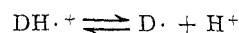


The ortho methyl group steric effect is exhibited in the reduced reactivity of all the species derived from *o*-MLECV vs. LECV. Under basic conditions, LECV yields the final dye. Reactivity of the ortho methyl groups of *o*-MLECV might explain the results if disproportionation occurred at these groups to give degradation products. However, the methyl groups are meta to the amino function and should not yield a highly resonance-stabilized benzyl radical; in fact, reactivity little greater than that of toluene might be expected. Furthermore, the effect of acid could not be explained by reaction at the methyl groups, because protonation would reduce the reactivity of the triphenylmethane carbon-hydrogen bond to the same extent as the meta methyl group, and thus no change in chemistry would be expected.

Assuming that 0.036 sec is the normal "unhindered" rate of disproportionation of unprotonated 4600-Å species, it is seen that with the ortho methyl groups present in *o*-MLECV the rate is significantly slower (0.10 sec). In the normal "unhindered" reaction we know oxidation at the triphenyl methane carbon-hydrogen bond occurred since color is formed. In the hindered case reaction at some other point must occur since no color will form on acidification. A reasonable suggestion is either oxidation at the *N*-ethyl function or ring addition products. Reaction at the α -C-H bond of the *N*-ethyl group yields a relatively stable amidinium compound. Further reaction with solvent leads to ethers, etc. Acid or even chloride ion might interfere with

this reaction, since they tie up the nonbonding nitrogen electrons and make the α hydrogens less reactive. In this case the color forming reaction has time to occur.

To check to see if it is possible to bring about the destructive reaction with LECV by adding base to the solution, the photooxidation with lophine was carried out in the presence of methanolic sodium methoxide. Even 0.1 *M* alkoxide ion in methanol is not sufficient to interfere with the color reaction with LECV. This must mean that, even if the equilibrium



is completely to the right, the triphenylmethyl radicals will disproportionate with LECV to produce the cation. Using these same arguments for *o*-MLECV, it is interesting to speculate how an apparently small change in acidity can have a dramatic effect on both the rate and course of the disproportionation reaction. A tentative set of intermediates that explain these results are shown in Scheme I, p 2279.

Registry No.—L., 29897-74-3; L₂, 1707-68-2; *o*-MLECV, 4482-70-6; *o*-MLECV·3HCl, 4482-56-8; LECV, 4865-00-3.

Acknowledgments.—We wish to thank R. Dessauer, L. A. Cescon, G. R. Coraor, and C. Yembrick for developing our interest in this problem. We also thank V. F. Hanson for the flash photolysis apparatus and J. M. White for assistance in carrying out the experiments.

Substituent Effects on the Reactivity of Triarylimidazolyl Free Radicals toward Tris(2-methyl-4-diethylaminophenyl)methane

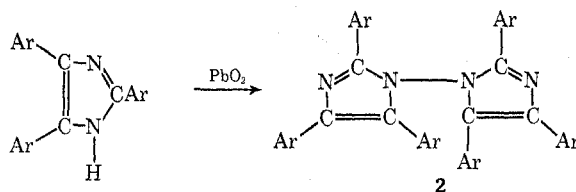
ROBERT L. COHEN

Contribution No. 448 from the Jackson Laboratory, Research and Development Division, Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received February 12, 1970

The effect of aryl substituents on the reactivity of substituted triarylimidazolyl free radicals, photolytically generated from their corresponding dimers, in an electron-exchange reaction with an aminotriphenylmethane substrate was studied by flash photolysis. The reaction rate was retarded by electron-donating substituents and enhanced by electron-withdrawing groups on the imidazolyl radical. Bulky substituents, ortho to the imidazole ring, also increased the reactivity. These results are consistent with the previously proposed mechanism for the reaction.

The preparation of 2,4,5-triphenylimidazole (lophine) was first reported in 1882.¹ In 1960, Hayashi and Maeda reported that oxidation of lophine **1** and its de-



rivatives yields dimeric products which are photo-, piezo-, and thermochromic due to the reversible formation of a colored 2,4,5-triarylimidazolyl free radical. They proposed a hydrazine-type structure **2** to account

for the dimer's properties.² The same structure was suggested by Zimmermann and coworkers³ who prepared a series of these compounds. On the basis of infrared spectral data, White and Sonnenberg⁴ proposed that the thermally unstable dimer originally formed in the oxidation of unsubstituted lophine is the 4,4' isomer **3** which isomerizes in solution to the thermally stable 1,2' dimer **4** through the intermediacy of the free radical **5**. The stable 1,2' isomer is the only dimer readily obtained on oxidation of lophines containing an

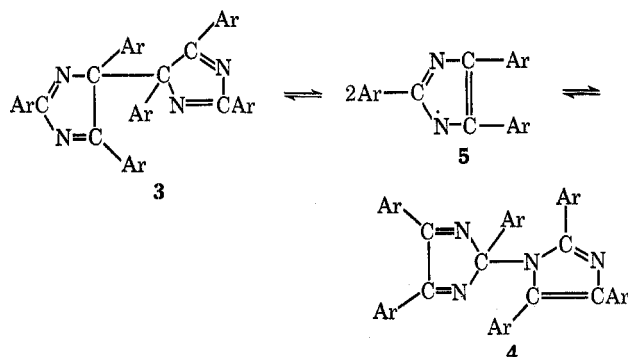
(1) (a) F. R. Japp and H. H. Robinson, *Ber.*, **15**, 1268 (1882); (b) B. Radziszewski, *ibid.*, **15**, 1493 (1882).

(2) (a) T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jap.*, **33**, 565 (1960); (b) *ibid.*, **35**, 2057 (1962); (c) T. Hayashi, K. Maeda, S. Shida, and K. Nakada, *J. Chem. Phys.*, **32**, 1568 (1960).

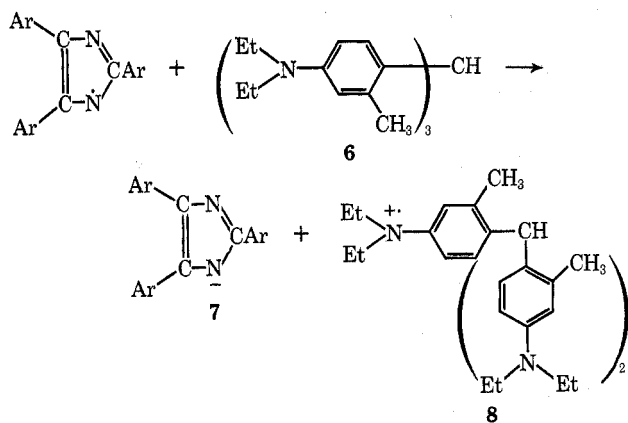
(3) (a) H. Zimmermann, H. Baumgärtel, and F. Bakke, *Angew. Chem.*, **73**, 808 (1961); (b) H. Baumgärtel and H. Zimmermann, *Z. Naturforsch.*, **18b**, 406 (1963).

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

ortho substituent in the 2-phenyl ring.^{4,5} An X-ray crystallographic study⁶ on the dimer obtained from the 2-ortho bromo substituted lophine which showed it to be the 1,2' isomer lends further credence to this conclusion.



The triarylimidazolyl free radicals formed by homolytic cleavage of the respective dimers in an inert solvent will, in the absence of light, revert to a dimeric form.^{5,7-9} The radicals are relatively unreactive toward molecular oxygen, vinyl monomers, aromatic hydrocarbons, and aliphatic alcohols,¹⁰ but are converted by reducing agents such as amines and phenols to the corresponding imidazole.^{3b,7,10} The effect of aryl substituents on the rate of radical dimerization has been studied.⁵ In this paper, the effect of aryl substituents on the rate of the electron-exchange reaction between triarylimidazolyl radicals and an aromatic amine, tris(2-methyl-4-diethylaminophenyl)methane (6) will be discussed. This reaction has been shown to involve electron exchange at the amino nitrogen atom yielding the lophyl anion 7 and the aminium ion 8.¹¹



If the reaction is carried out in the presence of acid, the aminium ion reacts further to form a triarylmethane dye by a mechanistic route¹¹ similar to that proposed by MacLachlan for the photochemical reaction between tris(*p*-*N,N*-diethylaminophenyl)methane and carbon tetrachloride.¹² In the absence of acid, the condition employed in this study, no dye is formed from the tri-

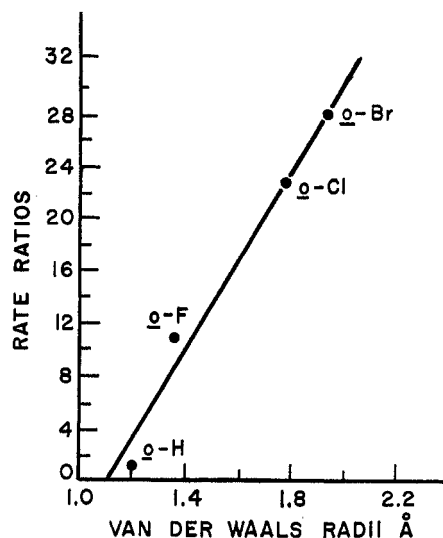


Figure 1.—Reactivity of 2-ortho-substituted phenyl-4,5-diphenylimidazolyl radicals as a function of size of ortho substituent.

arylmethane, but rather the aminium ion proceeds to unidentified, noncolored products.

Results and Discussion

The triarylimidazolyl free radicals were photochemically produced from the corresponding dimers in the presence of the aminotriarylmethane and the reaction kinetics measured using flash photolysis. Imidazolyl radical decay was followed at 5480 or 3900 Å. The reaction followed first-order kinetics under the conditions employed: methanolic solutions $2 \times 10^{-4} M$ in hexaarylbiumidazole and 1×10^{-3} to $2 \times 10^{-5} M$ in tris(2-methyl-4-diethylaminophenyl)methane. Riem and MacLachlan⁷ showed that these kinetics were actually pseudo first order when the concentration of amine is much larger than that of the photogenerated radical, as it is in this case. In a few instances, the rate and order of aminium ion appearance at 4600 Å¹¹ was checked against imidazolyl radical decay and good agreement was found. The true second-order rate constants for the reaction were obtained by dividing the pseudo-first-order rate constants, calculated from the observed transient half-lives, by the amine concentration. The resulting values are given in Tables I and II. The individual determinations were generally reproducible within 20%. In most cases, the rate constants for a single imidazolyl radical determined at two different amine concentrations were in good agreement. If future studies show that these second-order rate constants are responsive to imidazolyl dimer concentration, as was found by Wilks and Willis for the radical dimerization reaction,⁹ then the constants presented herein would include a dimer concentration term. Since dimer concentration was held constant in this study, none of the conclusions would be changed thereby.

Substituent Effects in the 4- and 5-Phenyl Rings.—

The rate constants for several series of substituted imidazolyl radicals and rate ratios using the simple 2-ortho substituted species as the standard are given in Table I. The data illustrate the effect of both electronic and steric factors on the reaction rate. Electron-donating groups on the 4- and 5-phenyl

(5) L. A. Cescon, G. R. Coraor, *et al.*, *J. Org. Chem.*, **36**, 2262 (1971).

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

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

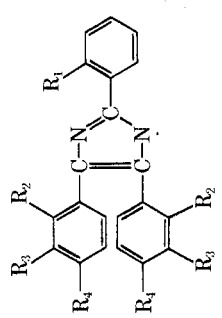
(8) (a) T. Hayashi, K. Maeda, and M. Moriga, *Bull. Chem. Soc. Jap.*, **37**, 1563 (1964); (b) T. Hayashi, K. Maeda, and M. Takeuchi, *ibid.*, **37**, 1717 (1964); (c) H. Neda, *J. Phys. Chem.*, **68**, 1304 (1964).

(9) M. A. J. Wilks and M. R. Willis, *J. Chem. Soc. B*, 1526 (1968).

(10) L. A. Cescon, G. R. Coraor, *et al.*, *J. Org. Chem.*, **36**, 2267 (1971).

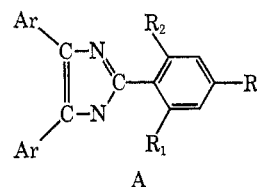
(11) A. MacLachlan and R. Reim, *ibid.*, **36**, 2275 (1971).

(12) A. MacLachlan, *J. Phys. Chem.*, **71**, 718 (1967).

TABLE I
RATE OF ELECTRON ABSTRACTION BY SUBSTITUTED TRIARYLMIDAZOLYLIS


Row	$R_1 = H^e$		$R_1 = F^f$		$R_1 = Cl^{g,h}$		$R_1 = Br^i$		$R_1 = NO_2^j$					
	k^a	b (k/k_{III}^c)	k^a	b (k/k_{III}^c)	k^a	b (k/k_{III}^c)	k^a	b (k/k_{III}^c)	k^a	b (k/k_{III}^c)				
a	1.5 ± 0.2^d	2	1.25	2	15.5 ± 0.5	2	1.14	2	32.0 ± 4.5	2	1.16	27.5 ± 0.5	2	0.69
b	1.0	1	0.83	3	23.7 ± 0.9	3	0.86	3	13	1	0.47			
c	0.5 ± 0.07	3	0.42	3	3.4 ± 0.3	3	0.12	3	2.6 ± 0.2	3	0.08			
d	0.25	1	0.21	2	0.27 ± 0.05	2	0.01	2						
e	0.026	1	0.022	2										

^a Rate constant $\times 10^{-6} M^{-1} sec^{-1}$. ^b Number of kinetic runs. ^c Rate constant for compound divided by that for corresponding 2-ortho-substituted phenyl-4,5-diphenylimidazolyls obtained from Table II. ^d Average deviation. ^e Registry no. are as follows. ^f 29883-62-3 (a); 29883-66-7 (b); 29883-68-9 (c); 29883-72-5 (d); 29883-75-5 (e). ^g 29883-63-4 (a). ^h 29883-64-5 (a); 29883-67-8 (b); 29883-69-0 (c); 29883-70-3 (d); 29883-71-4 (d). ⁱ 29883-65-6 (a); 30041-83-9 (e).

TABLE II
RATE OF ELECTRON ABSTRACTION BY A FROM
TRIS(2-METHYL-4-DIETHYLAMINOPHENYL)METHANE

No.	Registry no.	R_1	R_2	R_3	$k \times 10^{-6} M^{-1} sec^{-1}$	a
i	1724-47-6	H	H	H	1.2 ± 0	2
ii	29864-07-1	F	H	H	13.5 ± 0.5^b	2
iii	29897-74-3	Cl	H	H	27.6 ± 1.8	3
iv	29898-50-8	Br	H	H	32.5 ± 1.5	2
v	29864-09-3	CH ₃	H	H	1.4 ± 0.1	2
vi	29979-75-7	OCH ₃	H	H	1.5 ± 0.1	3
vii	29864-10-6	OCH ₂ CH ₃	H	H	1.1 ± 0	3
viii	29864-11-7	NO ₂	H	H	40.0 ± 9.0	3
ix	29864-12-8	Cl	Cl	H	953 ± 62	3
x	29898-51-9	CH ₃	CH ₃	CH ₃	23.5 ± 1.5	2

^a Number of kinetic runs. ^b Average deviation.

rings tend to reduce the rate of reaction with the amine, a finding consistent with the electron-exchange mechanism proposed by MacLachlan and Reim.¹¹

The tenfold decrease in reactivity between the ortho and para methoxy substituted compounds shows the influence of steric factors on the reaction rate. There are two steric factors which combine to produce the rate difference observed. Forced rotation of both the 4- and 5-phenyl rings out of the imidazole ring plane because of the bulk of the ortho substituents tends to reduce conjugation with the imidazole ring. This steric inhibition of resonance acts to increase the reactivity of the ortho relative to the more stable para substituted free radicals. The forced rotation of the 4- and 5-phenyl rings also further facilitates the close approach of the aminotriarylmethane in the plane of the imidazolyl ring, thus promoting the electron-transfer reaction.

Substituent Effects in the 2-Phenyl Ring.—Substituents on the 2-phenyl ring of the imidazolyl radical also influence its reactivity by electronic and steric effects, as shown in Table II. The latter factor is particularly important because of this ring's ability to be completely coplanar with the imidazole ring when unsubstituted, and its tendency, as shown by molecular models, to twist out of plane when ortho substituted. The 4- and 5-phenyl rings cannot both be coplanar with the imidazole nucleus at the same time, even when unsubstituted.¹³

In the series of 2-ortho halogen substituted radicals, the rate of reaction with the amine increases as a linear function of the substituent's van der Waals radius (Figure 1). In view of the similarity of the polar effects exerted by the halogens from the ortho position,¹⁴ this relationship exemplifies the steric acceleration of the electron-exchange reaction which results when the imidazole ring is exposed to close approach of the aminotriarylmethane because of forced rotation of the 2-phenyl ring. The electrical influence of the substituent on the rate is seen if one tries to extend the relationship found for the halogens to electron-supplying substituents.

(13) M. A. J. Wilks and M. R. Willis, *J. Phys. Chem.*, **72**, 4717 (1968).

(14) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 590.

TABLE III
 2-SUBSTITUTED ARYL-4,5-DIPHENYLIMIDAZOLES
 AND DIMERS^a

2-Phenyl substituent	Registry no.	Recrystn solvent	% yield	Mp, °C	λ_{\max} , m μ	Source
<i>o</i> -F	29864-14-0	EtOH·H ₂ O	78	139-165		<i>b</i>
						<i>c</i>
<i>o</i> -CH ₃	29864-15-1	PhH-PE	62	114-125		<i>b</i>
						<i>c</i>
<i>o</i> -CH ₃ O	7292-18-4	EtOH	87	169-200		<i>b</i>
						<i>c</i>
<i>o</i> -EtO	5496-42-4	EtOH	97	168-169	232	<i>c</i>
					310	
	29864-18-4	EtOH·H ₂ O	76	138-154		<i>c</i>
<i>o</i> -NO ₂	29864-19-5	Acetone-EtOH	94	233-234	292	<i>c</i>
	29864-20-8	PhH-PE	78	219-220 ^d		<i>e</i>
<i>o,o'</i> -Cl ₂	29864-21-9	EtOH	95	230-231	220	<i>e</i>
	29859-94-7	PE	74	210-225 ^f		<i>e</i>

^a For each pair of compounds, the properties of the imidazole are listed first, followed by those of the corresponding dimer. Satisfactory combustion analytical data ($\pm 0.4\%$) were provided for all of the compounds of this table: Ed. ^b Described in ref 9. ^c Prepared and kindly donated by Drs. L. A. Cescon and R. Dessauer. ^d Mol wt calcd 681; found 653. ^e Prepared and kindly donated by E. Urban. ^f Mol wt calcd 1458; found 1360 (tetramer).

sluggish reactivity is observed for radicals substituted with electron-supplying alkoxy groups at the ortho position of the 2-phenyl ring (IIvi, vii). The strongly electron-withdrawing nitro group, which has a smaller effective size than chlorine on the basis of rates of racemization of hindered biphenyls,¹⁵ promotes the electron-exchange reaction at a rate even faster than bromine.

These data suggest that imidazolyl radicals substituted in both ortho positions of the 2-phenyl ring with fairly large electron-withdrawing substituents would be particularly reactive toward an electron donor. This prediction was borne out by the determination of a second-order rate constant of $9.5 \times 10^8 M^{-1} \text{sec}^{-1}$ for the reaction of di ortho chloro substituted radical IIIi with the aminotriarylmethane. Addition of the second ortho chloro substituent increased the reaction rate by a factor of 35 compared with the mono ortho chloro substituted radical. Species IIix showed the greatest reactivity of any of the free radicals examined and, in fact, reacted 30,000 times faster than the most sluggish radical, 2-phenyl-4,5-bis(*p*-methoxyphenyl)imidazolyl (IIix). In this case, both steric and electronic factors

 TABLE IV
 SUBSTITUTED TRIARYLIMIDAZOLES AND DIMERS^a

Registry no.	2-Phenyl substituent	4- and 5-phenyl substituent	Recrystn solvent	% yield	Mp, °C	λ_{\max} , m μ	Source
29864-22-0	H	<i>m</i> -CH ₃ O	EtOH	82	188-189	307	<i>b</i>
29864-23-1			PhH-PE ^f	85	105-110		<i>b</i>
29969-82-2	H	<i>m</i> -EtO	EtOH	92	180-181	223	<i>b</i>
29864-24-2			EtOH-H ₂ O	81	110-120		<i>b</i>
29864-25-3	H	<i>m</i> -CH ₃	THF-EtOH	72	261-262	308	<i>b</i>
29969-83-3			PE	94	156-157		<i>b</i>
29864-26-4	H	<i>o</i> -CH ₃ O	EtOH	91	175.5-176.5	307	<i>c</i>
29864-27-5			PhH-PE	86	134-150		<i>b</i>
7044-99-7	H	<i>p</i> -CH ₃ O	PhH	99	197.5-198	298	<i>c</i>
30041-84-0			EtOH-H ₂ O	51	147-155		<i>c</i>
29864-29-7	<i>o</i> -F	<i>m</i> -CH ₃ O	EtOH	97	142.5-143.5	306	<i>d</i>
29864-30-0			PhH-PE	98	110-112		<i>d</i>
29864-31-1	<i>o</i> -Cl	<i>m</i> -CH ₃ O	MeOH	85	135-136.5	303	<i>e</i>
29864-32-2			EtOH	81	175-178.5		<i>e</i>
29864-33-3	<i>o</i> -Cl	<i>m</i> -EtO	EtOH	87	135.5-137.5		<i>e</i>
29864-34-4			EtOH	75	151-151.5		<i>e</i>
29864-36-6	<i>o</i> -Cl	<i>m</i> -CH ₃	EtOH	79	158-159	233	<i>b</i>
29864-35-5			PhH-PE	99	133-135		<i>b</i>
30041-85-1	<i>o</i> -Cl	<i>o</i> -CH ₃ O	EtOH	98	118-119	312	<i>b</i>
29864-37-7			PhH-PE	93	135-165		<i>b</i>
29864-38-8	<i>o</i> -Cl	<i>p</i> -CH ₃ O	EtOH	92	136-137	293	<i>b</i>
29969-84-4			PhH-PE	90	157-158		<i>b</i>
29864-39-9	<i>o</i> -Br	<i>o</i> -CH ₃ O	EtOH	78	124-125	309	<i>d</i>
29864-40-2			PhH-PE	85	133-135		<i>d</i>
29864-41-3	<i>o</i> -NO ₂	<i>m</i> -CH ₃ O	EtOH	69	188-190		<i>e</i>
29864-42-4			MeCl ₂ -PE	94	124-134		<i>e</i>
29864-43-5	<i>o</i> -NO ₂	<i>p</i> -CH ₃ O	PhH-PE	70	169-170	290	<i>e</i>
29864-44-6			PhH-PE	66	165-167		<i>e</i>

^a For each pair of compounds, the properties of the imidazole are listed first, followed by those of the corresponding dimer. Satisfactory combustion analytical data ($\pm 0.4\%$) were provided for all of the compounds of this table: Ed. ^{b-d} Prepared and kindly donated by ^b E. Urban; ^c Drs. L. A. Cescon and R. Dessauer; ^d Dr. W. M. Hardham. ^e Prepared by author. ^f Petroleum ether, bp 30-60°.

uents. The methyl-substituted radical (IIv) reacts only slightly faster than the unsubstituted one (III) even though the van der Waals radius for methyl is approximately the same as that for bromine. Similarly,

work together to produce an extremely potent radical with respect to electron abstraction.

As a further check on the importance of steric effects in the 2-phenyl ring, the reaction rate of 2-mesityl-4,5-diphenylimidazolyl (IIx) was measured and compared with that for 2-*o*-tolyl-4,5-diphenylimidazolyl (IIv). If steric considerations were important, the former compound should react faster, while, if the electronic effect of the methyl groups were the primary determinant of the rate, the latter compound would be the more reactive. The rate constant for the mesityl compound is $2.35 \times 10^7 M^{-1} \text{sec}^{-1}$, some 17 times greater than that for the ortho methyl substituted radical. This difference is probably a lower limit, since the steric effect of the ortho methyl groups in the mesityl compound is negated somewhat by the electronic effect of that radical's para methyl substituent.

It is interesting to note that, whereas ortho disubstitution in the 2-phenyl ring tends to increase the imidazolyl radical's reactivity toward electron abstraction, it decreases its dimerization rate.¹⁶ These two phenomena have the same basic cause. The formation of the thermally stable 1,2' isomer is severely hindered in a ortho disubstituted radical with the 2-phenyl ring preferring a conformation nearly perpendicular to the imidazole ring plane. In this conformation, the ortho substituents on the 2-phenyl ring lie above and below the carbon at position two, effectively shielding it from bond formation with a second radical's imidazole nitrogen. Thus, the same steric factor which tends to make im-

idazole radicals more reactive toward electron abstraction also makes them more resistant to dimerization.

Experimental Section

Materials.—Tris(2-methyl-4-diethylaminophenyl)methane was kindly donated by E. Urban, Organic Chemicals Department, Du Pont. Samples of triphenyl-, 2-*o*-chlorophenyl-4,5-diphenyl-, 2-*o*-bromophenyl-4,5-diphenyl-, and 2-mesityl-4,5-diphenylimidazolyl dimer were prepared by Cescon, Coraor, *et al.*⁵ The properties of new hexaarylbiimidazoles used in this study and their triarylimidazole precursors are listed in Tables III and IV. They were prepared by methods described by Cescon, Coraor, *et al.*⁵ The wide melting ranges reported for many of the dimers are due to their thermal instability and, perhaps, in part to their tendency to strongly retain solvent of crystallization.⁵ The latter is most probably the cause of the occasional lack of exact agreement between calculated and found microanalytical values.

Apparatus.—The flash photolysis apparatus was of conventional design.^{7,17} Light from the analysis lamp was filtered through a Corning 3-69 filter before entering the sample cell and through a Corning 3-72 filter before entering the monochromator. The photolyzing radiation was restricted to the ultraviolet with a Corning 7-54 filter. The kinetic studies were performed at $25 \pm 2^\circ$.

Registry No.—6, 4482-70-6.

Acknowledgment.—The author is grateful to Drs. Richard G. Bennett and Alexander MacLachlan for permission to use the flash photolysis equipment at the Radiation Physics Laboratory of the Du Pont Company.

(17) G. Porter, *Proc. Roy. Soc., Ser. A*, **200**, 284 (1950).

(16) Unpublished data, R. L. Cohen.

Substituent Effects on the Basicity of Pyridine. Elucidation of the Electronic Character of β -Substituted Vinyl Groups

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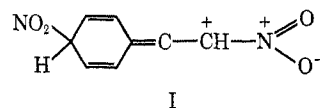
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Pyridines substituted in the 3 and 4 positions by groups $-\text{CH}=\text{CHX}$, where $\text{X} = \text{NO}_2$ (only the 3-substituted compound), CN , CHO , COCH_3 , COOC_2H_5 , COC_6H_5 , $\text{COC}_6\text{H}_4\text{NO}_2$, have been synthesized and their $\text{p}K_a$ values measured. The correlation of $\text{p}K_a$ values of substituted pyridines with the Hammett equation is discussed, with particular regard to the above substituents. Also prepared were *m*- and *p*-vinylbenzoic acids, and substituent constants for the vinyl group of 0.08 (σ_m) and -0.08 (σ_p) have been established.

Halogeno substituents are well known for their ability to direct electrophilic attack at the positions ortho and para to their point of attachment to a benzene ring, but reducing the rate of attack below that of benzene itself. This is attributed in simple terms to the opposing influence of the mutually independent inductive and resonance effects. A similar situation arises in the case of the β -nitrovinyl substituent and other substituents made up of attachment of a group of $-\text{I}$ or $(-\text{I}, -\text{M})$ character to the β position of the vinyl group. Thus Truce and Simms² found only 2% of meta nitration in β -styryltrimethylammonium picrate, while Baker and Wilson, Underwood and Kochmann, and Bordwell and Rohde obtained analogous results with β -nitrostyrene,³ cinnamic acid,^{4,5} and

β -styrenesulfonyl chloride.⁵ The latter workers also demonstrated correspondence between the rate of nitration of such compounds and that of chlorobenzene. These and other workers^{6,7} have consequently likened the electronic character of such substituents to that of the halogens, while at the same time remarking on the apparent high energy of the canonical form I



involving adjacent positive charges of the Wheland intermediate resonance hybrid for para nitration of β -nitrostyrene.

Stewart and Walker⁷ have also measured the dissociation constants for the *m*- and *p*- β -nitrovinyl derivatives of benzoic acid and thus shown that the σ_m and σ_p

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