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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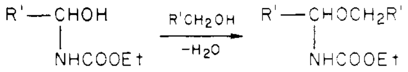
The reactions of ethoxycarbonylnitrene with hydrocarbons have been investigated systematically and extensively.[2] However, the reactions of the nitrene with compounds containing heteroatoms have been little investigated and there is no good agreement in the results. As for the reactions with ethers, 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.

Table I

	product, %		
alcohol	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.[6] [b] In addition, a rearrangement product in methanol was obtained in 13% yield.

Scheme I



5

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.

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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[1] College of General Education, Osaka University, Toyonaka, Osaka 560, Japan.

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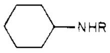
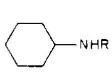
Table II. Photochemical and Thermal Decomposition of 1 in Alcohols

	product,^{a} %				
	insertion				
alcohol (3)	4		5		abstraction
A CH_3OH	A CH_3ONHR^b	55 (69)^d	A $CH_3O\underset{NHR}{C}H_2$ ND^c (ND)	ND^c (ND)	34 (25)
B CH_3CH_2OH	B CH_3CH_2ONHR	11 (4)	B $CH_3CH_2O\underset{NHR}{C}HCH_3$ 4 (trace)	4 (trace)	71 (72)
C $CH_3(CH_2)_2OH$	C $CH_3(CH_2)_2ONHR$	15 (8)	C $CH_3(CH_2)_2O\underset{NHR}{C}HCH_2CH_3$ 2 (2)	2 (2)	46 (52)
D $CH_3(CH_2)_3OH$	D $CH_3(CH_2)_3ONHR$	27 (16)	D $CH_3(CH_2)_3O\underset{NHR}{C}H(CH_2)_2CH_3$ 3 (2)	3 (2)	47 (52)
E $(CH_3)_2CHOH$	E $(CH_3)_2CHONHR$ ND	ND	E $(CH_3)_2CHO\underset{NHR}{C}(CH_3)_2$ ND	ND	95
F $(CH_3)_2CHCH_2OH$	F$_1$ $(CH_3)_2CHCH_2ONHR$	28 (22)	F $(CH_3)_2CHCH_2O\underset{NHR}{C}HCH(CH_3)_2$ 0.5 (2)	0.5 (2)	40 (34)
	F$_2$ $(CH_3)_2\underset{NHR}{C}CH_2OH$	3.8 (ND)			
G $(CH_3)_2CH(CH_2)_2OH$	G $(CH_3)_2CH(CH_2)_2ONHR$	18 (16)	G $(CH_3)_2CH(CH_2)_2O\underset{NHR}{C}HCH_2CH(CH_3)_2$	0.7 (2)	65 (54)

^{a} Calculated on the basis of the azide used. ^{b} R = $COOC_2H_5$. ^{c} ND = not detected. ^{d} Parenthesized values are those from themolyses of 1.

Table III. Photolysis of 1 in a Substrate Mixture

run	substrate mixture	insertion product,^{a} %		rel reactivity per C-H bond	
A	$CH_3(CH_2)_2OH$	$CH_3(CH_2)_2ONHR^b$	15	$\frac{\text{O-H}}{\alpha\ \text{C-H}} = 5.5$	$\frac{\alpha\ \text{C-H}}{\text{cycl C-H}} = 4.5$
	$CH_3(CH_2)_2CH_2OC_4H_9$	$CH_3(CH_2)_2\underset{NHR}{C}HOC_4H_9$	11		
B	$CH_3(CH_2)_2OH$	$CH_3(CH_2)_2ONHR$	18	$\frac{\text{O-H}}{\text{cycl C-H}} = 25$	
			8.7		$\frac{\text{O-H}}{\alpha\ \text{C-H}} = 5.5$
C	$CH_3(CH_2)_2CH_2OC_4H_9$	$CH_3(CH_2)_2\underset{NHR}{C}HOC_4H_9$	18	$\frac{\alpha\ \text{C-H}}{\text{cycl C-H}} = 4.5$	
			12		

^{a,b} See Table II footnotes.

of the products and the relative reactivities are summarized in Table III.

From the results of runs A and B in Table III, the relative reactivity of the α C–H bond of ether to the C–H bond of cyclohexane is estimated in value of 4.5. The estimated value was in complete agreement with that obtained from the photolysis in an acyclic ether–cyclohexane mixture (run C). Furthermore, a value 5.5 for the relative reactivity O–H/α C–H estimated from runs B and C was in good agreement with that obtained from run A.

The reactivity of the O–H bond per tertiary C–H bond gives a value of 7.4 from the result of the photolysis in isobutyl alcohol (Table III). The value 7.4 is close to that calculated from O–H/cycl C–H = 25 and tertiary C–H/cycl C–H = 3.0.[4] The relative reactivities of O–H bond, α C–H bond of ether, and C–H bonds of hydrocarbons are summarized in Figure 1.

Sensitized photolysis of 1 in alcohols gave no O–H insertion product.[3] This means that the O–H insertion products are formed only by the singlet nitrene. The large reactivity in the O–H insertion may be interpreted in terms of an O–N ylide intermediate formed from the singlet nitrene (Scheme II), as has been proposed in the reactions of the nitrene with acyclic[3] and cyclic[4] ethers.

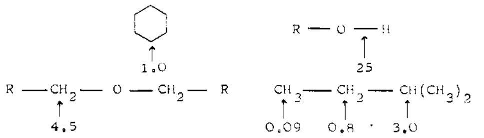
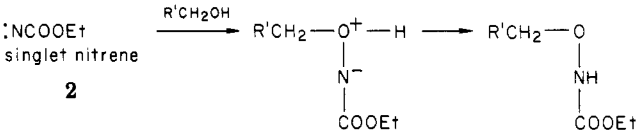


Figure 1. Relative reactivities of O–H and various C–H bonds at 0 °C.

Scheme II



2

O-N ylide

4

Experimental Section

Most of the equipment and techniques have been described in preceding papers.[4,9]

Photolysis of 1 in Alcohols. A solution of 1 (5.0 g, 0.043 mol) in alcohol (0.5 mol) was irradiated by using a low-pressure mercury lamp, with stirring and cooling at 0 °C, until the evolution of nitrogen was no longer observed. In the case of thermolysis, a solution of 1 (1.15 g, 0.01 mol) in alcohol (0.2 mol) was heated at 110 °C in a sealed tube for 8 h. The excess substrate and the volatile product, aldehyde or ketone, were trapped in a dry ice–methanol bath under reduced pressure. The trapped solution was added to a 2,4-dinitrophenylhydrazine solution, and the hydrazone was isolated. The residue was analyzed by VPC. The IR and the NMR data of **4B**, **4C**, **4D**, **4G**, **5B**, **5C**, **5D**, and **5G** were reported previously.[3] The insertion products (**4A**, **4F$_1$**, **4F$_2$**) and **5F** displayed strong absorptions in the 3260–3360- and 1700–1730-cm^{-1} regions due to the NH groups and the ester C=O groups, respectively.

N-Methoxyurethane (**4A**): NMR (CCl_4) δ 1.29 (t, 3, ester CH_3), 3.65 (s, 3, CH_3), 4.15 (q, 2, CH_2), 8.25 (brd s, 1, NH). Anal. Calcd for $C_4H_9O_3N$: C, 40.33; H, 7.62; N, 11.76. Found: C, 40.23; H, 7.56; N, 11.69.

N-Isobutoxyurethane (**4F$_1$**): NMR (CCl_4) δ 0.94 (d, 6, 2 CH_3), 1.60–2.15 (m, 1, CH), 2.29 (t, 3, ester CH_3), 3.57 (d, 2, CH_2), 4.14 (q, 2, ester CH_2), 7.85 (brd s, 1, NH). Anal. Calcd for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.07; H, 9.25; N, 8.76.

N-(1,1-Dimethyl-2-hydroxyethyl)urethane (**4F$_2$**): NMR (CCl_4) δ 1.25 (s, 6, 2 CH_3), 1.25 (t, 3, ester CH_3), 3.46 (s, 2, CH_2), 3.46 (s, 1, OH), 4.01 (q, 2, ester CH_2), 4.90 (brd s, 1, NH). Anal. Found: C, 52.11; H, 9.28; N, 8.80.

N-(2-Methyl-1-isobutoxypropyl)urethane (**5F**): NMR (CCl_4) δ 0.92 (d, 12, 4 CH_3), 1.29 (t, 3, ester CH_3), 1.74 (mult, 2, CH), 3.57 (d, 2, CH_2), 4.15 (q, 2, ester CH_2), 4.55 (mult, 1, NCH), 5.32 (brd s, 1, NH). Anal. Calcd for $C_{11}H_{23}O_3N$: C, 60.80; H, 10.67; N, 6.45. Found: C, 60.76; H, 10.59; N, 6.52.

Photolysis of 1 in a Substrate Mixture. A solution of 1 (5.0 g, 0.043 mol) in a substrate mixture (each 0.25 mol) was irradiated internally as has been described above. Then the reaction mixture was treated as mentioned above.

Acknowledgment. The authors are particularly indebted to Mr. Masao Inagaki of the College of General Education, Osaka University, for help in the preparation of this paper and for many useful suggestions.

Registry No. 1, 817-87-8; **2**, 2655-26-7; **4A**, 3871-28-1; **4B**, 38483-42-0; **4C**, 38483-43-1; **4D**, 38483-44-2; **4E**, 70084-52-5; **4F$_1$**, 63767-49-7; **4F$_2$**, 70084-53-6; **4G**, 38483-45-3; **5A**, 6781-01-7; **5B**, 1471-64-3; **5C**, 38542-87-9; **5D**, 38483-40-8; **5E**, 70084-54-7; **5F**, 70084-55-8; **5G**, 63767-45-3; methanol, 67-56-1; ethanol, 64-17-5; propanol, 71-23-8; butanol, 21-36-3; 2-propanol, 67-63-0; 2-methyl-1-propanol, 78-83-1; 3-methyl-1-butanol, 123-51-3; butyl ether, 142-96-1; cyclohexane, 110-82-7; ethyl cyclohexylcarbamate, 1541-19-1.

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A New Synthesis of the Isophosphindoline System[1]

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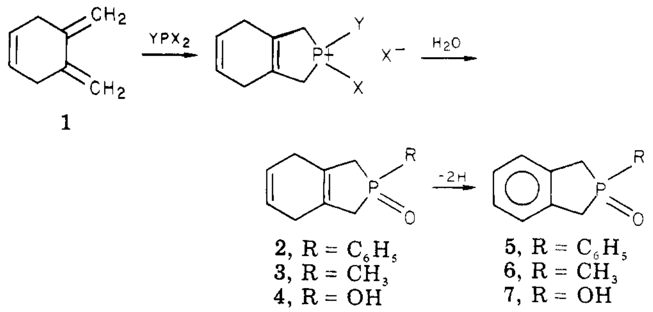
The isophosphindoline system was first constructed in the pioneering work of Mann and associates in 1954,[2] who later found that the *P*-phenyl derivative had especially valuable metal-complexing abilities.[3] Mann's synthesis of this ring system employed the principle of cyclization of an ortho-disubstituted benzene with a phosphorus compound, and all but one[4] of several subsequent syntheses[5] have made use of this principle with various reagents. The published methods have limited scope, however, and the number of known derivatives of this ring system remains quite small. We have now devised an entirely different approach to the isophosphindoline system which provides some variety in the phosphorus functionality produced (phosphine oxide or phosphinic acid) and for the former, in the carbon substituent on phosphorus.

Scheme I

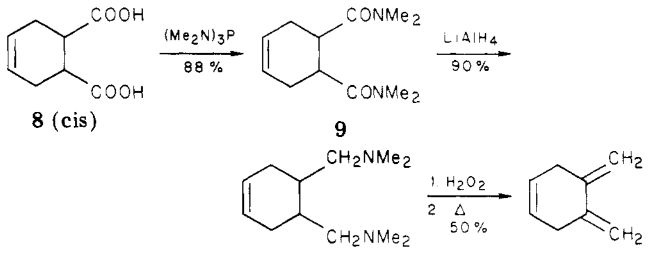


1

2, R = C_6H_5
3, R = CH_3
4, R = OH

5, R = C_6H_5
6, R = CH_3
7, R = OH

Scheme II



8 (cis) 9 10 1

Our approach involves the creation of the phosphorus-containing ring before development of the aromatic system and depends on the versatile McCormack cycloaddition reaction[6] to construct the requisite molecular framework (Scheme I). Many P(III) halides are known to participate in such cycloadditions, and in the present study we have used two phosphorus dihalides, CH_3PCl_2 and $C_6H_5PBr_2$, as well as PBr_3. Diene 1 has never before been used in a McCormack cycloaddition, but it responds exceptionally well to the usual mild conditions (standing at room temperature for several days) and leads to excellent yields of solid adducts. These were hydrolyzed without isolation to provide the new phospholene oxides 2 (85%) and 3 (92%) and the phosphinic acid 4 (78%). The value of our synthesis depends, of course, on the availability of known[7] diene 1, and in Scheme II is outlined

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[1] Supported by NSF Grant CHE77-17876 and ARO Grant DAAG29-76-G-0267.

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