PERFLUOROPHENYL-CONTAINING VERDAZYL RADICALS

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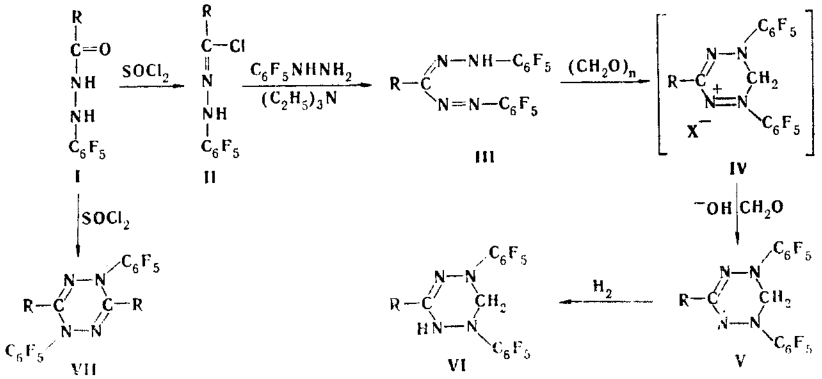
New formazans, tetrazines, and verdazyl radicals containing perfluorophenyl substituents were obtained on the basis of perfluorophenylhydrazides. The stabilities of mono-, bis-, and tris(perfluorophenyl)verdazyl radicals and their leuco compounds are compared qualitatively. The stabilities of the free radicals obtained considerably exceed the stability of the diphenylpicrylhydrazyl (DPPH) radical.

A preliminary study of the properties of 4- and 6-pentafluorophenyl- and 4,6-bis(pentafluorophenyl)verdazyl radicals has shown [1] that pentafluorophenyl residues have a considerable effect on the spectral characteristics and chemical properties of the radicals. Substantial changes in these properties are observed as a function of the position and number of perfluorophenyl substituents in the tetrazine ring. To ascertain the effect of the perfluoroaromatic ring on the properties of verdazyl radicals it seemed of interest to synthesize a systematic series of compounds containing different numbers of perfluorophenyl substituents in various positions of the tetrazine ring up to the tris(perfluorophenyl)verdazyl radical.

It has been previously shown [1] that perfluorophenyl substituents have a specific effect in the synthesis of verdazyl precursors, viz., 1- or 3-perfluorophenylformazans and 3,5-bis(perfluorophenyl)formazan. 1,5-Bis- and 1,3,5-tris(perfluorophenyl)formazans cannot be similarly synthesized, since the corresponding hydrazones couple with diazonium salts in strongly alkaline media, while the diazonium salt of perfluoroaniline is stable only in concentrated hydrofluoric acid [2].

Chlorohydrazones II* were obtained by the reaction of thionyl chloride with hydrazides I, while formazans III were obtained from II. In the case of hydrazide Ia the reaction may be accompanied by the formation of tetrazine VII. The nature of the solvent has a great effect on the direction of the reaction and the yields of the formazans. Tetrazine VII is primarily obtained when the reaction is carried out in benzene or ether, tetrazine VII and formazan III are formed in approximately equal amounts in ethanol, while the reaction mixture



I–VI a $R=C_6H_5$; b $R=C_6F_5$

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*Chlorohydrazone IIa was previously obtained [3] by chlorination of hydrazide Ia with phosphorus pentachloride.

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undergoes complete resinification in dimethylformamide (DMF). The most suitable solvent is diethylene glycol dimethyl ether, and formazans III are obtained in 40-60% yields when it is used.

The alkylation of formazans III with methyl iodide is accompanied by pronounced resinification, and verdazyl radicals are not formed. Formazans III undergo cyclization to tetrazines under the influence of paraformaldehyde in the presence of boron trifluoride etherate; in this case the products are salts IV, which, in contrast to the previously obtained verdazyl salts [4], on reaction with formalin give mixtures of verdazyl radicals V and leucoverdazyls VI, which can be explained by the greater stabilities of VI. Pure verdazyl radicals V were obtained by oxidation of the resulting mixture with a solution of potassium ferricyanide. Catalytic hydrogenation of radicals V with hydrogen leads to leucoverdazyls VI.

Perfluorophenyl-substituted verdazyl radicals V are crystalline substances that do not undergo decomposition during prolonged storage under ordinary conditions. Their EPR spectra consist of 9 groups of lines that are characteristic for verdazyl radicals [5]. The hyperfine splitting constant (a_N) is 6.7 G for the Va radical and 7.0 G for Vb. The g factor corresponds to the g factor of the triphenylverdazyl radical [5]. The stabilities of the verdazyl radicals obtained exceed the stability of the diphenylpicrylhydrazyl (DPPH) radical: The addition of the latter leads to the formation of the corresponding colored verdazyl radicals.

A qualitative comparison of the stabilities of the mono-, bis-, and tris(perfluorophenyl)-containing leucoverdazyls shows that the ease of their oxidation to verdazyl radicals decreases in the order mono- > bis- > tris(perfluorophenyl)verdazyl radical.

The introduction of fluorine atoms in place of hydrogen atoms in the aromatic ring changes the spectral properties of the radicals substantially: The maximum of the long-wave absorption band of the triphenylverdazyl radical lies at 720 nm, as compared with 675 nm for the mono(perfluorophenyl)-substituted radicals, 625 nm for the bis(perfluorophenyl)-substituted radicals, and 575 nm (in hexane) for the tris(perfluorophenyl)verdazyl radical. The hyperfine splitting constant (a_N) increases in the same order from 6.0 G for the triphenylverdazyl radical to 7.0 G for the tris(perfluorophynyl)verdazyl radical. Thus, the introduction of perfluorinated rings in the verdazyl radicals leads to an increase in the spin density on the nuclei of the nitrogen atoms of the verdazyl ring and to a hypsochromic shift of the maximum of the long-wave absorption band. This is apparently associated with disruption of the coplanarity of the orientation of the perfluorophenyl rings relative to the plane of the verdazyl ring or with a change in the polarity of the π system of the heteroring of the verdazyl radicals.

Of the various stable radicals, the triphenylverdazyl radical is distinguished by strong nucleophilic properties [6]. A preliminary study of the reactivities of the radicals that we obtained showed that perfluorophenyl-containing verdazyl radicals are stronger nucleophiles than the triphenylverdazyl radical and can serve as convenient models for comparison of the electrophilicity of various compounds.

EXPERIMENTAL

The UV spectra of solutions of the compounds in hexane were recorded with a Specord UV-vis spectrophotometer. The EPR spectra were recorded with an RÉ-1306 radiospectrometer. The PMR spectra were recorded with a Tesla BS-487 NMR spectrometer (80 MHz).

Benzoyl Chloride Perfluorophenylhydrazone (IIa). A mixture of 12 g (40 mmole) of hydrazide Ia and 100 ml of thionyl chloride was stirred at 65-70°C for 1.5-2 h until the liberation of gaseous products ceased. The thionyl chloride was removed by evaporation in the vacuum created by a water aspirator, after which the residue was washed with CCl_4 and petroleum ether and crystallized from hexane to give yellow needles of IIa (Table 1).

Perfluorobenzoyl Chloride Perfluorophenylhydrazone (IIb). A mixture of 5.9 g (15 mmole) of hydrazide Ib and 50 ml of thionyl chloride was refluxed until the liberation of gaseous products ceased (~4 h). The thionyl chloride was removed by evaporation in the vacuum of a water aspirator at no higher than 30°C, the residual oil was dissolved in dry CCl_4, and the solution was evaporated. This operation was repeated two to three times, as a result of which IIb was found in the residue in the form of an oily liquid (Table 1).

TABLE 1. Characteristics of the Compounds Obtained

Compound	mp., °C	Found, %		Empirical formula	Calc., %		Yield, %
		N	F		N	F	
IIa	129—130	8,9	29,7	$C_{13}H_6ClF_5N_2$*	8,7	29,6	80
IIb	—	6,9	46.4	$C_{13}HClF_{10}N_2$†	6,8	46,3	85
IIIa	185—186	11,6	39,0	$C_{19}H_6F_{10}N_4$	11,7	39,6	40
IIIb	121—122	10,1	49.8	$C_{19}HF_{15}N_4$	9,8	50,0	60
Va	137—138	11,7	38.9	$C_{20}H_7F_{10}N_4$	11,4	38,5	55
Vb	113—114	9,5	48,4	$C_{20}H_2F_{15}N_4$	9,6	48,9	70
VIa	196—197	11,0	37,9	$C_{20}H_8F_{10}N_4$	11,3	38,4	60
VIb	169—170	9,8	48.3	$C_{20}H_3F_{15}N_4$	9,6	48,8	60
VII	155—156	9,9	33,0	$C_{26}H_{10}F_{10}N_4$	9,8	33,4	75

*Found: Cl 10.8%. Calculated: Cl 11.0%.

†Found: Cl 8.3%. Calculated: Cl 8.6%.

1,4-Bis(perfluorophenyl)-3,6-diphenyl-1,4-dihydro-sym-tetrazine (VII). A mixture of 9 g (30 mmole) of hydrazide Ia and 60 ml of thionyl chloride was refluxed until the liberation of gaseous products ceased (~3 h). The thionyl chloride was removed by evaporation in the vacuum of a water aspirator, and the residue was cryatllized from petroleum ether—carbon tetrachloride to give yellow needles of tetrazine VII (Table 1). PMR spectrum ($CDCl_3$, with tetramethylsilane as the internal standard): 7.33 ppm (C_6H_5).

1,5-Bis(perfluorophenyl)formazan (IIIa) and 1,3,5-Tris(perfluorophenyl)formazan (IIIb). A 10-mmole sample of IIa or IIb was added in a dry atmosphere at 35-40°C to a solution of 3.96 g (20 mmole) of perfluorophenylhydrazine and 1.0 g (10 mmole) of triethylamine in 50 ml of diethylene glycol dimethyl ether. After all of the chlorohydrazone had been added, the mixture was stirred for another 2 h, and oxygen was then bubbled through the mixture for 1 h. The mixture was cooled and poured in small portions into 100 ml of water. The aqueous mixture was acidified with dilute hydrochloric acid, and the precipitated formazan IIIa or IIIb was removed by filtration. Formazan IIIa was crystallized from benzene—petroleum ether (9:1) to give dark-red needles (Table 1). UV spectrum, λ_{max} (log ε): 495 (4.0) and 285 nm (4.3). Formazan IIIb was crystallized from benzene—petroleum ether (1:4) to give red needles (Table 1). UV spectrum, λ_{max} (log ε): 446 (4.13) and 268 nm (4.24).

2,4-Bis(perfluorophenyl)-6-phenyl-3,4-dihydro-sym-tetrazin-1-(2H)yl (Va) and 2,4,6-Tris-(perfluorophenyl)-3,4-dihydro-sym-tetrazin-1-(2H)yl (Vb) Radicals. A mixture of 0.5 g of paraformaldehyde, 30 ml of dry chloroform, and 3 ml of boron trifluoride etherate was stirred for 20 min, after which a solution of 4.0 mmole of formazan IIIa or IIIb in chloroform was added slowly dropwise, and the mixture was stirred for 5 h. The solvent was removed by evaporation in the vacuum of a water aspirator at 20°C, 60 ml of benzene, 20 ml of 30% formaldehyde, and 30 ml of 1 N sodium hydroxide solution were added to the residual oily IVa or crystalline IVb, and the mixture was stirred for 30-45 min. The benzene solution of the leuco base and the partially formed radical was separated, washed with water, and stirred with 10 ml of a 0.5 M aqueous solution of potassium ferricyanide and 20 ml of a 2 N solution of sodium carbonate for 1 h. The benzene layer was separated, washed with water, dried with sodium sulfate, and evaporated *in vacuo*.

Radical Va was crystallized from benzene—hexane (1:5) to give the product in the form of azure needles (Table 1). UV spectrum, λ_{max} (log ε): 625 (3.4) and 360 nm (4.8).

Radical Vb was crystallized from benzene—hexane (1:9) to give the product in the form of violet needles (Table 1). UV spectrum, λ_{max} (log ε): 575 (3.45) and 314 nm (4.9).

2,4-Bis(perfluorophenyl)-6-phenyl-1,2,3,4-tetrahydro-sym-tetrazine (VIa) and 2,4,6-Tris(perfluorophenyl)-1,2,3,4-tetrahydro-sym-tetrazine (VIb). A 0.15-g sample of a catalyst (5% $Pd/BaSO_4$) was added to a solution of 1.0 mmole of radical Va or Vb in 30 ml of benzene, and a stream of hydrogen was bubbled through the mixture until the solution became colorless. The catalyst was removed by filtration, and the benzene was evaporated *in vacuo*. Tetrazine VIa was crystallized from carbon tetrachloride to give the product in the form of a yellowish powder (Table 1). UV spectrum, λ_{max} (log ε): 292 nm (4.0). Tetrazine VIb was crystallized from hexane—benzene (9:1) to give the product in the form of a yellowish powder (Table 1). UV spectrum: λ_{max} 266 nm (shoulder).

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