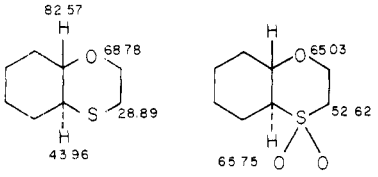
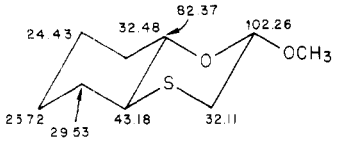
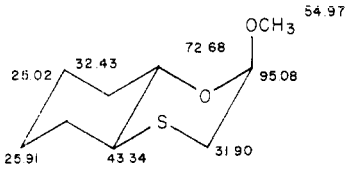


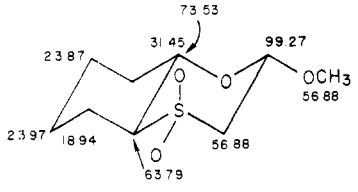
3 4



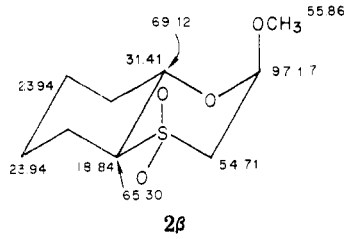
1α



1β



2α



2β

Microanalyses were performed by Galbraith Laboratories, Inc., and Integral Microanalytical Laboratories, Inc.

^{1}H NMR spectra were recorded on a JEOL Model C-60HL and a Varian Model XL-100-12 NMR spectrometer. The proton chemical shifts of samples as 5–8% (w/w) deuteriochloroform ($CDCl_3$) solutions are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si), and these values are considered accurate to ±0.01 ppm unless otherwise indicated. The coupling constants are given in hertz and are accurate to ±0.1 Hz unless otherwise specified. ^{1}H NMR coupling patterns are designated as s = singlet, d = doublet, m = multiplet, t = triplet, and dd = doublet of doublets. ^{13}C NMR FT spectra were recorded on a Varian Model XL-100-12 NMR spectrometer controlled by a 620/f computer. All FT spectra were obtained at ambient temperature (ca. 30 °C) and Fourier transforms were based upon 8K data points with off-resonance and noise decoupling.

Gas–liquid chromatography (GLC) analyses were performed on Hewlett-Packard Model 5754 research gas chromatographs. The diastereoisomers of 2-methoxy-*trans*-hexahydro-1,4-benzoxathiane, 1α and 1β, were prepared by methods previously described.[1]

α- and β-2-Methoxy-*trans*-hexahydro-1,4-benzoxathiane 4,4-Dioxides (2α, 2β). A solution of mCPBA (12.08 g, 70.0 mmol) in 65 mL of anhydrous chloroform was added dropwise over a period of 1 h to a solution of the isomeric 2-methoxybenzoxathianes 1α and 1β (6.8 g, 36 mmol) in anhydrous chloroform (20 mL) at 0–5 °C (ice bath). The solution was stirred for 17–18 h at ambient temperature and additional chloroform (90 mL) was added to dissolve *m*-chlorobenzoic acid. The solution was washed with a saturated solution of sodium bicarbonate (4 × 75 mL) and 100 mL of water and finally dried over magnesium sulfate. Removal of the solvent (rotary evaporator) gave 7.12 g (90%) of a colorless solid composed of 2α and 2β as determined by GLC.

Separation of the Diastereoisomeric Sulfones. Chromatographic separation of 2α and 2β was accomplished on a silica gel column (2.5 × 15 cm, 70–325 mesh, EM reagents, eluting with a 90:10 (v/v) chloroform–petroleum ether (bp 30–60 °C range) solution and collecting 20- to 40-mL fractions. The sulfones 2α and 2β were obtained analytically pure by this method. Alternatively, chromatographic separation could also be effected by using an alumina column and methylene chloride–ethyl acetate (75:25 (v/v)) solution as eluent. Under these conditions, 2β elutes first.

β-2-Methoxy-*trans*-hexahydro-1,4-benzoxathiane 4,4-Dioxide (2β): mp 155–157 °C; ^{1}H NMR ($CDCl_3$) δ 1.03–2.48 (m, 8 H, CH_2), 2.85 (m, 1 H, SO_2CH), 3.28 (d, J = 2.64 Hz, 2 H, SO_2CH_2), 3.40 (s, 3 H, OCH_3), 4.07 (m, 1 H, OCH), 5.01 (t, J = 2.64 Hz, 1 H, $OCHOCH_3$). Anal. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32. Found: C, 49.13; H, 7.35.

α-2-Methoxy-*trans*-hexahydro-1,4-benzoxathiane 4,4-Dioxide (2α): mp 130.0–130.5 °C; ^{1}H NMR ($CDCL_3$) δ 1.03–2.43 (m, 8 H, CH_2), 2.73 (m, 1 H, SO_2CH), 2.99 (dd, 1 H, J_{aa} = 8.20, J_{gem} = 13.28 Hz, SO_2CH_a), 3.48 (s, 3 H, OCH_3), 3.49 (m, 1 H, OCH), 3.28 (dd, 1 H, J_{ae} = 2.48, J_{gem} = 13.28 Hz, SO_2CH_e), 4.70 (dd, 1 H, J_{ee} = 2.48, J_{aa} = 8.20 Hz, $OCHOCH_3$). Anal. Found: C, 49.13; H, 7.40.

Equilibrations. Equilibrium concentrations of 2α and 2β were obtained by equilibrating pure samples of 2α and 2β from both sides at 300 K with boron trifluoride etherate as catalyst. Typically, 2α and 2β were separately dissolved in 2 mL of solvent along with 5 μL of BF_3·OEt_2 and sealed in ampules. After 1–2 h the reaction was complete and the reaction mixture was treated with 5% sodium hydroxide (10 mL), washed with water (15 mL), dried (anhydrous magnesium sulfate), and concentrated to dryness (rotary evaporator) to give crystalline material. GLC analyses were performed on samples of the solid material dissolved in chloroform on a 6 ft × 0.125 in. (i.d.) stainless steel column with 10% XE-60 nitrile on Chromosorb W-HP-AW-DMCS (100–120 mesh) at 200–210 °C. Response ratios were measured from the areas obtained from weighed samples.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the University Research Council (UNC) and the North Carolina Committee of Science and Technology for support of this research. We thank the National Science Foundation for a fellowship RPR and also Dr. David Harris for recording both noise-decoupled and off-resonance-decoupled ^{13}C NMR spectra.

Registry No. 1α, 60895-17-2; 1β, 60861-03-2; 2α, 70332-86-4; 2β, 70355-05-4.

Structure Elucidation of Polynitrated 2-Aminoperimidines

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One of the classic and most important approaches to determine trace quantities of sulfuric acid is to precipitate the quaternary salt of an organic amine, followed by its conversion to a product with a measurable, visible chromophore. Prior to 1970 this general procedure was limited

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(2) On leave with G.R.N. from Sambalpur University, Sambalpur (Orissa), India, 1975–1976.

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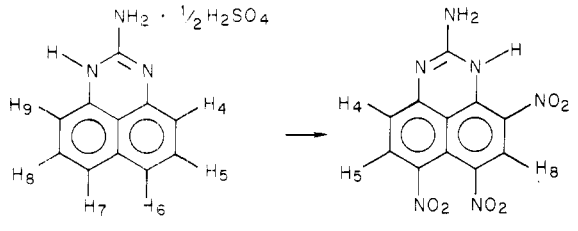
by the solubility of the resultant organic sulfate. Stephen[3] introduced 2-aminoperimidinylammonium chloride, which forms a sulfate salt (1) [$(PDA)_2SO_4$] possessing insolubility second only to barium sulfate! Initial synthetic procedures for the preparation of 1 were tedious at best,[4] until McClure[5] developed a convenient route to 2-aminoperimidinylammonium bromide (2, PDA-Br), which was later refined by Dasgupta et al.[6]

Generally, PDA-Br (2) is spontaneously converted to the insoluble 1 upon treatment with liquid sulfuric acid aerosol. The particulate sulfates are collected in the solid form and then the $(PDA)_2SO_4$ is nitrated with concentrated nitric acid to give a dominant product which possesses a usable chromophore for analytical monitoring.[7,8]

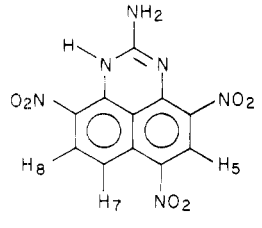
Although one major product results from the analytical procedure, attempts to mimic the reaction at macroscale levels with either 1 or 2 gave a number of nitro-substituted 2-aminoperimidines which could not be easily characterized. Similar structural assignment problems resulted when either perimidine[4] or 2-methylperimidine[10] was dinitrated. We herein report the unequivocal structural assignments to the products of the nitration of 1 and 2 as well as the structure of the major chromophoric product derived from the microgram and nanogram analytical procedure.

Results and Discussion

In an attempt to duplicate the analytical procedure at the macroscale level, 1 was nitrated with concentrated



1 3



4

nitric acid under mild reaction conditions (5 min; 30 °C); however, due to the extreme insolubility of 1 in water, an ultrasonic agitator was employed to ensure adequate mixing. Two major products were isolated and shown to be trinitro isomers 3 and 4, based on the following data. The dominant product, 4, crystallized as bright yellow needles and was demonstrated to possess the identical R_f and superimposable three-dimensional UV–pH plot (Figure 1) with that of the major component from the analytical procedure.

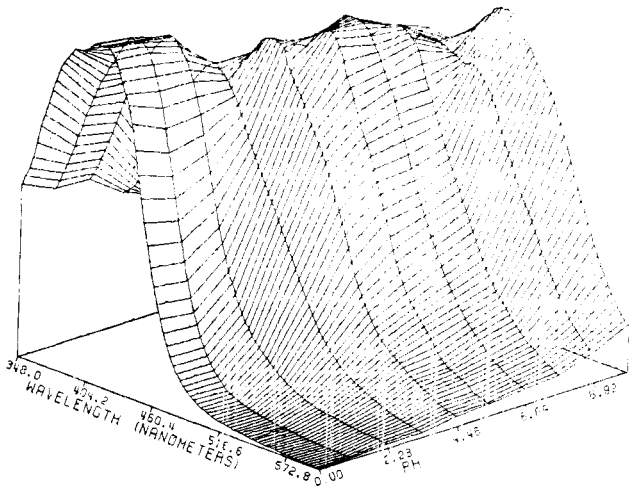


Figure 1. UV–pH three-dimensional plot for 4.

Table I. Polarographic Data for the Polynitrated 2-Aminoperimidines

		half-wave reduction potentials[a]			
		ortho		para	
compd	pH	[4 (9)]-NO_2		[6 (7)]-NO_2	
5	9.0	420	520	890	
	13.0	770	930	1330	1720
3	9.0	510	*b*	980	
	13.0	810	*b*	1300	1580
4	9.0	500	660	950	*b*
	13.0	820	1000	1390	*b*
6	9.0	480	*c*	970	
	13.0	770	*c*	1250	1560
7	9.0	490	610	960	*c*
	13.0	810	950	1340	*c*

[a] Negative millivolts vs. SCE. [b] Site of hydrogen. [c] Site of bromine.

Structurally, IR data for both 3 and 4 indicated the presence and proximity of the NH and a NO_2 group by the broad peak (3300–2400 cm^{-1}) of moderate intensity and ca. 150 cm^{-1} lower absorption than in the IR of 1;[13] this intramolecular hydrogen bonding under dilute conditions is suggestive of a strong peri NO_2–NH interaction. The NMR spectral data for 3 and 4 were nearly identical: singlet at δ 9.22 for the hydrogen flanked by two nitro groups and two doublets at δ 8.85 and 9.10 consistent with the anticipated electrophilic nitration of perimidine at the 4, 6, 7, and 9 positions. The location of the nitro groups can be derived from simple polarographic data. Aromatic nitro compounds belong to a functional class of ring substituents that have been subjected to extensive electrochemical investigation,[14] in that the nitro groups can be reduced to a hydroxylamine group via a direct four-electron reduction.[15] Subsequent reduction of the hydroxylamino group to an amino group does not occur normally *except* in high acid concentration.

From previous studies conducted by Holleck and Exner[16] on 2- and 4-nitroaniline, as well as 2,4-dinitroanilines (8), the reduction sequence of nitro groups in these anilines inidicates a well-separated (ca. 250 mV) distinction

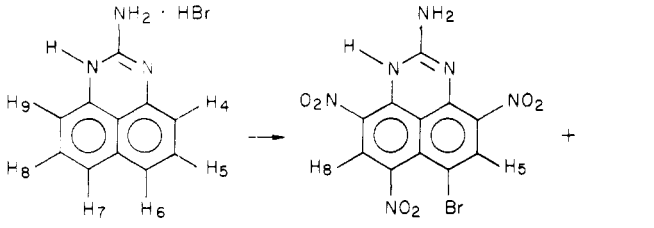
(3) Stephen, W. I. *Anal. Chim. Acta* **1970**, *50*, 413.
(4) Sachs, F. *Justus Liebigs Ann. Chem.* **1909**, *53*, 365.
(5) McClure, G. L. *Anal. Chim. Acta* **1973**, *64*, 289.
(6) Dasgupta, P. K.; Lundquist, G. L.; Reiszner, K. D.; West, P. W. *Anal. Chim. Acta* **1977**, *94*, 205.
(7) Dasgupta, P. K.; Lundquist, G. L.; West, P. W. *Atmos. Environ.*, in press.
(8) The limit of detection of aerosol sulfuric acid by this procedure[7] is 0.1 μg with spectrophotometry and an amazing **5 ng** with a ring over modification.[9]
(9) Dasgupta, P. K.; West, P. W. *Mikrochim. Acta* **1978**, 505.
(10) Whitehurst, I. S. *J. Chem. Soc.* **1951**, 226.
(11) du Pont de Nemours and Co., Inc., "Differential Thermal Analyzer-900", Wilmington, Del., 1965.
(12) For further information see: Southwick, L. M.; Willis, G. H.; Dasgupta, P. K.; Keszthelyi, C. P. *Anal. Chim. Acta* **1976**, *82*, 29.
(13) Pozharskii, A. F.; Koroleva, V. N. *Khim. Geterotsikl. Soedin.* **1975**, 550.
(14) Holleck, L.; Kostening, B. *Rev. Polarogr.* **1963**, *11*, 129.
(15) Kolthoff, I. M.; Lingane, J. J. "Polarography", 2nd ed.; Interscience Publishers: New York, 1952; Chapter 42.
(16) Holleck, L.; Exner, H. J. *Z. Electrochem.* **1952**, *56*, 677.

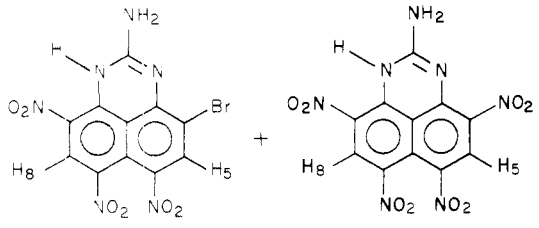
between the 2-nitro initially reduced and the 4-nitro group *at relatively low pH*. In fact, the 2-nitro group in 2,4-dinitroaniline (**8**) was more easily reduced than in 2-nitroaniline due to enhanced electron withdrawal caused by the second nitro group present, whereas the 4-nitro group in **8** was reduced with difficulty in comparison with 4-nitroaniline since, by the time the 4-nitro function in **8** is ready for reduction, the 2-nitro group was reduced to -NHOH and the electron donation of this function retards reduction at the 4 position.

The half-wave potentials of **5** at pH 7.2 and 9.0 (listed in Table I) indicate that the 4- and/or 9-nitro groups are reduced initially prior to those at the 6 and 7 positions. The differentiation in the 4- and 9-nitro groups is apparently caused by the intramolecular hydrogen bonding with only one group, whereas the juxtaposed peri-nitro groups (6- and 7-nitro) are similar and indistinguishable to these medium pH values. Differentiation of the 6- and 7-nitro groups can be realized at higher pH, in which all four nitro groups can be reduced at well-separated reduction potentials. Therefore by analogy with the nitrated anilines, in these polynitrated 2-aminoperimidines the "ortho" (4 and 9) nitro groups are reduced conspicuously easier than those in the "para" (6 and 7) positions.

Table I shows the half-wave reduction potentials for **3** and **4** at different pHs. These data, when compared to those of **5**, strongly support the isomeric assignments for both **3** (with the 4-NO_2 group missing) and **4** (with the 7-NO_2 group missing), especially in view of the large divisions ($\sim\Delta > 150$ mV) in these potentials.

Nitration of **2** under moderate conditions (80 °C, 2 h)





afforded two isomeric trinitro compounds *containing bromine* (**6** and **7**) as well as a single tetranitrated perimidine **5**, which was bromine free. From limited nitration[13] and halogenation[17] studies of 2-substituted perimidines, the 4,6,7,9-tetrasubstitution pattern was consistent under similar electrophilic conditions. The NMR data for **6** and **7** show the spike at δ 9.2 for H-8 which is flanked by two nitro groups and singlets at δ 8.98 and 9.02, respectively, for H-5 which is indicative of the expected upfield shift for substitution of a nitro group with a bromine atom. The structural assignments for **6** and **7** follow a similar deductive rationale, as used above.[18] The large differentiation in reduction potentials is supportive of bromine location: the bromine atom is located in the "para" (6 or 7) position in **7** and in an "ortho" (4 or 9) position in **6**.

In conclusion, electrophilic substitution of 2-aminoperimidine occurred exclusively at the 4, 6, 7, or 9 positions, in line with recent Russian work on other 2-substituted perimidines.[13,17] The unexpected electrophilic bromination can be rationalized in retrospect by application of the well-known reaction (eq 1) of bromide ion in the presence

$$H^+ + 3Br^- + HNO_3 \rightarrow NOBr + 2H_2O + Br_2 \quad (1)$$

of mild oxidizing agents, such as nitric acid. Either the nitrosyl bromide or "free" bromine would be sufficient sources of bromonium ion to halogenate this activated aniline moiety.

Experimental Section

General Procedures. All thermal data were obtained with a Du Pont 900 thermal analysis system in conjunction with a 950 thermogravimetric analyzer. Differential scanning calorimetry studies[11] were carried out in sealed capsules with a heating rate of 10 °C/min; thermocouple error was corrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 621 spectrophotometer. ^1H NMR spectra were obtained on a Varian HA-100 spectrometer in Me_2SO-d_6 with Me_4Si as the internal standard (δ 0). Mass spectral (MS) data were obtained on a Hewlett-Packard 5360A mass spectrometer. Polarographic studies with a dropping mercury electrode (DME) were conducted with a Sargent Model XV recording polarograph equipped with a Sargent Model A IR compensator. All polarographic data[12] were obtained with 1.5 μM solutions in 40% ethanol with NaCl as supporting electrolyte and Triton X-100 as maxima suppressor. The pH cited is the apparent pH as determined by an Orion 801 pH meter, calibrated with an aqueous buffer. Recorded R_f values were determined by a standardized thin-layer chromatograph (TLC) procedure: 0.25-mm Brinkmann silica gel HF-254 + 366 plates eluting with cyclohexane–ethyl acetate (1:1). Elemental analyses (C, H, N, Br) were performed by Galbraith Laboratories and were within acceptable tolerance.

In order to facilitate the collection and processing of UV–pH data, we interfaced, by special design, a Beckman DB-G UV–visible spectrophotometer with a Data General NOVA 1200 minicomputer system equipped with teletype and paper tape puncher. Subsequent processing of the data was accomplished by an IBM 360 coupled with a Varian electrostatic plotter affording the desired three-dimensional plots.

Perimidinylammonium Bromide (PDA-Br, **2**)[6] was synthesized and purified by recrystallization from water to afford a dihydrate, which can be dehydrated (80 °C in vacuo for 4 h) to give the anhydrous crystalline salt: mp 265 °C.

Nitration of $(PDA)_2SO_4$ (1). Macroscale Nitration of 1. A suspension of $(PDA)_2SO_4$ (500 mg, 1.1 mmol), prepared from **2** upon treatment with sodium sulfate, in water (25 mL) was agitated by an ultrasonic vibrator and concentrated nitric acid (25 mL) was added. After 5 min, the highly colored suspension was diluted with water, neutralized with aqueous sodium carbonate, and filtered. The precipitate was washed with water, dried in vacuo, and column chromatographed on silica gel-60 (200 mesh) eluting with cyclohexane–ethyl acetate (2:1) to afford two major fractions:

Fraction A afforded 2-amino-6,7,9-trinitroperimidine (**3**), as yellow crystals: 25 mg (5%); R_f 0.36; mp 287 °C (dec) [48% wt loss; $-\Delta H$ = 88 kcal/mol]; NMR δ 8.65 (bs, >NH, NH_2, 3 H), 8.85 (d, H-4, J = 6 Hz, 1 H), 9.10 (d, H-5, J = 6 Hz, 1 H), 9.22 (s, H-8, 1 H); IR (KBr) 3500 (br), 1610, 1490, 1360, 1300, 910 cm^{-1}; MS m/e 318 (M^+); UV–pH, see Figure 2 (supplementary material); the analytical determinations of C, H, and N for $C_{11}H_6N_6O_6$ are available in Table II (supplementary material).

Fraction B gave 2-amino-4,6,9-trinitroperimidine (**4**), as yellow needles: 100 mg (20%); R_f 0.34; mp 307 °C dec [45% wt loss; $-\Delta H$ = 88 kcal/mol]; NMR δ 8.65 (bs, >NH, NH_2, 3 H), 8.90 (d, H-7, J = 6 Hz, 1 H), 9.11 (d, H-8, J = 6 Hz, 1 H), 9.23 (s, H-5, 1 H); IR (KBr) 3500 (br), 1610, 1490, 1360, 1300, 910 cm^{-1}; MS m/e 318 (M^+); UV–pH, see Figure 1; mol wt (osmometry) 318.4 (average); analytical data for $C_{11}H_6N_6O_6$ (C, H, N) are available

(17) Kuzmenko, V. V.; Pozharskii, A. F. *Khim. Geterotsikl. Soedin.* **1978**, 1406.
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in Table II (supplementary material).

Microscale Nitration of 1. The general analytical procedure[7] for the specific determination of aerosol sulfuric acid in the presence of ammonium sulfate was followed. Insoluble $(PDA)_2SO_4$ (1), prepared from 2 upon treatment with aerosol sulfuric acid, was precipitated (coated) on a small piece of glass fiber filter, dried, and treated evenly with concentrated nitric acid (300 μL). After 1 min, the strong coloration due to the nitration product(s) appeared. The reaction mixture was carefully eluted into a volumetric flask with acetone (1 mL), diluted aqueous sodium hydroxide (2 mL, 4 N) was added, and distilled, deionized water was added. The solution was filtered, and the spectral and polargraphic data were collected. TLC of this reaction solution indicated a single major component with an R_f 0.35.

Nitration of Perimidinylammonium Bromide (2). A solution of 2 (1 g, 3.8 mmol) and nitric acid (100 mL, 10 M) was refluxed under reduced pressure and low heat (80 °C) for 2 h. The resultant brownish solution was diluted with water, and a bright yellow-orange solid formed. The mixture was neutralized with dilute aqueous sodium bicarbonate to pH 5. The solid was filtered, washed with water, dried in vacuo, and column chromatographed on silica gel-60 (200 mesh) by eluting with cyclohexane–ethyl acetate (1:2) to give three major colored components:

Fraction A afforded, after recrystallization from 95% ethanol, 2-amino-6-bromo-4,7,9-trinitroperimidine (7): 10 mg (2%); R_f 0.35; mp 283 °C dec [40% wt loss; $-\Delta H$ = 101 kcal/mol]; NMR δ 8.75 (bs, >NH, NH_2, 3 H), 8.98 (s, H-5, 1 H), 9.21 (s, H-8, 1 H); IR (KBr) 3500 (br), 1610, 1490, 1360, 1300, 980, 910 cm^{-1}; UV–pH, see Figure 3 (supplementary material); MS *m/e* 396, 398 (M^+), 317 (M^+ – Br); mol wt (osmometry) 397.1 (average); analytical data for $C_{11}H_5N_6O_6Br$ (C, H, N, Br) are available in Table II (supplementary material).

Fraction B afforded 2-amino-4-bromo-6,7,9-trinitroperimidine (6), as orange microcrystals: 100 mg (20%); R_f 0.32; mp 307 °C dec [42% wt loss; $-\Delta H$ = 103 kcal/mol]; NMR δ 8.75 (bs, >NH, NH_2, 3 H), 9.02 (s, H-5, 1 H), 9.20 (s, H-8 1 H); IR (KBr) 3500 (br), 1610, 1490, 1360, 1300, 980, 910 cm^{-1}; UV–pH, see Figure 4 (supplementary material); MS *m/e* 396, 398 (M^+), 317 (M^+ – Br); mol wt (osmometry) 397.2 (average); analytical data for $C_{11}H_5N_7O_8Br$ (C, H, N, Br) are available in Table II (supplementary material).

Fraction C yielded 2-amino-4,6,7,9-tetranitroperimidine (5), as yellow crystals: 300 mg (60%); R_f 0.26; mp 319 °C dec [53% wt loss; $-\Delta H$ = 171 kcal/mol]; NMR δ 8.93 (bs, >NH, NH_2, 3 H), 9.31 (s, H-5, 8, 2 H); IR (KBr) 3500 (br), 1610, 1490, 1360, 1300, 1260, 910, 820 cm^{-1}; UV–pH, see Figure 5 (supplementary material); MS *m/e* 363 (M^+); mol wt (osmometry) 363.1 (average). Analytical data for $C_{11}H_5N_7O_8$ (C, H, N) are available in Table II (supplementary material).

Acknowledgments. We thank the National Science Foundation for partial financial support to G.R.N.

Registry No. 1, 68046-88-8; 2, 40835-96-9; 3, 70160-60-0; 4, 68046-87-7; 5, 70160-61-1; 6, 70160-62-2; 7, 70160-63-3.

Supplementary Material Available: Three-dimensional UV–pH plots and analytical data for 3–7 (5 pages). Ordering information is given on any current masthead page.

Reactivity of Ethoxycarbonylnitrene toward Alcohols

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The reactions of ethoxycarbonylnitrene with hydrocarbons have been investigated systematically and extensively.[2] However, the reactions of the nitrene with compounds containing heteroatoms have been little investigated and there is no good agreement in the results. As for the reactions with ethers, we have reported that the nitrene generated from the photolysis of ethyl azidoformate (1) is inserted preferentially into the α C–H bonds of acyclic ethers[3] or of cyclic ethers[4,5] and that the insertion into the α C–H bonds proceeds predominantly via an O–N ylide intermediate formed with the singlet nitrene.

So far no clear-cut report on the photolysis of 1 in alcohols has been obtained as is shown in Table I (thermolysis of 1 in alcohols has not yet been reported).[6-8]

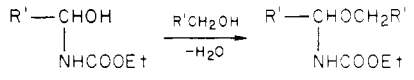
In this paper, the photolyses and the thermolyses of 1 in alcohols will be described in detail. Furthermore, reactivities of the nitrene insertion into the O–H bonds were compared with those into C–H bonds of hydrocarbons and ethers.

Table I

alcohol	product, % O–H insertion[a]	$H_2NCOOC_2H_5$	ref
CH_3OH	28	52	7
	44	20	8[b]
CH_3CH_2OH		90	6
	3	97	7
$(CH_3)_2CHOH$		98	6
	10	90	7

[a] Formation of *N*-(hydroxymethyl)urethane as a C–H insertion product in methanol is described without yield.[5] [b] In addition, a rearrangement product in methanol was obtained in 13% yield.

Scheme I



5

Results and Discussion

Photolysis and Thermolysis of 1 in Alcohols. A solution of 1 in alcohol (3) was irradiated by light (mainly 2537 Å) from a low-pressure mercury arc at 0 °C with stirring in an atmosphere of nitrogen. In the case of thermolysis, the solution was heated at 110 °C in a sealed tube. The insertion product (4) of ethoxycarbonylnitrene (2) into the O–H bonds was obtained, accompanied by the hydrogen-abstraction product, urethane. Aldehydes or ketone was detected in each reaction. In isobutyl alcohol, the insertion product into the tertiary C–H bond was isolated together with the O–H insertion product. In addition, *N*-(1-alkoxyalkyl)urethanes (5), derived probably from the α C–H insertion product,[6] were obtained in some of these reactions (Scheme I).

The yields of these products are listed in Table II.

Relative Reactivities. In order to compare the O–H bond with the C–H bonds of acyclic ethers and cyclohexane in the reactivities of the nitrene insertion, we carried out photolysis of 1 in a substrate mixture at 0 °C. The yields

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