INVESTIGATION OF NITROGEN-CONTAINING HETEROCYCLIC FREE RADICALS

XV.* MONO- AND DISUBSTITUTED TRIPHENYLIMIDAZOLYL RADICALS AND THEIR DIMERS

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The dependence between the rate of dissociation of dimers of 2,4,5-triarylimidazolyl radicals and the character of the substituent in the 2- and 4-phenyl rings was investigated. It was found that the rate of dissociation of 2,4-disubstituted dimers depends only on the character of the substituents in the 2-phenyl ring.

Continuing our study of the dependence between the structures of radicals of the triarylimidazolyl series and the rate of dissociation of their dimers, we decided to investigate the effect of substituents in the 4-phenyl ring on the rate of dissociation of the dimers.

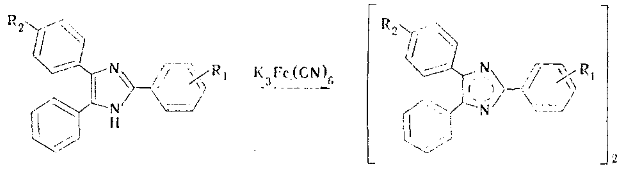
Substituted triphenylimidazoles (Tables 1 and 2) were synthesized via the Davidson method [2] by condensation of benzyls with aromatic aldehydes in the presence of ammonium acetate in glacial acetic acid. All of the imidazoles obtained are crystalline substances that are insoluble in water and moderately soluble in benzene and alcohol. Compounds I-IX, which have a p-methoxy group in the 4-phenyl ring, generally crystallize with incorporation of the solvent, which is removed with difficulty by vacuum drying.

The UV absorption spectra of alcohol solutions of the triarylimidazoles have two maxima at 225-290 nm and 300-395 nm. The introduction of substituents has little effect on the form of the curve and induces only a slight shift of the absorption maximum (the nitro group has the greatest effect) (Tables 1 and 2).

The triarylimidazoles are dehydrogenated by lead dioxide in benzene to give deeply colored solutions of radicals. The dehydrogenation of the intensely colored nitro derivatives is not accompanied by a visible change in the color, but ESR spectroscopic data attest to the presence of paramagnetic particles. The ESR spectrum of the 2,5(4)-diphenyl-4(5)-(p-nitrophenyl)imidazolyl radical is a singlet with an unresolved structure. The signal width is 23 Oe.

The absorption spectra of benzene solutions of the radicals in the visible region (400-700 nm) have one maximum. The introduction of substituents into the phenyl rings, regardless of their nature, induces a bathochromic shift of the absorption spectrum maximum as compared with the triphenylimidazolyl radical (λ_{max} = 555 nm) (Tables 1 and 2).

A number of dimers with substituents of different character in different positions of the phenyl rings (Table 3) were obtained by oxidation of the triarylimidazoles with potassium ferricyanide in aqueous alcoholic alkali [3].



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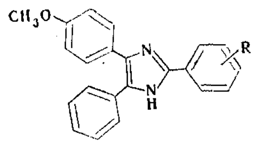
*See [1] for communication XIV.

N. P. Ogarev Mordovskii State University, Saransk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1676-1680, December, 1972. Original article submitted April 26, 1971.

TABLE 1. 2-R-Phenyl-4(5)-p-anisyl-5(4)-phenylimidazoles



Comp.	R	Mp, °C*	λ_{max} (log ε) of the imidazole (alcohol)	λ_{max} of the radical (benzene)	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	N	C	H	N	
I	H	225—226	230 (4,32); 304 (4,44)	570	$C_{22}H_{18}N_2O$	80,8	5,8	8,5	81,0	5,6	8,6	93
II	p-CH_3	184—185	302 (4,42)	586	$C_{23}H_{20}N_2O$	81,3	6,2	8,2	81,1	5,9	8,2	23
III	m-CH_3	253—254	302 (4,42)	580	$C_{23}H_{20}N_2O$	81,1	6,5	8,0	81,1	5,9	8,2	66
IV	p-Br	242—243	235 (4,38); 315 (4,47)	580	$C_{22}H_{17}BrN_2O$	65,4	4,6	6,5	65,2	4,2	6,9	60
V	m-Br	267—268	227 (4,35); 315 (4,40)	574	$C_{22}H_{17}BrN_2O$	65,2	4,5	6,5	65,2	4,2	6,9	40
VI	p-NO_2	229—230 †	265 (4,16); 395 (4,19)	—	$C_{22}H_{17}N_3O_3$	70,6	4,7	10,9	71,1	4,6	11,3	66
VII	m-NO_2	256—257	230 (4,32); 302 (4,30)	—	$C_{22}H_{17}N_3O_3$	71,0	5,0	11,0	71,1	4,6	11,3	72
VIII	p-OCH_3	182—183	232 (4,27); 300 (4,48)	614	$C_{23}H_{20}N_2O_2$	77,7	5,5	7,6	77,5	5,6	7,9	27,6
IX	p-$N(CH_3)_2$	110—111	317 (4,49)	—	$C_{24}H_{23}N_3O$	78,2	6,4	11,7	78,0	6,3	11,4	33

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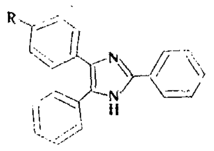
*Compounds I, II, and VIII were crystallized from acetone, III-VII were crystallized from ethanol, and IX was crystallized from isopropyl alcohol.

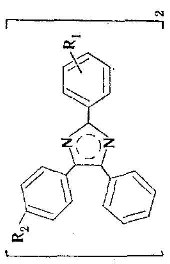
† The compound softens and darkens at 119-120° and then becomes lighter and begins to *harden*; it melts at 229-230°.

TABLE 2. 2,5(4)-Diphenyl-4(5)-R-phenylimidazoles



Comp.	R	Mp, °C (from alcohol)	λ_{max} (log ε) of the imidazole (alcohol)	λ_{max} of the radical (benzene)	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	N	C	H	N	
X	OC_2H_5	206—207	235 (4,32); 304 (4,45)	574	$C_{23}H_{20}N_2O$	80,9	5,7	8,3	81,1	5,9	8,2	61
XI	CH_3	219—220	225 (4,17); 303 (4,25)	565	$C_{22}H_{18}N_2$	84,7	5,9	8,9	85,1	5,8	9,0	37
XII	Cl	244—245	230 (4,34); 306 (4,43)	563	$C_{21}H_{15}ClN_2$	75,9	4,8	8,6	76,2	4,6	8,5	57
XIII	Br	253—254	230 (4,40); 304 (4,48)	562	$C_{21}H_{15}BrN_2$	67,5	4,2	7,1	67,3	4,0	7,5	58
XIV	I	237—239	225 (4,28); 306 (4,45)	570	$C_{21}H_{15}IN_2$	60,1	4,0	6,2	59,7	3,6	6,6	70
XV	NO_2	227—229	290 (4,32); 377 (4,10)	564	$C_{21}H_{15}N_3O_2$	73,7	4,5	11,9	73,9	4,4	12,2	79

TABLE 3. Dimers of Triarylimidazolyl Radicals



Comp.	R_1	R_2	Mp, °C	Dissociation rate constants, $K \cdot 10^2$ min^{-1}				E_a, kcal/mole	$K_0 \cdot 10^{-12}$, min^{-1}	Empirical formula	N, %		Yield, %
				65°	75°	80°	85°				found	calc.	
XVI	p-CH_3	OCH_3	155—160	1,92	4,24	6,21	8,94	20,0	0,15	$C_{46}H_{38}N_4O_2$	8,2	8,2	69
XVII	m-CH_3	OCH_3	125—130	1,60	3,57	5,37	8,02	20,7	0,36	$C_{46}H_{38}N_4O_2$	8,1	8,2	62
XVIII	H	OCH_3	95—110	1,22	2,60	4,32	6,73	21,5	0,90	$C_{44}H_{34}N_4O_2$	8,8	8,6	74
XIX	p-Br	OCH_3	142—145	1,06	2,58	4,14	6,50	22,5	3,62	$C_{44}H_{32}Br_2N_4O_2$	6,7	6,9	70
XX	m-Br	OCH_3	122—125	0,67	1,85	3,43	5,75	23,4	10,71	$C_{44}H_{32}Br_2N_4O_2$	6,6	6,9	65
XXI	H	OC_2H_5	90—110	1,08	2,54	4,25	6,27	21,7	1,1	$C_{46}H_{38}N_4O_2$	8,0	8,2	58
XXII	H	CH_3	115—120	1,17	2,90	4,70	6,90	21,8	1,4	$C_{44}H_{34}N_4$	9,1	9,0	67
XXIII	H	Cl	110—115	1,17	2,82	4,40	6,50	21,6	1,0	$C_{42}H_{28}Cl_2N_4$	8,2	8,5	72
XXIV	H	Br	100—110	1,16	2,65	4,28	6,74	21,7	1,2	$C_{42}H_{28}Br_2N_4$	7,3	7,5	75
XXV	H	H	200—201	1,18	3,62	—	8,06	22,4	3,9	$C_{42}H_{30}N_4$	9,1	9,5	90

The stable dimers are yellowish substances that melt with decomposition over a rather wide range of temperatures; this is apparently due to their thermal dissociation.

The rates of dissociation of the dimers into radicals were determined via the method in [4] and were described by a first-order equation.

As seen from Table 3, the rate of dissociation of dimers with substituents in the 4-phenyl ring is practically independent of the character of the substituent, although it is somewhat lower than the rate of dissociation of the triphenylimidazolyl dimer (XXV). The character of the substituent also does not affect the energy of activation of dissociation, but the presence of a substituent does lower it somewhat in comparison with that of unsubstituted bis(triphenylimidazolyl). A weaker effect of substituents in the 4-phenyl ring on the physicochemical properties of both triarylimidazoles and triarylimidazolyls was previously noted by Sümmermann and Cescon and coworkers [5,6], but in this case we are dealing more with the absence of this effect, at least over the investigated range of temperatures.

When substituents are simultaneously present in the phenyl rings in the 2 and 4 positions of the imidazole ring, the rate of dissociation of the dimers depends on the nature of the substituent in the 2-phenyl ring: electron-donor substituents facilitate dissociation of the dimers, while electron-acceptor substituents hinder it. The effect of substituents on the rate of dissociation of the dimers is described by the Hammett equation:

$$\lg K = -1{,}1149 - 0{,}335\sigma_I - 0{,}371\sigma_C \quad \text{at} \quad 85° \quad (r = 0{,}999)$$
$$\lg K = -1{,}2986 - 0{,}445\sigma_I - 0{,}540\sigma_C \quad \text{at} \quad 80° \quad (r = 0{,}999)$$
$$\lg K = -1{,}5003 - 0{,}622\sigma_I - 0{,}854\sigma_C \quad \text{at} \quad 75° \quad (r = 0{,}999)$$
$$\lg K = -1{,}8713 - 0{,}794\sigma_I - 1{,}076\sigma_C \quad \text{at} \quad 65° \quad (r = 0{,}998)$$

As seen from the table above, the presence of a p-methoxy group in the 4-phenyl ring (XVI-XX) increases the relative contribution of the mesomeric component to stabilization of the transition state as compared with bis(2-aryl-4,5-diphenylimidazolyls), for which the inductive component usually prevails over the mesomeric component:

$$\lg K = -1{,}0878 - 0{,}424\sigma_I - 0{,}472\sigma_C \quad \text{at} \quad 85° \quad (r = 0{,}993)$$
$$\lg K = -1{,}1895 - 0{,}507\sigma_I - 0{,}165\sigma_C \quad \text{at} \quad 80° \quad (r = 0{,}998)$$
$$\lg K = -1{,}4122 - 0{,}514\sigma_I - 0{,}382\sigma_C \quad \text{at} \quad 75° \quad (r = 0{,}999)$$
$$\lg K = -1{,}8485 - 0{,}562\sigma_I - 0{,}405\sigma_C \quad \text{at} \quad 65° \quad (r = 0{,}999)$$

[the rate constants for dissociation of bis(2-aryl-4,5-diphenylimidazolyls) presented in [7] were used for the calculations].

EXPERIMENTAL

2,5(4)-Diphenyl-4(5)-(p-methoxyphenyl)imidazole (I). A solution of 1.2 g (5 mmole) of p-methoxybenzyl, 0.53 g (5 mmole) of benzaldehyde, and 3 g of ammonium acetate in 25 ml of glacial acetic acid was refluxed for 1 h. It was then cooled and diluted to 250 ml with water. The precipitate was removed by filtration, washed with water, and dried to give 1.53 g (93%) of colorless crystals with mp 225-226° (from aqueous acetone).

Compounds II-XV were similarly obtained. In order to avoid the formation of resinous products in the preparation of II, III, VIII, and IX, the reaction mass should be poured into ammonium hydroxide.

2,5(4)-Diphenyl-4(5)-(p-methoxyphenyl)imidazolyl Dimer (XVI). A total of 450 ml of 1% potassium ferricyanide solution was added with continuous stirring at 5-10° in the course of 1.5 h to a solution of 1.1 g (3.4 mmole) of 2,5(4)-diphenyl-4(5)-(p-methoxyphenyl)imidazole in 100 ml of alcohol containing 12 g of potassium hydroxide. A blue color corresponding to the color of the resulting radical developed on addition of the first portions of the oxidizing agent. The blue color vanished as the ferricyanide solution was added, and a precipitate formed; this was removed by filtration and washed thoroughly with water. The light-colored product was dried and dissolved in a small amount of benzene. The intensity of the color of the solution fell quite rapidly. The benzene was vacuum evaporated to dryness, and the residue was triturated with ethanol to give 0.78 g (69%) of yellow crystals with mp 95-110°.

Dimers XVII-XXIV were similarly synthesized.

Kinetic Measurements. The reaction of the dimers with diphenylpicrylhydrazine [4] was used to determine the rate of dissociation of the dimers. The rate constants for dissociation of the dimers and the E_a values were determined graphically. Toluene, purified via the method in [8], was used as the solvent.

The reaction constants (ρ) and the correlation coefficients in the Hammett equation were calculated by the three-parameter correlation method [9]. The inductive and mesomeric components of the σ constants were taken from [10].

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