$$(-)\text{-}R_3Si^*NH_2 \xrightarrow[\ [\alpha]D\ -4.8°\ ]{n\text{-BuLi}} R_3Si^*NHLi \xrightarrow{(+)\text{-}R_3Si^*Cl}$$

$$(-)\text{-}R_3Si^*NHSi^*R_3 \quad (4)$$
$$[\alpha]D\ -8°$$

having half the specific rotation obtained for the product in reaction 4. Assignment of an invertive

$$(\pm)\text{-}R_3Si^*NH_2 \xrightarrow[\ [\alpha]D\ 0°\ ]{n\text{-BuLi}} R_3Si^*NHLi \xrightarrow{(+)\text{-}R_3Si^*Cl}$$
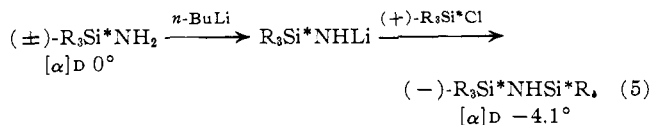
$$(-)\text{-}R_3Si^*NHSi^*R_4 \quad (5)$$
$$[\alpha]D\ -4.1°$$

path for the reactions of R_3Si^*Cl in (4) and (5) compels the conclusion that R_3Si^*Cl, $R_3Si^*NH_2$, and $R_3Si^*\text{-}NHSi^*R_3$ of the same sign of rotation also have the same configuration. Thus, reaction 3 must proceed with retention of configuration. It is interesting to note that reaction of R_3Si^*H and KOH_s to give $R_3\text{-}Si^*OK$ also proceeds with retention.[6]

The above correlations of configuration together with specific rotations are summarized in Table I. The preceding configurational relationships receive
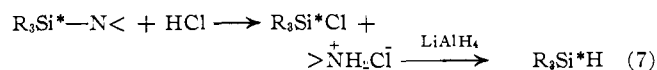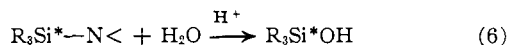
TABLE I

SILYLAMINES HAVING THE $(+)\text{-}R_3Si^*H$ CONFIGURATION[a]

Compd.	$[\alpha]D$	Concn.[b]
$(+)\text{-}R_3Si^*Pyr$	$+21.6°$	1.3
$(+)\text{-}R_3Si^*NHBu$	$+5.1°$	3.6
$(-)\text{-}R_3Si^*NH_2{}^c$	$-4.8°$	1.2
$(-)\text{-}R_3Si^*NHSiR_3$	$-8.2°$	4.4

[a] The absolute configuration of $(+)\text{-}R_3Si^*H$ has been determined (ref. 2). [b] All rotations were taken in pentane. [c] M.p. 91.9–94.3° (uncor.).

additional support from the largely parallel stereochemistry exhibited in the reactions of all four Si–N compounds.

Stereochemical studies of the above compounds were carried out with dilute aqueous acid (eq. 6) and anhydrous HCl (eq. 7). Hydrolysis was achieved by dissolving the appropriate Si–N compound in ethyl ether,

$$R_3Si^*\text{—}N< + H_2O \xrightarrow{H^+} R_3Si^*OH \quad (6)$$

$$R_3Si^*\text{—}N< + HCl \longrightarrow R_3Si^*Cl +$$
$$\overset{+}{>}NH_2\overset{-}{Cl} \xrightarrow{LiAlH_4} R_3Si^*H \quad (7)$$

and shaking with $\sim$0.25 N hydrochloric acid for 0.5 to 2 min.[7] After washing and drying, the silanol[2] was isolated. Reaction with HCl was accomplished by allowing the HCl to bubble into a solution of the silylamine in pentane. Reaction seemed to occur as rapidly as HCl was added. The product was usually worked up by reducing the chlorosilane to R_3Si^*H with $LiAlH_4$ (cf. ref. 2); however, in several reactions the chlorosilane was isolated to check the products and rotation. Stereochemical results are given in Table II and are based on present and previous[2] correlations of configuration.

All new compounds and products of reactions had the anticipated infrared spectra.[8] In addition, the proton magnetic resonance spectrum of $R_3Si^*NHSi^*R_3$ agreed with the structure proposed.

Full discussion of mechanistic implications of the above stereochemical results is deferred to a later full

(6) L. H. Sommer, et al., J. Am. Chem. Soc., 83, 2210 (1961).
(7) The disilazane did not hydrolyze under these conditions.
(8) A. L. Smith, Spectrochim. Acta, 16, 87 (1960); R. Fessenden, J. Org. Chem., 25, 2191 (1960).

TABLE II

REACTION OF SILYLAMINES WITH HCl AND H_2O

Reactant	Reagent	Product	Stereospecificity[a]
$(+)\text{-}R_3Si^*Pyr$	H_2O	$(-)\text{-}R_3Si^*OH$	76% inversion
$(+)\text{-}R_3Si^*NHBu$	H_2O	$(-)\text{-}R_3Si^*OH$	95% inversion
$(+)\text{-}R_3Si^*NH_2$	H_2O	$(+)\text{-}R_3Si^*OH$	96% inversion
$(+)\text{-}R_3Si^*Pyr$	HCl	$(-)\text{-}R_3Si^*H$	52% retention[b]
$(+)\text{-}R_3Si^*NHBu$	HCl	$(+)\text{-}R_3Si^*H$	80% inversion[b]
$(+)\text{-}R_3Si^*NH_2$	HCl	$(-)\text{-}R_3Si^*H$	91% inversion[b]
$(+)\text{-}R_3Si^*NHSiR_3$	HCl	$(-)\text{-}R_3Si^*H$	96% inversion[b]

[a] A stereospecificity of, say, 90%, means that the product was 80% optically pure (20% racemic), if optically pure reactant was used. [b] Stereospecificity for the reaction of HCl with the Si–N compound, assuming the $LiAlH_4$ reaction to be 100% inversion.[2]

article, but it may be noted here that predominant inversion of configuration for acid-catalyzed hydrolysis of Si–N probably reflects predominant operation of an S_N2–Si mechanism[9,10] involving displacement of a good leaving group formed by partial or complete protonation of the nitrogen-containing functional group. Although the reactions with hydrogen chloride in a nonpolar solvent provide circumstances which would appear to be favorable for operation of a quasi-cyclic four-center S_Ni–Si mechanism,[3,9,10] the finding of slight retention in one case and predominant inversion in the other three shows again that S_N2–Si is an exceedingly common mechanism path for silicon centers.

Acknowledgment.—We thank Dow Corning Corporation for continued generous support.

(9) L. H. Sommer, G. A. Parker, and C. L. Frye, J. Am. Chem. Soc., 86, 3280 (1964).
(10) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., in press.

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Chemiluminescent and Thermochemiluminescent Lophine Hydroperoxide

Sir:

The lophyl radical (2,4,5-triphenylimidazyl radical),[1] generated by solution of its piezochromic dimer[1b] and a 3% hydrogen peroxide solution, have been found to give rise to a 59% yield[2] of lophyl hydroperoxide, Ia, m.p. 110° with effervescence, then solidification and subsequent melting at 225–265° (Anal. Found: C, 77.0; H, 5.0; N, 8.1). Compound Ia can also be prepared in 68% yield by modifying the procedure of Dufraisse,[3] i.e., irradiating a chloroform solution of lophine in the presence of methylene blue and oxygen at 18°. The hydroperoxide is presumably the material which Dufraisse obtained in low yield in the absence of a photosensitizer and to which he assigned the endoperoxide structure II.[4]

Structure Ia is now assigned on the basis of spectral studies, analogous peroxide syntheses, and chemical

(1) (a) T. Hayashi and K. Maeda, Bull. Chem. Soc. Japan, 33, 565 (1960); (b) D. M. White and J. Sonnenberg, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 55M.
(2) Based on the stoichiometry: $(C_{21}H_{15}N_2)_2 + H_2O_2 \rightarrow Ia + C_{21}H_{16}N_2$ (lophine).
(3) C. Dufraisse, A. Étienne, and J. Martel, Compt. rend., 244, 970 (1957).
(4) The ultraviolet absorption of Ia at 283 mμ (ϵ 1.58 × 10⁴) is not consistent with structure II since model compounds such as 2,4,5-triphenylimidazoline and N-benzylbenzaldimine only absorb strongly at 250 mμ and lower.

Ia, R = OOH
b, R = OOC(CH₃)₂C₆H₅
c, R = OOC(CH₃)₃
d, R = C₆H₅

II

III
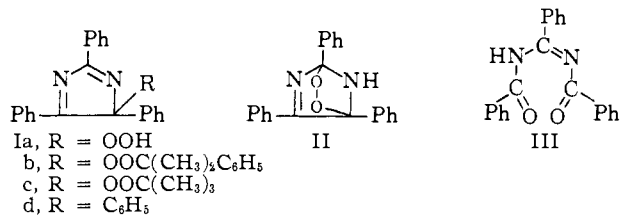
degradation. A strong infrared absorption band at 2820 cm.$^{-1}$ which is shifted on deuteration to 2105 cm.$^{-1}$ and an n.m.r. peak at 14.4 p.p.m. from TMS suggest the presence of a strong intramolecular N···H—O hydrogen bond.[5] Substitution of a hydroperoxide for hydrogen peroxide in the reaction with lophyl radical produces a mixed peroxide. Cumyl hydroperoxide is converted to Ib, m.p. 132–134° (*Anal.* Found: C, 80.9; H, 5.18; N, 6.2), and *t*-butyl hydroperoxide yields Ic, a liquid (*Anal.* Found: C, 78.3; H, 6.5; N, 7.5). The infrared spectra of Ia–c are very similar to that of 2,4,4,5-tetraphenyl-4H-isoimidazole (Id)[6] between 2000 and 650 cm.$^{-1}$.[7] This similarity of spectra and the formation of N,N'-dibenzoylbenzamidine III from the chemiluminescent reaction (see below) in 70% yield and from thermal degradation of Ia suggest the peroxidic group is on the C-4 position of the imidazole ring.

The hydroperoxide Ia exhibits several novel properties. It is thermochemiluminescent above 110° and is chemiluminescent on treatment with base. No additional oxidizing agent is required. The hydroperoxide Ia thus could be an intermediate in the known chemiluminescence of lophine. The action spectra from thermochemiluminescence and chemiluminescence of Ia have been found to be essentially identical with that of the chemiluminescence of lophine with the maximum occurring at approximately 530 mμ. For Ia, the quantum efficiency for thermochemiluminescence (*ca.* 3 × 10^{-7}) has been found to be about a factor of five smaller than that for chemiluminescence. The similarity of products, action spectra, and quantum yields suggests the possibility of a common emitting species from both thermal and base-induced chemiluminescence.

The chemiluminescence may arise from a triplet-to-singlet transition in the anion of lophine. Investigation of the spectral properties of the reaction products[8] has shown that at −196° lophine phosphoresces strongly at 523 mμ in alcoholic potassium hydroxide and weakly in absolute alcohol. It therefore seems possible that the excited anion of lophine is formed from the decomposition of the anion of Ia and is the light emitter in the chemiluminescence reaction.[9,10] In the

(5) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2900 (1961).
(6) D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964).
(7) Compounds Ia–d have characteristic absorptions of the same relative intensities near 1600, 1570, 1540, 1490, 1450, 1320, 1270, 1090, 1060, 1025, 940, 760, 720, and 690 cm.$^{-1}$ but they differ from 2,2,4,5-tetraphenyl-2H-isoimidazole (no corresponding 1570, 1320, 1060, and 720 cm.$^{-1}$ absorptions) and from N-substituted triarylimidazoles (no characteristic imidazyl 1502 cm.$^{-1}$ absorption).[6]
(8) The principal products from Ia after base or heat treatment are III, lophine, and oxygen.
(9) Compounds in liquid solution do not ordinarily appear to phosphoresce at room temperature because competing processes successfully quench the phosphorescence. At low temperature or in viscous solutions competing processes are minimized and phosphorescence can sometimes be observed. Using a sufficiently high energy source, such as those used in flash photolysis, it is possible to produce a high concentration of active species at one time to enable phosphorescence to be observed at room temperature. It is expected that a rapid chemical reaction can also generate a similar high concentration,

case of the weaker thermochemiluminescence either free lophine or its anion in smaller concentration may be the emitter.

Since phosphorescence is inefficient at room temperature and oxygen is a quenching agent, it appears reasonable that the decomposition of Ia which produces oxygen should give rise to a low quantum efficiency. The possibility that the chemiluminescence of lophine may arise from singlet-to-singlet transition is difficult to rule out unequivocally. There may be some trace reaction products which have not been examined as possible emitters and the low level of light emission requires large slit widths in the spectrophotometer which results in relatively poor resolution (*ca.* 5 mμ).

(10) For the chemiluminescence of 2-(*p*-dimethylaminophenyl)-4,5-diphenylimidazole (see M. J. C. Harding and E. H. White, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964, p. 34S), the light emission is attributed to a singlet-to-singlet transition in N,N-dibenzoyl-*p*-dimethylaminobenzamidine. For lophine chemiluminescence the analogous amidine (compound III) fluoresces very weakly in basic media at 508 mμ and seems unlikely as the emitting species.

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The Chemiluminescence of Lophine and Its Derivatives[1]

Sir:

The chemiluminescence of lophine (2,4,5-triphenylimidazole, Ia) was discovered in 1877 by Radziszewski who stated that, in the presence of air and a strong base, lophine yielded ammonia, benzoic acid, and enough light to illuminate the surroundings.[2] Kautsky and Kaiser later reported that a radical was formed in the oxidation of lophine and that the radical yielded light on reaction with a base.[3] Recently, however, Hayashi and Maeda showed that oxygen was required for the luminescence, and they suggested that peroxides were involved.[4] We found independently that peroxides could be made from the radical and its dimers,[5] and, furthermore, that an active peroxide could be made by the irradiation of lophine in the presence of oxygen. This peroxide had, in fact, been prepared earlier,[6] but its chemiluminescence had apparently not been noticed.

We have synthesized a number of substituted imidazoles (I) and from these, at low temperatures, the peroxides (II). The n.m.r. spectra (*sharp* singlet for

I　　　　　II　　　　　III

IV
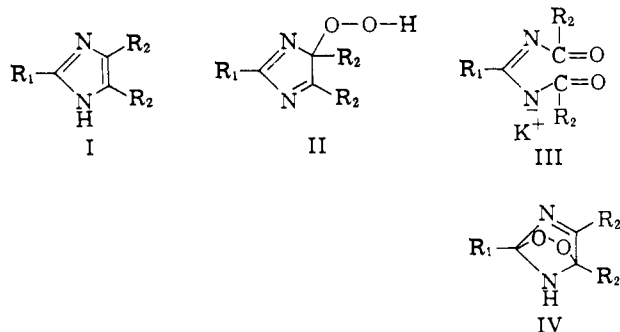
a, R₁ = R₂ = C₆H₅
b, R₁ = *p*-CH₃OC₆H₄, R₂ = C₆H₅
c, R₁ = R₂ = *p*-CH₃OC₆H₄
d, R₁ = *p*-(CH₃)₂NC₆H₄, R₂ = C₆H₅
e, R₁ = *p*-(CH₃)₂NC₆H₄, R₂ = *p*-CH₃OC₆H₄

(1) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964; Abstracts, p. 34S.
(2) Br. Radziszewski, *Ber.*, **10**, 70 (1877).
(3) H. Kautsky and K. H. Kaiser, *Naturwiss.*, **31**, 505 (1943).
(4) T. Hayashi and K. Maeda, *Bull. Chem. Soc. Japan*, **35**, 2057 (1962).
(5) We thank Dr. J. H. M. Hill for samples of various substituted lophine dimers.
(6) C. Dufraisse, A. Etienne, and J. Martel, *Compt. rend.*, 970 (1957).