INVESTIGATION OF NITROGEN-CONTAINING HETEROCYCLIC FREE RADICALS

XVI.* SYNTHESIS OF 2-ARYL-3,4-DIPHENYL-5-DIPHENYLYLPYRROLES AND INVESTIGATION OF FREE RADICALS BASED ON THEM

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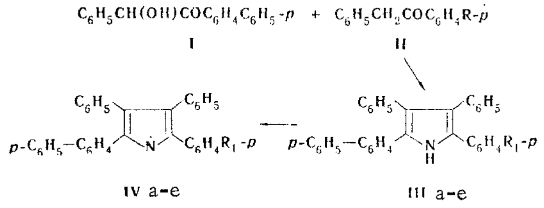
2-Aryl-3,4-diphenyl-5-diphenylylpyrroles and the corresponding radicals were synthesized. The rates of decolorization of the solutions of the radicals in air are described by a second-order equation with respect to the radical, and the logarithms of the rate constants of this reaction correlate with the total Hammett σ constants of the substituents.

It has been demonstrated that the character and number of substituents in the p position of the phenyl rings have a substantial effect on the stability of solutions of the corresponding pyrryl radicals [2]. Up until now, there have been no sufficiently clear concepts regarding the character of the effect of polycyclic residues on the stability of free radicals. Thus in triarylmethyl and triarylimidazolyl radicals, polycyclic hydrocarbon residues facilitate dissociation of the dimers into radicals [3,4]. However, in the case of tetraarylhydrazyls, on the other hand, replacement of the phenyl rings by diphenylyl rings causes a sharp decrease in their capacity for dissociation into radicals [5].

In the present research we have investigated the effect of replacement of the phenyl group by the diphenylyl group on the stability of radicals of the tetraarylpyrryl series, which are unusual analogs of diarylnitrogen radicals.

The synthesis of 2-aryl-3,4-diphenyl-5-diphenylylpyrroles was accomplished via the Davidson scheme [6]:



III, IV a $R_1 = H$; b $R_1 = CH_3O$; c $R_1 = C_2H_5O$; d $R_1 = CH_3$; e $R_1 = Cl$

Substituted deoxybenzoins were obtained via the Friedel–Crafts reaction from phenylacetyl chloride and the corresponding benzene derivatives; α-hydroxybenzyl diphenylyl ketone was synthesized by arylation of diphenylylglyoxal [7].

Compounds IIIa–e are colorless or yellowish crystalline substances that are soluble in glacial acetic acid and benzene, moderately soluble in ethanol, and insoluble in water.

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*See [1] for communication XV.

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TABLE 1. 2-(p-Aryl)-3,4-diphenyl-5-diphenylylpyrroles

Comp.	R_1	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %	K_{av},* liter/mole.min	λ_{max},† nm (in benzene)
				C	H	N	C	H	N			
IIIa	H	179—180	$C_{34}H_{25}N$	91,2	5,6	3,0	91,2	5,7	3,1	55	230±17	604
IIIb	OCH_3	234—235	$C_{35}H_{27}NO$	88,0	5,9	2,8	88,0	5,7	2,9	30	163±7	623
IIIc	OC_2H_5	180—181	$C_{36}H_{29}NO$	87,9	5,5	2,6	87,9	6,0	2,9	53	175±9	624
IIId	CH_3	119—120	$C_{35}H_{27}N$	90,9	6,1	3,2	91,1	5,9	3,0	59	185±9	612
IIIe	Cl	120—121	$C_{34}H_{24}NCl$	84,5	5,8	2,9	84,7	5,0	2,9	33	262±6	618

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*These are the effective rate constants for the destruction of IVa-e in benzene at 21 ± 1°C.

†These are the electronic absorption spectra of the corresponding radicals (IVa-e).

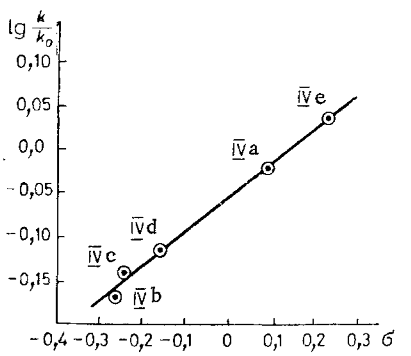

Fig. 1. Dependence of the rate constants for destruction of 2-aryl-3,4-diphenyl-5-diphenylylpyrryl radicals (IVa-e) (in benzene) on the total Hammett σ constants.

Deeply blue-green colored solutions containing an equilibrium mixture of the radical and its dimer are formed in the oxidation of IIIa-e with lead dioxide in benzene. These solutions have paramagnetic susceptibility and are decolorized in air in a few hours with loss of their paramagnetic properties and conversion of the radicals to the products of their reaction with air oxygen [8]. The destruction of the radicals in air is accelerated by heating and irradiation of solutions of them with UV light. The solutions of radicals IVa-e have a high dehydrogenating capacity and are instantaneously decolorized by diphenylamine, ethanol, and hydrochloric acid and react with α,α-diphenyl-β-picrylhydrazine to give α,α-diphenyl-β-picrylhydrazyl.

To estimate the effect of substituents on the stability of pyrryl radicals IVa-e, we studied the kinetics of the decolorization of benzene solutions of them in air within the limits of concentrations that are subject to the Lambert–Beer law. Under these conditions, the rate of decolorization of solutions of radicals IVa-e is described by a second-order equation with respect to the radical. The effective rate constants for decolorization of benzene solutions of the radicals were determined as in [2] (Table 1). The dependence of the logarithms of the rate constants of this reaction on the total substituent σ constants is described by the Hammett equation: $\log (k/k_0) = 0.412 \Sigma\sigma$, when $r = 0.983$ and $s = 0.2$; k_0 is the rate constant for decolorization of a benzene solution of unsubstituted tetraphenylpyrryl radical (242 liters · $mole^{-1}$ · min^{-1} [2]).

As seen from Table 1, the diphenylyl substituent does not increase the stability of the radical as compared with the unsubstituted tetraphenylpyrryl radical. However, by comparing the ρ values in the Hammett equation for monosubstituted 2-aryl-3,4,5-tetraphenylpyrryl radicals ($\rho = 0.329$) and 2-aryl-3,4-diphenyl-5-diphenylylpyrryl radicals IVa-e, for which $\rho = 0.412$, it can be noted that the diphenylyl residue promotes more distinct manifestation of the character of the substituent. The small effect of the diphenylyl group on the stability of the investigated radicals can probably be explained by the noncoplanarity of the diphenylyl group and, as a result, the small contribution of it to the distribution of the electron density of the unpaired electron over the radical molecule.

EXPERIMENTAL

The substituted deoxybenzoins were obtained via the method in [9].

α-Hydroxybenzyl Diphenylyl Ketone. A solution of 10 g (0.5 mmole) of diphenylylglyoxal in 50 ml of benzene was added dropwise with stirring in the course of 30 min to an ice-cooled mixture of 13.3 g of $AlCl_3$ in 200 ml of anhydrous benzene, and the mixture was held at 0° for 15 h. It was then treated with 250 ml of cold 20% hydrochloric acid solution, and the benzene layer was separated and dried with $CaCl_2$. The excess benzene was removed by vacuum distillation in a stream of nitrogen, and 30 ml of petroleum ether was added to the residue. The resulting ketone was removed by filtration to give 4.17 g (30%) of a product with mp 115-116° (from ethanol). Found,%: C 83.7; H 5.6. $C_{20}H_{15}O_2$. Calculated,%: C 83.7; H 5.3.

2,3,4-Triphenyl-5-diphenylylpyrrole (IIIa). A solution of 1.6 g (5.6 mmole) of α-hydroxybenzyl diphenylyl ketone in 25 ml of glacial acetic acid was added dropwise with stirring in the course of 30 min to a heated mixture of 1.06 g (5 mmole) of deoxybenzoin and 6 g of ammonium acetate in 25 ml of glacial acetic acid, and the mixture was heated for 1 h. Addition of hot distilled water to the mixture and crystallization of the precipitate from acetic acid and ethanol gave 1.23 g of 2,3,4-triphenyl-5-diphenylylpyrrole (Table 1).

2-(p-Tolyl)-3,4-diphenyl-5-diphenylylpyrrole (IId). A hot solution of 1.6 g (5 mmole) of α-hydroxybenzyl diphenylyl ketone in 25 ml of glacial acetic acid was added dropwise with stirring in the course of an hour to a refluxing mixture of 1.1 g (5 mmole) of p-tolyl benzyl ketone and 6 g of ammonium acetate in 25 ml of glacial acetic acid, and the mixture was refluxed until the initial red color changed to yellow. The product was isolated by the addition of hot distilled water and was crystallized from acetic acid and ethanol (Table 1).

The rate of decolorization of benzene solutions of radicals IVa-e was investigated as follows. A solution of 10-12 mg of IIIa-e in 25 ml of benzene was shaken with 1 g of lead dioxide for 3-5 min, and the sediment was removed by filtration. The concentration of radical IVa-e was determined by titration of a portion of the solution with hydroquinone. Colorimetry of the benzene solutions of the radicals was performed in a thermostatted cuvette with an FÉK-N-57 photocolorimeter in the λ_{max} region of the visible portion of the spectrum (Table 1). The initial concentration of the radicals was taken within the limits $2 \cdot 10^{-4}$-$4 \cdot 10^{-4}$ M. Within this range, the solutions of radicals followed the Lambert–Beer law.

"Cryoscopic" grade benzene, distilled twice over sodium metal, was used for the kinetic investigations. The mathematical treatment of the results was accomplished as in [10].

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