Articles

1-Aryl-*F*-1,3-butadienes and Unsymmetrical α,ω-Diaryl-*F*-polyenes

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Received January 30, 1996 (Revised Manuscript Received March 4, 1997®*)*

Para-substituted 1-aryl-*F*-1,3-butadiene derivatives p-R-C_6H_4-CF=CFCF=CF_2 (**2a**−**g**), where R = H, CH_3, OCH_3, OC_6H_{11}, $N(CH_3)_2$, Br, and CF_3, have been prepared by reaction of appropriate arylmagnesium bromides with *F*-1,3-butadiene. ^{19}F NMR chemical shifts correlate with σ_p Hammett substituent constants. Compounds **2a**−**e** react on their terminal perfluorovinyl group with C-nucleophiles and were used as intermediates in subsequent reactions with suitable organolithium compounds for the synthesis of a new series of unsymmetrically substituted α,ω-diaryl-*F*-polyenes $RC_6H_4(CF{=}CF)_nC_6H_4R'$, where $n = 2$ or 3 and R′ is one of the substituents specified above. A variety of new synthons containing α,ω-diaryl-*F*-1,3-butadiene skeleton and reactive Br, OH, CH=O, and COOH functionalities in *para*-positions on aromatic rings has been also prepared. Structural aspects, NMR spectra, and mesogenic properties of the title compounds are discussed.

Introduction

Synthetic methods for conjugated symmetrical α,ω-diaryl-*F*-polyenes, which have interesting chemical and physical properties are well established.[1] However, only a few unsymmetrical α,ω-diaryl-*F*-butadienes have been prepared so far using Ullmann coupling of *para*-substituted α,β-difluoro-β-iodostyrenes with copper[2] or by reaction of *p*-(*N*,*N*-dimethylamino)-α,β-difluorostyryllithium with α,β,β-trifluorostyrene.[3] Aryllithium compounds react with *F*-ethylene[4] and *F*-1,3-butadiene[5] to give their terminal bis-aryl derivatives preponderantly, because the initially formed monosubstituted products are obviously more susceptible to nucleophilic attack than the original *F*-alkenes. Only if suitable reaction conditions were chosen, namely low temperature (−78 °C) and an excess of *F*-alkenes,[6,4] or less reactive arylmagnesium halogenides were used[7,4] for reactions of phenyllithium with *F*-ethylene, isolable yields of monoaryl trifluorostyrene derivatives were obtained.

There is only one report in the literature on reactions of Grignard reagents with polyfluorodienes, describing reactions of *para*-substituted phenylmagnesium bromides with 1-chloropentafluoro-1,3-butadiene.[8] It was of interest to investigate reactions of the former with *F*-1,3-butadiene, a convenient synthesis of which we developed previously,[9] to prepare monoaryl pentafluoro-1,3-butadienes as potential synthetic precursors for unsymmetrically substituted α,ω-diaryl-*F*-polyenes obtainable in a subsequent addition−elimination reaction step with suitable organometallics.

Since many symmetrical α,ω-diaryl-*F*-polyenes are mesogenes, with a relatively wide range of mesophase transition temperatures,[10] it was also desirable to find out if the unsymmetrical ones would also display this behavior. Finally, we wished to introduce one or more functional groups into the title compounds for further synthetic utilization and investigation of structure−property relationships.

Results and Discussion

1-Arylpentafluoro-1,3-butadienes (2a−g). Our initial attention was focused on reactions of arylmagnesium bromides, prepared from corresponding bromo derivatives **1a**−**g**, with *F*-1,3-butadiene using tetrahydrofuran as solvent (method *A*). We obtained monosubstituted *F*-1,3-butadiene derivatives **2a**−**g** in good or moderate yields, Scheme 1.

A change of reaction conditions in metalation of *p*-dibromobenzene made it possible to obtain different reaction products in a subsequent reaction with *F*-1,3-butadiene. From the reaction of 2 equiv of magnesium, we obtained only low yields of fluorinated oligomers **3a**−**c** (0.8, 1.1, and 2%), Scheme 2.

Fractional crystallization from different solvents afforded fractions with different values of *n* (5−6, 7−8, 10−11) estimated from elemental analyses by the content of residual bromine. ^{19}F NMR indicated the prevalence of the *E*,*E* configuration in the tetrafluorobutadienyl units.

In contrast to the syntheses of monoaryl butadienes from organomagnesium halogenides (Scheme 1), the syntheses of compounds **2f**,**g** have been also accomplished

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® Abstract published in *Advance ACS Abstracts,* April 15, 1997.

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[10] (a) Yurchenko, V. M.; Yegorov, Yu. P.; Khranovskii, V. A. *Ukr. Phys. Zh.* **1978**, *23*, 337. (b) Moklyachuk, L. I.; Kornilov, M. Yu.; Fialkov, Yu. A.; Kremlev, M. M.; Yagupolskii, L. M. *Zh. Org. Khim.* **1990**, *26*, 1533.

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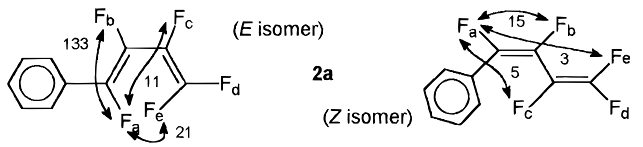
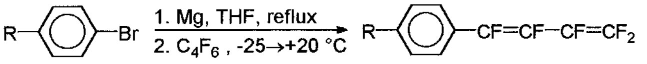


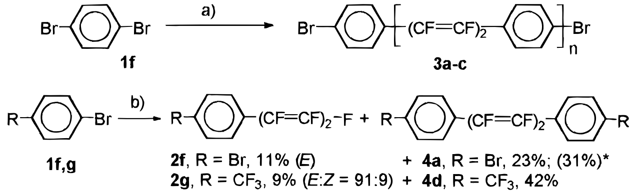
Figure 1. Selected J_{FF} for (*E* and *Z*)-**2a**.

Scheme 1



1a: R = H	**2a**: R = H, 36%, *E/Z* = 84/16
1b: R = CH_3	**2b**: R = CH_3, 30%, *E/Z* = 93/7
1c: R = OCH_3	**2c**: R = OCH_3, 46%, *E/Z* = 77/23
1d: R = OC_6H_{11}	**2d**: R = OC_6H_{11}, 55%, *E/Z* = 89/11
1e: R = $N(CH_3)_2$	**2e**: R = $N(CH_3)_2$, 65%, *E/Z* = 86/14
1f: R = Br	**2f**: R = Br, 21%, *E/Z* = 79/21
1g: R = CF_3	**2g**: R = CF_3, 5%, *E/Z* = 87/13

Scheme 2



(a) i) 2 Mg, THF, reflux, ii) C_4F_6, 5-20 °C, overnight;
(b) i) 1 BuLi, ii) 1.15 C_4F_6; -78 °C, *(1/2 C_4F_6)

by the "reverse" addition of the more reactive organolithium compound (Scheme 2), prepared by monolithiation of bromo derivatives **1g**[11] and **1f**, and reaction with an excess of *F*-1,3-butadiene at lower temperature (method B). The yields were low (9–11%), however, because of formation of 1,4-diaryl-*F*-1,3-butadienes **4a** and **4d**. The content of *E* isomers in these products was higher than in the same derivatives prepared by method A.

All new 1-aryl-*F*-1,3-butadienes **2a–g** prepared by method A were found as a mixtures of *E* and *Z* isomers, where *E* isomers predominated (77–93%), as established on the basis of ^{19}F NMR chemical shifts, J_{FF} coupling constants, and integration of the assigned signals.

There are significant differences in spin coupling constants between F_a and F_b, or F_a and F_e nuclei, due to the specific configuration and conformation of the individual isomers. Long range coupling $^5J_{a-e} = 20-22$ Hz in (*E*)-**2a–g** is relatively large, although smaller than $^5J_{F(1)F(4)}$ and $^5J_{F(3)F(6)} = 29.7-32.6$ Hz for the case of diaryl systems **6a–i** and **8a–e** discussed below, apparently caused by a significant contribution of the cisoid conformation.

The chemical shifts of fluorines in 1-aryl-*F*-1,3-butadienes depend upon its position on a polyene chain and are more influenced than δ ^1H in butadienes[8] by the benzene ring substituents. We found that chemical shifts of the F_b, F_c, F_d, and F_e nuclei in compounds **2a–g** are in good linear correlation with σ_p Hammett substituent constants[11] of corresponding substituents in the *para* position of aromatic ring. From δ_F/σ_p dependence, eq 1, it has been possible to determine reaction-susceptibility constants ρ for different molecular frameworks in the R-[core]-F systems for *E* and *Z* 1-aryl-*F*-1,3-butadienes, respectively.

$$\delta_F = \delta^\circ + \rho\sigma_p \qquad (1)$$

We have estimated the ρ values for *E* and *Z* aryl-*F*-polyene units occurring in isomers of 1-aryl-pentafluoro-1,3-butadienes **2a–c, e–g** (Table S2). Correlation with close ρ values has been found for α,β-difluoro-β-chlorostyrenes,[12] *trans*-α,β-difluorocinnamic, and *trans,trans*-5-aryl-2,3,4,5-tetrafluoro-2,4-pentadienoic acids.[8] For the case of cyclohexyloxy derivative **2d**, we could not find σ_p in the literature. However, from correlation **1** for the studied types of core, we can predict $\sigma_p = -0.32 \pm 0.02$ for a cyclohexyloxy substituent. The negative values of ρ for F_c indicate the "inverse" substituent effect on the δ $^{19}F_c$ along the conjugated framework of *E* and *Z* 1-aryl-*F*-butadienes. This phenomenon monitors the alternation in distribution of electron densities on carbons and fluorines attached to them along the *F*-butadiene conjugated chain.

The differences in chemical shifts of fluorines attached to C(1) and C(2), as well as to C(3) and C(4), reflect the degree of polarization of the double bonds in 1-aryl-*F*-1,3-butadienes **2a–g**. We found much better correlation of $\Delta\delta$ with classic σ_p Hammett substituent constants (eq 2):

$$(\Delta\delta_{F_x-F_y})_R - (\Delta\delta_{F_x-F_y})_H = \Delta\delta^\circ + \rho_{x-y}\sigma_p \qquad (2)$$

where $\Delta\delta_{F_x-F_y}$ are differences in chemical shifts between F_b and F_a, F_d and F_c, and F_e and F_c (Table S2), than with polar substituent parameters σ_{mb}, which were reported to correlate with the $\Delta\delta$ ^{19}F NMR in α,β,β-trifluorostyrenes.[13] The ^{19}F NMR chemical shifts as well as their differences, which reflect the polarization of the double bond, can help to specify the chemical activity of the carbon reaction centers and the double bonds. We studied ρ_b/ρ_d, ρ_b/ρ_e, ρ_{b-a}/ρ_{d-c}, and ρ_{b-a}/ρ_{e-c} relationships (Table S3) using ρ constants obtained by eqs 1 and 2, which, along with ρ_x/ρ_y ratios found earlier for the other aryl-*F*-polyene systems,[8,12] gave more precise picture of the electronic effects transmission.

From the comparison of ρ constants (Table S2) and ρ_x/ρ_y relations (Table S3) we can conclude: (a) the ρ values are larger for the same nuclei in the *E* than *Z* isomers in line with the presumed nonplanar conformation of *Z* isomers where more steric hindrance takes place unfavorable for transmission of electronic perturbations; b) the ρ_x/ρ_y values are in the range 1.3–3.0 for *E* isomers, which indicate a moderate decrease of the electronic effects transmission by addition of another CF=CF unit, if compared with the stronger decrease $\rho_x/\rho_y = 1.9-6.0$ for *Z* isomers; (c) the ρ values found for the F_d nuclei are larger than ρ for F_e (1.2 and 2.5 times for *E* and *Z* isomers, respectively); (d) $\rho_{b-a}/\rho_{d(e)-c}$ are approximately twice as small as the corresponding $\rho_b/\rho_{d(e)}$ values, which indicates a considerable ability of *para*-substituents to polarize the second π-bond in 1-aryl-*F*-1,3-butadienes.

A high reactivity of the terminal *F*-vinyl group in 1-aryl-*F*-1,3-butadienes toward organometallic nucleophiles was also observed in further reactions (Scheme 3). The reaction of **2b** with an excess of butyllithium proceeds under mild conditions and gives a mixture of the addition–elimination product (*E*,*E*)-1-(4-tolyl)-1,2,3,4-tetrafluoroocta-1,3-diene (**5a**), and products of further

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[11] March, J. *Advanced organic chemistry*, 3rd ed.; Wiley: New York, 1985; p 244. Trost, B. M.; Arndt, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 5288.

[12] Yagupolskii, L. M.; Sevastiyan, A. P.; Kremlev, M. M.; Khranovski, V. A.; Fialkov, Yu. A. *Zh. Org. Khim.* **1976**, *12*, 1967.

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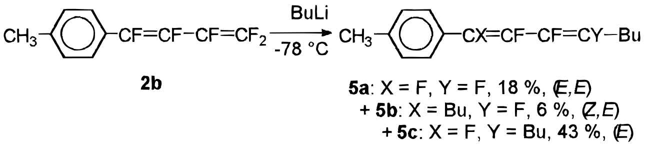
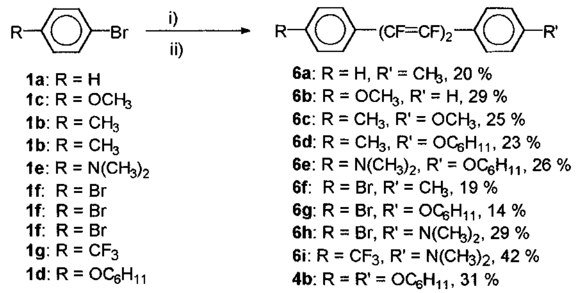
Scheme 3

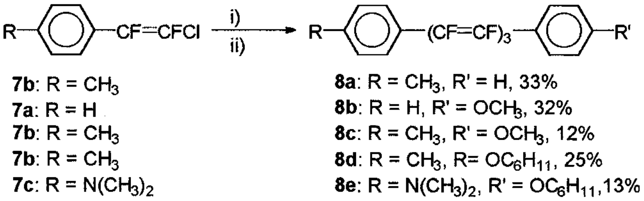


Scheme 4



i) Li, Et_2O, reflux, 1h for **1a-e**; BuLi, Et_2O, rt, 45 min for **1f**; BuLi, -70 °C for **1g**; ii) CF_2=CF-CF=CF-C_6H_4-R' **(2a-e)**, THF, -78 °C; 1/2 C_4F_6 for **4b**.

Scheme 5



i) BuLi, THF/Et_2O/hexane, -100 °C; ii) CF_2=CF-CF=CF-C_6H_4-R' **(2a,c,d)**

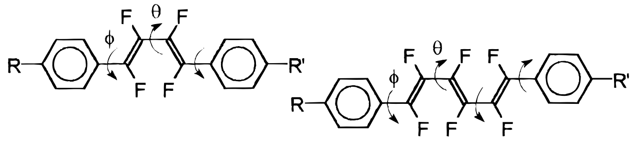


Figure 2. Geometry features of (*all-E*)-α,ω-diaryl-*F*-polyenes.

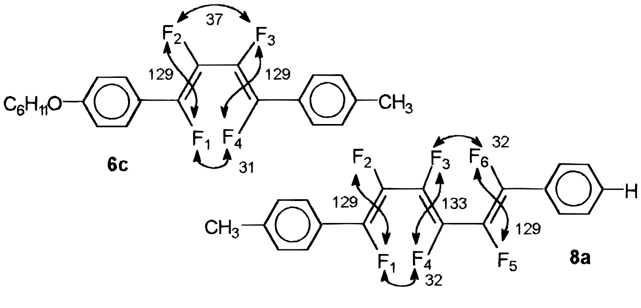


Figure 3. Selected J_{FF} for (*E*,*E*)-**6c** and (*E*,*E*,*E*)-**8a**.

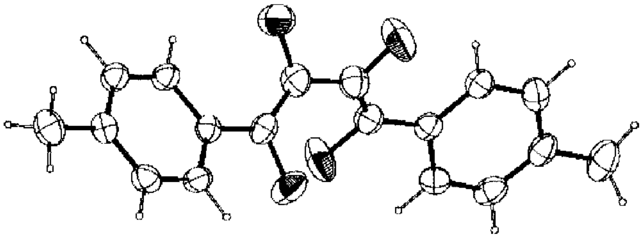


Figure 4. ORTEP drawing of (*E*,*E*)-*p*-tolyl-*F*-1,3-butadiene (**4c**).

attack of butyllithium with **5a** in positions 1 and 4 giving **5b** and **5c** in a ratio 1:6.8. The regioselectivity of the nucleophilic attack is in line with CNDO calculation[14] of electron density distribution in **5a**: C(1), 0.168, and C(4), 0.176, and the observed chemical shifts of F(1) and F(4).

Unsymmetrical α,ω-diaryl-*F*-polyenes. The reaction of *para*-substituted 1-aryl-*F*-1,3-butadienes with aryllithium and α,β-difluorostyryllithium derivatives containing different substituents in the *para*-position was used as a general synthetic approach to unsymmetrical α,ω-diaryl-*F*-polyenes, according to Schemes 4 and 5, respectively.

The reaction of the aryllithium compounds (prepared from bromobenzenes **1a−c, 1e−g** by Br/Li exchange) with 1-arylpentafluoro-1,3-butadienes **2a−e** proceeds smoothly at −78 °C in a diethyl ether/THF mixture to give unsymmetrical 1,4-diaryl-substituted tetrafluoro-1,3-butadienes **6a−i** (Scheme 4).

The lithiation of α,β-difluoro-β-chlorostyrenes **7a−c** proceeds by Cl/Li exchange.[15] The subsequent reaction with 1-arylpentafluoro-1,3-butadienes **2a**,**c**,**d** provided the unsymmetrical 1,6-diarylhexafluoro-1,3,5-hexatrienes **8a−e** (Scheme 5).

These novel unsymmetrical (**6a−i** and **8a−e**) and symmetrical (**4a**,**b**,**d**) α,ω-diaryl-*F*-polyenes were isolated as *all-E* isomers in 12−42% yields, easily separable by crystallization, due to their linear and conformationally rigid structure, analogous to the structurally similar symmetrical α,ω-diaryl-*F*-polyenes prepared before.[1] Other isomers (10−25% of the reaction mixture) with at least one (*Z*)-CF=CF linkage remained in the mother liquor along with the residual *E* isomers and were detected by ^{19}F NMR in the crude reaction mixture. The ^{19}F NMR assignment for *E* and *Z* unsymmetrical α,ω-diaryl-*F*-polyenes was based on an estimation using the additivity rule and the increments derived from the data found for monoaryl-substituted *F*-butadienes **2a−g**.

We suppose that the diarylbutadienes **6a−i** and diarylhexatrienes **8a−e** prefer to have a nonplanar s-cisoid conformation, similar to *F*-1,3-butadiene[16] and 1,6-bis-(*p*-anisyl)-*F*-1,3,5-hexatriene[17] .

The supposed out of plane s-cisoid conformations with the dihedral angles $\varphi = 5{-}23°$ and $\theta = 47{-}49°$, which were found in structurally similar systems and confirmed by X-ray and other spectral characteristics,[1] are supported by relatively large $^5J_{F(1)F(4)}$ and $^5J_{F(3)F(6)}$ coupling constants observed in the ^{19}F NMR spectra. Their range 29.7−32.6 Hz for **6a−i**[18] and **8a−e** are similar to that published.[19] Their magnitude is apparently due to through-space interaction, as shown for **6c** and **8a** in Figure 3.

We have recently proved the *E* stereochemistry about both double bonds and s-cisoid conformation of **4c** by X-ray analysis (Figure 4).[20]

Most of the new unsymmetrical α,ω-diarylsubstituted *F*-polyenes were found to be thermostable mesogens, and their phase transition temperatures are listed in Table

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[14] HyperChem Release 2 for Windows, Molecular Modeling System, 1991, Hypercube, Inc. and Autodesk, Inc.

[15] Prober, M. *J. Am. Chem. Soc.* **1953**, *75*, 968.

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[18] For the case of 2nd order ^{19}F NMR spectra of **6c,e,g, 10b** (ABXY system) and **4a,b** (AA′XX′ system), the coupling constant values were obtained from simulated spectrum performed with "High resolution NMR spectra analysis" CALM version 2.00 (C) 1991 Resonance Co.

[19] Yurchenko, V. M.; Kremlev, M. M.; Fialkov, Yu. A.; Sass, V. P.; Khranovskii, V. A.; Egorov, Yu. P.; Yagupolskii, L. M. *Theoret. Exper. Khim.* **1982**, *6*, 745.

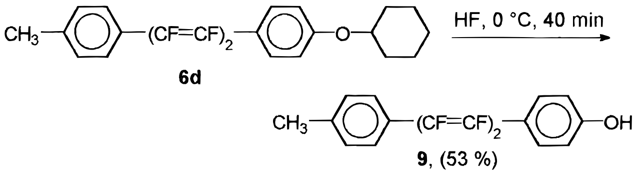
[20] Detailed X-ray crystallographic data for **4c** will be published.

Table 1. Phase Transition Temperatures (°C)[a] of (*all-E*)-α,ω-Diaryl-*F*-polyene Mesogens: $RC_6H_4(CF{=}CF)_nC_6H_4R'$

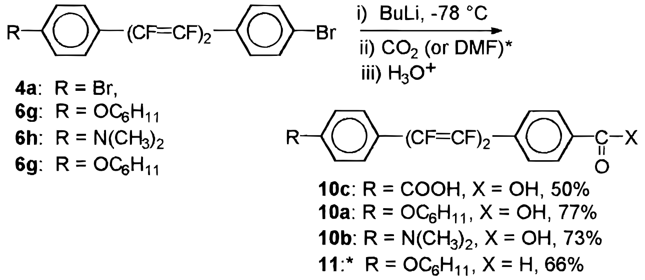
	comp			transition temp (°C)		
	n	R	R′	C	S	N
6a	2	CH_3	H	• 61	–	–
8a	3			• 65	• 74	• 80
6b	2	CH_3O	H	• 85	–	–
8b	3			• 63	–	• 109
6c	2	CH_3O	CH_3	• 74	–	• 156
8c	3			• 82	–	• 178
6d	2	$C_6H_{11}O$	CH_3	• 65	–	• 75
8d	3			• 80	–	• 132
6e	2	$(CH_3)_2N$	OC_6H_{11}	• 134	–	–
8e	3			• 147	–	• 167
6f	2	Br	CH_3	• 100	–	• 116
6g	2	$C_6H_{11}O$	Br	• 82	–	• 85
10a	2	HOOC	OC_6H_{11}	• 236	–	• 242

[a] C, crystalline; S, smectic; N, nematic.

Scheme 6



Scheme 7



1. The extension of the perfluoropolyene chain with one difluorovinylene unit from butadienes **6a**–**e** to hexatrienes **8a**–**e** caused the appearance of a nematic phase or extended its range.

Functional Group Transformations. We have also been interested in developing new routes for introducing useful functional groups into the α,ω-diaryl-*F*-polyene skeleton for further synthetic and practical exploitation. The presence of the protected hydroxyl group in **2d** made it possible to prepare **6d**, and after deprotection with hydrogen fluoride, to obtain the hydroxy derivative **9**, suitable for the preparation of new monomers or further functionalization (Scheme 6). For chemical proof, **9** was also treated with diazomethane on a preparative scale, and the methoxy derivative **6c** was thus obtained in an independent way.

Compounds **6g**, **6h**, and **4a** containing bromine atoms in the *para*-position of the benzene ring were transformed to corresponding derivatives with one (**10a,b**) or two (**10c**) COOH functions or one CH=O (**11**) function by usual procedures, as shown in Scheme 7.

Using diazomethane, **10c** was transformed to the dimethyl ester **12** for identification.[5]

Conclusion

New syntheses of 1-aryl-*F*-1,3-butadienes and unsymmetrical α,ω-diaryl-substituted *F*-1,3-butadienes and *F*-1,3,5-hexatrienes have been developed. Both symmetrical and unsymmetrical α,ω-diaryl-substituted *F*-polyenes and their derivatives prepared so far were found to be relatively stable substances chemically, useful for further applications.

Experimental Section

Melting points and phase transitions temperatures (Table 1) were determined on a Nagema PHMK 05 apparatus with an ortho-ocular (16×) attachment and polarizing filter. Infrared spectra (IR) were obtained using KBr disks for solids or films of liquid substances except where otherwise stated. All NMR analyses were undertaken with $CDCl_3$ as a solvent unless otherwise indicated. ^1H NMR spectra were recorded at 300 MHz on a Varian AM 4000 spectrometer with TMS as internal reference. ^{19}F NMR spectra were recorded at 75.4 MHz on a Bruker WP-80 SY spectrometer or at 376.5 MHz on a Bruker VMX 400 (in $CDCl_3$, $CFCl_3$ internal reference, δ negative upfield). ^{13}C APT NMR spectra were measured with TMS as internal reference. Mass spectra (MS, *m/z*) were recorded on a JEOL DX 303 JMA 5000 instrument (electron impact, 70 eV, ion source temp. 250 °C). The yields were not optimized.

General Procedure for Preparation of (*E,Z*)-1-Aryl-1,2,3,4,4-pentafluoro-1,3-butadienes ((*E,Z*)-2a–g). Method A. Magnesium activated by iodine vapor (1.1 equiv based on the bromo derivatives **1a**–**g**) and tetrahydrofuran were placed in a flame-dried flask previously flushed with dry nitrogen. A solution of bromo aromatics **1a**–**g** in THF (1–2 mL per 1 mmol) was added dropwise for 45 min at room temperature. When addition was completed, the mixture was refluxed for 1 h. The flask was cooled to −25 °C, and a precooled (−50 °C) ~1 M solution of *F*-1,3-butadiene (1.05 equiv based on **1a**–**e**) in THF was added dropwise during 10–20 min. The mixture was stirred for 1 h, and the cooling bath was allowed to warm up slowly to ambient temperature and was stirred overnight. The reaction mixture was worked up with a 5% solution of hydrochloric acid, extracted three times with ether, and washed with a 5% solution of $NaHCO_3$ and twice with water. The ethereal layer was dried over $MgSO_4$. The solvent was rotary evaporated, and the residue in the case of **2a**–**e**,**f**,**g** was distilled in vacuum (**2d**,**e** were purified by column chromatography). The compounds **2f**,**g** were further purified by column chromatography on SiO_2 for analysis; **2d** was used for further reactions as a crude product. Yields of **2a**–**g** and *E/Z* ratios are introduced in Scheme 1.

1-(4-Bromophenyl)-1,2,3,4,4-pentafluoro-1,3-butadiene ((*E*)-2f). Method B. Butyllithium ethereal solution (43 mL, 0.7 M, 0.03 mol) was added dropwise to a solution of *p*-dibromobenzene (7.8 g, 30 mmol) in 15 mL of ether at room temperature during 45 min and stirred for 1 h. The resultant organometallic was transferred to a dropping funnel, cooled to −75 °C, and added dropwise to a solution of *F*-1,3-butadiene (5.5 g, 34 mmol in 15 mL of THF) at −70 °C during 1 h. The mixture was stirred for 2 h at −75 °C and then allowed to warm up to 0 °C. The reaction mixture was worked up as in the previous method.

(*E,E*)-1,4-Bis(4-bromophenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4a). BuLi (20 mL of 0.75 M in hexane, 16.8 mmol) was added to a solution of 1,4-dibromobenzene (**1f**) (3.96 g, 16.8 mmol) in 24 mL of Et_2O at room temperature. After 1 h this solution was cooled to −78 °C, and a precooled solution of C_4F_6 (1.5 g, 9.3 mmol) in 8 mL of THF was added by cooled dropping funnel, keeping the reaction temperature below −70 °C. After 1 h the cooling bath was allowed to warm to −25 °C. The reaction mixture was quenched with 50 mL of NH_4Cl water solution, extracted with Et_2O (3 × 50 mL). The combined organic layer was washed with of H_2O (2 × 40 mL) and 40 mL of brine and dried over $MgSO_4$. The solvent was rotary evaporated. The residue was crystallized from ethanol (1.15 g, yield 31%). Yellow powder, mp 160 °C. MS *m/z* 438, 436 (95), 434 M^+; 416 (2.5); 357, 355 (65); 307 (18), 305 (18); 276 (100); 256 (80); 225 (23); 207, 205 (21); 200 (28); 138 (22); 126 (16); 107 (16); 75 (21); 51 (13). ^{19}F NMR (75.4 MHz) AA′XX′ system, δ −142.68 (m, F-1 and F-4), −158.56 (m, F-2 and F-3); J (1, 2) = (3,4) = −131.8, (1,3) = (2,4) = 12.4, (1,4) 32.6, (2,3) −36 Hz.[18] ^{1}H NMR (300 MHz) δ 7.62 and 7.63 (AB system, J = 9 Hz).

(*E,E*)- and (*E,Z*)-1,4-Bis[4-(cyclohexyloxy)phenyl]-1,2,3,4-tetrafluoro-1,3-butadiene (4b). Lithium as fresh cut flakes (0.4 g, 57 mmol) and 20 mL of ether were placed in a flame-dried flask previously flushed with nitrogen. A solution of 1-bromo-4-(cyclohexyloxy)benzene (**1d**) (5.1 g, 20 mmol) in 20 mL of ether was added dropwise for 20 min and then refluxed for 1.5 h. The flask was cooled to −78 °C, and a precooled (CO$_2$−ethanol bath) solution of *F*-1,3-butadiene (1.9 g, 11.7 mmol) in 15 mL of THF was added dropwise for 30 min. The mixture was stirred for 1.5 h and the cooling bath allowed to warm to −10 °C. The reaction mixture was worked up as usual. The crude product contained *E,E* and *E,Z* isomers of **4a** (86:14%, by ^{19}F NMR). **4b** *E,E* isomer was separated as yellow crystals, (1.46 g, 31%), mp 133 °C (from hexane). Anal. Calcd for $C_{28}H_{30}F_4O_2$: C, 70.87; H, 6.37. Found: C, 71.15; H, 6.50. MS m/z 476 (2); 475 (10); 474 (46) M$^+$; 392 (14); 311 (19); 310 (100); 290 (14); 261 (4); 236 (6); 217 (6); 216 (7); 186 (7); 169 (3); 167 (3); 143 (9); 94 (9); 83 (15); 81(12); 71 (10); 69 (7); 57 (12); 55 (59). IR 1634, 1606. ^{19}F NMR (75.4 MHz) AA′XX′ system, δ −142.67 (m, F-1 and F-4), −161.40 (m, F-2 and F-3); J (1−2) = (3−4) = −130.4, (1−3) = (2−4) 12.2, (1−4) 30.2, (2−3) −37.3 Hz.[18] ^{1}H NMR (300 MHz) δ 1.38−2.02 (m, 10H), 4.33 (m, 1H), 6.97 (d, J = 9 Hz, 2H), 7.69 (d, J = 9 Hz, 2H). (*E,Z*)-**4b** remained in the mother liquor (0.44 g, yellow oil), being 76% pure, containing 34% of (*E,E*)-**4b**. (*E,Z*)-**4b**: ^{19}F NMR (75.4 MHz) δ −141.34 (ddd, J = 132.7, 13.3, 6.5 Hz), −157.26 (ddd, J = 132.9, 40.4, 7 Hz), −143.05 (ddd, J = 40.4, 18.5, 13.3 Hz), −121.38 (ddd, J = 18.5, 7, 6.5 Hz).

(*E,E*)-1,4-Bis(4-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4c).[5] This was prepared following the procedure for preparation of **4b.** ^{13}C{^{1}H}-APT NMR (100.6 MHz) δ 21.43 (CH$_3$), 126.0 (m, quat C), 126.19 (p, J = 8.7, 4.3 Hz, CH), 129.37 (CH), 139.3 (dm, $J \approx$ 220 Hz), 140.48 (quat C), 150.1 (dm, $J \approx$ 246 Hz).

Reaction of *E,Z*-1-(4-Tolyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (2b) with Butyllithium. A precooled (−70 °C) solution of **2b** (1.31 g, 5.61 mmol in 20 mL of THF) was added to butyllithium (60 mL, 0.6 M, 36 mmol, solution in diethyl ether diluted with 20 mL of ether) at −72 °C for 30 min. The mixture was stirred at −78 to −72 °C for 1 h and allowed to warm up to +5 °C, worked up with 5% HCl and NaHCO$_3$ solutions, and extracted with ether. After rotary evaporation of the solvent, 2.06 g of the residual oil remained. A 1.2 g amount of it was separated by column chromatography on SiO$_2$ (75 g, 40/100) using pentane−benzene (25:1) as eluent. Fraction I, colorless oil (0.34 g, R_f 0.7) was identified as (*E*)-1-(4-tolyl)-1,2,3-trifluoro-4-butylocta-1,3-diene (**5c**), purity 88% (overall yield calcd on fractions I and II, 43%). Fraction II, colorless oil (0.25 g, R_f 0.65) contained 65% of (*E,E*)-1-(4-tolyl)-1,2,3,4-tetrafluoroocta-1,3-diene (**5a**) (yield 18%), and 35% of **5c** (by ^{19}F NMR). Fraction III, colorless oil (42 mg, R_f 0.62) contained (*Z,E*)-1-(4-tolyl)-2,3,4-trifluoro-1-butylocta-1,3-diene (**5b**), purity 70%, yield 6%.

General Procedure for Preparation of Unsymmetrical (*E,E*)-α,*ω*-Diaryl-1,2,3,4-tetrafluoro-1,3-butadienes (6a−i). An excess of lithium (1.5 equiv based on bromo derivative) in ether was placed in a flame-dried flask previously flushed with dry nitrogen. A solution of the bromoaromatic **1a**−**e** in ether was added dropwise at room temperature. When addition was completed, the mixture was refluxed for 1 h. The flask was cooled to −78 °C, and a precooled (by CO$_2$−ethanol mixture) solution of 1-aryl-*F*-1,3-butadiene **2a**−**e** in THF was added dropwise during 30−40 min. The mixture was stirred for 1.5 h and the cooling bath allowed to warm slowly to 0 °C. The reaction mixture was worked up with a 5% solution of hydrochloric acid, extracted with ether, and washed with a 5% solution of NaHCO$_3$ and twice with water. Ethereal layer was dried over MgSO$_4$. The product was purified by crystallization.

(*E,E*), (*E,Z*), (*Z,E*)-1-[4-(*N,N*-Dimethylamino)phenyl]-4-[4-(cyclohexyloxy)phenyl]-1,2,3,4-tetrafluoro-1,3-butadiene (6e). This was prepared from **2d** and **1e** (26% yield, *E,E* isomer, from hexane). Anal. Calcd for $C_{24}H_{25}F_4NO$: C, 68.72; H, 6.01; N, 3.34. Found: C, 69.11; H, 6.15; N, 3.31. ^{19}F NMR (75.4 MHz) ABXY system, δ −143.24 (m, 2F, F-1), −163.86 (m, 1F, F-2), −160.52 (m, 1F, F-3), −143.30 (m, 2F, F-4); J (1,2) = −129.2, (1,3) 12.5, (1,4) 29.7, (2,3) −37.7, (2,4) 12.6, (3,4) −130.8 Hz.[18] ^{1}H NMR (400 MHz) δ 1.3−2.04 (m, 10H), 3.02 (6H), 4.32 (tt, J = 8.9, 3.7 Hz, 1H), 6.72 (d, 2H, J = 9 Hz), 7.15 (d, J = 9 Hz, 2H), 7.63 (d, J = 9 Hz, 2H), 7.66 (d, J = 9 Hz, 2H). Other isomers (*E,Z*:*Z,E* = 4:3) remained in the mother liquor solution. **6e** (*E,Z* isomer): ^{19}F NMR (75.4 MHz) δ −141.7 (ddd, 1F, J = 134, 15, 8 Hz), −159.78 (ddd, 1F, J = 134, 39, 7.5 Hz), −142.05 (ddd, 1F, J = 39, 21, 15 Hz), −121.65 (ddd, 1F, J = 21, 8, 7.5 Hz). **6e** (*Z,E* isomer): ^{19}F NMR (75.4 MHz) δ −122.85 (ddd, 1F, J = 21, 8, 8 Hz), −145.43 (ddd, 1F, J = 41, 21, 14 Hz), −156.73 (ddd, 1F, J = 133, 41, 8 Hz), −142.1 (ddd, 1F, J = 133, 14, 8 Hz).

Preparation of Unsymmetrical (*E,E,E*)-α,*ω*-Diaryl-1,2,3,4,5,6-hexafluoro-1,3,5-hexatrienes (8a−e). The reaction was done in a flame-dried flask flushed with dry nitrogen. A precooled solution of butyllithium in hexane was added dropwise using a dropping funnel with jacket (cooling by CO$_2$−ethanol mixture) to a solution of an equimolar amount of a *para*-substituted *β*-chloro-α,*β*-difluorostyrene **7a**−**c** (76−80% of *Z* isomer, prepared by the reaction of Grignard reagent with chlorotrifluoroethylene[21]) in THF−ether (5:2) mixture at −100 °C and stirred for 1 h. A precooled (CO$_2$−ethanol mixture) solution of 1-aryl-*F*-butadiene **2a**,**c**,**d** (1.1 equiv) in THF was added dropwise for 30 min. The mixture was stirred for 1.5 h, and the cooling bath was allowed to warm to −25 °C. The reaction mixture was worked up with a 5% solution of hydrochloric acid, extracted with ether, and washed with a 5% solution of NaHCO$_3$ and twice with water. The organic layer was dried over MgSO$_4$ and the solvent was rotary evaporated. The obtained crude product was then purified by crystallization.

(*E,E,E*)-1-[4-(Cyclohexyloxy)phenyl]-6-(4-tolyl)-1,2,3,4,5,6-hexafluoro-1,3,5-hexatriene (8d). This was prepared from **2d** and **7b** (yield 25%, from hexane). Anal. Calcd for $C_{25}H_{22}F_6O$: C, 66.37; H, 4.90. Found: C, 66.37; H, 5.13. MS m/z 452 (47) M$^+$; 370 (81); 356 (9); 350 (10); 335 (9); 330 (6); 315 (7); 268 (43); 238 (16); 215 (9); 143 (93); 141 (68); 83 (19); 55 (100). IR 1675, 1637, 1606. ^{19}F NMR (376.5 MHz) δ −141.49 (ddd, 1F, J = 127, 31.5, 15.5 Hz), −168.19 (ddd, 1F, J = 127, 35, 14.5 Hz), −149.29 (dddd, 1F, J = 134.5, 35, 31, 14.5 Hz), −150.75 (dddd, 1F, J = 134.5, 34.5, 31.5, 15 Hz), −164.96 (ddd, 1F, J = 129, 34.5, 14.5 Hz), −141.31 (ddd, 1F, J = 129, 31, 15 Hz). ^{1}H NMR (300 MHz) δ 1.38−2.0 (m, 10H), 2.43 (3H), 4.33 (m, 1H), 6.97 (d, 2H, J = 9 Hz), 7.28 (d, J = 9 Hz, 2H), 7.65 (d, J = 9 Hz, 2H), 7.68 (d, J = 9 Hz, 2H). ^{13}C-{^{1}H}-APT NMR (75 MHz) δ 21.63 (CH$_3$), 23.80 (CH$_2$), 25.70 (CH$_2$), 31.77 (CH$_2$), 75.53 (CH), 115.82 (d, J = 2 Hz, CH), 120.2 (m, J = 25, 7 Hz, quat C), 125.5 (m, J = 25.3, 7.3 Hz, quat C), 126.26 (t, J = 8.5 Hz; CH), 128.06 (t, J = 8.9 Hz, CH), 129.35 (d, J = 2 Hz, CH), 140.92 (quat C), 138−156 (many overlapping multiplets), 159.57 (quat C).

(*E,E*)-1-(4-Hydroxyphenyl)-4-(4-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (9). A 67 mg amount of 1-[4-(cyclohexyloxy)-phenyl]-4-(4-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (**6d**) was put in a polyethylene bottle with a magnetic Teflon-covered stirring bar and cooled in brine bath (−10 °C). Liquid HF (3 mL) was added and stirred for 30 min. Then the flask was flushed with nitrogen for 20 min, and the rest of acid was neutralized with a NaHCO$_3$ solution, extracted with diethyl ether, washed with water, and dried over MgSO$_4$. Ether was rotary evaporated. The product was purified by TLC on SiO$_2$ eluted with CHCl$_3$ to obtain **9** (28 mg, 53%) R_f 0.2, as a pale yellow solid, mp 137 °C (purified by sublimation). IR (CHCl$_3$) 3591 (O−H), 1669, 1611. ^{19}F NMR (75.4 MHz) ABXY system, δ −142.2 (m, 1F), −161.52 (m, 1F), −159.83 (m, 1F), −143.10 (m, 1F). ^{1}H NMR (300 MHz) δ 2.42 (3H), 6.99 (d, J = 9 Hz, 2H), 7.25 (d, J = 9 Hz, 2H), 7.37 (d, J = 9 Hz, 2H), 7.98 (d, J = 9 Hz, 2H).

Preparation of (*E,E*)-1-(4-Carboxyphenyl)-4-aryl-1,2,3,4-tetrafluoro-1,3-butadienes (10a,b). The bromo derivative

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(21) Yagupolskii, L. M.; Kremlev, M. M.; Khranovskii, V. A.; Fialkov, Yu. A. *Zh. Org. Khim.* **1976**, *12*, 1372.

6g or **6h** (0.3 mmol), respectively, was placed into a flame-dried flask previously flushed with dry nitrogen and dissolved in 4 mL of ether and 3 mL of THF. BuLi (0.45 mL, 0.8 M in hexane) was added for 20 min by syringe at −78 °C, and the mixture was stirred for 1.5 h and allowed to warm to −20 °C. The color of the mixture changed from bloody-red at start to yellow-green at the end of stirring. Then the organometallic was poured onto dry ice. A yellow insoluble precipitate was formed. The reaction mixture was worked up with a 10%solution of KOH and washed with ether. The water layer was neutralized with a 5% solution of HCl, extracted with a benzene−THF (5:1) mixture, and washed twice with water. The organic layer was dried over $MgSO_4$. After rotary evaporation of solvents and crystallization, a yellow precipitate of acids **10a** (77%, benzene) and **10b** (73%, mp 113 °C, ethanol) was obtained.

(*E,E*)-1,4-Bis(4-carboxyphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (10c). A solution of **4a** (210 mg) in 25 mL of ether was cooled to −78 °C, and BuLi (2 mL, 0.85 M solution in ether) was added by syringe and stirred for 30 min. The mixture was allowed to warm to +10 °C for 1.5 h. The organometallic was poured on a dry ice and then worked up with KOH. The water layer was treated with HCl, and a pale yellow precipitate of **10c** was filtered (160 mg, yield 50%, mp 340 °C dec, (345 °C dec[5]).

Acknowledgment. We thank the Institute of Organic Chemistry, Ukrainian Academy of Sciences, for a leave of absence to Dr. M. M. Kremlev, and the Institute of Chemical Technology, Prague, for financial support of this work.

Supporting Information Available: ^{19}F NMR data of **2a**−**g** (Table S1); parameters of regression eq 1 and 2 (Table S2); table of ρ_x/ρ_y relationships (Table S3); analytical and spectral data of **2a**−**g**, **3a**−**c**, **5a**−**c**, **6a**−**i**, **8a**−**e**, **4a,b,d**, **9**, **10a,b**, **11**, **12**; UV absorption maxima for compounds **6a**−**i**, **10a,b**, **4a**−**d**, and **8a**−**e** (Table S4); ^{19}F NMR and MS data with assignment; copies of ^{1}H NMR spectra of **2b**−**e**, **4a**, **5a**−**c**, **6b**−**d**, **6h**, **8a,c**, **9**, **10b**, **11** (33 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960196E