INVESTIGATION OF NITROGEN-CONTAINING HETEROCYCLIC FREE RADICALS

XVIII.* SYNTHESIS AND RATE OF DISSOCIATION OF BIS-α-NAPHTHYLDIARYLIMIDAZOLYL RADICALS

A. A. Bardina, B. S. Tanaseichuk,
and I. M. Nekaeva

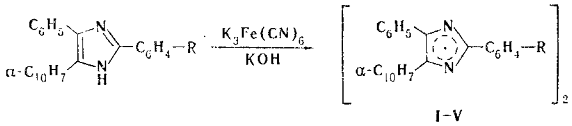
UDC 547.781'2.07:541.515

Dimers of 4(5)-phenyl-5(4)-(α-naphthyl)-2-R-phenylimidazolyl radicals were synthesized, and the rate constants and energies of activation for their dissociation were determined.

As previously demonstrated [2], replacement of one of the phenyl rings in the triphenylimidazole molecule by a β-naphthyl group promotes the formation of imidazolyl radicals. It seemed of interest to investigate the effect of replacement of the phenyl ring in the 4(5) position of the imidazole ring by an α-naphthyl group, which has a stronger stabilizing effect on triarylmethyl radicals than the β-naphthyl group [3].

The aim of the present communication is the synthesis of dimers of 4(5)-phenyl-5(4)-(α-naphthyl)-2-R-phenylimidazolyl radicals and an investigation of their dissociation as a function of the substituent in the phenyl ring.

The dimers were synthesized by oxidation of α-naphthyldiarylimidazoles [4] with potassium ferricyanide in aqueous alcoholic alkali solution [5]:



I–V

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

A previously proposed method [6], based on the reaction of the dimer with α,α-diphenyl-β-picrylhydrazine, was used to study the rate of dissociation of the dimers. The rate of dissociation of bis-4(5)-phenyl-5(4)-(α-naphthyl)-2-R-phenylimidazolyl radicals is described by a first-order equation. The rate constants for dissociation (k) were calculated from the slope of the anamorphosis in coordinates of $\log[D_\infty/(D_\infty-D_t)]$ and t; the average rate constants are presented in Table 1. The energy of activation for the dissociation of the dimers was determined from the temperature dependence of the dissociation rate constants, and the pre-exponential factors (A) in the Arrhenius equation were calculated.

As seen from the data obtained, the rate of dissociation of the dimers increases when both electron-donor groups and halogens are introduced. The introduction of an α-naphthyl group probably changes the character of the stabilization of the transition state; in fact, the peculiarities of the structures of α-naphthyl derivatives were emphasized in [7, 8].

---

*See [1] for communication XVII.

N. P. Ogarev Mordovskii State University, Saransk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1688-1689, December, 1972. Original article submitted May 6, 1971.

TABLE 1. Bis-4(5)-phenyl-5(4)-(α-naphthyl)-2-R-phenylimidazolyl Radicals and Rate Constants for Their Dissociation

Comp.	R	Mp, °C (from aq. methan.)	Empirical formula	Found, %			Calc., %			$\kappa \cdot 10^2$ min^{-1}				E_a, kcal · mole	A, min^{-1}	Yield, %
				C	H	N	C	H	N	70°	80°	85°	90°			
I	H	175—179	$C_{50}H_{34}N_4$	86,7	5,4	8,0	86,9	5,0	8,1	1,80	5,18	8,02	12,00	23,8	$2,2 \cdot 10^{13}$	82
II	*p*-CH_3	155—158	$C_{52}H_{38}N_4$	87,1	5,5	8,0	86,9	5,3	7,8	2,30	6,29	8,02	12,00	20,5	$2,7 \cdot 10^{11}$	77
III	*m*-CH_3	196—200	$C_{52}H_{38}N_4$	86,7	5,5	7,7	86,9	5,3	7,8	1,90	5,38	8,05	11,75	22,8	$6,0 \cdot 10^{12}$	85
IV	*p*-Br	136—140	$C_{50}H_{32}Br_2N_4$	70,6	4,0	6,6	70,7	3,8	6,6	2,20	5,25	8,00	11,00	19,2	$4,4 \cdot 10^{10}$	76
V	*m*-Cl	129—131	$C_{50}H_{32}Cl_2N_4$	78,9	4,1	7,2	79,0	4,2	7,2	2,52	7,29	9,10	13,55	20,9	$2,5 \cdot 10^{11}$	87

EXPERIMENTAL

The synthesis of α-naphthyldiarylimidazoles has been described [4].

Bis-2,4(5)-diphenyl-5(4)-(α-naphthyl)imidazolyl Radical (I). A total of 450 ml of a 1% aqueous solution of potassium ferricyanide was added with vigorous stirring in the course of 2 h to 1 g of 2,4(5)-diphenyl-5(4)-(α-naphthyl)-imidazole, dissolved in 100 ml of 95% ethanol containing 12 g of KOH, while maintaining the temperature at 5-10°. The precipitate was removed, washed with water, dried, and dissolved in cold benzene. The benzene solution was filtered, and the filtrate was evaporated. The residual oil was triturated with ethanol until yellow crystals appeared.

Dimers II-V were similarly obtained as yellow crystalline substances that were insoluble in water, slightly soluble in alcohol, and quite soluble in benzene and toluene (Table 1).

The kinetic investigations were carried out with solutions in toluene (purified by the method in [2]) with an SF-14 spectrophotometer.

LITERATURE CITED

1. S. V. Vlasova, B. S. Tanaseichuk, and E. N. Morozov, Khim. Geterotsikl. Soedin., 1684 (1972).
2. B. S. Tanaseichuk, A. A. Bardina, and A. A. Khomenko, Khim. Geterotsikl. Soedin., 1255 (1971).
3. E. Hückel, Z. Elektrochem., 43, 752 (1937).
4. A. A. Bardina, B. S. Tanaseichuk, and A. A. Khomenko, Zh. Organ. Khim., 7, 1267 (1971).
5. D. M. White and J. Sonnenberg, J. Am. Chem. Soc., 88, 3825 (1966).
6. B. S. Tanaseichuk, K. V. Stanovkina, A. N. Sunin, and L. G. Rezepova, Zh. Organ. Khim., 5, 2054 (1969).
7. C. C. Price and P. H. Michel, J. Am. Chem. Soc., 74, 3652 (1952).
8. V. A. Koptyug and V. A. Plakhov, Zh. Obshch. Khim., 2, 32 (1962).