by vpc. From its nmr pattern the compound was identified as α-chloroethyldimethylchlorosilane. The remaining three peaks could not be isolated and purified by vpc because of the rather poor resolution obtained for these peaks. Since there must be only three possible monochlorination products, one would imagine some side reaction occurring with this starting material. However, such complications do not preclude obtaining the relative site reactivity for the α position of ethyldimethylchlorosilane in view of the present method of calculation. The possibility for the decomposition of the α-chloro isomer during the vpc analysis could be eliminated by the success of vpc isolation and purification. A typical set of the competitive data is presented in Table II.

Chlorination Products of Ethyltrichlorosilane.[3]—Ethyltrichlorosilane (189 g) was heated under reflux with 187 g of sulfuryl chloride in the presence of 2 g of benzoyl peroxide to give 34 g of α-chloroethyltrichlorosilane (bp 135°) and 48 g of β-chloroethyltrichlorosilane (bp 150°). These were used as authentic samples. Each of the samples collected by vpc from the competitive runs agreed, in every respect (infrared absorptions, retention times, chemical shifts, and refractive indices) with the corresponding authentic sample.

Chlorination Products of Ethylmethyldichlorosilane.[23]—Ethylmethyldichlorosilane (179 g) was chlorinated with 268 g of sulfuryl chloride in the presence of 0.1 g of benzoyl peroxide yielding 49 g of α-chloroethylmethyldichlorosilane (bp 137°) and 63 g of β-chloroethylmethyldichlorosilane (bp 153°). These were used as authentic samples and their physical properties were compared with those of the samples obtained from the competitive chlorination mixtures by vpc.

Chlorination of Ethyldimethylchlorosilane.—A chlorination mixture of ethyldimethylchlorosilane was subjected to vpc analysis (silicone DC 550, 120°), there being noticed four product peaks in a ratio of 53:18:22:7. The compound responsible for the largest peak was obtained by vpc collection and identified as α-chloroethyldimethylchlorosilane by its nmr spectrum (Table I).

Chlorination Products of *n*-Propyltrichlorosilane.—There were three peaks on the chromatogram (QF-1, 120°). Each of the compounds was obtained by vpc collection and identified by nmr measurement. The first was (1-chloropropyl)trichlorosilane, the second the 2-chloro isomer, the last the 3-chloro isomer.

Chlorination Products of *n*-Propylmethyldichlorosilane.—There were again three product peaks on the chromatogram (QF-1, 120°). The compounds were separately collected by vpc; the structures were determined based on their nmr spectra (Table I). The order of retention times was found to be 1-chloro < 2-chloro < 3-chloro isomer.

Chlorination Products of *n*-Butyltrichlorosilane.—Vpc analysis (Versilube F-50, 135°) of a chlorination mixture of the silane disclosed four product peaks. Pure samples of the second, third, and fourth compounds were obtained by vpc collection. These were the 2-chloro, 3-chloro, and 4-chloro isomers, respectively (Table I). The first peak was, therefore, due to the 1-chloro isomer.

Chlorination Products of *n*-Butylmethyldichlorosilane.—Vpc analysis (QF-1, 125°) of a noncompetitive chlorination mixture of *n*-butylmethyldichlorosilane disclosed four product peaks. Each of pure samples of these products was isolated and purified by preparative scale vpc. Nmr determination of these compounds (Table I) confirmed the identity of the first peak as the 1-chloro isomer, the second as the 2-chloro isomer, the third as the 3-chloro isomer, and the fourth as the 4-chloro isomer.

Registry No.—**1**, 7787-82-8; **2**, 6233-20-1; **3**, 7787-84-0; **4**, 7787-85-1; **5**, 7787-86-2; **6**, 7787-87-3; **7**, 7787-88-4; **8**, 7787-89-5; **9**, 2550-06-3; **10**, 7787-91-9; **11**, 7787-92-0; **12**, 7787-93-1; **13**, 7787-94-2; **14**, 1000-58-4; **15**, 2322-28-3; **16**, 7787-97-5; **17**, 7787-98-6; **18**, 1591-20-4; **19**, 1591-21-5.

Acknowledgment.—The authors greatly appreciate the generous support by the General Electric Co.

The Chemiluminescence of Some Monoacylhydrazides

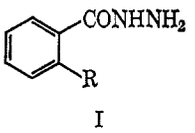
EMIL H. WHITE, MAURICE M. BURSEY,[1] DAVID F. ROSWELL,[2] AND JOHN H. M. HILL

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Received November 14, 1966

Some correlations between the structures of acylhydrazines and N,N′-diacylhydrazines and their chemiluminescence efficiencies have been determined. A comparison of the chemiluminescence spectra of the hydrazides of 1-hydroxy-2-naphthoic acid and of 1-hydroxy-2-anthroic acid and the fluorescence spectra of the corresponding carboxylate ions in dimethyl sulfoxide indicates that the latter compounds may be the emitters in the chemiluminescent reaction. A hydrazide related to firefly luciferin was prepared and shown not to be efficient in chemiluminescence.

Because of the low intensity of their chemiluminescence, monoacylhydrazides have not been studied by many workers with the purpose of establishing a relationship between structure and chemiluminescent reactivity. In aqueous systems, some *ortho*-substituted benzhydrazides (I, R = OH, NH_2) are weakly chemiluminescent.[3,4] Recrystallized *o*-, *m*-, and *p*-nitrobenzhydrazides do not emit light, although the crude materials (possibly containing the aminohydrazides) do in aqueous systems.[5] Among disubstituted hydrazines, N,N′-dianthranoylhydrazine was found to be weakly chemiluminescent.[3] The hydrazide of benzenesulfonic acid is not chemiluminescent[6] and so resembles benzhydrazide, which is nonchemiluminescent.[5] Other references to earlier work have been summarized.[7] This paper reports the results of a search for efficient acyclic hydrazides.



I

From the observations above, it appeared that chemiluminescent activity was conferred on linear hydrazides by electron-supplying substituents. This correlation had been noted for derivatives of phthalic hydrazide by Drew and Pearman.[8] Accordingly, examination of substituent effects was directed toward the amino, hydroxy, and methoxy substituents.

(1) National Science Foundation Cooperative Graduate Fellow, 1960–1963.
(2) National Science Foundation Summer Fellow, 1963.
(3) E. S. Vasserman and G. P. Miklukhin, *Zh. Obshch. Khim.*, **9**, 606 (1939); *Chem. Abstr.*, **33**, 7665[7] (1939).
(4) H. Ojima, *Naturwiss.*, **48**, 600 (1961).
(5) A. A. M. Witte, *Rec. Trav. Chim.*, **54**, 471 (1935).
(6) C. Courtot and A. Bernanose, *Compt. Rend.*, **205**, 989 (1937).
(7) A. Bernanose, *Bull. Soc. Chim. France*, 567 (1950).
(8) H. D. K. Drew and F. H. Pearman, *J. Chem. Soc.*, 586 (1937).

Monoacylhydrazines.—Chemiluminescent efficiency seems to follow rationalizable correlations with the position of the substituent and the size of the aromatic system. A series of hydrazides was tested in dry dimethyl sulfoxide (DMSO), reproducing the system found to be most efficient for the luminol reaction.[9,10] The efficiency of the monosubstituted compounds is so low that for the first members of the series only visual comparison was possible. For systems with more than one aromatic ring, an instrumental study was feasible. Data for the linear hydrazides examined are given in Table I.

TABLE I

CHEMILUMINESCENCE OF LINEAR HYDRAZIDES COMPARED WITH THE FLUORESCENCE OF PRODUCTS AND THE FLUORESCENCE OF CARBOXYLATE IONS IN DIMETHYL SULFOXIDE

A. Visual Estimation

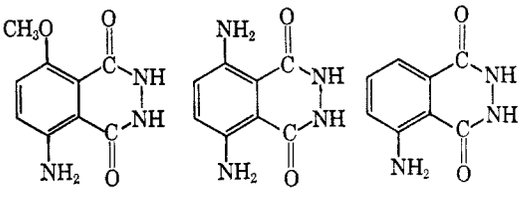
	Chemiluminescence of $RCONHNH_2$	Fluorescence: Of $RCOO^-$	Fluorescence: Of reaction mixture[a]
R = C_6H_5	Nil	Nil	Nil
R = *o*-HOC_6H_4	Dim whitish	Bluish	Bluish
R = *m*-HOC_6H_4	Dim whitish	Bluish	Bluish
R = *p*-HOC_6H_4	Nil	Nil	Nil
R = *o*-$H_2NC_6H_4$	Dim bluish	Bluish	Bluish
R = *m*-$H_2NC_6H_4$	Dim whitish	Bluish	Bluish
R = *p*-$H_2NC_6H_4$	Nil	Nil	Nil
R = 2,5-$(HO)_2C_6H_3$	Nil	Bluish	Nil
R = 3,5-$(HO)_2C_6H_3$[b]	Nil	Bluish	Nil
R = 3,4,5-$(HO)_3C_6H_2$	Nil		

B. Instrumental and Visual Estimation

Compd (RCO-$NHNH_2$)	Chemiluminescence: Emission max, mμ	Chemiluminescence: Quantum yield rel to luminol[c]	Fluorescence, mμ: Of $RCOO^-$	Fluorescence, mμ: Of reaction mixture[a]
V[b]	485 ± 10	1.25×10^{-3}	488 ± 5	483 + 5
VI	Yellowish		Yellowish	Yellowish
VII	Yellowish		Yellowish	Yellowish
VIII[b]	660 ± 10	4.00×10^{-3}[d]	671 ± 10	652 + 10

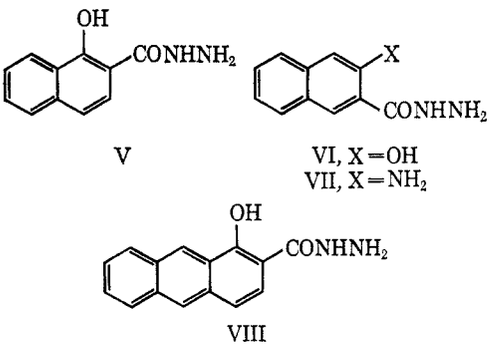
[a] Spent solutions from the chemiluminescence. [b] No light was observed in the H_2O–H_2O_2–NaOH–hemin system. [c] Luminol = 0.0125: J. Lee and H. H. Seliger, *Photochem. Photobiol.*, **4**, 1015 (1965). [d] Correcting our previous report of 0.33: E. H. White, O. Zafiriou, H. H. Kägi, and J. H. M. Hill, *J. Am. Chem. Soc.*, **86**, 940 (1964).

The first seven compounds in Table I would indicate that the effect of an amino or a hydroxy substituent on chemiluminescence of the hydrazide parallels its effect on visible fluorescence of the corresponding carboxylate anion. It is interesting to note that substituents in the *para* position do not modify the chemiluminescence of benzhydrazide or the fluorescence of the corresponding benzoate ion, whereas in the *ortho* and *meta* positions they enhance both the fluorescence and chemiluminescence efficiencies, at least in the visible region. This interaction of the *ortho* and *meta* substituents, but not the *para*, is in agreement with the electron distribution proposed for other excited-state reactions which allows direct resonance interaction of the reaction site with the *ortho* and *meta* substituents, but not the *para* substituents.[11] On the other hand, attempts to take advantage of cumulation of substituents in interacting positions were not successful. The polyhydroxyhydrazides did not emit light, although the corresponding anions were fluorescent (Table I). Under our conditions these hydrazides apparently suffer ring oxidation, since the product solutions were highly colored. An analogy may be drawn to the greatly decreased efficiency of II and III[12–14] relative to luminol (IV) itself.



II III IV

The most interesting trend, for the purpose of producing a compound with sufficient intensity for quantitative study, is the increase in efficiency on progressing from a benzene through a naphthalene to an anthracene nucleus. Measurements of the chemiluminescent efficiencies were possible for 1-hydroxy-2-naphthoic acid hydrazide (V) and 1-hydroxy-2-anthroic acid hydrazide (VIII) in the dimethyl sulfoxide system. The quantum yield of chemiluminescence is three times larger for the larger aromatic system (this value is probably no larger because of the greater susceptibility of the anthracene nucleus to oxidation). Paper chromatograms of the reaction products show the formation of nonfluorescent side products in both cases.



V VI, X=OH VII, X=NH_2

VIII

The chemiluminescence maxima of these two compounds, the fluorescence maxima of the corresponding carboxylate anions, and the fluorescence maxima of the reaction mixture after chemiluminescence had ceased were compared; the latter solution contained the corresponding carboxylate ion as the sole fluorescent species as shown by paper chromatography. Within the limits of error of the experiments, rather large because of the low light intensities available and the high speed of the reactions, the results (Table I) suggest that chemiluminescence involves the production of the carboxylate anion in an excited singlet state, followed by fluorescence of this ion (eq 1). A similar

(9) E. H. White, *J. Chem. Educ.*, **34**, 275 (1957).

(10) E. H. White and M. M. Bursey, *J. Am. Chem. Soc.*, **86**, 941 (1964).

(11) Early acknowledgement of differing positional effects in excited states are found in C. Reid ("Excited States in Chemistry and Biology," Butterworths, London, 1957) and E. Havinga, R. O. de Jongh, and W. Dorst [*Rec. Trav. Chim.*, **75**, 378 (1956)]. The first application of Hückel theory to the explanation of excited-state positional reactivities was by H. E. Zimmerman, *Tetrahedron, Suppl.*, **2**, 393 (1961).

(12) H. D. K. Drew and F. H. Pearman, *J. Chem. Soc.*, 586 (1937).

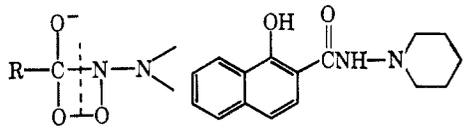
(13) K.-D. Gundermann and M. Drawert, *Chem. Ber.*, **95**, 2018 (1962).

(14) See discussion by K.-D. Gundermann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 566 (1965).

$$RCONHNH_2 \xrightarrow{OH^-} RCOO^{-*} \longrightarrow RCOO^- + h\nu \quad (1)$$

sequence of events has been established for the chemiluminescence of luminol,[10] the reaction of cyclic analogs of luminol,[15] and for lophine chemiluminescence.[16]

To determine whether the possibility of forming a four-membered peroxide (IX) (leading to a fluorescent product) would be a sufficient condition for chemiluminescence,[16] the trisubstituted hydrazine X was synthesized. The compound, however, was not chemi-



IX X

luminescent at 25° in either the DMSO–butoxide–O_2 system or the peroxide–base–hemin system; in the former system at 60°, a weak emission was seen. Compound X is thus far less efficient in light production than the unsubstituted hydrazide V.

A complete product study of these reactions has not been achieved; in addition to the paper chromatographic results, ultraviolet spectra of the reaction mixtures indicate that a plurality of products is formed. In a model system, autoxidation of benzhydrazide in dimethyl sulfoxide–*t*-butyl alcohol with potassium *t*-butoxide as base gave benzoic acid in yields inversely dependent on the concentration of the benzhydrazide (Table II).

TABLE II

DEPENDENCE OF BENZOIC ACID YIELDS ON INITIAL CONCENTRATION OF BENZHYDRAZIDE

Initial Concn of $C_6H_5CONHNH_2$, *M*	Yield of C_6H_5COOH, %
0.52	11
0.32	48
0.062	75
0.054	79
0.0047	97

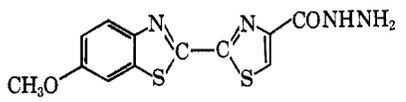
In more concentrated solutions, a second product, the benzoylhydrazone of benzaldehyde[17–19] (eq 2, 3) was

$$RCONHNH_2 \xrightarrow[O_2]{base} [RCON{=}NH] \xrightarrow[RCHO]{O_2} RCOOH \quad (2)$$

$$RCONHNH_2 + RCHO \longrightarrow RCONHN{=}CHR \quad (3)$$

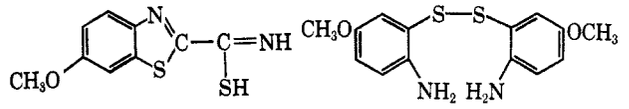
formed. No other products[20–22] were detected by thin layer chromatography. With 0.465 *M* potassium *t*-butoxide in pure *t*-butyl alcohol, 0.12 *M* β-naphthoic acid hydrazide gave 41% of the β-naphthoylhydrazone of β-naphthaldehyde and 56% naphthoic acid after 6 days under O_2 at room temperature; again no other products were detected by thin layer chromatography. Whether such products of bimolecular reactions contribute to the side reactions at the concentration used for chemiluminescence studies with the other hydrazides (*ca.* 1×10^{-3} *M*) remains problematical at this time.

One other hydrazide, O-methyldehydroluciferylhydrazide (XI) was prepared in conjunction with



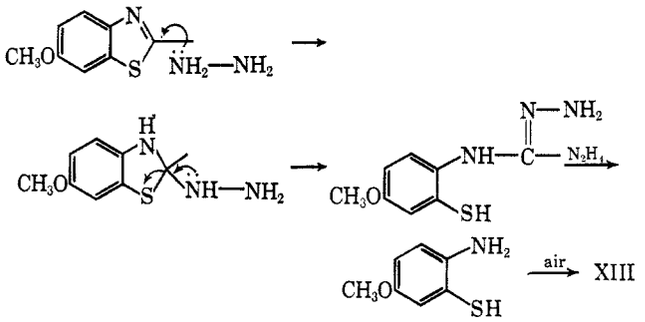
XI

studies on analogs of bioluminescent systems.[23,24] A condensation of the thioamide XII and ethyl bromopyruvate in methyl alcohol yielded O-methyldehydroluciferin ethyl ester analogously to the preparation of the methyl ester.[23] The hydrazide XI was prepared from the ethyl ester in ethanol solution. Under more vigorous conditions (95% hydrazine as the solvent)



XII XIII

bis(2-amino-5-methoxyphenyl)disulfide (XIII) was the main product, possibly by this sequence of steps.[25,26]



Despite the fact that highly fluorescent acids are formed in the reaction, the hydrazide was not chemiluminescent in the water–hydrogen–peroxide–hemin system (or with ferricyanide) and only very weakly chemiluminescent in the dimethyl sulfoxide–*t*-butoxide system. This points up the lack of direct correlation between the chemiluminescence efficiency of a hydrazide and the fluorescence efficiency of the product acid anion.

All the synthetic compounds discussed in the section were shown to be paper chromatographically singular.

N,N′-Diacylhydrazines.—Several disubstituted hydrazines were prepared to extend the observations made earlier on such compounds.[3,6,7] None of the compounds which are tabulated in Table III was found to exhibit chemiluminescence in the dimethyl sulfoxide–*t*-butoxide system.

(15) E. H. White and M. M. Bursey, *J. Org. Chem.*, **31**, 1912 (1966).
(16) E. H. White and M. J. C. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965).
(17) T. Curtius, *Chem. Ber.*, **33**, 2559 (1900).
(18) T. Curtius and H. Melsbach, *J. Prakt. Chem.*, **81**, 501 (1910).
(19) L. Kalb and O. Gross, *Chem. Ber.*, **59**, 727 (1926).
(20) T. Curtius and G. Struwe [*J. Prakt. Chem.*, **50**, 300 (1894)] produced N,N′-diacylhydrazines by HgO or I_2 oxidation of acylhydrazines.
(21) A. Darapsky, *ibid.*, **76**, 494 (1907).
(22) A. Darapsky [*Chem. Ber.*, **40**, 3033 (1907)] produced N,N′-diacylhydrazines by hypochlorite oxidation of acylhydrazines.
(23) E. H. White, F. McCapra, and G. F. Field, *J. Am. Chem. Soc.*, **85**, 337 (1963).
(24) E. H. White, H. Wörther, G. F. Field, and W. D. McElroy, *J. Org. Chem.*, **30**, 2344 (1965); E. H. White and H. Wörther, *ibid.*, **31**, 1484 (1966).
(25) See H. Hodgson and F. W. Handley, *J. Chem. Soc.*, 625 (1928), for an analogy.
(26) See K. Fries and W. Buchler, *Ann. Chem.*, **454**, 233 (1927), for an analogy.

TABLE III
NONCHEMILUMINESCENT HYDRAZIDES[a] (RNHNHR')

Acyl Substituent	
R = R' =	C_6H_5CO
R = R' =	o-$H_2NC_6H_4CO$
R = R' =	o-$CH_3OC_6H_4CO$
R = R' =	m-$CH_3OC_6H_4CO$
R = R' =	p-$CH_3OC_6H_4CO$
Phthalimidophthalimide[b]	
R =	o-$O_2NC_6H_4CO$; R' = $C_6H_5SO_2$
R =	o-$H_2NC_6H_4CO$; R' = $C_6H_5SO_2$[b]

[a] DMSO–*t*-butoxide–O_2 system. [b] In addition, no light in the H_2O–H_2O_2–NaOH–hemin system.

Experimental Section

Syntheses.—The hydrazides of Table I were prepared by the reaction of the corresponding methyl or ethyl esters with hydrazine according to the usual procedure, except as noted: benzhydrazide, mp 112, 113–114°, and lit.[27] mp 112.5°; *o*-aminobenzhydrazide, from isatoic anhydride (Maumee Chemical Co.) and hydrazine,[28,29] mp 123° and lit.[28] mp 123°; *m*-aminobenzhydrazide, mp 76–77°, and lit.[30] mp 77°; *p*-aminobenzhydrazide, mp 222–224° and lit.[31] mp 220°; *o*-hydroxybenzhydrazide, mp 147–148° and lit.[30,32] mp 145 and 147°; *m*-hydroxybenzhydrazide, mp 149–150° and lit.[30] mp 150°; *p*-hydroxybenzhydrazide, mp 259.5–261° and lit.[30] mp 260°; 2,5-dihydroxybenzhydrazide, mp 213–214°, and lit.[33,34] mp 209–210 and 207°; 1-hydroxy-2-naphthoic acid hydrazide (V), mp 212–213° and lit.[35] mp 212–213°; 2-hydroxy-3-naphthoic hydrazide (VI), mp 201.5–203° and lit.[36] mp 203–204°; 2-amino-3-naphthoic hydrazide (VII), mp 203–205° dec (bath at 200°) and lit.[37] mp 206–210° dec (bath at 200°).

3,4,5-Trimethoxybenzhydrazide was prepared from the acid chloride and hydrazine in ether–benzene,[38] mp 160.2–161.6° and lit.[39] mp 157–158°.

3,5-Dihydroxybenzhydrazide was prepared in a manner analogous to that for the 2,5-dihydroxybenzhydrazide, mp 264.5–265°.

Anal. Calcd for $C_7H_8N_2O_3$: C, 50.00; H, 4.80. Found: C, 49.60; H, 4.96.

1-Hydroxy-2-anthroic Acid Hydrazide (VIII).—Dienel's procedure was used to prepare 1-anthrol from 1-aminoanthracene (Aldrich),[40] mp 155–156.5° and lit.[40] mp 150–153°. The hydroxy compound was then subjected to a Kolbe carboxylation step[41] to give 1-hydroxy-2-anthroic acid, mp 200° dec and lit.[41] mp 200° dec. Esterification of the anthroic acid using methanol and HCl or H_2SO_4 gave poor yields of the ester and led to recovery of the acid. The triazene method[42] of esterification was, therefore, used. Crude 1-hydroxy-2-anthroic acid (1.5 g, 6.3 mmoles) was dissolved in 200 ml of ethyl ether and 3 g (20 mmoles) of 1-methyl-3-*p*-tolyltriazene was added. After stirring for 12 hr, the solution was extracted with 1 *N* HCl, water, dilute bicarbonate, water, and saturated NaCl. Drying and evaporation of the ether gave 1.2 g of crude ester, which was chromatographed on 30 g of silica gel with CCl_4 and recrystallized from isooctane to give 860 mg (3.3 mmoles, 53%) of methyl 1-hydroxy-2-anthroate, mp 143.5–145°; nuclear magnetic resonance (nmr) spectrum ($CDCl_3$) δ 7.2–9.2 (multiplet, 8 H), 12.4 (singlet, 1 H), and 4.1 (singlet, 3 H) (from tetramethylsilane).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 75.83; H, 4.74.

The methyl ester (50 mg, 0.2 mmole) was added to 2 ml of hydrazine hydrate in a 12-mm tube, which was then sealed off under *ca.* 20 mm of pressure and heated in a steam bath 2 hr. The tube was opened and the reaction mixture was poured into 20 ml of water, whose pH was adjusted to 5 with dilute HCl. The product was filtered, washed with water, and recrystallized from 95% ethanol, giving 33 mg (0.13 mmole, 66%); mp >250° dec; infrared spectrum 1640 and 1610 cm^{-1}; λ_{max} (in DMSO) 309 mμ (ϵ 33,600), 370 (9550), 387 (19,200).

Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10. Found: C, 71.61; H, 4.98; N, 11.28.

When the hydrazide was prepared in the presence of air, an impure product was obtained that was very difficult to purify by recrystallization or sublimation.

O-Methyldehydroluciferin (Ethyl and Methyl Ester Mixture).—To a suspension of 6-methoxybenzothiazole-2-thiocarboxamide[23] (XII) (0.40 g, 1.78 mmoles) in 40 ml of methyl alcohol was added ethyl bromopyruvate (1.25 g, 3.9 mmoles). The reaction mixture was stirred at room temperature for 15 hr, then heated on a steam bath for 2 hr, to yield cream-colored needles, 0.39 g (1.2 mmoles, 68%), mp 202° (sinters 186°), λ_{max} (in EtOH) 273 mμ (ϵ 351) (similar to the methyl ester[23]).[43] Partial ester interchange had occurred during the reaction and the elemental analysis indicated a mixture of 47% methyl ester and 53% ethyl ester.

Bis(2-amino-5-methoxyphenyl) Disulfide (XIII).—A suspension of O-methyldehydroluciferin (ethyl and methyl esters; see above) (0.17 g, 0.54 mmole) in 2.5 ml of 95% hydrazine was heated on a water bath for 13 hr. The reaction mixture was evaporated under vacuum to give an oily residue. Ethyl alcohol (4 ml) was added (and then water) until the solution became turbid. On cooling to 0°, yellow needles separated which were recrystallized twice from ethyl alcohol–water to give 65 mg of product (0.31 mmole, 39%). A sample for analysis was prepared by one more recrystallization from ethyl alcohol–water; mp 73–75°; λ_{max} (in 95% EtOH) 226 mμ (ϵ 24,100), 361 mμ (ϵ 5600); nmr (in $CDCl_3$) δ 6.75 (singlet, fine structure 6 H), 4.02 (singlet, 4 H), 3.62 (singlet, 6 H).[43]

Anal. Calcd for $C_{14}H_{16}N_2O_2S_2$: C, 54.54; H, 5.23; N, 9.09; S, 20.77. Found: C, 54.64; H, 5.53; N, 8.86; S, 20.62.

O-Methyldehydroluciferyl Hydrazide (XI).—To a solution of O-methyldehydroluciferin (methyl and ethyl esters; see above) (0.10 g, 0.31 mmole) in 50 ml of ethyl alcohol at 40° was added 0.15 ml of 95% hydrazine. The mixture was heated on a steam bath 6 hr, then condensed to 15 ml; hydrazine (3 ml) was added and the mixture was reheated for 10 min. On cooling, a product with mp 214–225° dec (73 mg, 0.23 mmole, 74%) was collected. The analytical sample was recrystallized twice from methyl alcohol; mp 243–243.5° dec; λ_{max}^{EtOH} 216 mμ (ϵ 22,000), 267 (6300), 353 (11,800).[43]

Anal. Calcd for $C_{12}H_{10}N_4O_2S_2 + CH_3OH$: C, 46.16; H, 4.17. Found: C, 46.49; H, 4.13.

Diacylhydrazines.—These were prepared as follows: 1,2-dibenzoylhydrazine, from benzhydrazide and benzoyl chloride in pyridine, mp 240–241° and lit.[44] mp 241°; dianthraniloylhydrazine, from *o*-aminobenzhydrazide by pyrolysis, mp 212–214° and lit.[28,45] mp 213°, or as below; phthalimidophthalimide, from phthalic anhydride and hydrazine hydrate in acetic acid, mp 311–312° and lit.[46] mp 311–313°.

1,2-Dianthraniloylhydrazine was also prepared by reduction of 1,2-di-*o*-nitrobenzoylhydrazine[47] (from *o*-nitrobenzoyl chloride and 94% hydrazine in pyridine (80% yield) (5.5 g, 16.7 mmoles) in ethyl acetate with 10% Pd–C (0.5 g, previously blanked) at atmospheric pressure. The solution was filtered, concentrated, and cooled to yield product (3.94 g, 87%), mp 202–204° and lit.[28,45] mp 213°.

1,2-Di-*o*-anisoylhydrazine.—After refluxing *o*-methoxybenzoic acid (3.0 g, 20 mmoles) in thionyl chloride for 3 hr, excess $SOCl_2$ was distilled and the product, in benzene (10 ml), was added dropwise to a vigorously stirred mixture of 94% hydrazine (0.35 g, 10 mmoles) and pyridine (10 ml). After 6 hr the mixture was diluted with 3:1 aqueous ethyl alcohol (100 ml) and the insoluble

(27) C. Naegeli and G. Stefanovitsch, *Helv. Chim. Acta*, **11**, 636 (1928).
(28) C. Thode, *J. Prakt. Chem.*, **69**, 92 (1904).
(29) We thank Dr. Charles P. Kulier for the preparation of this compound.
(30) A. Struve and R. Radenhausen, *J. Prakt. Chem.*, **52**, 227 (1895).
(31) T. Curtius, *ibid.*, **95**, 327 (1917).
(32) G. Bondi, *Z. Physiol. Chem., Hoppe-Seyler's*, **52**, 170 (1907).
(33) H. H. Fox and J. T. Gibas, *J. Org. Chem.*, **17**, 1653 (1952).
(34) A. E. Wilder Smith, *Arch. Pharm.*, **295**, 455 (1962).
(35) H. Beyer and H. Schulte, *Chem. Ber.*, **74B**, 98 (1941).
(36) H. Franzen and T. Eichler, *J. Prakt. Chem.*, **78**, 164 (1908).
(37) I. M. Heilbron, A. H. Cook, H. M. Bunbury, and D. H. Hey, "Dictionary of Organic Compounds," Oxford University Press, London, 1965.
(38) We thank Dr. Eugene Galántay for the preparation of this compound.
(39) I. A. Pearl and D. L. Beyer, *J. Am. Chem. Soc.*, **77**, 3660 (1955).
(40) H. Dienel, *Chem. Ber.*, **38**, 2862 (1905).
(41) S. S. Lele, N. H. Shah, and S. Sethna, *J. Org. Chem.*, **21**, 1293 (1956).
(42) E. H. White and H. Scherrer, *Tetrahedron Letters*, 758 (1961).
(43) We thank Dr. Kohtaro Matsuo for the preparation of these compounds.
(44) A. Benrath, P. Giesler, and O. Gaertner, *J. Prakt. Chem.*, **107**, 211 (1924).
(45) G. Heller, W. Dietrich, and G. Reichardt, *ibid.*, **118**, 138 (1928).
(46) H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 16 (1937).
(47) L. Horner and F. Fernekess, *Chem. Ber.*, **94**, 712 (1961).

residue was filtered and recrystallized from ethyl alcohol to give product (2.06 g, 69%), mp 201–202°.

Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.32. Found: C, 64.12; H, 5.28; N, 9.66.

1,2-Di-*m*-anisoylhydrazine was prepared analogously (74%), mp 199–200°.

Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.32. Found: 63.87; H, 5.67; N, 9.66.

1,2-Di-*p*-anisoylhydrazine was prepared analogously (65%), mp 228–228.5° and lit.[48] mp 224–225°.

Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.32. Found: C, 64.21; H, 5.62; N, 9.40.

1-*o*-Nitrobenzoyl-2-phenylsulfonylhydrazine.—After refluxing *o*-nitrobenzoic acid (4.0 g, 24 mmoles) with thionyl chloride for 3 hr, the excess $SOCl_2$ was distilled and the residue was dissolved in benzene (10 ml). This solution was added with stirring and cooling to phenylsulfonylhydrazine (4.1 g, 24 mmoles) in pyridine (25 ml). After 3 hr at 0° and 3 hr at room temperature, it was diluted with water (500 ml) and the product was filtered, washed with water and hexane, and recrystallized from ethyl alcohol (5.3 g, 68%), mp 183–184° and lit.[49] mp 181–182°.

Anal. Calcd for $C_{13}H_{11}N_3O_5S$: C, 48.60; H, 3.45; N, 13.08. Found: C, 48.33; H, 3.67; N, 13.01.

1-Anthraniloyl-2-phenylsulfonylhydrazine.—The previous compound (4.0 g, 12.5 mmoles) was suspended in ethyl alcohol (100 ml) and 10% Pd–C (0.5 g) was added. The mixture was hydrogenated in a Parr apparatus (initial pressure, 29 psi; final pressure after theoretical H_2 uptake, 26 psi). The solution was filtered, concentrated to 50 ml, and cooled to −40° to yield product (2.8 g, 77%), mp 147–149°.

Anal. Calcd for $C_{13}H_{13}N_3O_3S$: C, 53.60; H, 4.50; N, 14.42. Found: C, 53.28; H, 4.72; N, 14.09.

1-Hydroxy-N-(1-piperidino)-2-naphthamide (X).—Dicyclohexylcarbodiimide (1.03 g, 5.0 mmoles) was added in one portion to a solution of 1-hydroxy-2-naphthoic acid (0.94 g, 5.0 mmoles) in 40 ml of dry ether. After the mixture had stood for 18 hr at room temperature, the copious, white precipitate of dicyclohexylurea which had formed was filtered off and dried (1.19 g, 97%). The filtrate was evaporated and the residue was taken up in chloroform and chromatographed on 30 g of silica gel. After removal of 0.35 g of viscous oil from the column with benzene, elution with chloroform yielded fractions which on evaporation gave a clear oil (0.1 g) which solidified on standing. This material was crystallized once from benzene–carbon tetrachloride (1:2), and then from isooctane, to yield the product (0.07 g, 6%); mp 191–192°; infrared spectrum ($CHCl_3$) 3450, 3200, 3050, 2940, 1640, 1610, and 1600 cm^{-1}; nmr spectrum ($CDCl_3$) δ 8.4–6.7 (multiplet, 6.0 H), 4.66 (broad singlet, 0.8 H), 2.88 (triplet, J = 5 cps, 3.9 H), and 1.7 (multiplet, 6.1 H).[50]

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.99; H, 6.90; N, 10.22.

Chemiluminescence. Visual Estimation.—Hydrazides too weak to be examined instrumentally were compared visually with each other and with phthalic hydrazide under similar conditions; about 30 mg of hydrazide was dissolved in 5 ml of dry distilled DMSO, and a large excess (*ca.* 100 mg) of potassium *t*-butoxide was added in a completely darkened room. A very small amount of light was generally emitted under these conditions for all samples of DMSO prepared in this study, but the intensity and duration of emission from the hydrazide solutions exceeded this emission in all positive cases by a factor of at least *ca.* 10.

Emission Spectra.—The emission spectra of 1-hydroxy-2-naphthoic hydrazide and 1-hydroxy-2-anthroic hydrazide were measured in the DMSO–butoxide system by a grating spectrophotometer with an EMI 9558 phototube and a rapid recorder (340–730 mμ in 6 sec) and corrected for instrumental sensitivity variation with wavelength. Correction for decay was estimated by recording several scans of the same run and back calculating.[51]

Fluorescence Spectra—The fluorescence of products of 1.25×10^{-3} *M* 1-hydroxy-2-anthroic hydrazide and 1.25×10^{-3} *M* 1-hydroxy-2-naphthoic acid hydrazide in DMSO was measured with an Aminco-Bowman spectrophotofluorometer with a Dry Ice cooled RCA 7102 phototube or an IP21 phototube, respectively, as detector, in the spectral region of maximum sensitivity of the tube. The molarity of the solution was the same as that used for measuring emission since, in other cases, the fluorescence maximum shifts to shorter wavelength on dilution. The corresponding anions were produced in solution by treating 1.08×10^{-3} *M* 1-hydroxy-2-anthroic acid and 2.00×10^{-3} *M* 1-hydroxy-2-naphthoic acid solutions in dimethyl sulfoxide with solid potassium *t*-butoxide; fluorescence of the anions was measured with the appropriate phototube.

Paper Chromatographic Analysis of Products.—In the chemiluminescence of both the hydroxynaphthoic hydrazide and the hydroxyanthroic hydrazide, the sole fluorescent product was the corresponding carboxylic acid (Whatman No. 1 paper, descending, 8:1:1 ethyl alcohol–concentrated ammonia–water) (R_f of anthroate, 0.80; R_f of naphthoate, 0.82). After spraying with 0.1% acridine in ethanol, a dark violet spot of unknown identity appeared under ultraviolet light in both cases (R_f 0.22 in both cases).

Products of Oxidation of Linear Hydrazides.—A solution of β-naphthoic hydrazide (2.2343 g, 12.00 mmoles) in 0.465 *N* potassium *t*-butoxide in *t*-butyl alcohol (100 ml) was stirred for 6 days under O_2. At the end of this time a small amount of precipitate had formed but was kept in suspension by vigorous stirring. A 10-ml aliquot was pipetted into 1 *N* $NaHCO_3$ and extracted three times with 50-ml portions of chloroform. Evaporation of the extract gave 0.0828 g of thin layer chromatographically singular β-naphthoylhydrazone of β-naphthaldehyde. This material was sublimed at 200° to give 0.0807 g of the compound (0.239 mmole, 41%), mp 229.5–230.5°, lit.[52] mp 230°, and mmp 229–233°. The aqueous layer was acidified and extracted three times with chloroform (50 ml); the extract was evaporated, leaving 0.1241 g of acidic material. Paper chromatography showed one spot with the same R_f value as authentic β-naphthoic acid. The acidic material on sublimation gave 0.1157 g of β-naphthoic acid (0.672 mmole, 56%), mp 183–184°, lit.[53] mp 182–182.5°, and mmp 183.5–185°.

Experiments with benzhydrazide reported in Table II were conducted under similar conditions in 85:15 DMSO–*t*-butyl alcohol solutions.

Registry No.—3,5-Dihydroxybenzhydrazide, 7732-32-3; methyl 1-hydroxy-2-anthroate, 7732-33-4; VIII, 7732-34-5; O-methyldehydroluciferin ethyl ester, 7732-35-6; O-methyldehydroluciferin methyl ester, 7775-89-5; XIII, 7732-36-7; XI, 7732-37-8; 1,2-di-*o*-anisoylhydrazine, 7732-38-9; 1,2-di-*m*-anisoylhydrazine, 7732-39-0; 1,2-di-*p*-anisoylhydrazine, 849-82-1; 1-*o*-nitrobenzoyl-2-phenylsulfonylhydrazine, 7732-41-4; 1-anthraniloyl-2-phenylsulfonylhydrazine, 7732-42-5; X, 7732-43-6; V, 7732-44-7; VI, 5341-58-2; VII, 7732-46-9.

Acknowledgments.—We are grateful for the support of the National Institutes of Health (GM-10849).

(48) T. Kato, H. Yamanaka, and F. Hamaguchi, *Yakugaku Zasshi*, **85**, 45 (1965); *Chem. Abstr.*, **62**, 13068*h* (1965).

(49) H. Shirai, H. Oda, R. Amano, and E. Ishidi, *Nagoya Shiritsu Daiguku Yakugakubu Kiyô*, **5**, 61 (1957); *Chem. Abstr.*, **52**, 6252*i* (1958).

(50) We thank Dr. Oliver C. Zafiriou for the preparation of this compound.

(51) We thank Dr. Richard Morton for obtaining these spectra.

(52) A. Pinner, *Ann. Chem.*, **298**, 1 (1897).

(53) A. Kailan, *Monatsh. Chem.*, **28**, 1069 (1907).