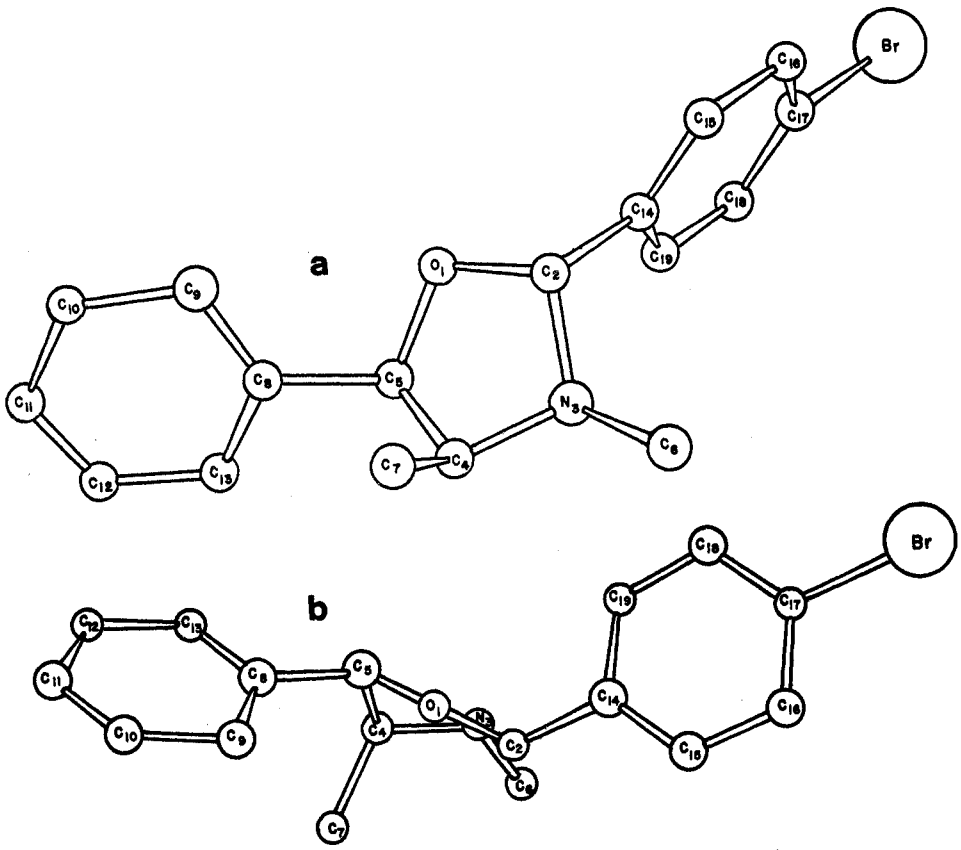

Figure 1.

Acknowledgment.—The authors wish to express their thanks to the University of Chicago for the use of the X-ray diffractometer. Special thanks are due to Dr. Dan W. Urry, Director, Division of Molecular Biophysics, for the use of laboratory facilities and for salary and computer support. Thanks are also due to the Mental Health Board of Alabama for partial financial assistance.

Some Properties of Triarylimidazolyl Radicals and Their Dimers

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Received February 12, 1970

The electronic spectra of 2,4,5-triarylimidazolyl radicals **1** are strongly influenced by substitution on phenyl rings; spectra of dimers **2** are not. The rates of disappearance of **1** in benzene at 27° vary over 100-fold with substitution of phenyl rings. Any ortho substituent in Ar increases the rate constant relative to position isomers, a fact consistent with radical destabilization by ortho substituents through steric disruption or ring coplanarity.

Colored triarylimidazolyl free radicals **1** are formed from the thermal or photolytic dissociation of hexaarylbiimidazoles, the oxidation products of triarylimidazoles **4**.[2] Two hexaarylbiimidazole isomers have been reported.[3] In solution, the more stable **2** is produced at room temperature and **3** is formed below −20°. Interconversion of **2** and **3** involves **1**. Structures were inferred from infrared data.[3] Dimer **2** is referred to by some authors as the photochromic dimer and **3** as the thermochromic dimer. The kinetics of radical recombination have been reported to be second order in radical concentration.[2c,d] Longer reaction times reveal deviation from second-order kinetics. Wilks and Willis reported 3/2 order which, after several half-lives, changed to first-order kinetics in radical disappearance.[4]

We have prepared some new hexaarylbiimidazoles, particularly a group bearing ortho substituents in the aromatic rings, and report here the effect of substitution on the rate of radical disappearance and on spectra of

(1) To whom inquiries should be addressed.

(2) (a) T. Hayashi and K. Maeda, *Bull. Soc. Chem. Jap.*, **33**, 565 (1960); (b) T. Hayashi and K. Maeda, *ibid.*, **35**, 2057 (1962); (c) T. Hayashi, K. Maeda, and M. Morinaga, *ibid.*, **37**, 1563 (1964); (d) T. Hayashi, K. Maeda, and M. Takenchi, *ibid.*, **37**, 1717 (1964); (e) T. Hayashi and K. Maeda, *ibid.*, **38**, 685 (1965); (f) T. Hayashi and K. Maeda, *J. Chem. Phys.*, **32**, 1568 (1960); (g) L. A. Cescon, Belgium Patent 509,415 (Aug 30, 1963); (h) S. M. Blinder, M. J. Peller, N. W. Lord, K. C. Aamodt, and N. S. Ivanclinkov, *J. Chem. Phys.*, **36**, 540 (1962); (i) H. Zimmerman, H. Baumgartel, and F. Bakka, *Angew. Chem.*, **73**, 808 (1961).

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

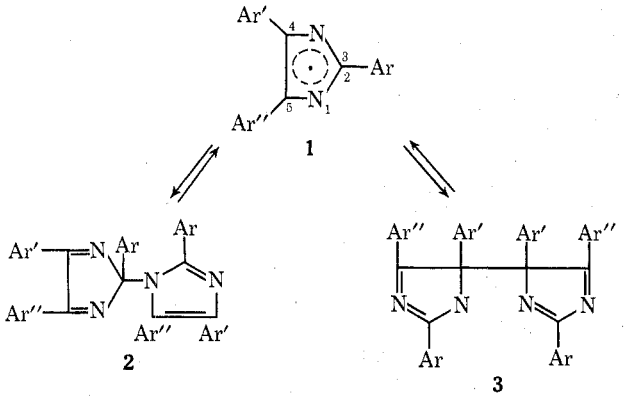
(4) H. Neda, *J. Phys. Chem.*, **68**, 1304 (1964); M. A. J. Wilks and M. R. Willis, *J. Chem. Soc.*, 1526 (1968); M. A. J. Wilks and M. R. Willis, *Nature (London)*, **212**, 500 (1966).

TABLE I

SPECTRAL PROPERTIES AND RATE CONSTANTS OF THE DIMERIZATION OF SOME SUBSTITUTED TRIPHENYLIMIDAZOLYL RADICALS IN BENZENE AT 27 ± 1°

	Substituents			Biimidazoles 2				Imidazolyl radicals 1		Dimerization at 27 ± 1° to 2				
				In CH_3OH		Cm^{-1}, KBr pellets								
No.	Ar	Ar′	Ar″	mμ	$10^{-4}\epsilon$			λ_{max}, mμ	$10^{-3}\epsilon$, l. mol^{-1} cm^{-1}	Benzene $10^3k/\epsilon$	Benzene $k^{b,d}$	1:1 methanol-benzene, k^b	Methanol, $k^{b,e}$	Toluene,[c] k^b
a						1550 s	1497 m	550	3.28	7.7	25.2			12.4
b	4-Methoxy			263	3.09	1552 m	1506 s	610	6.90	1.5	10.3			9.4
c	2,4-Dimethoxy			262	2.99	1554 m	1501 m	620	8.13	13.7	111.0	2820		
d	2-Chloro			265	2.79	1548 s	1495 m	540	2.80	122.0	342.0	3242	7800[d]	315
e	4-Chloro			267	2.74	1550 m	1498 m	570	4.49	6.8	30.5			
f	4-Bromo			265	2.89	1552 s	1498 w	560	3.90	6.0	23.4			
g	4-Nitro					1550 sh		530	1.38	6.2	8.56			
h	4-Cyano			264[a]		1547 s	1500 sh	560	2.19	10.0	21.9			
i	3-Chloro			265	2.78	1550 m	1500 m	550	2.90	16.2	47.0			
j	3-Nitro			265	3.92	1550 sh		540	1.14	12.8	14.6			
k	2-Bromo			265	2.69	1549 s	1493 w	560	4.07	123.0	501.0	1304		
l	2,4,6-Trimethyl					1540 m	1490 m	590	5.10	16.7	85.2			
m	2,4-Dichloro			265	2.53	1551 s	1498 w	570	4.60	283.0	1302.0	5888		
n			2-Chloro	262[a]		1552	1500	530	2.94	3.3	9.7			
o		2-Chloro	2-Chloro	261	2.15	1550 sh	1488 m	560	1.32	18.5	24.4			

[a] In acetonitrile solvent. [b] In l. mol^{-1} sec^{-1}. [c] From D. C. Reitz, private communication (in toluene at 26°). [d] Assumes that $\epsilon_{benzene} = \epsilon_{benzene-methanol}$. [e] $\epsilon_{methanol} = 1940$.



radicals and dimers. In the following paper, some reactions of **1** other than dimerization are covered. Subsequently, three additional papers appear which deal with the mechanism of certain oxidation reactions of **1**.

Results and Discussion

All hexaarylbiimidazoles studied, including those, with ortho substituents on aromatic rings, were readily prepared in good yields.

Substitution on **2** resulted in little spectral change in the ultraviolet (6 mμ in λ_{max} and less than a factor of two in ϵ_{max}). See Table I. Spectra of **1**, on the other hand, were more sensitive to structural changes (80 mμ in λ_{max} and a factor of seven in extinction coefficients). These results are consistent with the assumption that the radicals are more nearly planar than parent dimers. Absorption maxima correlated roughly with electron-releasing ability of substituents, *e.g.*, λ_{max} p-OCH_3 > p-Br > p-NO_2.[5]

The infrared spectra of the dimers (Table I) exhibited the 1550- and 1500-cm^{-1} bands considered diagnostic of **2**.[3] All dimers also could be converted into their less stable isomers **3** by irradiating a solution below −20° as previously reported by White and Sonnenberg.[3] If the 2 position in Ar was unsubstituted, **3** could be obtained which contained very little **2**, by evaporating the solvent under vacuum or by adding a nonsolvent; however, only very crude **3** was obtained with biimidazole having groups in the 2 position in Ar. A third dimer, first discovered by Reitz,[6,7] was observed for all dimers studied. It could be detected by cooling a solution of **2** to −85° and irradiating for 10–15 min. Radical color disappeared after irradiation was stopped. (Reitz reports concommitant esr signal loss.) When this solution was slowly warmed to room temperature, the following changes occurred. At about −40° radical color (and esr signal according to Reitz) reappeared. The solution once again became colorless on standing at about −35°. Further warming above −20° caused dissociation of dimer **3** to radical with final loss of color as the temperature reached about 12°. Dimer **2** was the predominant product at the end. Dimer **3** was identified in this experiment by its instability in solution at room temperature and by its uv spectrum. (The λ_{max} of **3** are about 10 mμ higher than of **2**.) The structure of the third dimer was not determined. The important fact is that all dimers behaved the same way, at about the same conditions.

Dissociation constants of **2** have been reported to be higher for dimers with electron-donating substituents in the para positions of the phenyl rings.[8] We found that these groups in ortho positions resulted qualitatively in very different properties. Any ortho substituent in Ar decreased dissociation. Thus, a benzene solution of the stable dimer of 2-(2-chlorophenyl)-4,5-diphenylimidazolyl radical **2d** exhibited no radical absorption spectrum below 80°, whereas the 4-chloro compound **2e** was partially dissociated in solution at room temperature. Ortho substituents in Ar′ and Ar″ affected the equilibrium quite modestly but appeared to

(5) A similar trend has been reported for the substituted benzyl radicals: J. E. Hodgkins and E. D. Megarity, *J. Amer. Chem. Soc.*, **87**, 5322 (1965). The similarity in the two groups of radicals still holds if one includes the following 2-(para-substituted phenyl)-4,5-diphenylimidazolyl radicals: CH_3, λ_{max} 565 mμ; C_6H_5, λ_{max} 600 mμ; and F, λ_{max} 545 mμ.

(6) D. C. Reitz, private communication.

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

(8) H. Baumgärtel and H. Zimmermann, *Z. Naturforsch*, **18**, 406 (1963).

have the opposite effect, that is, increased dissociation. Qualitatively, meta substituents had little effect on the equilibrium of dissociation.

The wide variation in thermal stability of dimers and (where ortho groups are present in Ar) the high reactivity encountered at temperatures where dissociation was readily observable discouraged our measuring equilibria or thermal dissociation kinetics. Photodissociation was complete at the end of a 5-μsec flash with no evidence for short-lived intermediates.

Radical disappearance, however, was readily followed spectrally. Benzene solutions at 27 ± 1° were irradiated and absorbance, A, at λ_{max} was determined at measured time intervals. A graphic method was utilized to obtain rate constants. Linear plots of $1/A$ *vs.* t were obtained until A was about half of A_0, when deviations from a second-order plot became apparent. The slopes of the linear first half-life was taken as equal to $k/\epsilon l$ in cm sec^{-1} (l = 1 cm) from which the rate constants, k, were obtained. The values of k/ϵ and k are in Table I.

Our presentation of results in terms of second-order rate constants fitted to initial rates during about one half-life does not imply knowledge of the detailed mechanism of radical disappearance. We observed, as did Wilks and Willis, that 3/2 order plots are linear for longer reaction times, but that these too deviate from linearity as well as vary in slope with A_0 and with the presence of sensibly inert additives. This information convinces us that the detailed mechanism of radical disappearance will remain to be understood until all reaction components can be measured quantitatively as reaction proceeds. We are attempting to develop such techniques.

At this time we are concerned with the effect of structure on radical dimerization and assume only that a common mechanism prevails for all. The low-temperature dimerization experiment, in which all compounds behaved comparably under similar conditions, supports this assumption.

A method was devised to determine extinction coefficients of radicals. A flash photolysis unit with filters to confine irradiation to a spectral region where only biimidazoles absorbed was utilized to generate radicals **1** whose initial absorbance was recorded photographically from an oscilloscope. In the same cell another solution was then photolyzed as above. This second solution contained an identical concentration of biimidazole to the first plus leuco crystal violet dye, tris-(4-dimethylaminophenyl)methane, and toluenesulfonic acid. The absorbance of dye produced by oxidation of leuco dye by **1** was observed at an unobstructed wavelength. The extinction of the dye at this wavelength in this medium was determined experimentally. The stoichiometry of radical attack on dye was known[2g,7] and the quantum yield of this reaction under these conditions had been previously determined experimentally by Kellogg and Kooser to be unity[9] (that is, one dye molecule is formed per biimidazole dissociated or per two radicals). Calculation of initial radical concentration corresponding to dye produced allowed calculation of radical extinction coefficient in the usual fashion from observed absorbance.

(9) R. E. Kellogg and R. H. Kooser, private communication in advance of publication. These workers report that ϕ varies substantially with acid concentration and leuco dye structure but is invariant with radical structure.

Our value for ϵ of 3280 cm^{-1} for **2a** in benzene–methanol compares with Wilks and Willis value 4150 cm^{-1} in dioxane–water and 3900 in benzene–pyridine. We consider these values in agreement.

The disparity in rates required use of different experimental techniques for different solvents. Radical absorbance was followed with a spectrometer when benzene was solvent, whereas a flash photolysis unit was employed in the methanol-containing solvent runs. In the latter, a photograph was made of the oscilloscopic trace of radical transmittance *vs.* time.

Radical extinction coefficients were measured in 50:50 vol benzene–methanol and, in one case, in methanol as well. It proved impossible to determine extinction coefficients by this method in benzene, the preferred solvent for kinetic runs, because of reagent insolubility. Rate constants in benzene are, therefore, equal to those reported multiplied by the experimentally unattainable ratio, $\epsilon_{benzene}/\epsilon_{benzene-methanol}$. The ratio is assumed to be relatively constant for the radicals studied. The method is the best compromise which would allow all rates to be measured by a common method.

Our rate constants agree reasonably well with those of Reitz,[6] determined by epr in toluene at 26°. The rate constant for disappearance of **1a**, 25.2, compares with second-order values approximated from Hayashi's data of 3.3 at 19° and 7.4 at 23° and from Wilks and Willis' data of between 7 and 18, depending on **2a** concentration.

The solvent exerts a profound influence; dimerization is 30-fold faster in methanol than in benzene. The degree of rate enhancement by methanol is disturbingly large. Efforts to characterize photolysis products other than dimer after prolonged periods of irradiation of methanol solutions showed a variety of products in trace amounts insufficient to characterize by liquid chromatography and inseparable by other techniques. Second-order plots showed the same deviations as were found in benzene. Rate studies were attempted in other solvents in the hope of shedding some light on medium effect. Unfortunately, a combination of problems precluded measurement of extinction coefficients in most of these. The k/ϵ values of dimerization of **1a** in various solvents are listed in Table II.

TABLE II
DIMERIZATION OF
2,4,5-TRIPHENYLIMIDAZOLYL RADICAL AT 27°

Solvent	$10^3k/\epsilon$, cm sec^{-1}
Benzene	25.2
Anisole	24.6
Benzonitrile	21.0
tert-Butylbenzene	43.2
1,2-Dimethoxybenzene	28.2
Nitrobenzene	31.8

A substituent in the ortho position of Ar but not of Ar′ or Ar″ unmistakably enhances the rate of radical combination. Thus, the 2-*o*-chlorophenyl compound **1d** (Table I) dimerized seven and ten times as fast as its meta and para isomers **1i**, and **1e**, respectively, 30 times as fast as the isomer with an ortho chloro group in Ar′ (**1n**), and an order of magnitude faster than the analog having ortho chloro groups in Ar′ and Ar″ (**1o**).

Bromo-substituted radicals followed a similar trend, the ortho isomer **1k** being 50-fold faster than the para isomer **1f**; the methoxy compounds **1b** and **1c** behaved similarly. The largest rate constant of dimerization was shown by **1m**.

The influence on rate by meta and para substituents was not great. Compare **1a** with **1b**, **1g**, **1h**, **1i**, and **1j**. Groups which are either strongly electron donating or attracting appear to retard the rate by a small factor.

From the equilibrium constants of Baumgärtel and Zimmerman[8] obtained in toluene at 25° and our rate constants for association, the rate constants of dissociation are calculated to be about 4.4×10^{-5} and 2.6×10^{-4} sec^{-1} for **2a** and **2b**, respectively.

The unusual aspect of these data is that the most hindered dimers, namely, those having ortho groups in Ar, form fastest. The effect is clearly steric since all groups have a similar influence. The results are consistent with two hypotheses. Ortho substituents in Ar result in (a) a different product, at least initially, or (b) a lower transition state of **2**, due to destabilization of **1**.

Hypothesis a implies, for example, that hexaarylbiimidazoles without substituents in Ar would be represented by the energy diagram in Chart A, due to White and Sonnenberg,[3] whereas those with ortho substituents on Ar would be represented by that in Chart B. The similar low temperature behavior of all rad-

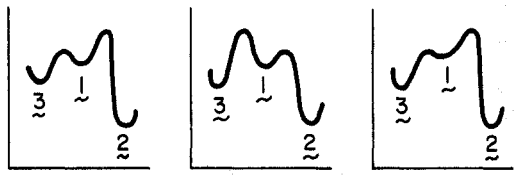


CHART A CHART B CHART C

icals, that is, their dimerization to the same isomers at similar temperatures, argues against this hypothesis. The products at the completion of kinetic runs did not differ observably among radicals studied. Hypothesis a, furthermore, would imply that ortho substitution in Ar somehow stabilizes that transition state which involves coupling closest to the hindrance. We can find no precedent for this in the literature.

Hypothesis b allows the unsubstituted biimidazole system still to be represented by Chart A. The diagram for biimidazoles with ortho groups in Ar can be depicted by Chart C. Radical destabilization is to be expected from steric hindrance of ring coplanarity. X-Ray crystallography has shown that crystalline dimer **2k** has no two rings which are coplanar.[10] Models of the radical, however, show that unsubstituted Ar can achieve coplanarity with the heterocyclic nucleus. They also show that ortho substitution in Ar does greatly interfere with rotation to achieve ring coplanarity of Ar and the imidazole nucleus. Models further reveal that Ar′ and Ar″ cannot simultaneously be coplanar with the imidazole ring and strongly suggest that individually this may also be impossible. Because neither radical nor dimer gains appreciable resonance stabilization from Ar′ and Ar″, kinetics and equilibria of reactions of radicals or dimers should not be greatly effected by ortho substituents on these rings.

A further test of ring coplanarity should be found in spectral data. The high sensitivity of radical spectra, both λ_{max} and ϵ, to substituents contrasts markedly with the biimidazoles (Table I). Parallel observations in the biphenyl series have been related to ring coplanarity.[11]

Experimental Section

Triarylimidazoles were prepared by the method of Davidson, Weiss, and Jelling[12] on a 0.01-mol scale. The reaction mixture was refluxed until unreacted benzil could no longer be detected by paper chromatography. If the product did not precipitate when the mixture was added to 200 ml of distilled water, the diluted mixture was neutralized in the cold with 15 *N* ammonium hydroxide. The product was recrystallized twice from an appropriate solvent. Spectra were obtained in methanol. Melting points were measured on a Thomas-Hoover apparatus. Analytical data are presented in Table III.

Hexaphenylbiimidazoles.—The two methods employed are exemplified. Method B is preferred for its wider applicability and for its suitability for preparing larger quantities. Analytical data are presented for individual compounds in Table IV. Spectroscopic data are in Table I.

Method A is essentially that reported by Hayashi and Maeda.[2a] The precipitated product was washed with water until added ferrous ion failed to give a positive ferricyanide test and dried overnight in a vacuum oven at 50° and subsequently for 8 hr at 56° (0.1 mm). Recrystallization from benzene–ethanol and redrying as before gave an 88% yield of product, mp 199–201° (recrystallization mp 200–201°).

Method B.—Solid 2-(2,4-dimethoxyphenyl)-4,5-diphenylimidazole (5.35 g) and 150 g of benzene were added to a solution of 6.0 g of sodium hydroxide and 9.9 g of potassium ferricyanide in 100 ml of water, and the resulting mixture was strirred vigorously for 16 hr. The benzene layer was separated and washed three times with 150 ml of water, dried over sodium sulfate, and concentrated to about 20 ml (preferably under vacuum for easily dissociated dimers). The product was allowed to crystallize. Purification procedure is the same as in method A, yield 91%, mp 120–121°.

Drying.—Irrespective of the method of preparation or solvent used for crystallization, the products held solvent tenaciously. Most normal drying methods proved ineffective. For most compounds, it was necessary to hold the sample at 110° (0.1 mm) for 24 hr to obtain solvent-free samples for analytical purposes. The appearance of color due to the radical during this process did not damage the samples so far as could be detected by their analytical, spectroscopic, and chemical properties. Benzene proved to be the easiest solvent to remove in most cases.

Spectral Studies.—Infrared absorption spectra were obtained with a Perkin-Elmer Model 221. Fluorescence measurements utilized a 0.75-m Jarrell-Ash spectrograph. Electronic absorption spectra were determined with a Cary Model 14M spectrophotometer. Molar extinction coefficients of radicals were determined by flash photolysis in an apparatus similar to that described by Porter.[13] Two Corning filters, 0-52 and 760, were inserted between the sample and the flash lamp, whose pulse duration at half peak width was 4 μsec. This array, in conjunction with concentration of materials employed, ensured that the dimer absorbed >95% of the radiation. The analyzing lamp was operated from a 6-V storage battery. Solutions were degassed with argon, although this procedure was shown not to be necessary.

Radical absorbance was measured at λ_{max} for each radical in the apparatus. Radical concentration was obtained by flash photolysis of a second solution (50:50 vol methanol–benzene) of biimidazole of identical concentration (2×10^{-4} *M*) but which

(10) G. Teufer, private communication in advance of publication.

(11) For leading references, see J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, 1963, pp 238–246. Drawing conclusions about the relative effect on coplanarity of position isomers on the basis of magnitudes of λ_{max} and ϵ is not valid without condsideration of the magnitude and direction of the dipole due to the substituent.

(12) D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937).

(13) G. Porter, *Proc. Roy Soc., London*, **200**, 284 (1950).

Table III

Preparation of Triarylimidazoles (4)[a]

Compd 4	Yield, %	Mp, °C	Crystn solvent	λ_{max} (MeOH), mm	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Halogen, % Calcd	Halogen, % Found	Mol wt	Lit. Mp, °C	Lit. Ref
a	92	273–275	MeOH	298	$C_{21}H_{16}N_2$	85.1	85.0	5.4	5.4	9.5	9.4			296.36	275	b
b	83	231–232	MeOH	297	$C_{22}H_{18}N_2O$	81.0	80.7	5.6	5.6	8.6	8.8			326.38	229	c
c	90	164–165	EtOH–H_2O	304	$C_{23}H_{20}N_2O_2$	77.5	77.8	5.7	5.7	7.9	8.0			356.41		
d	94	196–197	EtOH–H_2O	286	$C_{21}H_{15}N_2Cl$	76.2	76.4	4.6	4.6	8.5	8.2	10.7		330.8	197.3–197.8	d
e	98	263.5–264	EtOH–H_2O	303	$C_{21}H_{15}N_2Cl$	76.2	76.3	4.6	4.4	8.5	8.3	10.7	10.5	320.8	266–268	d
f	94	263–263.5	EtOH–H_2O	310	$C_{21}H_{15}N_2Br$	67.2	67.1	4.0	3.9	7.5	7.5	21.3		375.27	253–254	e
g	99	237–238	EtOH–PhH		$C_{21}H_{15}N_3O_2$	73.9	74.2	4.4	4.4	12.3	12.4			341.36	240	d
h	97	272.5–273	EtOH–PhH	338	$C_{22}H_{15}N_3$	82.2	82.0	4.7	4.7	13.1	13.1			321.37		
i	90	295–296	THF–EtOH–H_2O	300	$C_{21}H_{15}N_2Cl$	76.2	76.5	4.6	4.6	8.5	8.4	10.7		320.8		
j	94	f	f	f	$C_{21}H_{15}N_3O_2$	73.9	73.6	4.4	4.4	12.3	12.3			338.44	f	g
k	97	205.5–206.5	EtOH–H_2O	288	$C_{21}H_{15}N_2Br$	67.2	67.1	4.0	4.0	7.5	7.4			375.27		
l	89	230–230.5	EtOH–H_2O	~267	$C_{24}H_{22}N_2$	85.2	84.9	6.6	6.9	8.3	8.0			338.44		
m	96	174.5–175	EtOH		$C_{21}H_{14}N_2Cl_2$	69.1	69.2	3.9	4.0	7.7	7.4	19.4		365.24	176.5–177.0	d
n	95	232.5–233.5	PhH	298[h]	$C_{21}H_{15}N_2Cl$	76.2	76.0	4.6	4.7	8.5	8.3	10.7		320.8		
o	94	245.5–246.5	PhH	290	$C_{21}H_{14}N_2Cl_2$	69.1	69.0	3.9	4.0	7.7	7.6	19.4		338.44		

[a] Satisfactory combustion analytical data (±0.4) were provided for all of the compounds of this table: Ed. [b] B. Radziszewski, *Ber.*, **10**, 70 (1877). [c] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941). [d] D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964). [e] K. Skoichiro and S. Narisawa, *Asahi Garasu Kenkyu Hokoku*, **12**, 55 (1962); *Chem. Abstr.*, **59**, 1622 (1963). [f] Insoluble, mp >360°. Troegger[g] reports that it did not melt to 295°. [g] J. Troegger, *J. Prakt. Chem.*, **64**, 532 (1901). [h] In acetonitrile.

Table IV

Preparation of Hexaarylbiimidazoles II[a]

Compd 2	Yield, %	Method	Crystn solvent	Drying (24 hr), °C (mm)	Mp, °C	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Halogen, % Calcd	Halogen, % Found	Lit. Mp, °C	Lit. Ref
a	88	A	PhH–EtOH	110 (0.1)	200–201	$C_{42}H_{30}N_4$	85.4	85.4	5.1	5.0	9.5	9.3			198–201	2a
b	85	A	PhH–EtOH	110 (0.1)	127–128	$C_{44}H_{34}N_4O_2$	81.2	81.0	5.3	5.3	8.6	8.5			146	8
c	91	B	PhH	110 (0.1)	120–121	$C_{46}H_{38}N_4O_4$	77.7	77.8	5.4	5.2	7.9	7.8				
d	89	B	PhH–EtOH	56 (760)	202–203	$C_{42}H_{28}N_4Cl_2$	76.5	76.8	4.3	4.5	8.5	8.4	10.7	10.4	115–120	3
e	85	B	Ph–PH ether	110 (0.1)	210.5–212	$C_{42}H_{28}N_4Cl_2$	76.5	76.7	4.3	4.4	8.5	8.2	10.7	10.8	203–205	3
f	82	B	Ether	110 (0.1)	210–211	$C_{42}H_{28}N_4Br_2$	67.4	67.3	3.8	3.8	7.5	7.6	21.4			
g	85	A		110 (0.1)		$C_{42}H_{28}N_6O_4$	74.1	74.2	4.1	4.3	12.3	12.2				
h	70	B	PhH	110 (0.1)	~162–168	$C_{44}H_{28}N_6$	82.5	82.5	4.4	4.4	13.1	13.0				
i	81	B	PhH	110 (0.1)	167.5–168.5	$C_{42}H_{28}N_4Cl_2$	76.5	76.7	4.3	4.4	8.5	8.6	10.7	10.5	165–167	3
j	74	B	PhH	110 (0.1)	~150	$C_{42}H_{28}N_6O_4$	74.1	73.9	4.2	4.1	12.4	12.5				
k	90	A	PhH–EtOH	110 (0.1)	190–191	$C_{42}H_{28}N_4Br_2$	67.4	67.4	3.8	3.8	7.5	7.6	21.4			
l	78	A	PhH–EtOH	110 (0.1)	195–203	$C_{48}H_{42}N_4$	85.4	85.5	6.3	6.2	8.3	8.1				
m	95	B	PhH	110 (0.1)		$C_{42}H_{26}N_4Cl_4$	69.2	69.4	3.6	3.7	7.7	7.8	19.5	19.4	Glass	3
n	43	B	PhH	110 (0.1)	~190	$C_{42}H_{28}N_4Cl_2$	76.5	76.7	4.3	4.1	8.5	8.3	10.7			
o	94	A	PhH–EtOH	110 (0.1)	~210	$C_{42}H_{26}N_4Cl_4$	69.2	69.3	3.6	3.8	7.7	7.5	19.5			

[a] Satisfactory combustion analytical data were provided for all of the compounds in this table: Ed.

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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