was also 10^{-4} *M* in leuco crystal violet and 2×10^{-4} *M* in toluenesulfonic acid. From the amount of crystal violet dye obtained as determined spectrally, and from the reaction stoichiometry (1 mol of dye per biimidazole dissociated) and quantum yield of unity,[9] both experimentally determined, radical concentration immediately after the flash was obtained.

Rates of Triarylimidazolyl Radical Dimerization.—A Perkin-Elmer "Spectrachord" Model 400A was set up in a dark room to record absorbance (at λ_{max} of each radical) *vs.* time. A solution of biimidazole in carefully purified benzene was irradiated until a steady state was established and absorbance was recorded for several half-lives and determined eventually at "$t = \infty$." From the usual second-order expression, the slope of $1/A$ plotted *vs.* *t* gave k/ϵ (cell length = 1 cm) reported in Table I. From these values *k* was calculated.

Extreme care was necessary to free solvents of impurities which react with radicals. Normally, three distillations of reagent grade solvent sufficed. Even with carefully purified solvents, radical dimerization was not the exclusive fate of radicals in the media studied. A small but detectable deviation from strict second-order was apparent sometime during the second half-life[4] and A_∞ was slightly greater than *A* measured prior to irradiation. Rate constants were taken from the first half-life.

Rates in 50:50 vol methanol-benzene were measured both in the spectrometer and in the flash photolysis apparatus used to determine extinction coefficients. An oscillographic trace of absorbance *vs.* time was photographed.

Registry No.—**1a**, 1724-47-6; **1b**, 29898-43-9; **1c**, 29898-44-0; **1d**, 29897-74-3; **1e**, 29898-46-2; **1f**, 29898-47-3; **1g**, 29898-48-4; **1h**, 29898-49-5; **1i**, 29843-47-8; **1j**, 29843-48-9; **1k**, 29898-50-8; **1l**, 29898-51-9; **1m**, 29898-52-0; **1n**, 29898-53-1; **1o**, 29843-49-0; **2a**, 7189-41-5; **2b**, 29898-55-3; **2c**, 29898-56-4; **2d**, 7189-82-4; **2e**, 7189-80-2; **2f**, 29936-66-1; **2g**, 29898-58-6; **2h**, 29843-51-4; **2i**, 7189-78-8; **2j**, 29898-60-0; **2k**, 29843-52-5; **2l**, 29898-61-1; **2m**, 7189-83-5; **2n**, 29898-63-3; **2o**, 29898-64-4; **4a**, 484-47-9; **4b**, 1728-95-6; **4c**, 1740-23-4; **4d**, 1707-67-1; **4e**, 5496-32-2; **4f**, 5496-33-3; **4g**, 5496-39-9; **4h**, 29898-72-4; **4i**, 29898-73-5; **4j**, 5496-38-8; **4k**, 1740-25-6; **4l**, 29898-76-8; **4m**, 1740-05-2; **4n**, 29898-78-0; **4o**, 29898-79-1.

Acknowledgment.—We sincerely thank Dr. Catherine E. Looney for the infrared spectral work and for many helpful discussions. The generous support and assistance of the Radiation Physics Laboratory are gratefully acknowledged, especially Drs. A. MacLachlan, Richard Bennett, Roland Riem, David Reitz, Reid Kellogg, and Victor Hanson who were most generous in providing facilities and assistance.

Some Reactions of Triarylimidazolyl Free Radicals

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Received February 12, 1970

Triarylimidazolyl free radicals **2** were found to oxidize electron-rich substances by rapid electron abstraction from *tert*-amines, iodide ion, and metal ions and hydrogen atom abstraction from phenols, mercaptans, primary and secondary amines, and activated C–H compounds. The rate constants for electron abstraction from *tert*-amines were related to σ^+ values *via* oxidation potentials which were determined by cyclic voltametry.

The formation of triarylimidazolyl free radicals **2** from the thermal or photolytic dissociation of hexaarylbiimidazoles **1** has been reported.[2-6] These radicals are known to dimerize to regenerate a hexaarylbiimidazole, usually one of the two favored isomers **1** or **3** (Scheme I).[3,5,7] They are also known to react with nitric oxide to give *N*-nitrosotriarylimidazoles[2] and to react with hydrogen peroxide to give 4-hydroperoxytriarylimidazoles.[8]

We report here further exploration of triarylimidazolyl radical chemistry. Two types of oxidations by **2** were studied: abstraction of electrons and of hydrogen atoms. Both reactions normally yield triarylimidazole **4** as the reduction product, the proton being obtained from the solvent if necessary. Results are summarized in Scheme II. Examples of representative reactions are the subject of mechanistic studies reported in subsequent papers.[9-13]

Radicals **2** do not react with aromatic hydrocarbons, aliphatic alcohols, oxygen, or vinyl monomers at rates which compete detectably with dimerization or the oxidation reactions studied. Thus, benzene and methanol could be used as solvents under conditions employed without observing side products due to their presence. Reactions proceeded equally well with or without degassing. When radicals **2a** or **2b** were produced photolytically in neat monomers such as ethyl acrylate, acrylonitrile, or pentaerythritol triacrylate, no polymerization could be detected.

The reactivity of photolytically and thermally produced **2** was identical. Hence, in the reactions studied, only the ground state **2** is presumed to be involved.

Reactions 1–4 (Scheme II) involve as the first step electron abstraction by **2** which is two to three orders of magnitude faster than dimerization of **2**.[9,13,14]

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(1) To whom inquiries should be addressed.

(2) T. Hayashi and K. Maeda, *Bull. Soc. Chem. Jap.*, **33**, 565 (1960).

(3) T. Hayashi and K. Maeda, *ibid.*, **35**, 2057 (1962).

(4) T. Hayashi and K. Maeda, *J. Chem. Phys.*, **32**, 1568 (1960).

(5) H. Zimmermann, H. Baumgartel, and F. Bakka, *Angew. Chem.*, **73**, 808 (1961).

(6) S. M. Blinder, M. J. Peller, N. W. Lord, L. C. Aamodt, and N. S. Ivanclinkov, *J. Chem. Phys.*, **36**, 540 (1962).

(7) L. A. Cescon, Belgium Patent 509,415 (Aug 30, 1963).

(8) J. Sonnenberg and D. M. White, *J. Amer. Chem. Soc.*, **86**, 5685 (1964).

(9) A. MacLachlan and R. H. Riem, *J. Org. Chem.*, **36**, 2275 (1971).

(10) R. E. Kellogg and R. H. Kooser, personal communication.

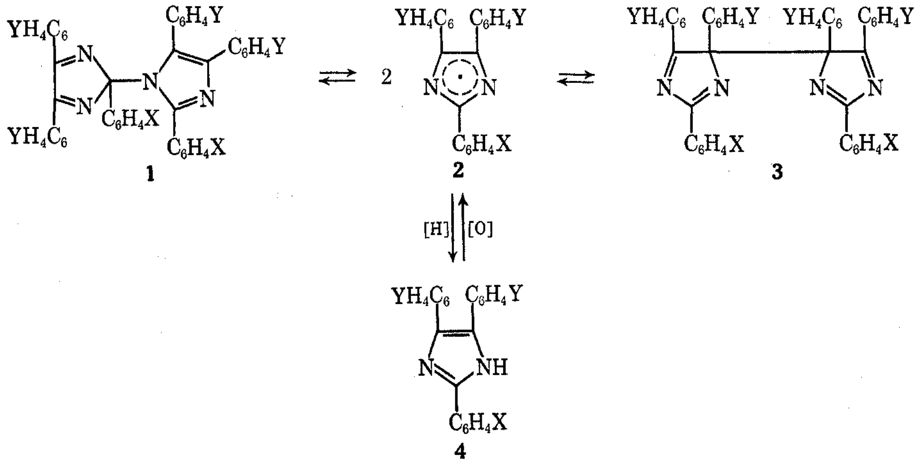
(11) R. L. Cohen, *J. Org. Chem.*, **36**, 2280 (1971).

(12) R. L. Cohen, private communication.

(13) R. H. Riem, A. MacLachlan, G. R. Coraor, and E. J. Urban, *J. Org. Chem.*, **36**, 2272 (1971).

(14) L. A. Cescon, G. R. Coraor, R. Dessauer, E. F. Silversmith, and E. J. Urban, *J. Org. Chem.*, **36**, 2262 (1971).

SCHEME I



a, X = H; Y = H c, X = 4-MeO; Y = H
b, X = 2-Cl; Y = H d, X = 2-Br; Y = H

The inability of 2 to initiate vinyl polymerization is not due to an energetic deficiency since the intermediate products (radicals or radical ions) formed in reactions 1 and 4 do initiate polymerization. Thus, if a mixture of *N,N'*-dimethylaniline, a biimidazole, and a monomer such as pentaerythritol triacrylate is photolyzed, a hard polymer is formed. If the *N,N*-dimethylaniline is omitted, no polymerization occurs, no monomer double bond loss is evident from the infrared spectrum, and radical dimerization is observed at a rate normal for inert solvents.

The failure of 2 to initiate polymerization may result from steric or resonance factors; however, justification for neither is evident. However, other delocalized radicals which contain nitrogen atoms, especially when hindered, do not initiate polymerization and sometimes inhibit it.[15]

Reaction 4 involves stoichiometrically 1 mol of leuco dye salt, 1 mol of biimidazole, and 1 equiv of acid. MacLachlan and Reim[9] found the mechanism to be

$$1 \longrightarrow 2$$

$$7 + 2 \xrightarrow{k} 4 + 7\cdot^{+}$$

$$7\cdot^{+} \rightleftarrows 7\cdot + H^{+}$$

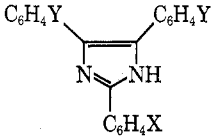
$$7\cdot + 7\cdot^{+} \longrightarrow 8 + 7$$

where $7\cdot^{+}$ and $7\cdot$ are the intermediate radical ion and radical, respectively, of the triarylmethane leuco dye 7. With proper choice of components and conditions, this reaction can give unit quantum yield of dye even in the presence of oxygen.[10]

Cohen[11] examined the effect of substitution on the rate of disappearance of 2 in reaction 4. His selection of compounds was designed to emphasize steric variations in 2. A plot of Cohen's rate constants *vs.* $-E_{p/2}$ values for various imidazole–imidazolyl radical redox couples (Table I) (Figure 1) is linear. The linear relationship of $E_{p/2}$ and σ^{+} values is shown by Table II and Figure 2. Rate differences in reaction 4 which result from substituents X are thus strongly influenced by electron delocalization.

TABLE I

CYCLIC VOLTAMMETRIC OXIDATION–REDUCTION OF TRIARYLIMIDAZOLES IN ACETONITRILE SOLUTION



X	Y	Registry no.	$-E_p$, V *vs.* sce	$-E_{p/2}$, V *vs.* sce	Log *k* (step 1), reaction 4[a]
H	H	484-47-9	0.923[b]	0.808[b]	6.08
2-Cl	H	1707-67-1	0.994	0.891	7.45
2-F	H	1740-26-7	1.024	0.904	7.13
2-Br	H	1740-25-6	1.036	0.931	7.50
2-Me	H	13730-60-4	0.889	0.774	6.15
2-NO_2	H	29864-19-5	1.088	0.963	7.63
2-MeO	H	1965-19-1	0.899	0.862	6.20
H	4-MeO	7044-99-7	0.738	0.668	4.41
H	2-MeO	29864-26-4	0.898	0.718	5.40

[a] From Cohen.[11] [b] Compare with values obtained by reduction of 2a; $-E_p = 0.976$, $-E_{p/2} = 0.816$.

Rate constants of reaction 4 with variously substituted leuco dyes have been found by Cohen[12] to correlate with σ. Delocalization effects were specifically excluded in the leuco dyes employed in that study. Reaction 1 actually is an exact model of the first step in reaction 4 with the added degree of freedom that substituents para to the dimethylamino group can be varied to include those capable of strong delocalization effects. This reaction has been studied kinetically with various para substituents, and rate constants were found to correlate with σ^{+}.[13]

Reactions 6–10, formally, involve hydrogen atom abstraction. The lower rate constant observed by MacLachlan, *et al.*, when O-deuterated phenols were used instead of normal phenols, was consistent with a rate-determining hydrogen atom abstraction in reaction 6.[13] Reactions 7–10 have not been studied mechanistically as yet; all are sufficiently fast to preclude observable radical dimerization. Rate constants of reactions 5 and 6 (with variously substituted phenols and hydroquinones) were found to be several orders of magnitude greater than that for radical dimerization.

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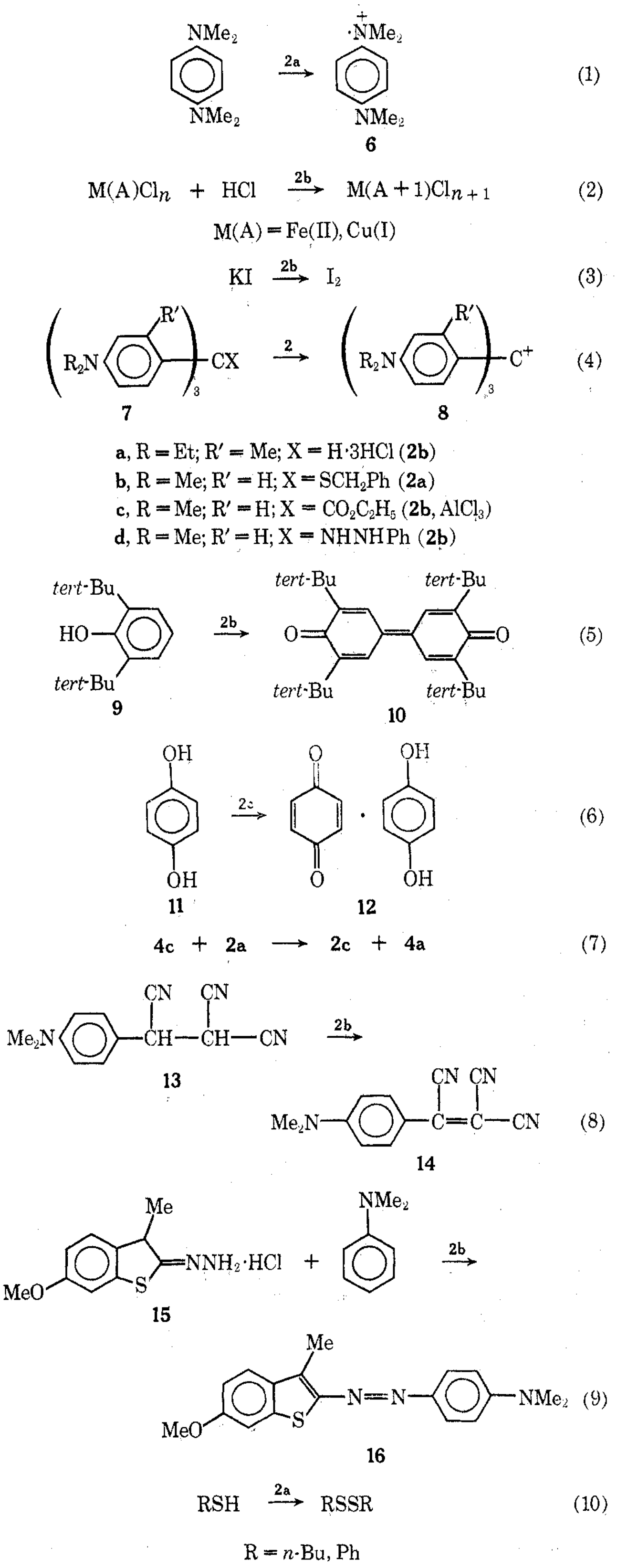
[15] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 163.

SCHEME II



Because visible spectra of radicals **2** vary considerably, reaction 7 can serve as a convenient method for determining the relative oxidation potential of different radicals. For example, reddish purple **2a** (formed by adding to the reaction mixture its less stable dimer **3a**) rapidly oxidized the colorless imidazole **4c** to a blue radical **2c**. Colorless imidazole **4a** was the other product.

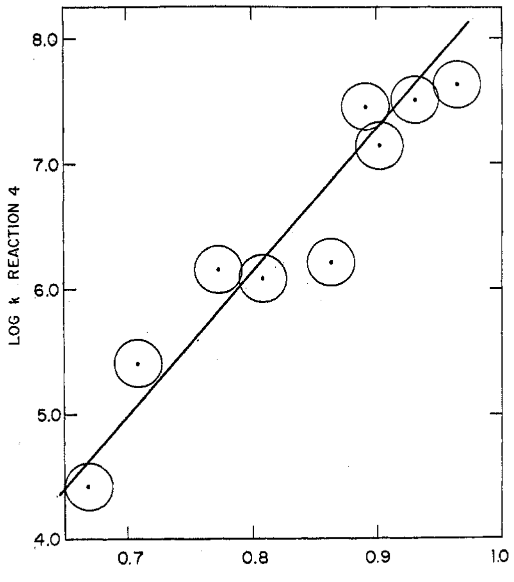
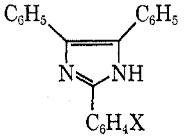


Figure 1.—Plot of rate constants of various imidazolyl free radicals in reaction with tris(4-diethylamino-2-methylphenyl)-methane trihydrochloride *vs.* the half-wave potential of the reversible oxidation of parent triarylimidazoles.

TABLE II

OXIDATION POTENTIALS OF SOME TRIARYLIMIDAZOLES IN ACETONITRILE SOLVENT



X	Registry no.	$-E_p$ V *vs.* sce	$-E_{p/2}$ V *vs.* sce	σ^a	$\sigma^{+\,a}$
H		0.923	0.808	0.00	0.00
4-MeO	1728-95-6	0.716	0.641	−0.27	−0.78
3-Cl	29898-73-5	0.918	0.778	0.37	0.37
4-Cl	5496-32-2	0.978	0.928	0.23	0.11
3-Br	29913-29-9	1.038	0.878	0.39	0.39
4-Br	5496-33-3	0.981	0.856	0.27	0.15
4-I	29936-60-5	0.974	0.768	0.30	0.13
3-F	29913-31-3	0.990	0.840	0.34	0.35
4-F	2284-96-0	0.931	0.836	0.06	−0.07
4-Me	5496-31-1	0.850	0.765	−0.17	−0.31
3-NO_2	5496-38-8	1.236	0.986	0.71	0.66
4-NO_2	5496-39-9	0.969	0.919	0.78	0.78
4-CN	29898-72-4	1.121	0.936	0.66	0.66
3,4-Benzo[b]	13866-85-8	0.882	0.787	0.48	−0.13
4-Me_2N	1728-97-8	0.461	0.376	−0.83	−1.70

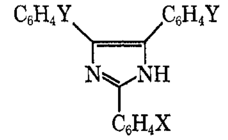
[a] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 2, 334 (1964). [b] That is, "C_6H_4X" = β-naphthyl.

Redox potentials, $-E_{p/2}$, of imidazole–radical systems provide a quantitative ranking of the oxidizing ability of different radicals. Some $-E_{p/2}$ values determined by cyclic voltammetry appear in Tables I and II.

A number of additional reactions were carried out on a crude scouting basis to test the generality of this oxidation technique. Thus, irradiation of a 1:4 dimethylformamide–methanol solution of *N*,*N*-diethyl-*p*-phenylenediamine, thenoylacetonitrile, and **1b** gave a magenta-colored product as expected for the "oxidative coupling" product, 2-(4-diethylaminophenylimino)-3-thenylpropionitrile. Similarly, irradiation of a solu-

TABLE III

PREPARATION OF TRIARYLIMIDAZOLES



X^a	Y	Recrystn solvent	Yield, %	Mp, °C	λ_{max},[b] mμ	Formula	Lit. Mp, °C	Lit. Ref
4-F	H	EtOH–H_2O	98	254–255	303	$C_{21}H_{15}N_2F$	243–244 dec	*c*
2-OMe	H	EtOH	89	207.5–208.5	308	$C_{22}H_{18}N_2O$	210–210.5	*d*
2-Me	H	PhH–EtOH	98	252.5–253.5	294	$C_{22}H_{18}N_2$	244–246	*e*
H	2-OMe	PhH–Hexane	88	175.5–176.5	303	$C_{23}H_{20}N_2O_2$		
H	4-OMe	PhH	99	197.5–198.0	298	$C_{23}H_{20}N_2O_2$		
3-Br	H	PhH–Tetrahydrofuran	91	302–303	312	$C_{21}H_{15}N_2Br$		
4-I	H	PhH	100	267.5–268.5	315	$C_{21}H_{15}N_2I$		
3-F	H	EtOH–H_2O	98	254.5–255.0	295	$C_{21}H_{15}N_2F$		
2-F	H	EtOH–H_2O	99	254.5–255.0	295	$C_{21}H_{15}N_2F$		
4-Me	H	EtOH	91	234.5–235.5	300[f]	$C_{22}H_{18}N_2$	237–237.5	*d*
4-NMe$_2$	H	EtOH	100	258–259		$C_{23}H_{21}N_3$	259.5–260	*d*
3,4-Benz[g]	H	EtOH	84	277–278	*h*	$C_{25}H_{18}N_2$		

[a] Satisfactory combustion analytical data for C, H, and N (±0.3%) were provided for all of the compounds of this table: Ed. [b] In MeOH. [c] G. E. Philbrook, M. A. Maxwell, R. E. Taylor, and J. R. Trotter, *Photochem. Photobiol.*, 4 (6), 1175 (1965). [d] D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964). [e] S. Kori and S. Narisawa, *Asaki Garasu Kenkyu Hokoku*, **12**, 55 (1962). [f] In acetonitrile. [g] Thus, the imidazole is substituted in its 2 position with α,β-naphthyl. [h] 232, 271, 281, 313 mμ.

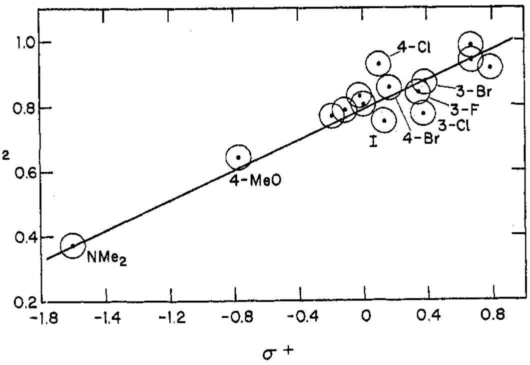


Figure 2.—Oxidation potentials of some substituted triphenylimidazoles plotted *vs.* σ^+ values for their substituents.

tion of *N*,*N*-dimethyl-*p*-phenylenediamine, phenol, and **1b** gave a blue color typical of 4-(*N*,*N*-dimethylaminophenylimino)cyclohexadienone. Also, irradiation of a benzene solution of phenothiazine and **1d** gave the blue-green color of oxidized phenothiazine; similarly, 10-propionyl-3,7-bis(dimethylamino)phenothiazine and **1b** in acetone produce methylene blue. In each case, products were identified by comparison with known dye spectra. If the biimidazole was omitted from the above mixtures, no color developed.

It is thus obvious that radicals **2** can serve as highly selective oxidizing agents. When generated from biimidazoles photochemically, a convenient and versatile means is provided for carrying out photoinduced oxidations with high quantum yield without the problem of triplet quenching by oxygen.

It is probably true that all reactions studied involve electron abstraction or hydrogen abstraction. However, formally, a wide variety of organic oxidation reactions are represented: O–H, N–H, S–H, and C–H bond cleavage (reactions 6, 7, 8, and 10), oxidative coupling (reactions 5, 9, and 10), and electron abstraction (reactions 1–4).

Experimental Section

Reagents. Triarylimidazoles (4).—Samples of **4** (Table III) were prepared by previously described methods.[11,14]

Hexaarylbiimidazoles (2).—Samples of **2** were obtained as described.[11,14] 2-Methoxyphenyl-4,5-diphenylimidazole gave **2c** in 87% yield: λ_{max} ~270 mμ; ir 1497, 1551 cm^{-1} (lit.[16] mp 182–185°; ir 1502, 1555 cm^{-1}).

Tris(4-dimethylaminophenyl)benzylthiomethane (7b).—A solution of 8.1 g of crystal violet in 50 ml of dry dimethylformamide was added to a mixture of 20 ml of α-toluenethiol, 50 ml of dry dimethylformamide, 50 ml of dry benzene, and 1 g of a 52% dispersion of sodium hydride in mineral oil. Removal of the solvent under vacuum left a colorless solid. Recrystallization (acetone) gave 8.4 g of white solid, mp 190°.

Anal. Calcd for $C_{32}H_{37}N_3S$: C, 77.5; H, 7.5; N, 8.5; S, 6.5. Found: C, 77.5; H, 7.5; N, 8.3; S, 6.5.

Tris(4-dimethylaminophenyl)ethoxycarbonylmethane (7c).—The method of Guyot[17] was used.

1-Tris(4-dimethylaminophenyl)methyl-2-phenylhydrazine (7d).—Tris(4-dimethylaminophenyl)methanol (8 g) was heated with 10 g of phenylhydrazine at 100–120° for 1 hr under nitrogen. Ether (50 ml) was added to the cooled mixture followed by 75 ml of ethanol. A yellow solid (7.1 g, 59%) crystallized, mp 171–172°.

Anal. Calcd for $C_{31}H_{37}N_5$: C, 77.6; H, 7.8; N, 14.6. Found: C, 77.9; H, 7.6; N, 14.4.

1,2,2-Tricyanoethyl-*N*,*N*-diethylaniline (13).—A sample supplied by Dr. B. C. McKusick was used without further purification.

Other Reagents.—Eastman White Label or Reagent Grade (from other manufacturers) were used without further purification.

Acetonitrile in 1-l. batches was dried by passage four times through a 4-ft column in diameter containing 6 in. of Linde 3 Å molecular sieves on the bottom, and the remainder filled with 13X molecular sieves. Acceptability was determined by a good blank (flat) polarogram after the solvent was made 0.5 *M* with $LiClO_4$. Imidazoles were dried at 110° (0.1 mm) for 8 hr over P_2O_5.

Equipment. Radiation Sources.—The sun lamp, 275-W input, was manufactured by General Electric Co. The mercury-xenon flash lamp used had 100-W input, 2400 effective candle second output, (450 μF at 475 V), and spectral output centers at

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(16) D. M. White and J. Sonnenberg, *J. Amer. Chem. Soc.*, **88**, 3825 (1966).

(17) M. A. Guyot, *R. Acad. Sci.*, **144**, 1051 (1907); *ibid.*, 1122 (1907).

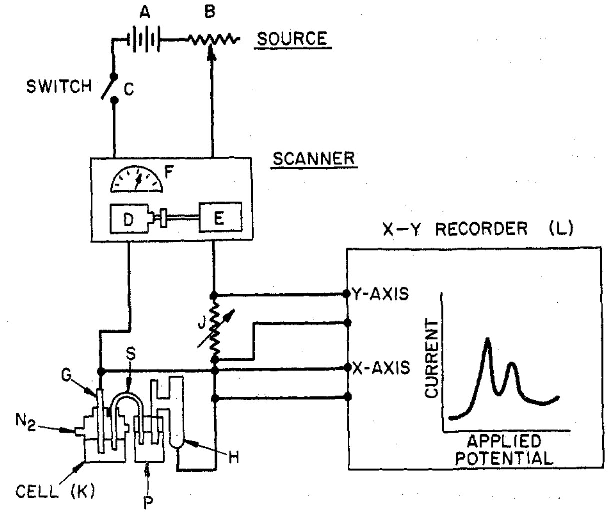

Figure 3.—Cyclic voltammeter: A, voltage source, 3-1.35-V mallory mercury batteries; B, 200-Ω 10-turn helipot; C, off-on switch; D, scan motor, bristol model 830-20, 60 cycles, 8-V; E, 25-Ω 10-turn helipot; F, voltmeter, 5 V, D.C. Simpson; G, platinum electrode, Beckman; H, saturated calomel electrode; J, decade box, Shallcross Mfg. Co., No. 8285; K, electrolytic cell; L, X-Y recorder, Mosley Autograf, Model 3S; P, vessel containing aqueous saturated KCl; S, agar-saturated KCl salt bridge.

420–430 mμ with detectable emission at 220 mμ. The low-pressure mercury resonance source emitted primarily at 253.7 mμ.

Cyclic Voltametry Equipment.—The equipment employed is described in Figure 3. Figure 4 provides details of cell construction.

Reactions of Triarylimidazolyl Radicals (2). 1. With ***N,N,N′,N′*****-Tetramethyl-4-phenylenediamine** (5).—To 0.5 g of 5 in 5 ml of water was added a solution of 0.17 g of sodium hydroxide in 6 ml of water to yield a white solid 5 which, after filtration, was stable in the dark over 4 hr. Addition of biimidazole **3a** to 2 ml of benzene containing a few mg of **5** gave a yellow solution which became blue when phenol was added. If, instead, water was added, a blue, lower layer formed. The blue product was shown by match in uv and visible spectra (600 mμ) to be identical with Wurster's blue prepared by boiling **5** in xylene and adding phenol or water.[18]

2. **With Metal Ions.**—Equal volumes of two solutions of 1.65 g of biimidazole **1b** in 300 ml of 95% ethanol and 0.31 g of freshly prepared ferrous chloride in 300 ml of 95% ethanol were mixed. The resulting solution was divided into four 5-ml portion A, B, C, and D. The $FeCl_2$ solution was also divided into 5-ml portions of E, F, G, and H. To each of B, D, G, and H was added 5 drops of concentrated HCl. A, B, E, and G were heated on the steam bath for 1 hr under an N_2 atmosphere, whereas C, D, F, and H were irradiated with the sun lamp for 1 hr. The initially colorless, very faintly yellow solutions of A, B, C, and D developed orange Fe(III) ion, whereas E, F, G, and H developed no Fe(III). Copper(I) chloride was treated similarly. The intense blue copper(II) ion was formed in A, B, C, and D, the portions in which radical **2b** was formed. The remaining solutions were essentially unchanged.

3. **With Iodide Ion.**—To a solution of 100 mg of biimidazole **1b** in 20 ml of methanol was added 5 ml of saturated methanolic potassium iodide. Irradiation with a sun lamp gave a yellow solution, a sample of which when added to a starch solution gave the purple color characteristic of a starch–iodine complex. Irradiation of methanolic KI alone did not give a positive starch–iodine test.

4. **With Triarylmethane Derivatives. a. Tris(2-methyl-4-diethylaminophenyl)methane Trihydrochloride (7a).**—A solution of 5.2 g of **7a** and 6.6 g of biimidazole **1b** in 350 ml of ethanol prepared in the dark was irradiated under nitrogen with a mercury resonance lamp for 8 hr. The solution changed from essentially colorless to dark blue. Solvent was stripped under vacuum. The solid residue was extracted with petroleum ether (bp 30–60°) and then with 4 l. of benzene. The benzene extract was stripped of solvent and the blue solid was chromotographed on neutral alumina. Compound **4b** (2.4 g) was eluted with benzene and minor bands with 1:1 and subsequently 2:1 by volume chloroform–benzene. The remaining blue band was eluted with 8:1:1 by volume benzene-chloroform-ethanol. Evaporation gave 0.6 g of the dye **8a** [λ_{max} 610 mμ (ethanol) (ϵ 128,000)] which was identical with a sample of the dye prepared from its leuco form by lead dioxide oxidation.[19]

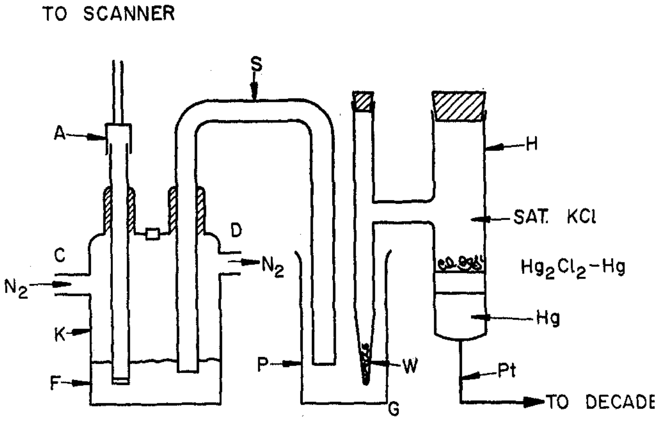

Figure 4.—Electrolysis cell-electrode system: A, flat platinum electrode, Beckman; C, nitrogen inlet; D, nitrogen outlet; K, electrolysis cell; F, supporting electrolyte and solvent (*e.g.*, 0.5 *M* $LiClO_4$ in acetonitrile); G, aqueous saturated KCl; H, saturated calomel electrode (aqueous); P, vessel containing saturated KCl (G); S, saturated agar-KCl salt bridge (aqueous); W, glass wool plug.

b. **Tris(4-dimethylaminophenyl)benzylthiomethane (7b).**—A solution of **7b** (0.15 g) and biimidazole **3a** (0.20 g) in 25 ml of acetone was irradiated with the flash lamp to give a solution of crystal violet dye **8b** as characterized by comparison to its uv and visible spectra with those of an authentic sample. Similar exposure of a solution of 0.15 g of the leuco dye in 25 ml of acetone gave no crystal violet dye **8b**.

c. **Tris(4-dimethylaminophenyl)ethoxycarbonylmethane (7c).**—A benzene solution of **7c** in the presence of aluminum chloride gave no color when irradiated with a flash lamp. Addition of biimidazole **1b** to a similar solution caused no change in color but, when this solution was irradiated, crystal violet dye **8b** was formed. Characterization was as above.

d. **1-Tris(4-dimethylaminophenyl)methyl-2-phenylhydrazine (7d).**—A solution of 4 g of **7d** and 6.6 g of biimidazole **1b** in 15 ml of ethanol was irradiated with one flash of the flash lamp. The yellow solution immediately became intensely colored. The product was identified spectrally as crystal violet **8b**. Similar treatment of a solution lacking the biimidazole did not cause a color change.

5. **With 2,6-Di-*****tert*****-butylphenol** (9).—A solution prepared in the dark from 1.3 g of **9**, 1.5 g of biimidazole **1b**, and 100 ml of benzene was irradiated 1 hr, 6 in. from a sun lamp. The colorless solution became bright yellow. Concentration on a steam bath gave a mixture of dark red and light yellow crystals. The mixture was treated with petroleum ether, and the insoluble yellow crystals of triarylimidazole **4b** were removed by filtering. Methanol was added to the filtrate to precipitate the product. Crystallization from petroleum ether–methanol gave 0.29 g of 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (**10**), mp 245.0–245.5°. The uv and infrared spectra of the product were identical with those of a sample prepared according to the procedure of Hart.[20]

Similarly, to a solution of 2,6-dimethoxyphenol was added solid biimidazole **3a**. A purple solid, the diphenoquinone, precipitated. It was identical in all respects with that prepared by dichromate oxidation.[21]

6. **With Hydroquinones.**—A solution of biimidazole **1c** and 0.44 g of hydroquinone **11** in 65 ml of benzene was heated at re-

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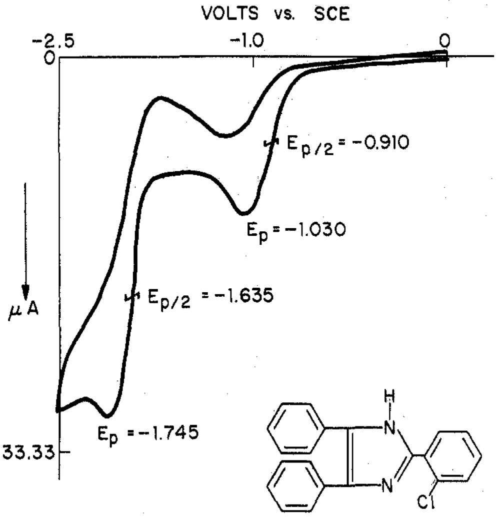
(18) V. Franzen, *Justus Liebigs Ann. Chem.*, **604**, 251 (1957).

(19) C. C. Barker, M. H. Bride, G. Hallas, and A. Stamp, *J. Chem. Soc.*, 1285 (1961).

(20) H. Hart and F. A. Cassis, Jr., *J. Amer. Chem. Soc.*, **73**, 3179 (1951).

(21) A. W. Hofmann, *Ber.*, **11**, 335 (1878).



2-(2-chlorophenyl)-4,5-diphenylimidazole, 0.00130 *M*

Figure 5.—Cyclic voltammetry: temperature 25 ± 0.1°; electrode system Pt *vs.* sce; 0.5 *M* $LiClO_4$ in acetonitrile.

flux 3.5 hr. A precipitate, formed when the solution cooled, was crystallized from benzene to give 0.33 g of 2-(4-methoxyphenyl)-4,5-diphenylimidazole (**4c**), mp 230–232°, $\lambda_{\max}$ 297 mμ. From the remaining solid product was isolated 0.14 g of dark green quinhydrone **12**, mp 169–171°.

7. **With 2-(4-Methoxyphenyl)-4,5-diphenylimidazole (4c).**—A 25-ml benzene solution of 0.05 g of biimidazole **1a** and 0.05 g of **4c** was irradiated with a sun lamp to give a blue solution of radical **2c**, $\lambda_{\max}$ 610 mμ. Irradiation of a benzene solution of **4c** in the absence of biimidazole **1a** gave no radical which could be detected spectrally or by esr.

8. **With 1,2,2-Tricyanoethyl-*N*,*N*-dimethylaniline (13).**—A solution of 1:1 by volume acetone–benzene, containing 0.5% each of **13** and biimidazole **1b**, was irradiated with the sun lamp. The known orange 4-(1,2,2-tricyanovinyl)-*N*,*N*-dimethylaniline (**14**) was identified spectrally.[22]

9. **With 3-Methyl-2-benzothiazole Hydrazone Hydrochloride (15). Oxidative Coupling with *N*,*N*-Dimethylaniline Hydrochloride.**—A solution prepared in the dark of 0.635 g of **15**, 0.468 g of *N*,*N*-dimethylaniline hydrochloride, and 1.0 g of biimidazole **1b** was irradiated for 10 min with the sun lamp. The solution was diluted with 100 ml of water and extracted with three 50-ml portions of petroleum ether, which were discarded. The aqueous methanol solution was concentrated on a steam bath, cooled to room temperature, and filtered. The filtrate was saturated with sodium chloride and a blue-black crystalline solid formed. The uv and visible spectra (methanol) of this solid were identical with those of 3-methyl-2,4-(dimethylaminophenylazo)benzothiazolium chloride (**16**) prepared according to Hünig.[23]

10. **With Mercaptans. a. 1-Butanethiol.**—Under an atmosphere of dry nitrogen, a mixture of 2.7 g of butanethiol, 3.3 g of biimidazole **1b**, and 20 ml of benzene was heated with stirring. The refluxing solution was irradiated (through Pyrex glass) with the sun lamp, 2 in. distant for 20 hr. The mixture was cooled and precipitate formed. This solid, mp 193.0–194.5°, was identical in infrared spectrum with authentic 2-(2-chlorophenyl)-4,5-diphenylimidazole (**4b**). The filtrate was shown by comparison of its ir spectrum and gas chromatographic analysis with those of authentic material to contain a high concentration of dibutyl disulfide.

b. Thiophenol.—A similar reaction was carried out with 0.44 g of thiophenol and 1.2 g of biimidazole **1a** in 15 ml of benzene. Triphenylimidazole **4a**, mp 190.0–191.5°, formed as a precipitate, and the phenyl difulfide was identified, as above, in the filtrate.

Spectral Determinations.—A Cary Model 14 spectrophotometer was used for uv and visible measurements. A Perkin-Elmer Model 221 instrument was employed for the infrared.

Cyclic Voltammetry.—The cell–electrode system was flushed with dry nitrogen and thermostated at 25 ± 0.5°. Acetonitrile (25 ml), 0.5 *M* in $LiClO_4$, and the sample (0.001–0.005 mol) were further flushed 5 min. The potential was scanned cyclically between 0 and +2.0 V *vs.* sce at a scan rate experimentally varied between 1 and 2.5 V/min. The cell was blanketed under nitrogen and shielded from light during the reaction. A representative polarogram is shown in Figure 5.

Reversibility of electrolytic triarylimidazole ⇄ biimidazole redox reaction was demonstrated by (a) observing no hysteresis in repetitive cycling and (b) obtaining the same cyclic trace from the biimidazole as from the corresponding imidazole.

Registry No.—**7b**, 21356-01-4; **7d**, 29920-21-6; **12**, 106-34-3.

Acknowledgment.—We are grateful to Drs. B. C. McKusick and R. Cohen for supplying samples, and to Dr. C. E. Looney for valuable discussions.

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[22] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and F. W. Mower, *J. Amer. Chem. Soc.*, **80**, 2806 (1958).

[23] S. Hünig and K. H. Fritsch, *Justus Liebigs Ann. Chem.*, **609**, 143 (1957).

The Flash Photolysis of a Substituted Hexaarylbiimidazole and Reactions of the Imidazolyl Radical

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Received February 12, 1970

The rate of reaction of 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl radicals (L·) with additives has been studied in various solvents. Evidence based on measured rate constants, including kinetic deuterium isotope effects, prove that the rate-determining step in the reaction L· + aromatic amine is an electron exchange reaction at the amino nitrogen, while in the reaction L· + hydroquinone the rate-determining step is hydrogen abstraction.

Lophine dimer [(bis(2,4,5-triphenylimidazole)] has been known and studied for many years. It was first prepared in 1960[1] although at the time the structure was incompletely characterized. The first clearly recognized synthesis[2] was published the following year. The observed photochromism[1] of the hexaarylbiimidazole was subsequently shown to be due to the formation of imidazolyl radicals[3,4] upon photodissociation of the parent compound. In the present study, the kinetics and mechanism of reactions of 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl radicals (L·) with aromatic

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[1] T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jap.*, **33**, 565 (1960).

[2] H. Zimmermann, H. Baumgärtel, and F. Bakke, *Angew. Chem.*, **73**, 808 (1961).

[3] H. Baumgärtel and H. Zimmermann, *Z. Naturforsch.*, *B*, **18**, 406 (1963).

[4] T. Hayashi, K. Maeda, and M. Takeuchi, *Bull. Chem. Soc. Jap.*, **37**, 1717 (1964).