VERDAZYL RADICALS WITH PERFLUOROPHENYL RINGS

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UDC 547.883'221.07

New formazans, tetrazines, and verdazyl radicals containing pentafluorophenyl residues were synthesized on the basis of the reaction of perfluorophenylhydrazones with benzenediazonium salts. The stabilities of the free radicals obtained considerably exceed the stability of the diphenylpicrylhydrazyl radical.

Polyhalophenyl substituents in free-radical molecules have a substantial effect on their stabilities, reactivities, and spectral characteristics. For example, in contrast to the triphenylmethyl radical, the tris(pentachlorophenyl)methyl is extremely stable and is not decomposed even by strong mineral acids [1]. The perchlorodiphenylaminyl [2] and perchlorodiphenylnitroxyl [3] radicals are just as stable. The introduction of a perfluorinated benzene ring in the diphenylpicrylhydrazyl radical, on the other hand, lowers its stability and affects the reactivity of the diphenylpicrylhydrazyl radical and its ability to undergo complexing [4].

The formation of complexes with aromatic solvents is characteristic for verdazyl radicals [5]; this is associated with the high spin density of the heterocyclic ring [6]. A study of the dynamic polarization of the ^{19}F nuclei of hexafluorobenzene in the presence of the triphenylverdazyl radical showed [6, 7] that contact interaction makes a substantial contribution to polarization. It may be assumed that the introduction of high-complexing nuclei into the verdazyl molecule has a significant effect on its properties. In this connection, for the first time we have synthesized verdazyl radicals with perfluorinated aromatic substituents.

A comparison of the conditions for the synthesis of verdazyl, triphenylverdazyl [8], and other triarylverdazyl radicals [9] with perfluorophenyl rings indicates that the presence of perfluorinated substituents has an appreciable effect not only on the stabilities of the radicals but also on the ease of formation of the starting formazans, their tendency to undergo cyclization to tetrazines, and on the oxidation of the latter to radicals.

Diazo coupling, which leads to the formation of formazans IIa, b, proceeds only under relatively severe conditions in alcoholic potassium hydroxide solution, whereas formazan IIc is readily obtained in pyridine.

The alkylation of formazans II with methyl iodide proceeds under approximately identical conditions. However, whereas in the case of formazan IIb the reaction stops with the formation of N-methylformazan IIIb, formazan IIc gives a mixture of products of alkylation of IIIc and cyclization products, and the principal reaction product in the alkylation of formazan IIa is tetrahydrotetrazine IVa. According to [10], the alkylation of unsymmetrical formazans takes place at the nitrogen atom bonded to the perfluorophenyl ring.

N-Methylformazans IIIb,c undergo cyclization in dimethylformamide (DMF) at 110-120°C. In this case tetrazine IVc cannot be isolated in the individual state, since it is readily oxidized to radical Vc. In contrast to the leuco bases of the triphenylverdazyl radical and tetrazine IVc, tetrazines IVa,b are stable under ordinary conditions, and this significantly expands the possibilities for the study of their physicochemical properties; they are converted to radicals only under the influence of lead dioxide or potassium ferricyanide.

Thus a perfluorinated substituent attached to the 3-C atom of formazans promotes the stability of tetrazines and hinders their oxidation to radicals; this is explained by the determining effect of this substituent on the configuration of the formazan chain [11]. The

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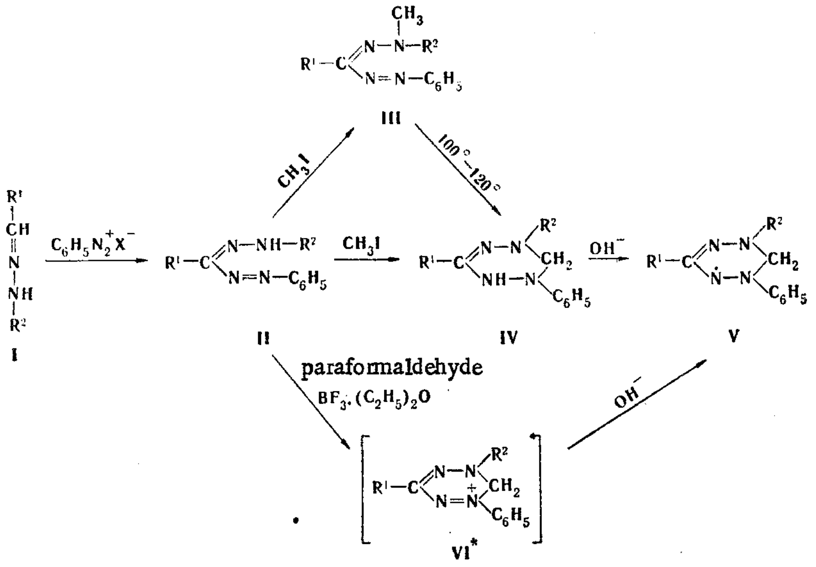
Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 266-269, February, 1978. Original article submitted February 22, 1977.

0009-3122/78/1402-0218$07.50

presence of a perfluorinated ring attached to the nitrogen atom increases the stability of the verdazyl radical.



I–V a $R^1 = C_6F_5$, $R^2 = C_6H_5$; b $R^1 = R^2 = C_6F_5$; c $R^1 = C_6H_5$, $R^2 = C_6F_5$

The verdazyl radicals with perfluorophenyl substituents are crystalline substances that do not undergo decomposition on prolonged storage under ordinary conditions. Their stabilities considerably exceed the stability of the well-known stable diphenylpicrylhydrazyl radical. Thus the addition of the latter to benzene solutions of the leuco bases of verdazyl radicals leads to the instantaneous formation of the corresponding colored perfluorinated verdazyl radicals. The ESR spectra of radicals V consist of nine lines (Va) or nine groups of lines (Vb,c), and this constitutes evidence for the approximate equivalence of the four nitrogen atoms. The hyperfine splitting constant (a_N) is 6.25 G for Va and 6.5 G for Vb,c. The g factor corresponds to the g factor of the triphenylverdazyl radical [8]. The character and the parameters of the ESR spectra indicate that the introduction of perfluorinated rings in the verdazyl radicals leads to an increase in the spin density on the heteroring of the verdazyl radical, and additional splitting on the fluorine nuclei is observed only if the perfluorinated ring is attached to the nitrogen atom.

EXPERIMENTAL

The UV spectra of the compounds were recorded with a Specord UV-vis spectrophotometer. The ESR spectra were recorded with a Varian E-3 radiospectrometer.

1,5-Diphenyl-3-pentafluorophenylformazan (IIa) and 1-Phenyl-3,5-bis(pentafluorophenyl)formazan (IIb). A solution of 25 mmole of hydrazone I in 200 ml of ethanol and 4.2 g (30 mmole) of an aqueous solution of benzenediazonium chloride were added simultaneously with stirring at 0-3°C to a solution of 5 g of potassium hydroxide in 200 ml of ethanol. After 30 min, the cooling bath was removed, and the mixture was stirred at 20°C for 3 h. Water (500 ml) was added, and the mixture was acidified to pH 6 with dilute acetic acid. The precipitated formazan was removed by filtration and crystallized from ethanol to give the product in the form of red plates (see Table 1).

1,3-Diphenyl-5-pentafluorophenylformazan (IIc). A total of 7 g (50 mmole) of an aqueous solution of benzenediazonium chloride was added at 0-3°C to a solution of 14.3 g (50 mmole) of Ic in 150 ml of pyridine. After 1 h, the temperature was raised to 20°C, and the mixture was stirred for 3 h. It was then diluted with 200 ml of water, and the precipitated formazan was removed by filtration and crystallized from acetone to give the product in the form of dark-red plates (see Table 1).

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[*] The formation of radical V in the case of cyclization of formazans II with paraformaldehyde or formalin through a step involving the formation of salt VI was proved in [8, 9].

TABLE 1. Formazans, sym-Tetrahydrotetrazines, and Verdazyl Radicals with Perfluorophenyl Rings

Compound	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	N	F		C	H	N	F	
IIa	187—188	58,4	2,8	14,3	24,1	$C_{19}H_{11}F_5N_4$	58,5	2,8	14,4	24,3	52
IIb	154—155	47,4	1,1	11,5	39,2	$C_{19}H_6F_{10}N_4$	47,5	1,3	11,7	39,6	75
IIc	168—169	58,4	2,8	14,3	24,1	$C_{19}H_{11}F_5N_4$	58,5	2,8	14,4	24,3	60
IIIb	110—120[a]	48,5	1,5	11,3	38,3	$C_{20}H_8F_{10}N_4$	48,6	1,6	11,3	38,4	53
IVa	155—156[b]	59,4	3,2	13,8	23,3	$C_{20}H_{13}F_5N_4$	59,4	3,2	13,8	23,5	53
IVb	176—177[b]	48,5	1,6	11,3	38,2	$C_{20}H_8F_{10}N_4$	48,6	1,6	11,3	38,4	55
Va	144—145	59,5	2,9	13,9	23,5	$C_{20}H_{12}F_5N_4$	59,6	3,0	13,9	23,6	60
Vb	118—119	48,6	1,4	11,1	38,3	$C_{20}H_7F_{10}N_4$	48,7	1,4	11,4	38,5	40
Vc	120—121	59,5	2,9	13,8	23,2	$C_{20}H_{12}F_5N_4$	59,6	3,0	13,9	23,6	58

[a] Undergoes cyclization. [b] Sealed capillary.

1-Phenyl-3,5-bis(pentafluorophenyl)-5-methylformazan (IIIb) and 1,3-Diphenyl-5-pentafluorophenyl-5-methylformazan (IIIc). A 14-g sample of BaO and 0.7 g of $Ba(OH)_2 \cdot 8H_2O$ were added to a solution of 2.4 g (5 mmole) of formazan IIb in 100 ml of dimethylformamide (DMF) cooled to 0-3°C, and 15 ml of methyl iodide was added dropwise to the resulting mixture. The mixture was then stirred at 0-3°C for 1 h and at 20°C for 3 h, after which it was filtered to remove the inorganic substances. The filtrate was mixed with benzene, and the mixture was washed with water until the wash waters were neutral. The benzene solution was dried with sodium sulfate and vacuum evaporated. The solid residue was crystallized from methanol—acetone (3:1) to give the product in the form of yellow plates. UV spectrum (in benzene), λ_{max} (log ε): 352 nm (4.5).

Alkylation of IIc under similar conditions gave a mixture consisting of 5-methylformazan IIIc and its transformation products (tetrazine IVc and verdazyl radical Vc). 5-Methylformazan was isolated in 5% yield in the form of orange plates by chromatography with a column filled with silica gel (elution with benzene). Formazan IIIc was oxidized immediately to radical Vc at 110-120°C in a sealed capillary. Found: N 13.6: F 23.3%. $C_{20}H_{13}F_5N_4$. Calculated: N 13.8; F 23.5%.

2,4-Diphenyl-6-pentafluorophenyl-1,2,3,4-tetrahydro-sym-tetrazine (IVa). A 12-ml sample of methyl iodide was added dropwise with stirring to a cooled (to 0°C) mixture of 1.95 g (5 mmole) of formazan IIa in 50 ml of DMF, 5 g of BaO, and 0.5 g of $Ba(OH)_2 \cdot 8H_2O$, and the mixture was stirred at 0°C for 1 h and at 20°C for 2 h. It was then worked up as in the preparation of IIIb and crystallized from ethanol to give the product in the form of colorless needles (see Table 1).

2-Phenyl-4,6-bis(pentafluorophenyl)-1,2,3,4-tetrahydro-sym-tetrazine (IVb). A solution of 2 g (4 mmole) of IIIb in 15 ml of DMF was heated at 115°C for 5 min, after which 10 ml of benzene was added, and the mixture was washed with water, dried with sodium sulfate, and vacuum evaporated. The residue was crystallized from methanol—acetone (3:1) to give the product in the form of colorless needles. UV spectrum (in acetonitrile): inflection at 242 nm.

2,4-Diphenyl-6-pentafluorophenyl-3,4-dihydro-sym-tetrazin-1(2H)-yl Radical (Va) and 2-Phenyl-4,6-bis(pentafluorophenyl)-3,4-dihydro-sym-tetrazin-1(2H)-yl Radical (Vb). A total of 20 ml of a 1 N solution of sodium carbonate and 5 ml of a 0.5 mole/liter solution of potassium ferricyanide were added to a solution of 2.5 mmole of IVa or IVb in 100 ml of benzene, and the mixture was stirred for 10 min (IVa) or 50 min (IVb). The benzene layer was separated, washed to neutrality with water, dried with sodium sulfate, and vacuum evaporated. The residue was crystallized from ethanol to give green needles of tetrazine Va. UV spectrum (in benzene), λ_{max} (log ε): 319 (4.12), 380 (4.04), and 675 nm (3.78). Tetrazine Vb was obtained as blue needles. UV spectrum (in benzene), λ_{max} (log ε): 315 (4.05), 372 (3.97), and 625 nm (3.67).

2,6-Diphenyl-4-pentafluorophenyl-3,4-dihydro-sym-tetrazin-1(2H)-yl Radical (Vc). A mixture of 1 g of paraformaldehyde, 40 ml of dry chloroform, and 5 ml of boron trifluoride etherate was stirred for 20 min, after which a solution of 2 g (5 mmole) of IIc in 200 ml of chloroform was added dropwise in the course of 2.5 h. The mixture was then stirred for 6 h, after which 30 ml of 40% formalin was added, and the mixture was stirred for 10 min. It was then transferred to a separator funnel, and 1 N sodium hydroxide was added until the color changed from violet to green. The organic layer was worked up as in the case of IIIb, and the residue was crystallized from acetone–methanol (1:2) to give the product in the form of green needles. UV spectrum (in benzene), λ_{max} (log ε): 385 (4.02) and 675 nm (3.63).

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