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SHORT COMMUNICATION

Perfluoro-9-phenylfluorenyl Anion Generation, Spectra and Thermodynamic Stability

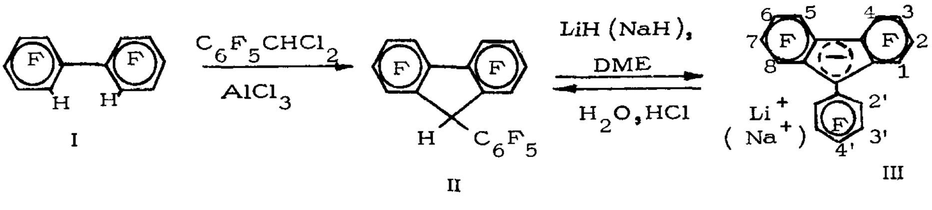
V.M. VLASOV, G.G. YAKOBSON

Institute of Organic Chemistry, Siberian Division of the Academy of Sciences, 630090, Novosibirsk (U.S.S.R.)

E.S. PETROV, A.I. SHATENSHTEIN

L.Ya. Karpov Physico-Chemical Institute, Moscow (U.S.S.R.)

In the present paper we have described the generation and properties (spectra and thermodynamic stability) of perfluoro-9-phenylfluorenyl anion - the first example of a perfluorinated benzocyclopentadienyl anion . The interaction of 2,2'-dihydrooctafluorobiphenyl (I) with pentafluorobenzal chloride in the presence of excess of anhydrous $AlCl_3$ results in the formation of 9-hydroperfluoro-9-phenylfluorene (II). Pmr spectrum of the compound (II) contains one singlet signal at 6.15 ppm. ^{19}F NMR spectrum contains five signals at 1.5 ($2F_{3'}$, m), 9.1 ($1F_{4'}$, $2F_{2,7}$, $2F_{3,6}$), 19.7 ($2F_{1,8}$, m), 20.9 ($2F_{2'}$, m) and 28.3 ppm ($2F_{4,5}$, m) (cf. ^{19}F NMR spectrum of octafluorofluoren-9-one [1].



Perfluoro-9-phenylfluorenyl anion has been generated by action of lithium or sodium hydride on the compound (II) in DME. The reaction is finished over a period of 1 h at 20–25°. ^{19}F NMR spectrum of the carbanion (III) in DME /cation Li^+ (Na^+)/ contains seven signals (ppm): −17.3 (−17.2)/$2F_{3,6}$/, −6.6 (−6.5)/$2F_{2,7}$/, −3.8 (−3.9)/$2F_{3'}$/, 0.0 (0.0)/$1F_{4'}$/, +2.9 (+2.8)/$2F_{1,8}$/, +19.8 (+19.4)/$2F_{4,5}$/ and +23.2 (+22.9)/$2F_{2'}$/. Fluorine assignments in this spectrum were straightforwarded from the coupling patterns. Spin-spin coupling constants J(F–F)(Hz) for the compound (III) are the following: J(F_1–F_2) 20.5, J(F_1–F_3) 9, J(F_1–F_4) ~9, J(F_2–F_3) 20.5, J(F_3–F_4) 19, J(F_1–$F_{2'}$) ~4, J($F_{3'}$–$F_{4'}$) 21.5. The spectra of lithium and sodium compounds are nearly similar. Neutralization of the solution of carbanion (III) recovered the starting compound (II) in a quantitative yield.

The larger upfield shift of the fluorine atom F_3 comparatively with that of the fluorine atom $F_{4'}$ (in C_6F_5 group) when going from the precurser (II) to carbanion (III) indicates greater delocalization of the negative charge on π system of the fluorenyl ring of carbanion (III).

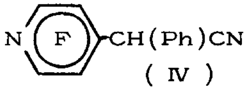
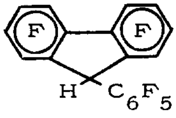
^{19}F NMR spectrum of a solution of the compound (II) in hexamethylphosphoramide (HMPA) contains fluorine atom signals of this compound as well as that of the carbanion (III). The concentration of the carbanion (III) in this solution is equal 30 %. It was estimated from the relationship of integral intensities of signals in ^{19}F NMR spectrum.

Equilibrium acidity of the compound (II) has been determined spectrophtometrically by the overmetallation method [2] in DME (cation Li^+). Malonic ether whose the pK has been determined relative to 9-phenylfluorene [3] and the range of polyfluoroarylcontaining compounds [4] have been used as the indicator carbon acids of intermediate acidity. Equilibrium constants of the overmetallation reactions (K, the number of measurements, /n/), the pK's and the electronic spectra parameters of studied carbanions are given in the Table.

The mentioned data suggest the relative great thermodynamic stability of perfluoro-9-phenylfluorenyl anion: the pK of the compound (II) /5.3/ is smaller that of 9-phenylfluorene by about 13 pK units. It may be concluded from the approximate estimates [5] that the influence of the C_6F_5 group in (II) may be evaluated ca. 5 pK units. Hence the contribution of each tetrafluorinated condensed ring in the acidity of the compound (II) may be estimated ca. 4 pK units.

TABLE

Equilibrium constants of the overmetallation reactions (K), pK's and the characteristics of the electronic spectra of carbanions (DME, Li^+, 25^0)

Compound	Indicator (pK)	K (n)	pK	λ_{max}, nm ($\mathcal{E}$ x 10^{-3}, l/mole. cm)
 (IV)	$CH_2(COOEt)_2$ (V) (8.4)	6.8 ± 0.5 (6)	7.6	378 (28)
$(C_6F_5)_2CHCN$ (VI)	(V) (8.4)	106 ± 12 (3)	6.4	360 (25)
	(IV) (7.6)	20 ± 1 (3)	6.3	
$p-CH_3C_6F_4CH(COOEt)_2$ (VII)	(VI) (6.4)	240 ± 25 (4)	4.0	-
 (II)	(VI) (6.4)	10.3 ± 0.5	5.4	420 (8)
	(VII) (4.0)	0.070 ± 0.007	5.2	

EXPERIMENTAL

^1H and ^{19}F NMR spectra were recorded on a Varian A 56-60 A spectrometer at 60 and 56.4 MHz respectively, the internal standards being TMS and C_6F_6 (the downfield shift was positive); the concentration of the specimens were 10 mole %; the spectra were recorded at 37^0. The IR spectra were recorded on an UR-20 spectrometer using a 5 % solution in CCl_4. The UV spectrum of (II) was recorded on a Specord UV Vis spectrometer using a solution in EtOH (1.10^{-4} mole/l).

The determination of equilibrium acidity of the compounds (II), (V - YII) was made by the overmetallation method described earlier [2].

9- Hydroperfluoro- 9- phenylfluorene (II) (nc)

To a stirred mixture of the compound (I) (1.85 g) [6] and anhydrous $AlCl_3$ (3.5 g), pentafluorobenzal chloride (1.65 g) [7] was added dropweise at 20- 25°. The reaction mixture was stirred successively for 1 h at 50°, 2 h at 70° and 0.5h at 80°. After cooling it was poured on ice water . The precipitate was filtered off, washed with water and dried; 2.6 g (87 %) of compound (II) was isolated, m.p. 145- 146° (from EtOH). Analysis: Found: C, 48.3; H, 0.34; F,52.1 %. Mol. wt., 468. $C_{19}HF_{13}$ requires C, 47.9; H, 0.21; F, 51.9 %. Mol. wt., 476. IR spectrum: ν_{max} 2940 (w), 1525-1500 (s)(multiplet), 1425 (m), 1360 (m), 1335 (m), 1325 (w), 1300 (w), 1150 (m), 1135- 1130 (s)(doublet), 1108 (s), 1065 (s), 1015-1000 (s)(doublet), 955 (w), 695 (w), 685 (w), 645 (m), 600 (w), 556 (w), 480 (w) cm^{-1}. UV spectrum: λ_{max} 210 shoulder, 262 and 292 shoulder, nm (log ε 4.50, 4.28 and 3.38).

Perfluoro- 9- phenylfluorenyl anion (III)

To a suspension of lithium hydride (0.015 g) / or of sodium hydride (0.04 g)/ in anhydrous DME (0.5- 0.6 ml), compound (II) (0.24 g) was added in a stream of dry argon at 20- 25°. After bubbles of hydrogen had ceased to be evolved, the resulting brown solution was kept for 1 h at 20- 25° and poured into a tube for recording the ^{19}FNMR spectrum of the carbanion (III). The tube was then sealed. After recording of spectrum, the solution was diluted with diethyl ether (4 ml) and neutralized with a 5 % solution of HCl (5 ml). Diethyl ether was evaporated, the precipitate was filtered off, washed with water and dried. The compound (II) was isolated (0.2- 0.22 g) and identified by IR spectrum.

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