Synthesis and cycloaddition of *N*-substituted pyrroles with polyfluorinated substituents

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Reactions of *N*-pyrrolylpotassium with fluorinated electrophiles yielded *N*-substituted pyrroles containing polyfluoroalkyl, polyfluoroalkenyl, polyfluoroalkylsulfonyl, and polyfluoroaryl substituents. *N*-Polyfluoro-substituted pyrroles did not isomerize at ≥ 100 °C; they were found to be reactive in [4+2] cycloaddition reactions with perfluorobut-2-yne.

Key words: *N*-(polyfluoroalkenyl)pyrroles, *N*-(polyfluoroalkylsulfonyl)pyrroles, *N*-(penta-fluorophenyl)pyrrole, 7-azabicyclo[2.2.1]heptadiene, cycloaddition.

First representatives of *N*-polyfluoroalkylpyrroles (1,1,2,2-tetrafluoroethyl, 2-chloro-1,1,2-trifluoroethyl, and 1,1,2,3,3,3-hexafluoropropylpyrroles) were obtained rather long ago^{1,2} by addition of pyrrole to polyfluorinated alkenes at 100 °C in the presence of metallic potassium. In the same studies,^{1,2} two examples of the synthesis of*N*-(polyfluoroalkenyl)pyrroles, namely,*N*-(2-chloro-difluorovinyl)pyrrole and 2-fluoro-2-phenyl-1,1-dipyrrolylethylene, were reported, although the researchers themselves were doubtful about their structures. 3,4-Dimethyl-1-pentafluorophenylpyrrole was obtained by desulfooxidation of the corresponding thiazine oxide with a solution of alkali in aqueous alcohol and this was the only example of the synthesis of fluorinated arylpyrrole.³

The goal of the present study was to investigate the preparative possibility of using *N*-pyrrolylpotassium to obtain pyrroles containing polyfluorinated substituents at the N atom. Earlier, ⁴ *N*-pyrrolylpotassium was prepared by a reaction of pyrrole with solid KOH followed by drying. Our attempted synthesis of *N*-substituted pyrroles by reactions of the reagent thus prepared with polyfluoroolefins failed. The major process was mineralization of fluoroolefins by the action of KOH.

We found that reactions of chlorotrifluoroethylene and perfluoropropylene with *N*-pyrrolylpotassium (*in situ* prepared by dissolution of metallic potassium in an excess of pyrrole (1 : 1.2) in ether) occur even at -60 °C and proceed exothermically to give 2 : 7 and 2 : 5 mixtures of *N*-polyfluoroalkyl- and *N*-polyfluoroalkenylpyrroles **1**, **2** and **3**, **4**, respectively. Repeated fractionation of these mixtures allowed individual compounds **1**, **3** and **2**, **4** to be isolated in low ($\leq 5\%$) yields (Scheme 1).

It should be noted that pyrrole does not react with fluoroolefins in the absence of potassium.

Scheme 1



 $R = Cl(1, 2), CF_3(3, 4)$

N-Polyfluoroalkenylpyrroles were selectively obtained with N-pyrrolylpotassium dried in vacuo. Reactions of the dispersed N-pyrrolylpotassium thus prepared with chlorotrifluoroethylene, perfluoropropylene, and perfluoroisobutylene in ether proceed exothermically at -60 °C to give polyfluoroalkenylpyrroles 2, 4, and 5 in satisfactory yields (Scheme 2). The reaction with the most reactive polyfluoroalkene (perfluoroisobutylene) also yielded disubstituted olefin 6. Pyrroles 2 and 4 were obtained as mixtures of the geometrical Z, E-isomers in the 7 : 5 ratio for compound 2 and of the E,Z-isomers in the 8 : 1 ratio for compound 4. Pyrroles 2 and 4 were distilled over dry KOH to remove minor amounts of polyfluoroalkylpyrroles 1 and 3, which can form in the presence of water or pyrrole traces. The Z-isomer of compound 2 and the *E*-isomer of compound **4** were dominant (>95%). This follows from the constants of F–F spin-spin coupling in the ¹⁹F NMR spectra ($J_{trans} = 126.2$ and 127.7 Hz, respectively) characteristic of the *trans*-arranged F atoms relative to the double bond. The increase in the content of

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the Z-isomer of pyrrole $\mathbf{2}$ and the E-isomer of pyrrole $\mathbf{4}$ is probably due to Z, E-isomerization in the presence of fluoride ions.

Scheme 2



Polyfluoroalkenylpyrroles 2 and 4-6 are stable compounds. Pyrroles 2 and 4 are resistant to hydrolysis; in a homogeneous acetone—water solution, the double bond of the alkenyl fragment remains unchanged for a long period of time.

N-Sulfonyl-containing pyrroles were obtained by reactions of polyfluoro sulfonyl fluorides with *N*-pyrrolyl-potassium at low temperatures. *N*-Pyrrolylpotassium exothermically reacted with trifluoromethanesulfonyl fluoride at -70 °C. The resulting product was *N*-trifluoromethylsulfonylpyrrole **7** (~70%, ¹H NMR) and up to 30% of the starting pyrrole was recovered, which were not separated by fractionation. Pyrrole **7** was separated from the starting pyrrole by treating the resulting mixture with HCl, which causes pyrrole polymerization. *N*-Substituted pyrrole **7** polymerizes to a lesser degree (Scheme 3). The reaction of *N*-pyrrolylpotassium with perfluoro-2-ethoxy-ethanesulfonyl fluoride also occurred at low temperatures: in this case, substituted pyrrole **8** can be easily purified by fractionation *in vacuo*. The reaction of *N*-pyrrolyl-

Scheme 3



potassium with trifluoromethanesulfonyl chloride afforded no pyrrole 7; instead, polymerization of the reaction mixture took place. The ambiguity of the reactions of polyfluoroalkanesulfonyl chlorides with amines was reported earlier.⁵

The reaction of *N*-pyrrolylpotassium with perfluorobenzene occurred only upon prolonged heating to give mono- and disubstitution products **9** and **10** (Scheme 4) separated by fractional sublimation.





In contrast to hydrocarbon analogs,⁴ *N*-substituted pyrroles **2**, **4**, and **9** were not isomerized at high temperatures (200-250 °C) even upon prolonged heating.

The high stabilities of the pyrroles obtained made it possible to study their properties in [4+2] cycloaddition reactions. It is known⁶ that pyrrole itself behaves ambiguously in such reactions.

It turned out that alkenylpyrroles 2 and 4 react with such a reactive dienophile as perfluorobut-2-yne even at 20 °C; however, the process was accompanied by oligomerization giving rise to unidentified resinous products.

The [4+2] cycloaddition reactions of *N*-substituted pyrroles **8**, **9**, and **11*** with perfluorobut-2-yne afforded 7-azabicyclo[2.2.1]heptadienes **12**, **13**, and **14**. *N*-Penta-fluorophenylpyrroles **9** and **11** slowly reacted at room temperature, while the reaction with sulfonylpyrrole **8** occurred only at 120 °C. The cycloaddition rate of pyrrole **9** was appreciably higher at 100 °C (Scheme 5).

According to NMR data, compounds 12, 13, and 14 contain no syn-anti-isomers, as has been noted⁷ for 7-azanorbornadienes with an alkyl substituent at the N atom.

The [4+2] cycloaddition reaction of tetrafluoro-1,4dipyrrolylbenzene **10** with perfluorobut-2-yne at 20 °C yielded a mixture of di- and monocycloadducts **15** and **16** (¹H and ¹⁹F NMR data); however, only bis(7-azanorbornadienyl)tetrafluorobenzene **15** was isolated in the individual state (Scheme 6).

^{* 3,4-}Dimethyl-*N*-pentafluorophenylpyrrole **11** was prepared as described earlier.³







7-Azanorbornadienes are stable compounds, which decompose only at high temperatures according to the retro [4+2] cycloaddition mechanism. For instance, *N*-perfluorophenyl-7-azabicyclo[2.2.1]hepta-2,5-diene **13** underwent retrodiene decomposition at ~170 °C to give a 5 : 1 mixture of pyrroles **9** and **17** (¹H and ¹⁹F NMR and GC-MS data) (Scheme 7).



Compounds 9 and 17 are close in physicochemical properties and cannot be separated by fractional sublimation.

Thus, the reactions of *N*-pyrrolylpotassium with fluoro-containing reagents provide additional preparative possibility of obtaining a number of new *N*-substituted pyrroles with polyfluoroalkenyl, polyfluoroaryl, and polyfluoroalkylsulfonyl substituents. Compounds of this type are thermodynamically stable and resistant to hydrolysis but they are sufficiently reactive in [4+2] cycloaddition to such a strong dienophile as perfluorobut-2-vne.

Experimental

¹H and ¹⁹F NMR spectra were recorded on Bruker AC-300 and Bruker WP-200 SY spectrometers (300.13 and 188.31 MHz, respectively). Chemical shifts were referenced to Me₄Si (¹H) and CF₃COOH (¹⁹F) as the external standards. Mass spectra were recorded on a GC-MS spectrometer based on an HP 5890 II Series gas chromatograph with an HP 5972A MSD mass-selective detector. IR spectra (thin film) were recorded on a Hitachi 127-30 IR spectra, the elemental analysis data, ¹H and ¹⁹F NMR spectra, IR spectra, physicochemical characteristics, and yields of the compounds obtained are given in Table 1. Commercial reagents were used. Solvents were prepared according to known recommendations.⁸ Compound **11** was synthesized as described earlier.³

Synthesis of mixtures of *N*-substituted pyrroles 1 and 2, 3 and 4 (general procedure). Powdered metallic potassium (2.9 g, 75 mmol) was added to a stirred solution of pyrrole (6.0 g, 90 mmol) in anhydrous diethyl ether (30 mL). The mixture was stirred for 20 h and then the corresponding polyfluoroalkene (90 mmol) was rapidly added at -60 °C. After warming to ambient temperature, the reaction mixture was filtered and the precipitate was washed with ether (3×10 mL). The combined filtrates were fractionated *in vacuo* to collect mixtures of compounds 1 and 2 (b.p. = 31–34 °C (15 Torr)) and 3 and 4 (b.p. = 54–58 °C (45 Torr)) in the 2 : 7 and 2 : 5 ratios, respectively. Triple fractionation of these mixtures on an efficient column allowed individual compounds 1–4 to be isolated in $\leq 5\%$ yields. The physicochemical properties of compounds 1 and 3 agree with the earlier reported data.^{1,2}

Synthesis of N-(polyfluoroalkenyl)pyrroles (general procedure). N-(2-Chlorodifluorovinyl)pyrrole (2), N-(pentafluoroprop-1-envl)pyrrole (4), N-(heptafluoroisobut-1-envl)pyrrole (5), and hexafluoro-1,1-bis(pyrrol-1-yl)isobutylene (6). Powdered metallic potassium (2.9 g, 75 mmol) was added to a stirred solution of pyrrole (6.0 g, 90 mmol) in anhydrous diethyl ether (30 mL). The reaction mixture was stirred for 20 h and the solvent and the excess of pyrrole were removed in vacuo (2 Torr, 1 h). N-Pyrrolylpotassium was dried and dry diethyl ether (30 mL) was added with stirring, whereupon the corresponding polyfluoroalkene (90 mmol for pyrroles 2 and 4 and 50 mmol for pyrroles 5 and 6) was rapidly added at -60 °C. The occurring reaction was exothermic. After warming to ambient temperature, the reaction mixture was filtered, the precipitate was washed with ether (3×10 mL), and the filtrates were fractionated. Pyrroles 2 and 4 were isolated as mixtures of the Z, E-isomers with possible admixtures of N-polyfluoroalkylpyrroles 1 and 3. The individual Z- and E-isomers of compounds 2 and 4, respectively, were obtained by distillation over powdered KOH (760 Torr). In the case of perfluoroisobutylene, no polyfluoroalkylpyrroles were detected.

N-(Trifluoromethylsulfonyl)pyrrole (7). Powdered metallic potassium (2.9 g, 75 mmol) was added to a stirred solution of pyrrole (6.0 g, 90 mmol) in anhydrous diethyl ether (30 mL). The reaction mixture was stirred for 20 h and then trifluoromethanesulfonyl fluoride (12.9 g, 85 mmol) was rapidly added at -70 °C. After warming to ambient temperature, the reaction mixture was filtered, the precipitate was washed with ether (3×10 mL), and the filtrate was fractionated. The resulting mixture of *N*-substituted pyrrole 7 and the starting pyrrole was dis-

Com- pound	Yield (%)	B.p./°C (<i>p</i> /Torr) [m.p./°C]	<i>n</i> _D ²⁰	Found Calculated (%)		Molecular formula	NMR, δ (<i>J</i> /Hz)		IR, v/cm^{-1}
				СН	Ν		¹ H	¹⁹ F	
1 ^{<i>a</i>}	4	52—53 (50)	1.4428	<u>39.42</u> <u>2.73</u> 39.23 2.72	<u>7.65</u> 7.63	C ₆ H ₅ ClF ₃ N	6.32 (ddd, 1 H, CFH, $J_{H,F} = 48.4$, $J_{H,F_A} = 4.2$, $J_{H,F_B} = 4.2$); 6.38, 6.95 (both br.s, 2 H each CH)	14.73 (ddd, 1 F, CF ^B , $J_{AB} = 213.8$, $J_{F,F_{vic}} = 13.2$, $J_{F,H_{vic}} = 4.2$); 18.23 (ddd, 1 F, CF ^A , $J_{AB} =$ 213.8, $J_{F,F_{vic}} = 13.9$, $J_{F,H_{vic}} = 4.2$); 74.95 (ddd, F, CHFCl, $J_{F,H} = 48.4$, $J_{F,H_{vic}} = 13.2$)	2980 (CH); 1480 (C=C)
2 ^b	75	128	1.4749	<u>44.48</u> <u>2.46</u> 44.36 2.45	<u>8.59</u> 8.56	C ₆ H ₄ ClF ₂ N	2 H each, CH) $c_{6.35}, 6.85$ (both br.s, 2 H each, CH) $d_{6.36}, 6.90$ (both br.s, 2 H each, CH)	$J_{F,F} = 15.2, J_{F,F} = 15.9$ $48.11 (d, F, CF, J_{F,F} = 126.2); 50.66 (d, F, CFCl, J_{F,F} = 126.2)$ $26.65 (d, F, CF, J_{F,F} = 25.8);$ $34.09 (d, F, CFCl, J_{F,F} = 25.8);$	1675 (C=C)
3	5	40—41 (20)	1.3820	<u>38.55</u> <u>2.32</u> 38.71 2.30	<u>6.51</u> 6.45	C7H5F6N	2 H each, CH) 5.12 (dddq, 1 H, CFH, $J_{H,F} = 43.5,$ $J_{H,F_A} = 10.7,$ $J_{H,F_B} = 8.2,$ $J_{H,CF_3} = 23.2);$ 6.35, 6.99 (both br.s, 2 H each (CH)	$J_{F,F} = 23.8$) 1.02 (dd, 3 F, CF ₃ , $J_{CF_3,F} =$ 11.1, $J_{CF_3,H} = 23.2$); 9.93 (dd, 1 F, CF ^B , $J_{AB} = 207.1$, $J_{F,F_{vic}} = 21.7$, $J_{F,H_{vic}} = 10.7$); 16.39 (ddd, 1 F, CF ^A , $J_{AB} =$ 207.1, $J_{F,F_{vic}} = 24.8$, $J_{F,H_{vic}} =$ 8.2); 132.06 (dddq, F, CHF, $J_{H,F} = 43.5$, $J_{H,F} = 10.7$, $J_{H,F} = 8.2$, $J_{H,F} = 10.7$,	2990 (CH); 1470 (C=C)
4 ^e	65	108—110	1.4050	<u>42.71</u> <u>2.04</u> 42.64 2.03	<u>7.13</u> 7.10	C7H4F5N	 ² H each, CH) ^d6.41, 7.08 (both br.s, ² H each, CH) ^c6.35, 6.80 (both br.s, ² H each, CH) 	$J_{H,F} = 8.2, J_{H,CF_3} = 23.2)$ -9.4 (dd, 3 F, CF ₃ , $J_{CF_3,F} = 22.5, J_{CF_3,F} = 12.5);$ 51.0 (dq, F, CF, $J_{F,CF_3} =$ 22.5, $J_{F,F} = 127.7$); 105.9 (dq, F, CF, $J_{F,CF_3} = 12.5, J_{F,F} = 127.7$) -8.70 (dd, 3 F, CF ₃ , $J_{CF_3,F} = 12.0, J_{CF_3,F} = 9.6);$ 13.00 (dq, F, CF, $J_{F,CF_3} = 9.6, J_{F,F} = 3.7);$ 83.10 (dq, F, CF	1680 (C=C)
5	26	117	1.4338	<u>38.97</u> <u>1.63</u> 38.86 1.62	<u>5.69</u> 5.67	$C_8H_4F_7N$	6.42, 6.97 (both s, 2 H each, CH)	$J_{F,CF_3} = 12.0, J_{F,F} = 3.7)$ -14.67 (qq, F, CF, $J_{F,CF_3} = 8.0, J_{CF_3,F} = 23.8);$ -17.99 (dq, 3 F, CF ₃ , $J_{CF_3,CF_3} = 8.0, J_{CF_3,F} = 23.8);$ -18.81 (dq, 3 F, CF ₃ ,	1690 (C=C)
6	32	53—54 (3)	1.4842	<u>49.18</u> <u>2.73</u> 48.98 2.72	<u>9.56</u> 9.52	$C_{12}H_8F_6N_2$	6.49, 6.78 (both br.s, 2 H each, CH)	$J_{CF_3,CF_3} = 8.0, J_{CF_3,F} = 8.0)$ -18.85 (s, 6 F, CF ₃)	2950 (CH); 1640
7	11	37—38 (22)	1.4069	$\frac{30.22}{30.15} \frac{2.02}{2.01}$	<u>7.05</u> 7.03	$C_5H_4F_3NO_2S$	6.49, 7.14 (both t, 2 H each, $CH, J = 2.1$)	-0.37 (s, 3 F, CF ₃)	(C=C) 2900 (CH)
8	47	58 (11)	1.3649	<u>26.38</u> <u>1.10</u> 26.30 1.09	<u>3.85</u> 3.83	C ₈ H ₄ F ₉ NO ₃ S	6.49, 7.15 (both br.s, 2 H each, CH)	4.39 (t, 2 F, CF_2 , $J = 11.8$); 9.65 (br.s, 3 F, CF_3); 11.31 (t, 2 F, CF_2 , $J = 11.8$); 38.09 (br.s, 2 F, $CF_2(C_2F_5)$)	2930 (CH)

Table 1. ¹H and ¹⁹F NMR and IR spectra, physicochemical characteristics, and yields of the compounds obtained

(to be continued)

Com- pound	Yield (%)	B.p./°C (<i>p</i> /Torr) [m.p./°C]	$n_{\rm D}^{20}$	Found (%) Calculated		Molecular formula	NMR, δ (<i>J</i> /Hz)		IR, ν/cm^{-1}
				C H	N	-	¹ H	¹⁹ F	
9	25	[63—64]	_	<u>51.62</u> <u>1.7</u> 51.50 1.7	<u>2 6.03</u> 1 6.01	$C_{10}H_4F_5N$	6.42, 6.88 (both br.s, 2 H each, CH)	$68.21 (d, 2 F, C_6F_5, J = 20.1);$ $76.58 (t, F, C_6F_5, J = 20.1);$ 81.44 (t, 2 F,	2080 (CH); 1540
10	15	[129—131]	_	<u>60.11</u> <u>2.8</u> 60.00 2.8	<u>37</u> <u>10.04</u> 36 10.00	$C_{14}H_8F_4N_2$	6.35, 7.01 (both br.s, 2 H each, CH)	$C_6F_5, J = 20.1)$ 68.69 (s, 4 F, C_6F_4)	(C=C) 2960 (CH); 1500 (C=C)
12	55	56—58 (1)	1.3511	<u>27.38</u> <u>0.7</u> 27.32 0.7	7 <u>2.66</u> 6 2.65	C ₁₂ H ₄ F ₁₅ NO ₃ S	5.58, 7.39 (both s, 2 H each, CH)	-13.49 (s, 6 F, CF ₃); 4.76 (t, 2 F, C ₂ F ₄ , $J = 12.4$); 10.21 (br.s, 3 F, CF ₃); 11.90 (t, 2 F, CF ₂ , $J = 12.4$); 40.12 (br.s. 2 F, CF ₂ , $J = 12.4$);	(C=C) 2970 (CH); 1690 (C=C)
13	71	[53—54]	_	<u>42.61</u> <u>1.0</u> 42.53 1.0	02 <u>3.55</u> 01 3.54	$C_{14}H_4F_{11}N$	5.58, 7.27 (both s, 2 H each, CH)	$\begin{array}{l} -13.07 \text{ (s, } 6 \text{ F, } \text{CF}_3\text{);} \\ 78.05 \text{ (d, } 2 \text{ F, } \text{C}_6\text{F}_5\text{, } J = 20.4\text{);} \\ 86.43 \text{ (t, } 2 \text{ F, } \text{C}_6\text{F}_5\text{, } J = 20.4\text{);} \\ 86.93 \text{ (t, } F \text{ C}_5\text{, } L = 20.4\text{);} \end{array}$	2950 (CH); 1700 (C=C)
14	77	[96—97]	_	<u>45.43</u> <u>1.9</u> 45.39 1.8	0 <u>0</u> 3.33 93.31	$C_{16}H_8F_{11}N$	1.88 (s, 6 H, Me); 5.22 (s, 2 H, CH)	$\begin{array}{l} -15.01 (s, 6 F, CF_3); \\ 77.62 (d, 2 F, C_6F_5, J = 21.1); \\ 86.12 (t, 2 F, C_6F_5, J = 21.1); \\ 87.15 (t, F, C_2F_5, J = 21.1); \end{array}$	(C=C) 2985 (CH); 1700 (C=C)
15	30	[167—168] (decomp.)	—	<u>43.83</u> <u>1.3</u> 43.71 1.3	<u>3</u> <u>4.65</u> 2 4.63	$C_{22}H_8F_{16}N_2$	5.55, 7.22 (both s, 4 H each, CH)	-13.57 (s, 12 F, CF ₃); 77.62 (s, 4 F, C ₆ F ₄)	(C=C) (C=C)
16	_	—	_			$C_{18}H_8F_{10}N_2$	5.67, 6.38, 6.87, 7.29 (all s, 2 H each, CH)	-13.57 (s, 6 F, CF ₃); 73.79 (d, 2 F, C ₆ F ₄ , $J = 13.9$); 77.18 (d, 2 F, C ₆ F ₄ , $J = 17.1$)	_
17	_	_	_			$C_{12}H_2F_{11}N$	7.28 (s, 2 H, CH)	$-18.02 (s, 6 F, CF_3); 71.69 (d, 2 F, C_6F_5, J = 20.3); 75.11 (t, 2 F, C_6F_5, J = 20.3); 82.88 (t, F, C_6F_5, J = 20.3)$	_

Table 1 (continued)

^{*a*} The physicochemical characteristics were reported earlier.²

^b The mixture of the Z- and E-isomers in the 7 : 5 ratio.

^c The Z-isomer.

^d The *E*-Isomer.

^e The mixture of the *E*- and *Z*-isomers in the 8 : 1 ratio.

solved in CH_2Cl_2 (5 mL) and HCl (5 mL) was added with vigorous stirring. The precipitate that formed was filtered off and washed with CH_2Cl_2 (3×5 mL). The organic layer was separated, dried with MgSO₄, and fractionated.

N-(Perfluoro-2-ethoxyethyl-1-sulfonyl)pyrrole (8). Powdered metallic potassium (2.9 g, 75 mmol) was added to a stirred solution of pyrrole (5.4 g, 80 mmol) in anhydrous diethyl ether (30 mL). The reaction mixture was stirred for 20 h and 2-fluorosulfonylperfluorodiethyl ether (24.0 g, 75 mmol) was added at -70 °C. The occurring reaction was exothermic. After warming to ambient temperature, the reaction mixture was filtered, the precipitate was washed with ether (3×10 mL), and the filtrate was fractionated *in vacuo*.

N-Pentafluorophenylpyrrole (9) and perfluoro-1,4-bis(pyrrol-1-yl)benzene (10). Powdered metallic potassium (2.9 g, 75 mmol) was added to a stirred solution of pyrrole (5.4 g, 80 mmol) in anhydrous diethyl ether (30 mL). The reaction mixture was stirred for 20 h and then perfluorobenzene (17.7 g, 95 mmol) was added at room temperature. The resulting mixture was refluxed for 14 h, cooled to ambient temperature, and filtered. The precipitate was washed with ether (2×10 mL). The combined filtrate was concentrated and the residue was separated by fractional sublimation *in vacuo* (1 Torr).

Reactions of N-substituted pyrroles 8, 9, and 11 with perfluorobut-2-yne (general procedure). 7-(Perfluoro-2-ethoxyethyl-1-sulfonyl)-2,3-bis(trifluoromethyl)-7-azabicyclo[2.2.1]hepta-2,5-diene (12), 7-perfluorophenyl-2,3-bis(trifluoromethyl)-7azabicyclo[2.2.1]hepta-2,5-diene (13), and 5,6-dimethyl-7-pentafluorophenyl-2,3-bis(trifluoromethyl)-7-azabicyclo[2.2.1]hepta-2,5-diene (14). A mixture of the corresponding N-substituted pyrrole (7.5 mmol) and perfluorobut-2-yne (2.4 g, 15 mmol) was kept in a sealed glass tube at 120 °C for 6 h, Reaction of perfluoro-1,4-bis(pyrrol-1-yl)benzene (10) with perfluorobut-2-yne. 7-{4-[2,3-Bis(trifluoromethyl)-7-azabi $cyclo[2.2.1]hepta-2,5-dien-7-yl]-2,3,5,6-tetrafluorophenyl}-$ 2,3-bis(trifluoromethyl)-7-azabicyclo[2.2.1]hepta-2,5-diene (15)and 7-[2,3,5,6-tetrafluoro-4-(pyrrol-1-yl)phenyl]-2,3-bis(trifluoromethyl)-7-azabicyclo[2.2.1]hepta-2,5-diene (16). A mixture of perfluoro-1,4-bis(pyrrol-1-yl)benzene 10 (0.6 g,2.1 mmol) and perfluorobut-2-yne (2.1 g, 12.9 mmol) in drydiethyl ether (5 mL) was kept in a glass tube at room temperature for 30 days. The tube was cooled and volatile products wereremoved. After warming to 20 °C, the mixture was concentrated*in vacuo*(13 Torr) and the residue was recrystallized from heptane. 1,4-Disubstituted perfluorobenzene 15 and a 1 : 2 mixtureof di- (15) and monocycloadducts (16) were isolated (NMRdata). The components of the mixture were not separated.

Synthesis of a mixture of *N*-pentafluorophenyl-3,4-bis(trifluoromethyl)pyrrole (17) and *N*-pentafluorophenylpyrrole (9). 7-Azanorbornadiene 13 (1 g, 2.5 mmol) was heated at 170 °C for 16 h and the residue was sublimed *in vacuo* (1 Torr). The resulting mixture of pyrroles 17 and 9 (1 : 5) was characterized by NMR and GC-MS data. Compound 17: MS (EI, 70 eV), m/z (I_{rel} (%)): 369 [M]⁺ (100), 350 [M - F]⁺ (85), 300 $[M - CF_3]^+$ (37), 231 $[300 - CF_3]^+$ (6), 167 $[C_6F_5]^+$ (37), 69 $[CF_3]^+$ (92).

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