INVESTIGATION OF NITROGEN-CONTAINING HETEROCYCLIC FREE RADICALS

XIX.* 2-ARYL-4,5-(p-BROMOPHENYL)IMIDAZOLYL RADICALS AND THEIR DIMERS

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2-Aryl-4,5-di(p-bromophenyl)imidazolyl dimers were synthesized, and the dependence between the rate of dissociation of the dimers into radicals and the character of the substituents in the 2-phenyl ring was investigated. It was found that the effect of substituents on the rate of dissociation of the dimers is described by the Hammett equation. The presence of bromine atoms in the p positions of the 4-and 5-phenyl rings increases the contribution of the mesomeric component to stabilization of the transition state of the dissociation of dimers as compared with bis(triphenylimidazolyls).

The rate of dissociation of dimers of triphenylimidazolyl radicals that contain substituents in the 2- and 4-phenyl rings is determined by the presence and character of substituents in the 2-phenyl ring [2]. Moreover, the presence of a substituent in the 4-phenyl ring somewhat lowers the activation energy of the dissociation of the dimer (by 0.7-0.9 kcal/mole) without having a substantial effect on the dissociation rate.

In the present paper, we have studied the dissociation of dimers of triarylimidazolyl radicals that contain substituents in all three phenyl rings.

2-Aryl-4,5-di(p-bromophenyl)imidazoles were obtained by condensation of p,p'-dibromobenzil with aromatic aldehydes in the presence of ammonium acetate in glacial acetic acid via the Davidson method [3].

The UV absorption spectra of alcohol solutions of the imidazoles have two maxima at 235-300 and 300-375 nm (Table 1). The introduction of substituents into the phenyl ring of the imidazole molecule causes a considerable bathochromic shift of the absorption spectrum maximum as compared with triphenylimidazole (λ_{max} 225 and 301 nm).

When toluene solutions of 2-aryl-4,5-di(p-bromophenyl)imidazoles are shaken with lead dioxide, they take on an intense coloration, which is due to the formation of radicals. The radical character of the dehydrogenation products is confirmed by ESR spectroscopy. The electronic absorption spectra of toluene solutions of the radicals at 400-700 nm have one maximum (Table 1). The presence of substituents, regardless of their nature, in the 2-, 4-, and 5-phenyl rings causes a bathochromic shift of the absorption maximum as compared with the triphenylimidazolyl radical (by ~20 nm).

Radical dimers are obtained by oxidation of 2-aryl-4,5-di(p-bromophenyl)imidazoles with potassium ferricyanide in aqueous alcoholic alkali. The absorption spectra of alcohol solutions of the dimers have one maximum in the UV region (Table 2).

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*See [1] for communication XVIII.

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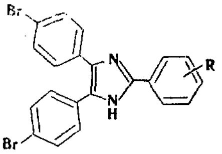
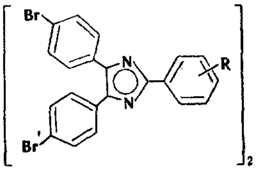
TABLE 1. 2-Aryl-4,5-di(p-bromophenyl)imidazoles



Compound	R	mp, °C	Empirical formula	Found, %			Calc., %			λmax, nm (log ε), of imidazole (alcohol)	λmax, nm, of radical (toluene)	Yield, %
				C	H	N	C	H	N			
I	H	279—280	$C_{21}H_{14}Br_2N_2$	55,3	3,2	6,1	55,5	3,1	6,2	302 (4,26)	572	50
II	*p*-CH_3	260—262	$C_{22}H_{16}Br_2N_2$	56,2	3,3	5,7	56,4	3,4	6,0	300 (4,39)	591	56
III	*m*-CH_3	314—315	$C_{22}H_{16}Br_2N_2$	56,0	3,4	5,6	56,4	3,4	6,0	305 (4,31)	585	36
IV	*p*-Br	275—276	$C_{21}H_{13}Br_3N_2$	47,5	2,5	5,2	47,3	2,5	5,3	235 (4,24), 310 (4,35)	591	52
V	*m*-Cl	323—324	$C_{21}H_{13}Br_2ClN_2$	51,3	3,0	5,7	51,6	2,7	5,7	305 (4,39)	580	65
VI	*p*-NO_2	327—328	$C_{21}H_{13}Br_2N_3O_2$	50,5	3,1	8,2	50,5	2,6	8,4	300 (4,12), 375 (4,15)		80

TABLE 2. 2-Aryl-4,5-di(p-bromophenyl)imidazolyl Dimers



Compound	R	mp, °C	Empirical formula	Found, %			Calc., %			λmax, (log ε), of dimer (alcohol)	Yield, %
				C	H	N	C	H	N		
VII	H	175—180	$C_{42}H_{26}Br_4N_4$	55,6	3,3	5,9	55,7	2,9	6,2	280 (4,61)	68
VIII	*p*-CH_3	214—218	$C_{44}H_{30}Br_4N_4$	56,8	3,6	5,7	56,6	3,2	6,0	285 (4,52)	69
IX	*m*-CH_3	173—177	$C_{44}H_{30}Br_4N_4$	56,8	3,4	6,2	56,6	3,2	6,0	280 (4,36)	65
X	*p*-Br	139—143	$C_{42}H_{24}Br_6N_4$	47,2	2,5	5,5	47,4	2,3	5,3	280 (4,52)	70
XI	*m*-Cl	136—139	$C_{42}H_{24}Br_4Cl_2N_4$	52,0	2,8	5,6	51,7	2,5	5,7	280 (4,43)	65
XII	*p*-NO_2	140—143	$C_{42}H_{24}Br_4N_6O_4$	51,0	2,5	8,2	50,6	2,4	8,4	275 (4,53)	30

TABLE 3. Thermodynamic Data for the Dissociation of 2-Aryl-4,5-di(p-bromophenyl)imidazolyl Dimers in Toluene

Compound	R	Dissociation rate constants, $K \cdot 10^2$, min^{-1}				E_a, kcal/mole	K_0, min^{-1}
		65°	75°	80°	85°		
VII	H	1,92	4,92	7,13	10,19	20,4	$3{,}0 \cdot 10^{11}$
VIII	*p*-CH_3	3,26	6,90	11,04	13,80	18,3	$0{,}2 \cdot 10^{11}$
IX	*m*-CH_3	2,83	5,64	9,09	12,02	19,2	$0{,}7 \cdot 10^{11}$
X	*p*-Br	2,51	5,98	10,51	14,15	21,6	$2{,}3 \cdot 10^{12}$
XI	*m*-Cl	1,13	3,22	4,81	7,60	22,5	$4{,}1 \cdot 10^{12}$
XII	*p*-NO_2	0,65	1,71	2,85	4,08	23,7	$13{,}0 \cdot 10^{12}$

The method in [4] was used to investigate the rate of dissociation of the dimers into radicals. The rate of dissociation of 2-aryl-4,5-di(p-bromophenyl)imidazolyl dimers is described by a first-order equation.

The thermodynamic data for the rate of dissociation of the 2-aryl-4,5-di(bromophenyl)imidazolyl dimers in toluene at 65-85° are presented in Table 3.

The rate of dissociation of 2-aryl-4,5-di(p-bromophenyl)imidazolyl dimers proved to be higher than the rate of dissociation of the analogous 2-aryl-4,5-diphenylimidazolyl dimers. Just as for bis(2-aryl-4,5-diphenylimidazolyls), electron-donor substituents (p- and m-CH_3) facilitate dissociation of the dimers, while electron-acceptor substituents hinder it. The presence of bromine in the p position of the 2-phenyl ring also increases the dissociation rate (Table 3) because of the strong mesomeric effect of bromine.

The effect of substituents on the rate of dissociation of the dimers is satisfactorily described by the Hammett equation with separation of the inductive and mesomeric components of the σ constants:

$$
\begin{aligned}
\lg K &= -0.9819 - 0.350\sigma_I - 1.032\sigma_C \text{ (at } 85°) \ (r = 0.962) \\
\lg K &= -1.1446 - 0.415\sigma_I - 1.093\sigma_C \text{ (at } 80°) \ (r = 0.983) \\
\lg K &= -1.4456 - 0.477\sigma_I - 1.151\sigma_C \text{ (at } 75°) \ (r = 0.983) \\
\lg K &= -1.6403 - 0.604\sigma_I - 1.178\sigma_C \text{ (at } 65°) \ (r = 0.986)
\end{aligned}
$$

Thus the introduction of substituents into the p position of 4- and 5-phenyl rings changes the character of the stabilization of the transition state by increasing the relative contribution of the mesomeric component of the substituents in the 2-phenyl group as compared with 2-aryl-4,5-diphenylimidazolyl dimers [2].

EXPERIMENTAL

2-Phenyl-4,5-di(p-bromophenyl)imidazole (I). A solution of 1.84 g (5 mmole) of 4,4'-dibromobenzil [5], 0.53 g (5 mmole) of benzaldehyde, and 3 g (40 mmole) of ammonium acetate in 25 ml of glacial acetic acid was refluxed for 1 h. It was then cooled and diluted with 220 ml of water, and the white precipitate was removed by filtration, washed with water, and dried to give 1.14 g (50%) of colorless needles with mp 279-280° (from alcohol).

Compounds II-VI were similarly prepared (Table 1).

Imidazoles V and VI began to separate out 10-15 min after the start of the reaction, but considerable dilution of the reaction mixture with water is necessary to isolate the rest of the compounds.

2-Phenyl-4,5-di(p-bromophenyl)imidazolyl Dimer (VII). A total of 450 ml of 1% potassium ferricyanide solution was added with stirring at 5-10° in the course of an hour to a solution of 1.54 g (3.4 mmole) of 2-phenyl-4,5-di(p-bromophenyl)imidazole in alcoholic alkali (12 g of KOH in 100 ml of alcohol). The addition of the first portions of the ferricyanide solution was accompanied by the appearance of an intense coloration peculiar to the radical, after which a precipitate formed. It was removed by filtration and washed thoroughly with water. The dried product was dissolved in benzene, which was then removed by vacuum distillation with a water aspirator. The residue, which is a transparent solid mass, was treated with alcohol, as a result of which 1.05 g (68%) of a yellowish-greenish product with mp 175-180° was isolated.

Dimers VIII-XII were similarly obtained (Table 2).

The kinetic measurements were made as in [4].

The three-parameter correlation method [6] was used to separate the inductive and mesomeric components of the Hammett σ constants. The σ_I and σ_C values were taken from [7].

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