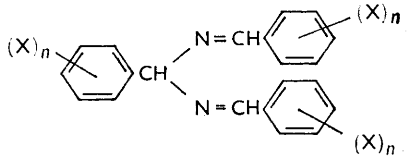
563. *The Effect of Substituent Orientation on Chemiluminescence*[1]

By Isadore Nicholson and Ronald Poretz

A series of chloro-derivatives of αα-bisbenzylideneaminotoluenes (hydrobenzamides) and 2,4,5-triphenylimidazoles (lophines) was synthesised. The molar average chemiluminescence intensities and chemiluminescence spectra on oxidation of the lophines were determined along with fluorescence, ultraviolet, and infrared spectra. The mechanism of the chemiluminescent oxidation of these compounds is discussed.

The chemiluminescent oxidation of substituted lophines (2,4,5-triphenylimidazoles) has been reported by Philbrook and Maxwell.[2] They studied the effects of different types of substituents on one of the three phenyl groups of lophine (XII; $X = NR_2$, OR, NH·COR, R, CO_2^-, O^-) on its chemiluminescence and noted a two-step light-intensity curve (an initial peak followed by a fairly long-lasting plateau). Based on their peak intensity readings, their ρ value from a Hammett plot was $-1{\cdot}96 \pm 0{\cdot}06$.

We independently studied the chemiluminescence of lophines having identically substituted phenyl groups, (VI)—(XI). Chlorine was chosen as the substituent since Dufford, Calvert, and Nightingale[3] (phenyl Grignard reagents) and Cook and Jones[4] (lophines) found that chloro-derivatives emitted the most intense chemiluminescence. Lophine was chosen as the base compound for chemiluminescence study since its three phenyl groups triple the effect of ring substitution.



$n = 1$

(I) X = H

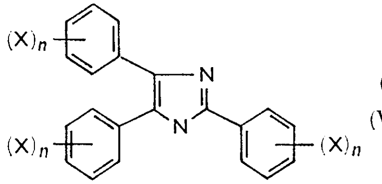
(II) X = *o*-Cl

(III) X = *p*-Cl

$n = 2$

(IV) X = 2,4-Cl_2

(V) X = 3,4-Cl_2



$n = 1$

(VI) X = H

(VII) X = *o*-Cl

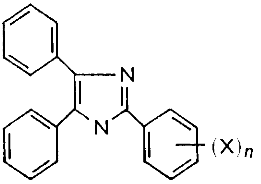
(VIII) X = *m*-Cl

(IX) X = *p*-Cl

$n = 2$

(X) X = 2,4-Cl_2

(XI) X = 3,4-Cl_2



The general synthetic approach was that of aminative condensation of the chlorinated benzaldehyde to the corresponding hydrobenzamide. Subsequent dehydrogenative pyrolysis of the hydrobenzamide yielded the desired chlorinated lophine. The reaction

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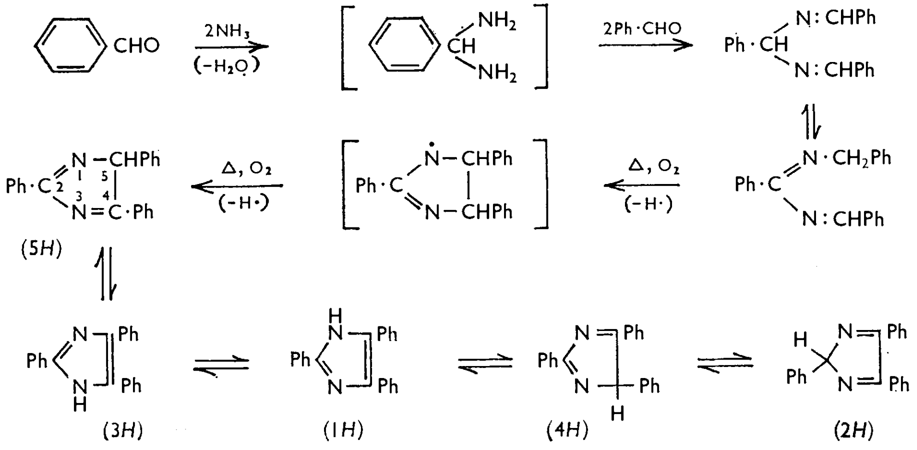
[1] Original data, R. Poretz, M.Sc. Thesis, Long Island University, 1963.

[2] G. E. Philbrook and M. A. Maxwell, *Tetrahedron Letters*, 1964, 1111.

[3] R. T. Dufford, S. Calvert, and D. Nightingale, *J. Amer. Chem. Soc.*, 1923, **45**, 2058; 1925, **47**, 95.

[4] A. H. Cook and D. G. Jones, *J.*, 1941, 278.

sequence is shown in the annexed Scheme, with possible intermediates as well as the tautomeric forms of the lophine.



A study of the pyrolysis step indicated the necessity of oxygen as the dehydrogenating agent. The new hydrobenzamides, (III), (IV), and (V), and four new lophines, (VII, VIII, X, and XI), have been synthesised.

Beside the usual absorptions for aromatic rings and aromatic substitution, the infrared spectra of the lophines (Figure 1) showed characteristic sharp absorption peaks at 735—743 (medium to strong) and 1200—1205 cm.$^{-1}$ (weak to medium). Similarly, the infrared spectra of the hydrobenzamides (Figure 1) showed a common sharp absorption peak at 1210—1220 cm.$^{-1}$ (weak to strong) and the characteristic very strong peak at 1630—1650 cm.$^{-1}$ for the C=N stretching vibration of Ar·CH=NR,[5] along with the expected absorption peaks for aromatic rings, aromatic substitution, and C–H stretching and deformation.

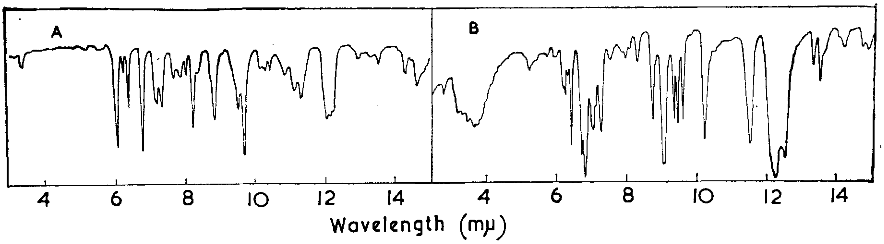


FIGURE 1. Representative infrared spectra: (A), 3,4-dichloro-αα-bis-(3,4-dichlorobenzylideneamino)toluene (V); (B), 2,4,5-tris-(2,4-dichlorophenyl)imidazole (X)

The ultraviolet spectra (Figure 2) of all hydrobenzamides examined showed two strong broad peaks, at 245—265 and 205—220 mμ. Two very weak absorptions appeared at 288—305 and 283—295 mμ. The ultraviolet spectra of lophines had two strong broad absorption regions, 300—320 and 225—240 mμ, the latter peak being stronger in the chloro-derivatives. The lack of typical absorption in the 220—800 mμ region with *o*-chlorolophine may be due to steric inhibition of resonance.[6]

The intensity of chemiluminescence from the oxidation of the lophines with an alkaline mixture of sodium hypochlorite and hydrogen peroxide was measured as a function of time (Figure 3). The lophines all gave similarly shaped curves, the general features being a sharp rapid rise in light-emission intensity followed by a typical gradual exponential

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[5] A. Kirrman and P. Laurent, *Bull. Soc. chim. France*, 1939, **6**, 1657.
[6] C. M. Moser and A. I. Kohlenberg, *J.*, 1951, 804.

decay curve. Only *o*-chlorolophine gave no appreciable emission when compared with the blank. The average maximum molar chemiluminescent intensity readings were determined (Table 1).

TABLE 1

	Average molar intensity			Average molar intensity	
Compound	Absolute (mA)	Relative	Compound	Absolute (mA)	Relative
(X)	39·3	1·0	(X)	40·0	1·0
(VIII)	257	6·6	(XI)	441	11·2
(IX)	171	4·4			

The relative intensities appear to be additive: the sum of the relative intensities of *meta* and *para* is 11, the value for the 3,4-derivative. The *meta*-substituent appears to be more powerful than the *para*-substituent in affecting intensity enhancement. *ortho*-Substitution diminishes the intensity, perhaps due to steric inhibition of electron delocalisation required in the excited state. These substitution effects are not in agreement with those obtained on the chemiluminescence from the reaction of chlorine-substituted Grignard reagents with molecular oxygen.[3]

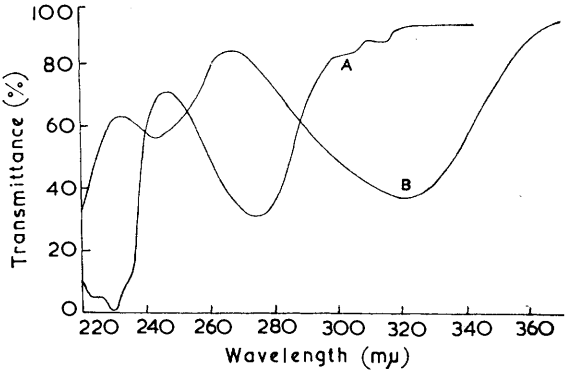


FIGURE 2. Representative ultraviolet spectra: (A), 3,4-dichloro-αα-bis-(3,4-dichlorobenzylideneamino(toluene (V); (B), 2,4,5-tris-(3,4-dichlorophenyl)imidazole (XI)

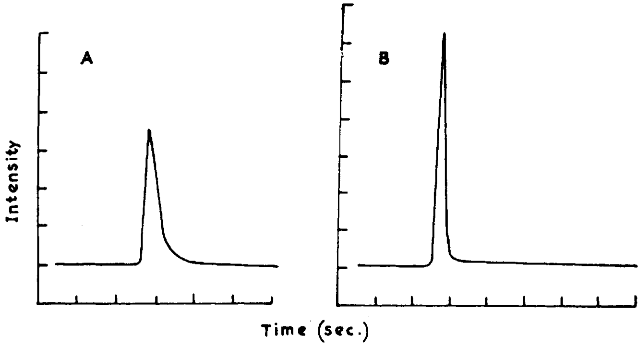


FIGURE 3. Chemiluminescence intensity duration recordings of (A) 2,4,5-tris-(3-chlorophenyl)imidazole (VIII); (B), 2,4,5-tris-(3,4-dichlorophenyl)imidazole (XI), at full-scale deflection of 1mA

From the second half of the time–intensity recordings (see Experimental under Time—Chemiluminescence Intensity Recordings), decay constants were derived using the equation, $I = I_0 \, e^{-(t/\alpha)}$, where I_0 is the intensity at time zero and α is a constant related to the time for total decay.

A plot of (log I) *vs* time (t) derived from the curve yielded α for each lophine. The half-lives, along with their reproducibilities, were calculated ($t_{\frac{1}{2}} = 2{\cdot}303\alpha \log 2$) for each lophine (Table 2). The data indicate that chlorine substitution speeds the decay of the light-emitting species and, in particular, *meta*-chlorine substitution increases the decay rate more than *para*-chlorine substitution.

TABLE 2

Half-lives (sec.) of lophine chemiluminescences

Compound ...	(VI)	(IX)	(VIII)	(X)	(XI)
$t_{\frac{1}{2}}$	3·7 ± 0·4	0·54 ± 0·06	0·26 ± 0·01	0·27 ± 0·01	0·011 ± 0·004

The essentially pure electron-withdrawing behaviour of *meta*-chlorine (inductive effect only) suggests that the excited-state species involved may be stabilised, and hence more readily formed, by an electron-rich environment, some of which can be supplied by resonance electron donation by *para*-chlorine substitution.

A Hammett relationship[7] was sought in replacing Hammett's equation, $\log K/K_0 = \rho\sigma$ by $\log I/I_0 = \rho\sigma$ where I_0 is the molar chemiluminescent peak intensity for lophine itself and I is the corresponding intensity for the substituted lophine.

The σ value for the 3,4-dichloro-substituted compound is taken as the sum of those of the *meta*- and *para*-substituents.[8]

Since lophine has three phenyl rings, the effect of the ring substituents was multiplied by that factor[8] (see Table 3).

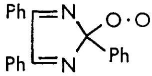
TABLE 3

Hammett ρ values of substituted lophines

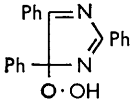
Compound	(VIII)	(IX)	(XI)
ρ	+0·729	+0·939	+0·829

The average ρ value is, therefore, +0·82 ± 12%. Jaffe[8] found a median precision of ±15% for ρ values of 3180 reactions. Obviously, these results are only suggestive and other isomers are being prepared to substantiate this value of ρ. The positive value of ρ indicates that the chemiluminescence peak intensity is increased by the presence of electron-withdrawing substituents. The abstraction of the tautomeric hydrogen (1*H*—5*H*, see reaction Scheme) may be closely related to the subsequent chemiluminescence intensity (concentration of the excited species or the rate of light emission by these species). Sonnenberg and White (see below) have found that, at —196°, lophine phosphoresces as strongly as 523 mμ in a basic solution. They therefore postulate that the chemiluminescence is due to the excited anion of lophine undergoing the transition of triplet (or singlet)-to-singlet.

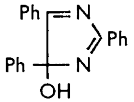
The most stabilised (*i.e.*, electron-withdrawing substituents) carbanions[9] and thioanions[10] are the most difficult to oxidise by molecular oxygen in basic solution. Bases are known to catalyse the peroxidation of active-hydrogen compounds[11] * and also to form hydroperoxide anion from hydrogen peroxide.[13] The course of the autoxidation of tetrahydrocarbazoles and other nitrogen heterocycles † suggests that a tertiary carbon (rather than nitrogen) hydroperoxide (XIII or XIV) is formed:



(XIII)



(XIV)



(XV)

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* Hayashi and Maeda[12] found that, as in luminol, alkylation of the imino-nitrogen prevents chemiluminessence.

† Hydroperoxides of heterocycles are prepared by the use of molecular oxygen or hydrogen peroxide.[14]

[7] L. P. Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 186.
[8] H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.
[9] G. A. Russell, A. J. Moye, and K. Nagpal, *J. Amer. Chem. Soc.*, 1962, **84**, 4154.
[10] T. J. Wallace, A. Shriesheim, and W. Bartok, *J. Org. Chem.*, 1963, **28**, 1313.
[11] A. V. Tobolsky and R. B. Mesrobian, " Organic Peroxides," Interscience, New York, 1954.
[12] T. Hayashi and K. Maeda, *Bull. Chem. Soc. Japan*, 1962, **35**, 2057.
[13] C. A. Burton, *Nature*, 1949, **163**, 444.
[14] See (*a*) A. G. Davies, " Organic Peroxides," Butterworths, London, 1961, p. 30; (*b*) E. G. Hawkins, " Organic Peroxides," Van Nostrand, Princeton, 1961, pp. 127—130.

A tertiary lophine hydroperoxide has now been reported isolated by J. Sonnenberg and D. M. White (*J. Amer. Chem. Soc.*, 1964, **86**, 5685) and the authors present some evidence to suggest (XIII) as its probable structure. The hydroperoxide was found to be chemiluminescent on treatment with base alone.

The decomposition of tertiary hydroperoxides by alkali has been investigated and the products were molecular oxygen and the tertiary alcohol, possibly by a cyclic mechanism.[15]

A tertiary alcohol (XIV) has been isolated as the product of photochemical oxidation of lophine.[16]

$$2R{\cdot}O{\cdot}OH \xrightarrow{\text{base}} O_2 + 2ROH$$

A complex of the excited products[17] (molecular oxygen[18] and the tertiary alcohol) might be yielding the observed chemiluminescence by the transitions $\pi^* \longrightarrow \pi$ or $\pi^* \longrightarrow n$.

E. H. White and M. J. C. Harding (*J. Amer. Chem. Soc.*, 1964, **86**, 5686) have isolated salts of dibenzoylphenylamidines, (A), from the chemiluminescent oxidation of lophine and they suggest the excited singlet or triplet state of the amidine salts, as the light emitters in the chemiluminescence. We propose the following scheme to account for the amidine formation:

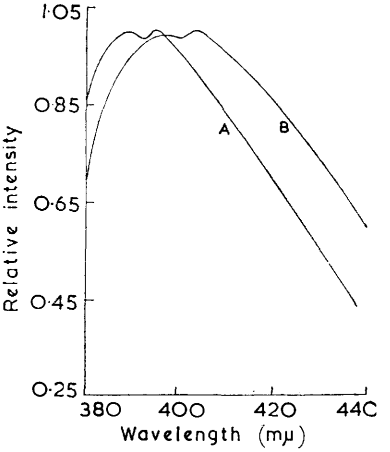


FIGURE 4. Fluorescence spectra of (A), lophine (VI); (B), 2,4,5-tris-(*m*-chlorophenyl)imidazole (VIII)

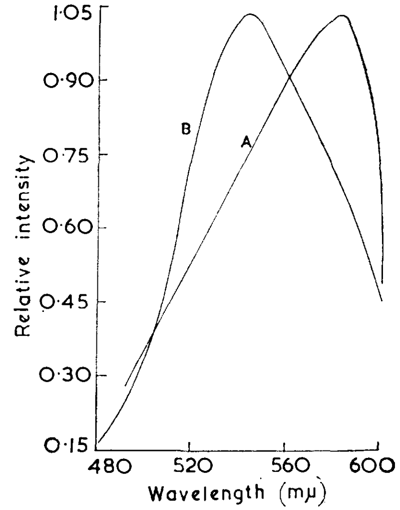
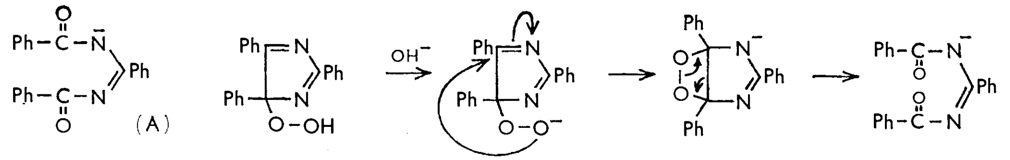


FIGURE 5. Chemiluminescence spectra of (A), lophine (VI); (B), 2,4,5-tris-(*p*-chlorophenyl)imidazole (IX)



Sonnenberg and White regard White and Harding's identification of the light emitter as " unlikely " since a basic solution of lophine amidine fluoresces very weakly. White and Harding, likewise, consider Sonnenberg and White's identification of the light emitter doubtful since triplet states in the liquid state at room temperature have been found to be completely quenched by oxygen.

[15] A. G. Davies, ref. 14*a*, p. 187.

[16] C. Dufraisse, A. Étienne, and J. Martel, *Compt. rend.*, 1958, **246**, 1337.

[17] E. H. White and M. M. Bursey, *J. Amer. Chem. Soc.*, 1964, **86**, 942.

[18] R. J. Browne and E. A. Orgyzlo, *Proc. Chem. Soc.*, 1964, 117.

Fluorescence spectra were obtained for lophine and its *m*-chloro-, *p*-chloro-, and 3,4-dichloro-derivatives. *o*-Chlorolophine gave no fluorescence.

Chlorine substitution, excepting the *ortho*-case, generally increases the fluorescence intensity (by galvanometer readings) and causes a bathochromic shift of the maximum fluorescence wavelength (Figure 4).

Chemiluminescence spectra of these same compounds were determined (Figure 5) and found not to be identical with the corresponding fluorescence spectra (see Table 4), indicating that regeneration of the starting compound does not occur. Etienne [19] noted the decomposition of *endo*-peroxides to the original aromatic hydrocarbon accompanied by chemiluminescence.

TABLE 4

Comparison of spectral peaks ($\lambda_{max.}$ in mμ)

Compound	Chemiluminescence	Fluorescence	Absorption
(VI)	580	389, 395	230, 309
(IX)	540	400—402	238, 317
(VIII)	550—570	398, 404	236, 314
(XI)	520—560	404	244, 323

The Stokes displacement of the lophines is, therefore, in the range 80—90 mμ. Chlorine substitution causes the chemiluminescence emission peak to be displaced toward shorter wavelengths indicating that the energy level of the excited state may be higher when electron-withdrawing substituents are present in the molecule.

EXPERIMENTAL

Substituted Hydrobenzamides.—*αα-Bisbenzylideneaminotoluene* (*hydrobenzamide*) (I). This compound was prepared by a method similar to that of Cottman.[20] Benzaldehyde (26·4 g., 0·246 mole) and concentrated ammonium hydroxide (90·0 g., 2·30 mole) were mixed, shaken vigorously, and set aside for 3 days in a stoppered flask at room temperature. The precipitated white cake was filtered, washed with 200 ml. of 20% aqueous methanol, and air dried. The crude product (24 g., 99·8%) gave white crystals, m. p. 104—105° (lit.,[20] 102°) (from ethanol).

o-*Chloro-αα-bis-*(o-*chlorobenzylideneamino*)*toluene* (II). This compound was prepared by the method of Hilbert *et al.*,[21] and had m. p. 106—107° (lit.,[21] 98—100°).

p-*Chloro-αα-bis-*(p-*chlorobenzylideneamino*)*toluene* (III). To 95% aqueous ethanol (75 ml.) was added *p*-chlorobenzaldehyde (31·0 g., 0·221 mole). Concentrated ammonium hydroxide (67·5 g., 1·78 mole) was added to this solution which was magnetically stirred at room temperature in a stoppered flask for 1 day, then set aside for 7 days. After the first 2 days of standing, a gummy oil separated, which solidified during the reaction period. The solid product was filtered, and washed with cold water and then cold ethanol. Attempted recrystallisation from methanol–water resulted in gums as well as small amounts of crystals. Upon recrystallisation from ethanol an emulsion was obtained, but with successive attempts using seed crystals of colourless crystals (17·8 g., 59·5%), m. p. 86·5—87·5°, were obtained. After three recrystallisations from ethanol, colourless *crystals*, m. p. 92·5—93·5°, were obtained (Found: C, 63·0; H, 3·85; Cl, 26·35; N, 6·4. $C_{21}H_{15}Cl_3N_2$ requires C, 62·8; H, 3·75; Cl, 26·45; N, 6·95%.

2,4-*Dichloro-αα-bis-*(2,4-*dichlorobenzylideneamino*)*toluene* (IV). To 2,4-dichlorobenzaldehyde (82·6 g., 0·490 mole) partly dissolved in 95% aqueous ethanol (270 ml.), was added concentrated ammonium hydroxide (259·2 g., 6·8 mole) with magnetic stirring. After 7 days at room temperature in a stoppered flask (without stirring), the precipitated white semi-solid gum was filtered and washed with cold water. The product was crystallised from ethanol giving colourless crystals (44·6 g., 55·1%), m. p. 113—117°. After recrystallisation once from acetone and twice from ethanol colourless *crystals*, m. p. 133·5—134°, were obtained (Found: C, 49·95; H, 2·4; Cl, 42·1; N, 5·55. $C_{21}H_{12}Cl_6N_2$ requires C, 50·5; H, 2·5; Cl, 41·0; N, 5·5%).

3,4-*Dichloro-αα-bis-*(3,4-*dichlorobenzylideneamino*)*toluene* (V). A solution of 3,4-dichlorobenzaldehyde (60·0 g., 0·34 mole) in 95% aqueous ethanol (200 ml.) was combined with concentrated ammonium hydroxide (194·4 g., 5·10 mole). After 6 days at room temperature in a

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[19] A. Étienne, " Traite de Chimie Organique," 1949, **17**, 1299.

[20] E. W. Cottman, *J. Chem. Educ.*, 1937, **14**, 236.

[21] G. Hilbert, L. Howard, R. Wiebe, and V. Gaddy, *J. Amer. Chem. Soc.*, 1932, **54**, 3128.

stoppered flask, a few crystals and a large white semi-solid mass formed. The precipitate was filtered and dissolved in hot ethanol. Upon slow cooling and with the addition of seed crystals, obtained from previous attempts, a mass of colourless crystals (38·2 g., 66·9%) was obtained. After two recrystallisations from ethanol, colourless *crystals*, m. p. 108·5—109·5°, were obtained (Found: C, 50·55; H, 2·55; Cl, 41·35; N, 5·45. $C_{21}H_{12}Cl_6N_2$ requires C, 50·5; H, 2·5; Cl, 41·0; N, 5·5%).

Substituted Lophines.—2,4,5-*Triphenylimidazole* (VI). This compound was prepared by the method of Laurent [22] and recrystallised from methanol, and twice from ethanol, m. p. 279·5—280° (lit.,[22] 275°).

2,4,5-*Tris*-(2-*chlorophenyl*)*imidazole* (VII). Tri-orthochlorohydrobenzamide (II) (58·0 g., 0·144 mole) was placed in a 125 ml. distilling flask. An oxygen inlet tube and thermometer were fitted into the neck of the flask. The material was heated in an electrically controlled sand-bath so that the temperature rose to 260° during 1 hr. Extra dry oxygen was bubbled into the molten mixture at a moderate rate. The temperature of the melt was held at 265—270° for 5½ hr., during which the melt changed from colourless to dark brown.

The cooled, dark glass-like solid was slurried in hot benzene (*ca.* 50 ml.) and chromatographed on a column (2·5 × 25 cm.) of alumina in light petroleum. On elution with benzene (1 l.), three major fractions were collected and elution with 50% chloroform in benzene (200 ml.) yielded a fourth fraction. A final fraction was obtained using 100% chloroform (50 ml.). Grey material remaining at the top of the column was removed and recrystallised from the minimum amount of benzonitrile. This product (1·5 g. had m. p. 266—269°). Further purification by digestion in acetonitrile, dissolution in hot water, and basification with concentrated ammonium hydroxide resulted in the precipitation of colourless crystals (0·65 g.). Recrystallisation from ethanol gave colourless crystals (0·20 g., 3·5%), m. p. 170·5—173° (lit.,[21] 169—170°).

2,4,5-*Tris*-(3-*chlorophenyl*)*imidazole* (VIII). In a flask equipped with a gas-inlet tube and thermometer, was placed the gummy reaction product (*ca.* 55 g., 0·16 mole) from 3-chlorobenzaldehyde and concentrated ammonium hydroxide. This material was heated for 1½ hr. up to 270° with the passage of oxygen at a slow rate and then at 270° for a further 4¾ hr.

Upon cooling, the reaction product was observed to consist of an amber-coloured glassy lower layer covered by a soft yellow material. The lower layer (*ca.* 50 g.) was removed and digested in ethanol yielding a yellow hard product (20·7 g.). A portion (9·6 g.) of this was separated into two fractions, (i) (1·5 g.) and (ii) (4·0 g.), m. p. 238—245°, by fractional crystallisation. Recrystallisation of fraction (i) from ethanol gave pale yellow *crystals* (0·18 g., m. p. 254—256·5° (Found: C, 63·45; H, 3·25; Cl, 26·5; N, 6·35. $C_{21}H_{13}Cl_3N_2$ requires C, 63·1; H, 3·3; Cl, 26·6; N, 7·0%).

2,4,5-*Tris*-(4-*chlorophenyl*)*imidazole* (IX). The hydrobenzamide (III) (15·7 g., 0·0390 mole) was placed in a distillation flask fitted with a gas-inlet tube and a thermometer. The material was heated to 250° during ¾ hr. and held at 245° for 5½ hr. with continuous passage of oxygen at a moderate rate. The amber, glass-like pyrolysis material was dissolved in hot ethanol which was then evaporated to about 25 ml. Upon cooling, a yellow product (9·07 g.) formed. Recrystallisation of 6·26 g. of this substance from benzene then ethanol gave greenish yellow crystals (0·59 g., m. p. 280—281·5° (lit.,[4] 268°) (Found: C, 62·9; H, 3·45; Cl, 25·85; N, 6·4. Calc. for $C_{21}H_{13}Cl_3N_2$: C, 63·1; H, 3·3; Cl, 26·6; N, 7·0%).

2,4,5-*Tris*-(2,4-*dichlorophenyl*)*imidazole* (X). In a 250 ml. distillation flask fitted with a gas-inlet tube and thermometer, the hexachloro-compound (IV) (28·36 g., 0·05615 mole) was heated to 275° during 1½ hr. and kept at 265—275° for 7 hr. with oxygen bubbling into the melt.

The cooled, dark reaction product was dissolved in refluxing ethanol (*ca.* 1·8 l.) in the presence of activated charcoal. After 2 hr. the solvent was removed and the residue chromatographed on a column (3·8 × 21·3 cm.) of activated alumina (heated at 400° for 2 hr.) in benzene. Elution with benzene (2·3 l.) gave three fractions. Evaporation to dryness and crystallisation from ethanol of the first two fractions gave a small amount of crystals. Extraction with dimethylformamide, followed by the addition of water, to the clear extract, gave tan crystals, m. p. 220—230°. Successive recrystallisations from dimethylformamide–water yielded light tan *crystals*, m. p. 228—230·5° (Found: C, 49·35; H, 2·1; Cl, 43·0; N, 5·65. $C_{21}H_{10}Cl_6N_2$ requires C, 50·05; H, 2·0; Cl, 42·2; N, 5·55%).

2,4,5-*Tris*-(3,4-*dichlorophenyl*)*imidazole* (XI). In a test-tube, fitted with oxygen inlet and

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[22] A. Laurent, *J. prakt. Chem.*, 1845, **35**, 455.

outlet tubes, was placed the hydrobenzamide (V) (2·19 g., 0·00434 mole). The material was heated for 5¼ hr. at 250—275° (sand-bath temp.).

After being cooled, the dark solid material was refluxed in excess of benzonitrile with activated charcoal for 30 min. After hot filtration, evaporation, and cooling, crystals (0·52 g.), m. p. 112—226° were collected. This material was twice recrystallised yielding 0·14 g. of product, m. p. 261—264°. Recrystallisation of 0·064 g. of this material produced light yellow *material* (0·036 g., m. p. 269—271° (Found: C, 50·9; H, 2·15; Cl, 41·1; N, 5·5. $C_{21}H_{10}Cl_6N_2$ requires C, 50·05; H, 2·0; Cl, 42·2; N, 5·55%).

Investigation of the Optimum Conditions for the Pyrolytic Production of 2,4,5-*Tris*-(3,4-*dichlorophenyl*)*imidazole*.—A series of experiments was conducted in order to study the effects of heat, time, and atmosphere on the pyrolytic production of the lophine from the hydrobenzamide (V). In successive runs, compound (V) (*ca.* 1·5 g., 0·0029 mole) was heated in a test-tube by an electrically controlled sand-bath. The bath was held at fixed temperature (150—330°) for a fixed period of time (1¾—46 hr.) under nitrogen or pure oxygen. After pyrolysis, the cooled reaction product was extracted with hot ethanol, cooled, and filtered, yielding crude alcohol-insoluble product. In general, lophine was found to be less alcohol-soluble than the corresponding hydrobenzamide. The results are summarised in Table 5.

TABLE 5

The effect of heat, time, and atmosphere on the preparation of 2,4,5-tris-(3,4-dichlorophenyl)imidazole by pyrolysis of 3,4-dichloro-αα-bis-(3,4-dichlorobenzylideneamino)toluene

Sand-bath temp.	Time (hr.)	Atmosphere	Product * (%)	M. p.
150—170°	22	Air	31	120—256°
190	46	Air	25	125—258
210—280	22	Air	55	130—255
310	2	Air	15	110—263
295—330	3	Air †	33	132—263
300	20	Nitrogen	4	—
295—305	7	Oxygen	54	112—265

* Yield of ethanol-insoluble material after extraction with hot solvent. † The air in this run was continuously bubbled into the melt.

Ultraviolet and Visible Spectra.—Hydrobenzamides. The ultraviolet and visible spectra of compound (I), (III), (IV), and (V) were obtained for approximately 1·5 × 10^{-5}M-solutions in cyclohexane using a Bausch and Lomb model Spectronic 505 with 1 cm. quartz cells.

Lophines. The ultraviolet and visible spectra of compounds (VI), (VII), (VIII), (IX), and (XI) were obtained for approximately 1·6 × 10^{-5}M-solutions in dioxan using the same instrument and cells as above.

Infrared Spectra.—Hydrobenzamides. A Perkin-Elmer model Infracord spectrophotometer was employed to obtain the infrared spectra (2·5—15 μ) of compounds (I), (II), (III), (IV), and (V) as KBr pellets (*ca.* 1% by weight).

Lophines. The infrared spectra of compounds (VI)—(XI) were obtained as KBr pellets (*ca.* 1% by weight) using the same instrument as above.

Fluorescence Spectra.—Lophines. The fluorescence spectra of 1·4 × 10^{-3}M ethanol solutions of compounds (VI), (VIII), (IX), and (XI) were obtained using a Beckman model DU spectrophotometer with a fluorescence accessory. Excitation was produced by the emission of the 361 mμ radiation of a mercury-vapour lamp.

Chemiluminescence Spectra.—Lophines. The approximate chemiluminescence spectra of compounds (VI), (VIII), (IX), and (XI) were obtained using a Beckman model DU spectrophotometer with a fluorescence accessory. This was accomplished by the preliminary mixing of 0·5 ml. of 1·4 × 10^{-3}M ethanolic solution of the lophine, 0·5 ml. of 0·32% hydrogen peroxide in ethanol, and 0·5 ml. of 0·8N-potassium hydroxide in 25% aqueous ethanol in a 1 cm. Pyrex cuvette. The reaction was initiated by the injection into the cell, in the sample compartment, of 1 ml. of 1% aqueous solution of sodium hypochlorite.

Time–Chemiluminescence Intensity Recordings.—Lophines. The chemiluminescence intensity duration experiments on compounds (VI)—(XI) were carried out using an RCA model 5819 photomultiplier tube with a current of 6 mA and a divided potential of 750 v.

The experiments were performed by initially mixing 10 ml. of the lophine (104×10^{-3}M), 10 ml. of potassium hydroxide (0·8N in 25% aqueous ethanol), and 10 ml. of hydrogen peroxide (0·32% in ethanol) in a florence flask, magnetically stirred. The reaction was allowed to proceed by the injection of 25 ml. of sodium hypochlorite (1% aqueous solution) into the flask which was in a light-tight compartment. The output (in mA) of the photomultiplier tube was recorded using a Bausch and Lomb model VOM-5 recorder at a chart speed of 20 in./min.

In this manner, " time *vs* light intensity " recordings were obtained for compounds (VI), (VIII), (IX), (X), and (XI). Analyses (see Discussion) of these curves yielded half-lives and maximum molar intensity values.

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DEPARTMENT OF CHEMISTRY, LONG ISLAND UNIVERSITY,
BROOKLYN 1, NEW YORK, N.Y., U.S.A.

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