity) 173.1413 (M⁺, 6, calcd for C₉H₁₉NO₂ 173.1415), 159 (3), 156 (2), 128 (3), 124 (3), 110 (4), 100 (8), 98 (10), 88 (26), 84 (16), and 58 (100).

In a separate experiment, TMT (8 g), norbornene (11 g), trifluoroacetic acid (25 g), and acetonitrile (200 mL) were irradiated under oxygen for 5 h at 0 °C. The photolysate gave 0.0045 mol equiv of oxidizing agents at the end of photolysis. The photolysate was separated into the acid (500 mg) and the base (4.6 g) fractions by the usual extraction method. The aqueous phase was continuously extracted to afford the second basic fraction (1.6 g). These fractions were analyzed by VPC on a 10% SE-30 column. The neutral fraction gave the major peak corresponding to the trifluoroacetate **4a** (<3%, vide infra) (9.0 min) in addition to 14 minor peaks, none of which correspond to epoxide **13**. The first basic fraction gave VPC peaks of 2-*exo*-dimethylaminonorbornane³³ (3.9 min), 3-dimethylaminonorbornane (**5**, 6.9 min), *exo*-amino alcohol **6** (7.5 min), and *endo*-amino alcohol **6** (8.1 min) in which the first peak was very small and the ratio of the next three was 6:1.5:1. The second basic fraction exhibited the intense NMR signals (τ 6.77 and 7.80) for the imine trimer **1** and weak signals for the amino ketone **5** in a ratio of 10:1. Ketone **5** was isolated by preparative VPC on the Dowfax column as a colorless oil: IR 2820, 2778 (s), 1746 (s), and 1440 (s) cm⁻¹ (lit.²⁹ 2815, 2770, 1742, and 1045 cm⁻¹).

3. In the Presence of 1,5-Cyclooctadiene. A solution of TMT (3 g), 1,5-cyclooctadiene (4 g), trifluoroacetic acid (23 g), and acetonitrile (200 mL) was photolyzed under oxygen at 0 °C for 2 h. The photo-

lysate was evaporated and the residue was diluted with ethanol (50 mL). To this, 40% KOH solution (5 mL) was added at -30°C followed by a solution of sodium borohydride (4 g) in aqueous ethanol (1:1, 50 mL). The basic products were worked up in the usual manner to give a light yellow oil (3.08 g). This extract, by VPC on the 20% Dowfax 9N9/10% TEP column showed two peaks with the retention times of 37 and 48 min in a ratio of 1:1.7 and an additional minor peak ($\sim 1\%$ of the first) at 12 min. By a peak matching technique, the 37-min peak was identified as the trans alcohol **10** and the 12-min peak as **9**. **9** was separated by preparative VPC as an oil: IR 3020, 2828, 2779 (s), 1688 (w), 1458 (s), 1264, 1177, 1154, 1043, 1032, 994, and 727 (s) cm^{-1} ; mass spectrum m/e (rel intensity) 153 (M^+ , 25), 138 (5), 136 (5), 125 (18), 124 (18), 110 (25), 84 (66), and 71 (100). The spectra were identical with those of an authentic sample prepared by another pathway.³³

The major products were separated by preparative VPC on the same column. The trans alcohol **10** was obtained as a colorless oil (27%) and had IR, NMR, and mass spectrum identical with those of the authentic compound.³² The second compound was the cis alcohol **10** isolated as prisms (46%): mp $72\text{--}76^{\circ}\text{C}$; IR 3130, 3020, 2794, 1635 (w), 1456 (s), 1370, 1173 (s), 1120 (s), 1023 (s), 982, 874, and 721 (s) cm^{-1} ; NMR τ 4.0–4.5 (m, 2 H), 5.93 (t, each peak further split, $J = 4$ Hz, 1 H), 6.90 (D_2O exchangeable, 1 H), 7.25 (ddd, $J = 10.7$, 4.2, 1 Hz, 1 H), 7.68 (s, 6 H), 7.40–8.55 (m, 8 H); mass spectrum m/e (rel intensity) 169 (M^+ , 19), 154 (3), 140 (17), 124 (5), 110 (19), 87 (13), 84 (17), and 71 (100).

Irradiation at either τ 7.95 or 8.35 changed the τ 5.93 signal to broad singlet but irradiation at τ 7.25 sharpened this signal slightly. Irradiation at either τ 5.93 or 8.35 changed the τ 7.25 signal to a doublet ($J = 10.7$ and 4.3 Hz) or a poorly resolved doublet ($J = 4.5$ Hz), respectively.

Photolysis of TMT under Neutral Conditions. A solution of TMT (8 g), norbornene (11 g), and acetonitrile (200 mL) was photolyzed under the same condition as described above. The photolysate was colorless during irradiation. To the photolysate, TFA (25 g) was added and worked up as above. The neutral fraction (354 mg) showed numerous minor VPC peaks, one of which matched that of **4a**. A trace amount of epoxynorbornene **13** was also detected by TLC. Both the first and the second basic fractions (2.6 and 1.4 g) gave an intense VPC peak corresponding to imine trimer **1** and many other small peaks all of which were $\sim 1\%$ or less.

Synthesis of 2,3-exo-Epoxynorbornene (13) and Its Solvolysis. Norbornene was treated with *m*-chloroperbenzoic acid to give the epoxide²⁷ **13**. The epoxide was briefly refluxed in formic acid to give an oil which was hydrolyzed with a 10% KOH solution.²⁸ The recovered oil was treated with *p*-nitrobenzoyl chloride to afford the bis benzoate of **4b**: mp $159\text{--}163^{\circ}\text{C}$; IR 3120, 3060, 1720, 1615, 1522, 1458, 1353, 1320, 1002, 1286, and 721 cm^{-1} ; mass spectrum m/e (rel intensity) 426 (M^+ , 1), 410 (1), 396 (1), 276 (4), 259 (16), 213 (5), 150 (100), 134 (20), 120 (17), 110 (37), 104 (52), 92 (64), 76 (30), and 66 (35).

The epoxide (100 mg) was stirred in a CH_2Cl_2 (2 mL) solution containing trifluoroacetic acid (100 mg) for 5 min at 20°C . The solution was washed with a dilute K_2CO_3 solution at 0°C , dried by passing through an alumina (2 g) column, and evaporated to give a colorless oil (150 mg): IR 3400, 2956, 1779, 1352, 1165, 1080, and 720 cm^{-1} . The oil showed one major VPC peak at 8.5 min for **4b** on

an SE-30 column and some minor peaks at higher retention times and was used immediately for peak matching with **4b** by VPC analysis. The mass spectra of the major peak for **4b** from gas chromatography–mass spectrometry gave m/e (rel intensity) at 207 (1), 206 (2), 169 (6), 153 (6), 125 (5), 115 (10), 110 (94), 95 (76), 92 (88), 81 (100), and 79 (92).

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