INVESTIGATION OF NITROGEN-CONTAINING HETEROCYCLIC FREE RADICALS

XVII.* SYNTHESIS OF 2-(β-NAPHTHYL)-3,4-DIPHENYL-5-ARYLPYRROLES

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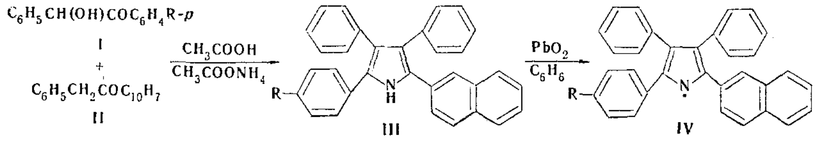
UDC 547.748:541.515.07

2-(β-Naphthyl)-3,4-diphenyl-5-(p-R-phenyl)pyrroles were synthesized in order to study the effect of polycyclic substituents on the stability of free radicals of the tetraphenylpyrryl series. Benzene solutions of these radicals were oxidized with lead dioxide to obtain the corresponding radicals. The rates of decolorization of the latter in air are described by a second-order equation with respect to the radical. The introduction of a β-naphthyl substituent into the α position of the pyrrole ring in place of a phenyl group increases the stability of the radicals.

As previously noted [1], the replacement of a phenyl ring in the α position of the tetraphenylpyrryl radical by a diphenylyl group does not substantially affect the rate of destruction of the radical in air in benzene solution; this is probably explained by the noncoplanarity of the diphenylyl group and, as a result of this, the insignificant conjugation of the unpaired electron of the radical with its π system. It is known that the introduction of a β-naphthyl substituent into a hexaarylethane increases its capacity for dissociation [2,3]. In triarylimidazolyl radicals, the effect of a β-naphthyl substituent is similar to its effect in the triarylmethyl radical [4]. The following derivatives were synthesized via the Davidson reaction in order to ascertain the character of the effect of the β-naphthyl group on the stability of radicals of the tetraphenylpyrryl series:



a R=H, b OCH_3, c OC_2H_5, d Cl, e Br

All of the synthesized 2-(β-naphthyl)-3,4-diphenyl-5-(p-R-phenyl)pyrroles (III) are colorless or slightly colored crystalline substances. Oxidation of benzene solutions of them with lead dioxide gives blue-green paramagnetic solutions of radicals that absorb in the visible region of the spectrum to form several maxima (Fig. 1). Solutions of the radicals in time are decolorized in air with loss of the paramagnetic properties because of irreversible reaction with air oxygen. The rate of decolorization of the solutions increases with temperature and during UV irradiation. The radicals are also formed during oxidation in toluene, dioxane, and chloroform. Benzene solutions of radicals IV have a high dehydrogenating capacity and are instantaneously decolorized by diphenylamine and ethanol and oxidize α,α-diphenyl-β-picrylhydrazine to the corresponding radical.

The kinetics of the destruction of radicals IV in air were investigated spectrophotometrically with an FÉK-N-57 photoelectrocolorimeter with a thermostatted cuvette holder. The measurements were made in

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*See [1] for communication XVI.

N. P. Ogarev Mordovskii State University, Saransk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1684-1687, December, 1972. Original article submitted June 4, 1971.

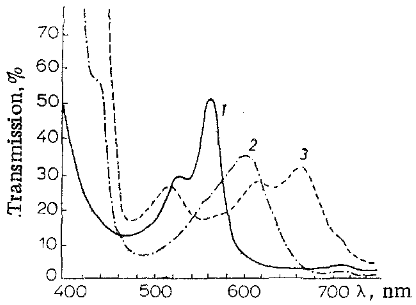

Fig. 1. Electronic absorption spectra of free radicals (in benzene): 1) tetraphenylpyrryl; 2) 2-diphenylyl-3,4,5-triphenylpyrryl; 3) 2-(β-naphthyl)-3,4,5-triphenylpyrryl.

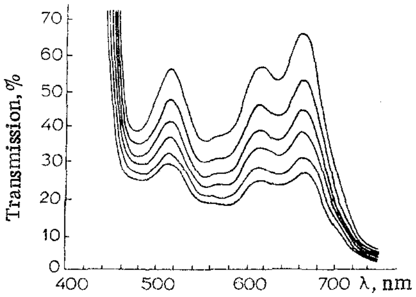

Fig. 2. Change in the intensity of the absorption maxima in the visible region of the 2-(β-naphthyl)-3,4,5-triphenylpyrryl radical with time (C_6H_6, $\Delta\tau$ = 20 min).

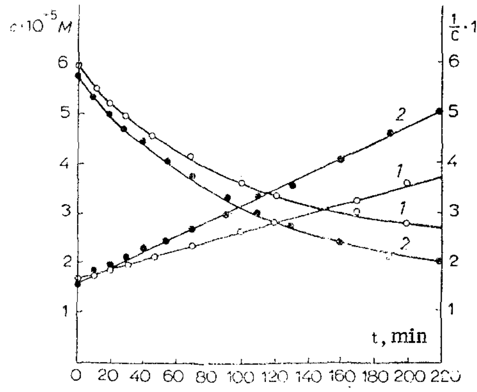

Fig. 3. Kinetic curves of the change in the concentration of the radicals with time and their anamorphoses in coordinates of 1/C and τ: 1) 2-(β-naphthyl)-3,4-diphenyl-5-(p-anisyl)pyrryl radical (c 6 · 10^{-5} M); 2) 2-(β-naphthyl)-3,4-diphenyl-5-(p-bromophenyl)pyrryl radical (c 5 · 8 M*).

cryoscopic benzene at 21 ± 0.5°C within the limits of concentrations that obey the Lambert–Beer law (2 · 10^{-4} to 4 · 10^{-4} M). The kinetic measurements were made from the rate of disappearance of the single absorption maximum of the benzene solution of the corresponding radical in the visible portion of the spectrum at 500-530 nm (Fig. 2).

As observed for the previously studied derivatives, the rate of decolorization of benzene solutions of the radicals in air is described by a second-order equation with respect to the radical [1,5,6]. The curves of the decolorization of benzene solutions of the radicals and their anamorphoses, which show that the experimental points lie satisfactorily on a line in coordinates of 1/C and τ, are presented in Fig. 3. The effective rate constants for destruction of the radicals, which are presented in Table 1, were determined from the slope of the anamorphoses.

Just as in the case of α-arylpyrryl and α,α'-diarylpyrryl radicals, electron-donor substituents increase (while electron-acceptor substituents decrease) the stability of solutions of β-naphthyl derivatives IV in air.

A comparison of the obtained constants with the constant for the unsubstituted tetraphenylpyrryl radical (K = 242 liter · mole^{-1} · sec^{-1}) indicates a considerable increase in the stability of 2-(β-naphthyl)-substituted pyrryl radicals, which is probably due to considerable conjugation of the unpaired electron of the radical with the π system of the β-naphthyl group. As seen from Fig. 1, in contrast to tetraphenylpyrryl and 2,3,4-triphenyl-5-diphenylylpyrryl radicals, a greater number of absorption maxima appear in the visible region for radicals IV, and there is a considerable bathochromic shift of the long-wave maximum. Moreover, as was previously noted [5,6], a qualitative correlation is observed between the stability of the radicals and the long-wave absorption maximum in the visible portion of the spectrum (Table 2).

EXPERIMENTAL

Aryl Benzyl Ketones. The aryl benzyl ketones necessary for the synthesis of the aryl hydroxybenzyl ketones were obtained by acylation of the appropriate arenes with phenylacetyl chloride via the Friedel–Crafts reaction.

Aryl Hydroxybenzyl Ketones (I). These compounds were synthesized by bromination (in light) of the hydrogen of the methylene group of the corresponding aryl benzyl ketones with subsequent reaction of the bromo derivatives with sodium ethoxide in absolute ethanol and hydrolysis of the resulting ethoxy derivative [6].

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*As in Russian original – Publisher.

TABLE 1. Effective Rate Constants for the Destruction of 2-(β-Naphthyl)-3,4-diphenyl-5-(p-R-phenyl)pyrryl Radicals in Benzene Solution (t = 21 ± 0.5°C)

Radicals	R	K_{av}, liter · $mole^{-1}$ · sec^{-1}
IVa	H	131±10
IVb	CH_3O	102±6
IVc	C_2H_5O	110±8
IVd	Cl	134±14
IVe	Br	137±14

TABLE 2. Electronic Absorption Spectra of Benzene Solutions of 2-(β-Naphthyl)-3,4-diphenyl-5-(p-R-phenyl)pyrryl Radicals in the Visible Region

Radicals	λ_1	λ_2	λ_3	λ_4
IVa	428	514	618	670
IVb	427	528	618	658
IVc	425	523	616	661
IVd	420	524	624	675
IVe	418	528	624	672

TABLE 3. 2-(β-Naphthyl)-3,4-diphenyl-5-(p-R-phenyl)pyrroles

Comp.	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	N	C	H	N	
IIIa	212—213	$C_{32}H_{23}N$	90,6	6,2	3,1	91,2	5,5	3,3	97
IIb	207—208	$C_{33}H_{25}NO$	88,0	5,7	3,1	87,8	5,6	3,0	62
IIIc	164—165	$C_{34}H_{27}NO$	88,0	6,1	3,0	87,7	5,8	3,1	79
IIId	108—109	$C_{32}H_{22}ClN$	84,3	5,1	2,9	84,3	4,9	3,1	79
IIIe	117—118	$C_{32}H_{22}BrN$	76,5	4,4	2,9	76,9	4,4	2,8	81

β-Naphthyl Benzyl Ketone (II). A solution of 12.8 g (0.1 mole) of naphthalene and 15.5 g (0.1 mole) of phenylacetyl chloride in 30 ml of nitrobenzene was added dropwise with stirring in the course of 75 min at 35° to a solution of 18 g of $AlCl_3$ in 30 ml of dry, freshly distilled nitrobenzene, and the mixture was heated at 60° for 15 min, cooled, and poured over a mixture of 50 ml of concentrated HCl and 400 g of ice. After the ice had melted, the product was extracted with 500 ml of ether. The ether extract was washed successively with 50 ml of 10% HCl, 50 ml of aqueous sodium carbonate solution, and twice with water, and it was then dried with magnesium sulfate. The ether was removed, and the residue (a brown oil) was vacuum distilled at a residual pressure of 10 mm to give 22.4 g (90%) of a rapidly solidifying light yellow product. Recrystallization from ethanol gave colorless crystals with mp 91-92°. Found,%: C 88.0; H 6.1. $C_{18}H_{14}O$. Calculated,%: C 87.7; H 5.7.

2-(β-Naphthyl)-3,4,5-triphenylpyrrole (IIIa). A 1.5-g (5.6 mmole) sample of β-naphthyl benzyl ketone and 1.1 g (5 mmole) of benzoin were refluxed with 3 g of ammonium acetate in 25 ml of glacial acetic acid for 1.5 h until the initial yellow color of the solution changed to orange. The product was precipitated with hot water to give 2.1 g (97%) of the pyrrole.

Repeated recrystallization from ethanol gave colorless crystals with mp 212-213°. Compounds IIIc-e (Table 3) were similarly obtained.

2-(β-Naphthyl)-3,4-diphenyl-5-(p-R-phenyl)pyrryl Radicals. These radicals were obtained by oxidation of benzene solutions of the corresponding derivatives (III) with lead dioxide in the course of 5 min.

The kinetics of destruction of radicals IV in air were investigated in cryoscopic benzene at 21 ± 0.5° with an FÉK-N-57 photoelectrocolorimeter with a thermostatted cuvette holder via the method described in [5].

The effective rate constants for destruction of the radicals in air were calculated from the slopes of the anamorphoses of the curves of the decolorization of benzene solutions of the radicals in coordinates of 1/C and τ via the method in [5].

LITERATURE CITED

1. S. L. Vlasova, B. S. Tanaseichuk, and E. N. Morozov, Khim. Geterotsikl. Soedin., 1681 (1972).
2. A. E. Chichibabin and S. E. Koryagin, Zh. Russk. Fiz.-Khim. Obshchestva, 45, 766 (1914).
3. W. Schleuk and A. Herzenstein, Ber., 43, 1753 (1910).
4. A. A. Bardina, B. S. Tanaseichuk, and A. A. Khomenko, Zh. Organ. Khim., 7, 1267 (1971).
5. B. S. Tanaseichuk, S. L. Vlasova, A. N. Sunin, and V. E. Gavrilov, Zh. Organ. Khim., 5, 144 (1969).
6. S. L. Vlasova, B. S. Tanaseichuk, and E. N. Morozov, Zh. Organ. Khim., 7, 1264 (1971).