INVESTIGATION OF NITROGEN-CONTAINING HETEROCYCLIC FREE RADICALS

XIV.* RATE OF DISSOCIATION OF DIARYL-β-NAPHTHYLIMIDAZOLYL RADICALS

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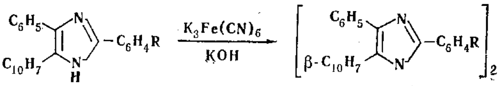
Dimers of 4(5)-phenyl-5(4)-β-naphthyl-2-phenyl-substituted imidazolyl radicals were synthesized in order to study the effect of a β-naphthyl group on the stability of triarylimidazolyl radicals, and the rate constants and energies of activation for dissociation of the dimers were determined. The presence of a β-naphthyl group in the bistriarylimidazolyl molecule facilitates its dissociation into radicals as compared with bistriphenylimidazolyl.

As demonstrated in [1], replacement of one of the phenyl rings in the triphenylimidazolyl molecule by a biphenyl group somewhat increases the rate of dissociation of the dimers of these radicals and reduces the energy of activation for the dissociation by 1.5-2.0 kcal/mole. It seemed of interest to us to investigate the effect of other polycyclic hydrocarbon groups in the radical molecule on the rates of dissociation of their dimers. The aim of this communication is a description of the synthesis of dimers of 4(5)-phenyl-5(4)-β-naphthyl-2-arylimidazolyls and an investigation of the effect of substituents in the 2-phenyl ring on the rate constants for dissociation of the dimers.

The dimers were synthesized by the oxidation of β-naphthyldiarylimidazoles [2] with potassium ferricyanide in aqueous alcoholic alkali:



I-V

I R H; II R = p-CH_3; III R = m-CH_3; IV R = p-Br; V R = m-Cl

TABLE 1. Dimers of 2-(R-Phenyl)-4(5)-phenyl-5-(4)-β-naphthylimidazolyls

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %	κ · 10², min⁻¹				E, kcal/mole	A, min⁻¹
			C	H	N	C	H	N		60°	70°	75°	80°		
I	126—129	$C_{50}H_{34}N_4$	87,4	5,2	8,1	86,9	5,0	8,1	63	1,99	3,84	6,44	8,54	17,0	$4,8\cdot10^7$
II	145—149	$C_{52}H_{38}N_4$	86,8	5,0	8,2	86,9	5,3	7,8	58	2,23	4,63	6,90	9,20	16,6	$2,8\cdot10^7$
III	158—162	$C_{52}H_{38}N_4$	86,8	5,6	7,9	86,9	5,3	7,8	60	2,18	3,93	6,51	8,68	16,5	$1,3\cdot10^7$
IV	137—140	$C_{50}H_{32}Br_2N_4$	70,6	4,2	6,2	70,8	3,8	6,6	70	1,59	3,47	6,40	7,25	18,0	$1,3\cdot10^8$
V	166—168	$C_{50}H_{32}Cl_2N_4$	79,3	4,0	7,6	79,0	4,2	7,4	57	1,38	2,90	6,21	6,90	18,6	$4,8\cdot10^8$

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*See [1] for communication XIII.

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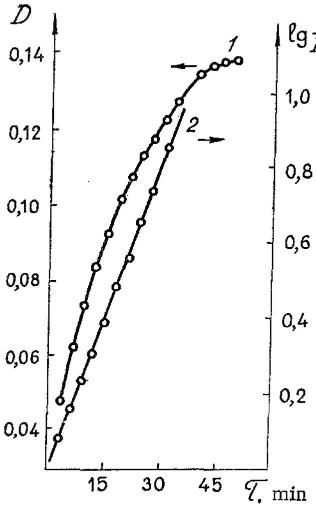

Fig. 1. Kinetic curve of the dissociation of bis-4(5)-phenyl-5(4)-β-naphthyl-2-(m-tolyl)imidazolyl in toluene (1) and its anamorphosis (2) at 75°C.

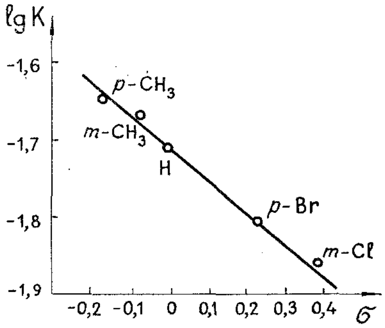

Fig. 2. Correlation of the rates of dissociation of bis-4(5)-phenyl-5(4)-β-naphthyl-2-(R-phenyl)imidazolyls with the Hammett σ constants at 60°.

The method proposed in [3], which is based on the reaction of the dimer with α,α-diphenyl-β-picrylhydrazine, was used to investigate the rate constants for dissociation of the dimers. The rate of dissociation of a dimer was determined from the rate of accumulation of α,α-diphenyl-β-picrylhydrazyl in solution.

As in the case of bistriphenylimidazolyl, the rate of dissociation of the dimer is described by a first-order equation (Fig. 1). The dissociation rate constant (K) was determined from the slope of the anamorphoses in coordinates of $\log[D_\infty / (D_\infty - D_\tau)]$ and τ. The rate constants were determined at four temperatures, the energies of activation for all of the dimers were determined from the temperature dependence of the constants, and the preexponential factors (A) were calculated (see Table 1).

The effect of substituents in the phenyl ring on the rate of dissociation of the dimers of β-naphthyldiarylimidazolyls is satisfactorily described by the Hammett equation (Fig. 2). However, judging from the absolute ρ values, the effect of substituents in this case is less than in the case of dimers of biphenyldiarylimidazolyls [1] and triphenylimidazolyls [4]. This is probably explained by the fact that the β-naphthyl group makes a considerably larger contribution to the energy of stabilization of the transition state than the phenyl or even biphenyl groups:

$$
\begin{aligned}
&\text{at } 60^\circ \lg K = -0{,}402\sigma + \ldots \ (r = 0{,}998;\ s = 0{,}20),\\
&\text{at } 70^\circ \lg K = -0{,}325\sigma + \ldots \ (r = 0{,}988;\ s = 0{,}25),\\
&\text{at } 75^\circ \lg K = -0{,}283\sigma + \ldots \ (r = 0{,}980;\ s = 0{,}23),\\
&\text{at } 80^\circ \lg K = -0{,}240\sigma + \ldots \ (r = 0{,}992;\ s = 0{,}21).
\end{aligned}
$$

In this case, just as in the case of bisbiphenylyldiarylimidazolyls [1], the effect of substituents on the energy of activation is insignificant, and lies at 17-18 kcal/mole, which is 5 kcal/mole less than the energy of activation for bistriphenylimidazolyl.

EXPERIMENTAL

The synthesis of the imidazoles was described in [2]. The dimers were obtained by oxidation of the imidazoles by the method in [5].

Bis-2,4(5)-diphenyl-5(4)-biphenylylimidazolyl (I). A total of 450 ml of 1% aqueous potassium ferricyanide was added with vigorous stirring at 5 to 10° in the course of 2 h to 1 g of 2,4(5)-diphenyl-5(4)-biphenylylimidazole dissolved in 100 ml of 95% ethanol containing 12 g of potassium hydroxide. The precipitate was removed by filtration, washed with water, dried, and dissolved in cold benzene. The filtrate was evaporated, and the oil was triturated with ethanol until crystals appeared. The crystals were recrystallized from aqueous methanol.

Dimers II-V were similarly obtained; their characteristics are presented in Table 1.

The α,α-diphenyl-β-picrylhydrazine necessary for the determination of the rate of dissociation of the dimers was synthesized according to the method in [6].

The toluene used as the solvent was purified by shaking with sulfuric acid, washing with water, sodium carbonate solution, and water, and distillation over sodium. The kinetic curves were recorded with an SF-5 spectrophotometer.

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