July, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *54*, *2045—2052 (1981)* 2045

Acetylenic and Polyacetylenic Compounds Derived from Thiophene, Furan, and *p*-Dibromobenzene Using 1,1-Dichloro-2,2-difluoroethene

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(Received September 1, 1980)

Compounds of the type $AZCF{=}CCl_2$, prepared from AZA (thiophene, furan, and *p*-dibromobenzene; Z= 2,5-thiophenediyl, 2,5-furandiyl, and *p*-phenylene; A=H or Br), were converted into $CCl_2{=}CFZC{\equiv}CH$, $CCl_2{=}CFZC{\equiv}CCF{=}CCl_2$, and $CCl_2{=}CFZC{\equiv}CSi(CH_3)_3$ in a one-flask procedure *via* $LiZC{\equiv}CLi$. The products were further converted into acetylenic compounds such as $(CH_3)_3SiC{\equiv}CZC{\equiv}CSi(CH_3)_3$ and $(CH_3)_3SiC{\equiv}CZC{\equiv}C{-}C{\equiv}CSi(CH_3)_3$. 1-Ethynyl-4-(1,3-butadiynyl)benzene was isolated. 2,5-Diethynylthiophene and -furan were prepared in two steps from thiophene and furan, respectively, *via* $CCl_2{=}CFZCF{=}CCl_2$. By treatment with copper (II) acetate hydrate in pyridine, $(CCl_2{=}CFZC{\equiv}C{-})_2$ were obtained not only from $CCl_2{=}CFZC{\equiv}CH$ but also from $CCl_2{=}CFZC{\equiv}CSi(CH_3)_3$.

For introduction of the ethynyl group, the method using $CF_2{=}CCl_2$ (**1**)[1] is useful where R is aryl[2,3] and the organolithium and/or magnesium compounds are available. The method is particularly attractive when

$$RLi \longrightarrow RCF{=}CCl_2 \longrightarrow RC{\equiv}CLi$$

an appropriate lithium compound is easily obtained by lithiation[4] rather than by halogen-lithium exchange.[5] Lithium compounds easily obtained by lithiation are also expected to give rise to the desired substitution in high proportion (undesirable Cl-Li exchange in low proportion) in the reaction with **1**, since the partial negative charge is considerably delocalized in such compounds.[6] A typical example is the preparation of 2-ethynylthiophene from thiophene.[1] A good overall yield is also expected for the preparation of 2-ethynylfuran from furan *via* 2-(2,2-dichloro-1-fluoroethenyl)furan (**4b**).[7]

In the previous study,[1] however, only one position in each compound[8] was used for introduction of Li followed by reaction with **1** and subsequent transformations even where more than one position are available. In the present study two positions in each compound have been used in order to expand the synthetic possibility of the proposed method. 2,5-Diethynylthiophene (**23a**) and 2,5-diethynylfuran (**23b**) were prepared from thiophene and furan by this method. For the synthesis of these new diethynyl compounds, other methods used for the synthesis of 2-ethynylthiophene[9–13] and 2-ethynylfuran[14–16] do not seem to be feasible.[17] *p*-Dibromobenzene was also subjected to similar conversions, though preparation of *p*-diethynylbenzene was not attempted because of its known preparation from divinylbenzene (isomeric mixture),[18] diethylbenzene,[19] and *p*-diacetylbenzene.[20]

Results and Discussion

Treatment of 2-(2,2-dichloro-1-fluoroethenyl)thiophene (**4a**) and 2-(2,2-dichloro-1-fluoroethenyl)furan (**4b**) with two equivalents of butyllithium affords lithium acetylides **5**[1] (Scheme 1). Further addition of butyllithium lithiated the 5-position of the heterocycles to give dilithium compounds (**6a** and **6b**). A similar dilithium compound (**6c**) was formed, together with butyl bromide, from **4c** *via* Li-Br exchange between **5c** and butyllithium. When a portion of a mixture obtained in this way was left standing in the absence of **1**, 1-butyl-4-lithioethynylbenzene (**18**) was formed by the reaction of **6c** with butyl bromide.

$$\underset{\mathbf{4c}}{p\text{-}BrC_6H_4CF{=}CCl_2} + 2\,n\text{-}C_4H_9Li$$

$$\longrightarrow \underset{\mathbf{5c}}{p\text{-}BrC_6H_4C{\equiv}CLi} + 2\,n\text{-}C_4H_9Cl + LiF$$

$$\mathbf{5c} + n\text{-}C_4H_9Li$$

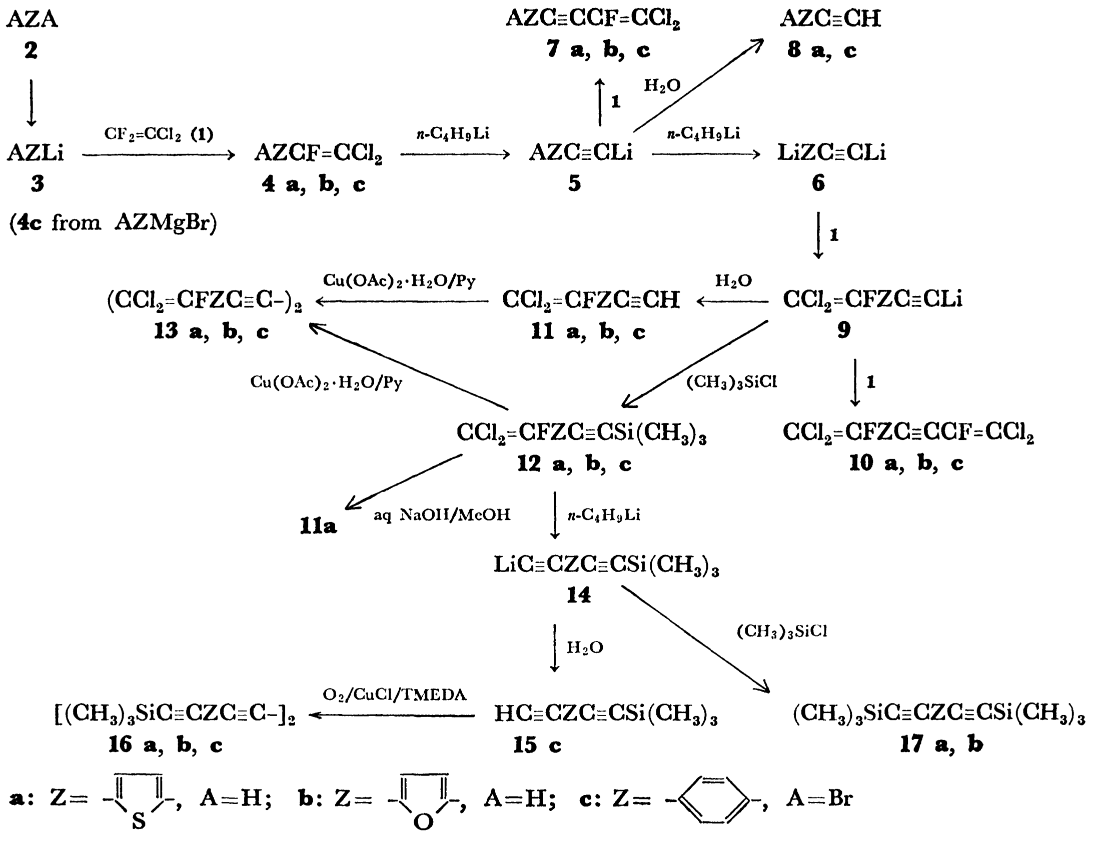
$$\longrightarrow \underset{\mathbf{6c}}{p\text{-}LiC_6H_4C{\equiv}CLi} + n\text{-}C_4H_9Br$$

$$\longrightarrow \underset{\mathbf{18}}{p\text{-}(n\text{-}C_4H_9)C_6H_4C{\equiv}CLi} + LiBr$$

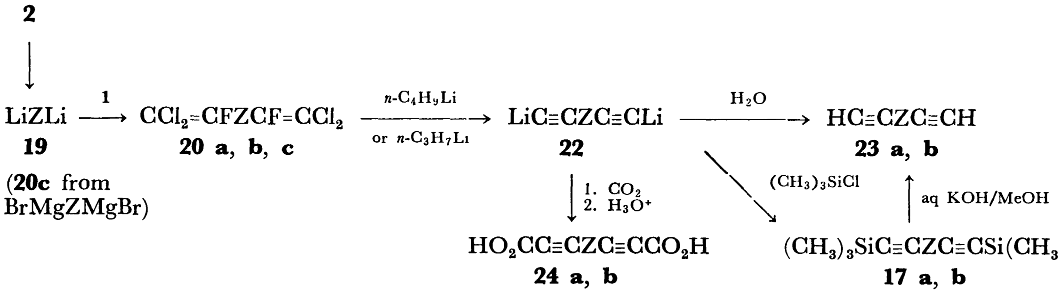
Compounds **6** serve as key intermediate in the transformations shown in Scheme 1. Treatment with **1** under refluxing conditions afforded compounds (**10**) having two $-CF{=}CCl_2$ groups. As the nucleophilicity of the acetylide carbanion is much smaller than that of the ring carbanion, the reaction can be carried out in such a way that only the latter takes part in the reaction. Thus the reaction of **6** with **1** at about 15 °C for a short time or at 0 °C for 1—2 h led to the formation of lithium acetylides **9** as the predominant product. Hydrolytic work-up afforded terminal acetylenes **11**, and quenching with chlorotrimethylsilane gave **12**. Compound **11a** was relatively unstable,[21] no procedure for its isolation in satisfactory yield being found. Thus the isolated yield of **11a** from **4a** was only 29%, whereas **12a** (a silylated acetylene)[22] was obtained in 78% yield together with 7% crude yield of **10a**. (At present the best way to prepare **11a** is the hydrolysis of **12a** by alkali.) Compounds **11b** and **11c** were much more stable than **11a**.

The 2,2-dichloro-1-fluoroethenyl group in **12** can also be converted into the lithioethynyl group by treatment with butyllithium. The conversion *via* **12** thus illustrates a method for the preparation of compounds of the type $A_1C{\equiv}CZC{\equiv}CA_2$, though there are limitations regarding the types of A_1 and A_2 for the conversion to be applicable. The conversions of **4** into **10**, **11**, and **12**, *via* several steps each, were conveniently carried out by a one-flask procedure.

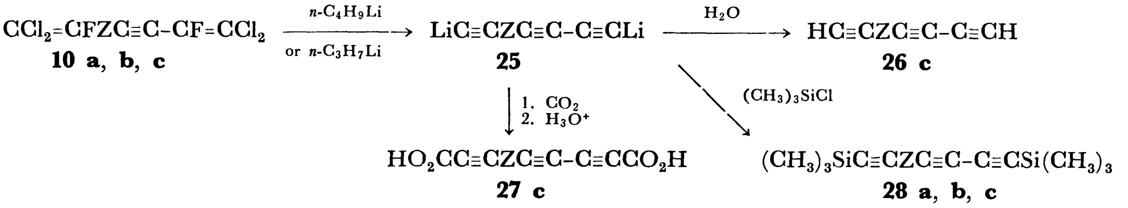
Terminal acetylenes were oxidatively coupled in order to obtain more stable crystalline "derivatives." Compounds **11a**, **11b**, and **11c** were satisfactorily converted into the symmetrically substituted butadiynes **13** by Eglinton coupling.[23,24] However, the use of



Scheme 1.



Scheme 2.



Scheme 3.

this method in the case of **15b** (curde product obtained from **12b**) resulted in the formation of a black, insoluble substance instead of **16b**, suggesting the cleavage of the Si–C (acetylenic) bond followed by a coupling reaction. Thus **12b** was subjected to the conditions for Eglinton coupling of **11b**, formation of **13b** being expected. Compound **13b** was indeed obtained in 77% isolated yield, higher than the yield (58%) of this compound obtained from **11b**. Likewise **13c** was obtained in an excellent yield from **12c** as well as from **11c**. On the other hand, the yield of **13a** obtained from **12a** was considerably lower than that obtained from **11a**. Under the reaction conditions compound **12a** (or a compound derived therefrom) probably undergoes a side reaction, such as ring cleavage, whereas compound **11a** is rapidly converted into the coupling product (**13a**). The coupling product formed from **11a** soon crystallizes, remaining mostly intact. The conversion of **15** into **16** was effected by use of Hay's procedure.[25]

Scheme 2 shows the conversion of thiophene and furan into 2,5-diethynylthiophene (**23a**) and 2,5-di-

Table 1. Yields, physical properties, and elemental analysis data of acetylenes and related compounds obtained by using $CF_2=CCl_2$

Compd	Yield/%[a]	Bp/°C(mmHg)	n_D^{20} or [Mp/°C]	^{19}F NMR[b,c] δ/ppm	^{1}H NMR[b] δ/ppm		IR[f] $\tilde{\nu}$/cm^{-1}	C (%) (Calcd) Found	H (%) (Calcd) Found
					I[d]	II[e]			
10a	73 (**4a**)		[46—47]	22.7		7.36+7.44(4.0)	1612	(35.96)	(0.60)
				(t 0.9)		(d 1.0) (t 0.7)	1620 sh	35.70	0.59
				24.8			**2190**		
				(d 0.6)					
11a	29 (**4a**)	96—98(6)	[42—43]	22.5	*3.48*	7.25+7.39(4.0)	1628	(43.46)	(1.37)
	97[g] (**12a**)			(t 0.9)	(d 0.5)	(d 0.9) (d 1.0)	**2110**	43.35	1.21
						(d 0.4)	*3300*		
12a	78 (**4a**)	126—128(2.5)	[76.5—78]	22.7	0.26	7.20+7.36 (4)	1620	(45.05)	(3.78)
				(t 0.9)		(d 0.9) (d 0.9)	**2145**	44.78	3.70
13a	77 (**11a**)		[197—198] dec	20.1[h]			1618	(43.66)	(0.92)
	38 (**12a**)						**2140**	43.41	0.97
16a	78 (**12a**)		[135.5—136.5]		0.25[i]	7.08+7.17[i] (3.9)	**2145**	(64.97)	(5.45)
								64.76	5.29
17a	95 (**12a**)		[82.5—83.5]		0.24	7.06	**2145**	(60.80)	(7.29)
	95 (**20a**)							60.70	7.51
20a	64 (**2a**)	130—133(2)	[85—86]	22.2		7.47	1616	(30.99)	(0.65)
				(t 0.9)		(t 0.9)		30.64	0.59
21a[j]	(**2a**)	*ca.* 80(2)	1.6114	24.0		6.90+7.25(4.2)	1628	(31.13)	(0.87)
				(t 0.9)		(d 0.6) (d 0.8)		31.30	0.90
23a	85 (**17a**)		1.636[k]		*3.35*[i]	7.11[i]	**2106**	(72.69)	(3.05)
	85 (**20a**)						*3290*	72.46	3.08
24a	72[g] (**20a**)		l)		5.11[m,n]	7.49[m]	**2210**	(54.54)	(1.83)
								54.17	1.54
28a	59 (**10a**)	*ca.* 182(2)	1.6231		0.23	7.09+7.12(3.8)	**2090**[o]	(63.93)	(6.71)
					0.24		**2135**[o]	63.63	6.79
							2180[o]		
10b	51 (**4b**)	130—135(2)	[52—53]	35.3		6.92	1624	(37.77)	(0.63)
				(t 1.1)		(d 1.0)	**2205**	37.66	0.62
				26.1					
11b	44 (**4b**)	85(7)	1.5912	35.1	*3.48*	6.73+6.83(3.6)	1630	(46.87)	(1.48)
				(d 1.3)	(d 0.4)	(d 1.4) (d 0.6)	**2119**	46.72	1.68
				(d 0.6)		(d 0.5)	*3295*		
12b	49[p] (**4b**)	118—122(2.5)	1.5673	35.0	0.26	6.69+6.82(3.5)	1628	(47.66)	(4.00)
				(d 1.4)		(d 1.5) (d 0.5)	**2153**	47.58	4.08
				(d 0.6)					
13b	58 (**11b**)		[123—124] dec	35.6[i]		6.88[i]	1637	(47.10)	(0.99)
	77 (**12b**)			(t 1.0)		(d 1.0)	**2149**	46.97	0.98
16b	64 (**12b**)		[128—129]		0.26	6.60+6.76(3.6)	**2154**	(70.54)	(5.92)
							2184 w	70.47	5.94
17b	88 (**12b**)		[72—72.5]		0.24	6.55	**2158**	(64.55)	(7.74)
	93 (**20b**)						**2192** w	64.41	7.58
20b	37 (**2b**)	116(4)	[65.5—66.5]	35.4		6.93	1625	(32.69)	(0.69)
				(t 1.0)		(t 1.0)		32.68	0.55
21b[j]	(**2b**)	*ca.* 75(5)	1.5556	35.3		6.31+6.83(3.6)	1635	(33.45)	(0.94)
				(d 1.4)		(d 1.4)		33.29	0.96
23b	72 (**17b**)		1.5654[k]		*3.39*[i]	6.62[i]	**2107**	(82.75)	(3.47)
	86 (**20b**)						*3290*	82.90	3.40
24b	73[g] (**20b**)		l)		5.30[m,n]	7.11[m]	**2225**	(58.83)	(1.98)
								58.89	1.97
28b	50 (**10b**)	153—158(2)	[50—52]		0.22	6.58+6.62(3.6)	**2100**[o]	(67.54)	(7.09)
					0.24		**2152**[o]	67.44	7.06
							2200[o]		
10c	72 (**4c**)		[74.5—75.5]	19.7 br		7.59+7.76(8.6)[q]	1624	(43.94)	(1.23)
				24.4 br			1630 sh	43.66	1.14
							2200		

Table 1. (continued)

Compd	Yield/%[a]	Bp/°C(mmHg)	n_D^{20} or [Mp/°C]	^{19}F NMR[b,c] δ/ppm	^{1}H NMR[b] δ/ppm I[d]	^{1}H NMR[b] δ/ppm II[e]	IR[f] $\tilde{\nu}$/cm^{-1}	C (%) (Calcd) Found	H (%) (Calcd) Found
11c	60 (**4c**)		[50—51]	19.2 br	*3.20*	7.57+7.71 (8.8)[q]	1634 r) *3275* *3300* w	(55.85) 55.74	(2.34) 2.42
12c	55 (**4c**)	129—137 (3)	[56—57]	19.3 br	0.26	7.52+7.66 (8.4)[q]	1628[s] **2154**	(54.36) 54.33	(4.56) 4.50
13c	93 (**11c**) 96[g] (**12c**)		[161—162]	19.7[i]		7.61+7.75[i] (9)[q]	1634 r)	(56.11) 55.64	(1.88) 1.77
15c[t]	71 (**12c**)		[55—56]		0.25 *3.16*	7.45	**2152** *3259*		
16c	78 (**12c**)		[231—232]		0.26[i]	7.44[i]	**2152**	(79.12) 78.98	(6.64) 6.45
20c[u]			[119—120.5]	19.6 br[i]		7.82[i]	1634	(39.51) 39.48	(1.33) 1.39
26c	79 (**10c**)		l)		*2.52*[i] *3.20*[i]	7.47[i]	**2205** *3295* sh *3270*	(95.97) 95.18	(4.03) 3.99
27c	85[g] (**10c**)		l)		4.90[m,n]	7.65[m]	**2165** w **2209** sh **2230**	(70.59) 70.10	(2.54) 2.71
28c	81 (**10c**)		[107.5—108.5]		0.22 0.24	7.43	**2103**[o] **2153**[o] **2205**[o]	(73.40) 73.32	(7.53) 7.53

a) Isolated yield, calculation being based on the starting compound indicated in parentheses. b) 20% Solution in CDCl$_3$ unless otherwise stated. ^{1}H and ^{19}F chemical shifts measured downfield relative to internal tetramethylsilane and upfield relative to external CF$_3$CO$_2$H, respectively. Splitting pattern and (apparent) coupling constant (Hz) indicated in parentheses. c) ^{19}F chemical shift for -C≡C-CF=CCl$_2$ indicated by bold face; broad signals at expanded scale (half-height width of roughly 1 Hz) denoted by br. ^{19}F chemical shifts and splitting patterns (in parentheses) not given in the Table are as follows: **4a**, 20.7(d 2.8)(t 1.1); **7a**, 23.9(d 0.6); **4b**, 34.1(t 1.4)(t 0.5); **7b**, 25.2 br; **4** (Z=*p*-phenylene, A=H), 15.6 br; **7** (Z=*p*-phenylene, A=H), 23.6; **4c**, 18.8 br; **7c**, 24.2 br. d) Si(CH$_3$)$_3$ (0.22—0.26 ppm), CO$_2$H (4.90—5.30 ppm), and C≡CH (2.52—3.48 ppm, in italics). e) Aromatic ring proton. Data for (gross) AB pattern: chemical shift of A+chemical shift of B (coupling constant: J_{AB} in Hz). Further splittings indicated under the respective chemical shifts. f) νC=C of -CF=CCl$_2$, νC≡C (in bold face), and νC-H of -C≡CH (in italics) are given. Neat for liquid and in KBr pellet for crystals. w, weak; sh, shoulder; br, broad. g) Crude yield. h) Saturated solution in thiophene. This compound is sparingly soluble in organic solvents. i) Concentration smaller than 10%. j) Obtained in *ca.* 7% crude yield as by-product of **20a** or **20b**. k) Melting point *ca.* 15 °C. l) No melting point observed; turning dark with rise in temperature. m) CD$_3$OD used as solvent. n) Chemical shift probably concentration-dependent due to the equilibrium: -COOH+CD$_3$OD$\rightleftharpoons$-COOD+CD$_3$OH. o) The three bands of νC≡C of comparable strength. p) 2-(Trimethylsilylethynyl)furan obtained in 17% yield. q) Approximate value of J_{AB} of AA′BB′ (or AA′BB′X) system. Since J_{AB} is the coupling constant between protons in mutually ortho positions and is expected to be much larger than other coupling constants, the spectrum has been treated as a (gross) AB pattern. r) νC≡C not observed: apparently IR-inactive. s) A stronger band, probably not due to the -CF=CCl$_2$ group, present at 1608 cm^{-1}. t) Previously reported (Ref. 23). u) Obtained in 9% yield together with 52% yield of **4c** when excess **1** was refluxed for a total of 19 h (in 3 days) in a Grignard reagent mixture prepared from *p*-dibromobenzene (0.5 mol) and magnesium (0.62 g-atom: Ventron chips).

ethynylfuran (**23b**), as well as their derivatives. The yields of 2,5-bis(2,2-dichloro-1-fluoroethenyl)thiophene (**20a**) and -furan (**20b**) obtained *via* lithiation of thiophene and furan followed by treatment with **1** were 64 and 37%, respectively. The low yields are apparently due to incomplete dilithiation of the heterocycles (and to possible decomposition of the dilithium compounds), particularly in the case of furan,[26] rather than to the yield of the reaction of the dilithium compounds with **1**. In the lithiation an increase in the proportion of butyllithium is expected to increase the extent of conversion of the heterocycles into dilithium compounds. However, the use of a large excess of butyllithium is undesirable since remaining butyllithium reacts with **20** as well as with **1**. In the present experiments a 50% excess of butyllithium (a total of three equivalents) was used for the dilithiation of thiophene and furan with a refluxing time of 9.5—11 h. In the reaction with **1**, the inverse addition method was not used since a significant portion of the butyllithium was considered to remain and to offset the advantage of use of this less convenient method.

The by-products of these reactions are 2-chloro-5-(2,2-dichloro-1-fluoroethenyl)thiophene (**21a**) and

-furan (**21b**) besides **4a** and **4b**, which were formed from the monolithiated compounds (**3a** and **3b**). Compounds **21a** and **21b** were isolated by preparative GC for identification. The formation of $\mathrm{ClZCF{=}CCl_2}$ (**21**) from LiZLi seems to proceed *via* ClZLi rather than *via* $\mathrm{LiZCF{=}CCl_2}$ since LiZLi is expected to give much higher proportion of the Li-Cl exchange to the substitution than $\mathrm{LiZCF{=}CCl_2}$, in view of stabilization to a much smaller extent of the negative charge[6] in LiZLi than in $\mathrm{CCl_2{=}CFZLi}$.

$$\begin{tikzcd}
 & \mathrm{CCl_2{=}CFZLi} \arrow[r, "1"] & \mathbf{20} \\
\mathrm{LiZLi} \arrow[ur, "1"] \arrow[dr] & & \\
 & \mathrm{ClZLi} \arrow[r, "1"] & \underset{\mathbf{21}}{\mathrm{ClZCF{=}CCl_2}}
\end{tikzcd}$$

Treatment of **20a** and **20b** with excess butyllithium (or propyllithium) followed by work-up and rotary evaporation of the solvent and butyl chloride (or propyl chloride) afforded crude 2,5-diethynylthiophene (**23a**) and 2,5-diethynylfuran (**23b**), respectively. The yields were high, but the samples contained hydrocarbon impurities, apparently originating from lithium reagent solutions and not effectively removable by rotary evaporation. 2,5-Diethynylthiophene (**23a**) was not sufficiently stable to be purified by preparative GC; purification was successfully performed through conversion into the disilver diacetylide. 2,5-Diethynylfuran (**23b**) was more stable, pure samples being obtained by careful preparative GC as well as through conversion into its disilver diacetylide.

Alkali hydrolysis of the bis(trimethylsilyl) derivatives (**17**), obtained by treatment of the dilithium diacetylides (**22**) with chlorotrimethylsilane as well as by a one-flask procedure from **12** (Scheme 1), also afforded 2,5-diethynylthiophene (**23a**) and -furan (**23b**). However, the crude samples obtained from **17** contained $\mathrm{(CH_3)_3SiOSi(CH_3)_3}$, and its removal required the use of the methods by which the samples obtained from **20** were purified.

The conversion of 1,4-bis(2,2-dichloro-1-fluoroethenyl)benzene (**20c**) into 1,4-diethynylbenzene (**23c**) was not undertaken. 1-Ethynyl-4-(1,3-butadiynyl)benzene (**26c**) was, however, prepared for the first time by treatment of **10c** with butyllithium (or propyllithium) as shown in Scheme 3. This is probably the easiest route for preparation of **26c**. The dicarboxylic acid (**27c**) and the bis(trimethylsilyl) derivative (**28c**) were also obtained. The corresponding bis(trimethylsilyl) derivatives (**28a** and **28b**) of thiophene and furan were similarly obtained. Compound **28a** remained as a viscous oil even after being purified by preparative GC.

Each of the compounds **28** obtained from **10** was accompanied by a by-product resulting from addition of butyllithium to **25** and subsequent replacement of three lithium atoms by trimethylsilyl groups. Propyllithium was not used for the preparation of **28**. On the basis of the infrared spectrum (ν C≡C 2122 and 2158 $\mathrm{cm^{-1}}$ for **30a** as compared with ν C≡C 2090, 2135, and 2180 $\mathrm{cm^{-1}}$ for **28a**) and from the fact that no addition of butyllithium to **22** takes place in the treatment of **20** with excess butyllithium, as confirmed by GC-mass spectroscopic examination of crude **17** obtained from the route given in Scheme 2, the by-product is considered as formed *via* 1,2-addition of butyllithium to one of the triple bonds in the lithiobutadiynyl group of **25**. Structure **29** is most likely for the adduct, structure **30** being tentatively assigned to the trisilylated compound. The addition of butyllithium to **25** was particularly conspicuous in the case of the thiophene derivative.

$\mathrm{LiC{\equiv}CZC(C_4H_9\text{-}\mathit{n}){=}C(Li)C{\equiv}CLi}$ (**29**)

$\mathrm{(CH_3)_3SiC{\equiv}CZC(C_4H_9\text{-}\mathit{n}){=}C[Si(CH_3)_3]C{\equiv}CSi(CH_3)_3}$ (**30**)

The following remarks are given on the NMR data summarized in Table 1: (1) The unusually high ^{19}F NMR chemical shifts of the $\mathrm{-CF{=}CCl_2}$ group of furan derivatives are clearly associated with a similar trend of the ^{1}H NMR chemical shifts of the ring protons. Note that the ^{19}F NMR and ^{1}H NMR chemical shifts are measured in mutually opposite directions. (2) The coupling patterns in ^{1}H NMR spectra of thiophene and furan derivatives are much simpler than those of benzene derivatives. In many cases, the coupling constant between the fluorine of the $\mathrm{-CF{=}CCl_2}$ group (attached to the 2-position of the ring) and the proton at the 3-position is comparable to the one between the fluorine and the proton at the 4-position. However, of the two coupling constants or of the two ^{1}H chemical shifts, it is not clear which one is for the proton at the 3-position.

Experimental

Caution should be taken in the handling of acetylenic compounds. Some terminal acetylenes are liable to exothermic decompostion upon heating (*cf.* descriptions for **11a** and **23a**).

Temperature readings are uncorrected. Pressure readings are given in terms of mmHg (1 mmHg=133.322 Pa). ^{19}F NMR and ^{1}H NMR spectra were recorded on a Hitachi R-20BK operated at 56.451 MHz and on a Hitachi R-22 operated at 90 MHz, respectively. IR spectra were recorded on a Hitachi EPI-G3, and mass spectra[27] on a Shimadzu GCMS-7000. All reactions of butyllithium and propyllithium were conducted under an atmosphere of nitrogen with use of sodium-dried ether. Butyllithium and propyllithium were prepared from butyl bromide and propyl bromide, respectively, by the reaction with cut pieces of lithium in ether and stored at −20 °C. The amounts of these reagents are calculated from nominal concentration.

*2-Ethynyl-5-(2,2-dichloro-1-fluoroethenyl)thiophene (**11a**).* Compound **4a**[1] (19.06 g, 96.7 mmol) was treated with butyllitium, **1** being added as described in the section for **12a**. The resulting mixture was allowed to warm to 0 °C, at which it was stirred for 1.3 h. The worked-up mixture was crystallized by cooling to −20 °C, crystals of **11a** (4.32 g) remaining unmelted at room temperature being filtered off. Vacuum distillation of the mother liquor afforded an additional amount of **11a** (1.95 g, bp 96—98 °C/6 mmHg), increasing the total isolated yield to 29%. A large amount (11.86 g) of distillation residue remained. The experiment was repeated, and the total worked-up mixture was subjected to vaccum distillation. A few minutes after air[28] had been admitted into the apparatus in order to replace the condenser, in which the first portion of **11a** had crystallized, the content of the still pot decomposed with ignition. The analytical sample (mp 42—43 °C) of **11a** was obtained by recrystallization (from methanol) of a sample obtained by alkaline hydrolysis of **12a**. MS *m/e*, 220 (M).

2-(2,2-Dichloro-1-fluoroethenyl)-5-(trimethylsilylethynyl) thiophene (12a). Ethereal butyllithium (322 mmol, 192 ml) was added to a stirred solution of **4a** (19.70 g, 100 mmol) in ether (100 ml) cooled with Dry Ice–acetone below −50 °C. The resulting mixture was stirred for 1.5 h at *ca.* 20 °C and re-cooled with Dry Ice-acetone. After addition of **1** (36 g, 270 mmol) in one portion, the Dry Ice-acetone bath was replaced by an ice–water bath. The internal temperature rose rapidly to reach a maximum of 20 °C and then began to fall. The resulting mixture was stirred at 13—17 °C for 16 min after that moment, re-cooled with Dry Ice–acetone, and chlorotrimethylsilane (24.5 g, 225 mmol) was added. After the cooling bath had been removed, the whole mixture was stirred for 2 h and poured onto a mixture of crushed ice and concd hydrochloric acid. Distillation of 94% of the worked-up mixture afforded 21.47 g (78% yield) of **12a**, bp 126—128 °C/2.5 mmHg. The distillation residue (2.2 g, corresponding to 7% yield) was found to be mainly **10a** by IR and ^{19}F NMR spectroscopy. No crystallization of **12a** took place in the condenser during the course of distillation, though crystallization was easily induced by seeding. The analytical sample (mp 76.5—78 °C) was obtained by recrystallization from ethanol. MS *m/e* (rel intensity), 292 (M, 46), 277 (M−CH$_3$, 100).

Bis[5-(2,2-dichloro-1-fluoroethenyl)-2-thienyl]butadiyne (13a). Compound **11a** (2.00 g, 9.0 mmol) and copper(II) acetate hydrate (3.00 g) was stirred in pyridine (30 ml) in a bath at 50 °C. The solution turned into a bright brown slurry in a few minutes. After being stirred for 30 min, the resulting mixture was poured onto water (*ca.* 500 ml) with agitation. The precipitate was collected by filtration and dried (mp 195—199 °C; 1.93 g, corresponding to 97% yield of **13a**). The first crop of recrystallization of **13a** from dioxane was 1.54 g, (77%; mp 197—198 °C with decomposition as judged from formation of a black melt). MS *m/e* (rel intensity), 438 (M, 100), 368 (M−2Cl, 22).

When compound **12a** (2.00 g, 6.8 mmol) was subjected to essentially the same treatment as described above, the crude product obtained by pouring the reaction mixture onto water amounted to 1.44 g, corresponding to 96% yield of **13a**. However, only 38% yield (0.57 g) of **13a** was obtained from this. The rest of the material was more strongly adsorbed on alumina and is suggested to be a mixture by its elution behavior.

2,5-Bis(trimethylsilylethynyl) thiophene (17a). Ethereal butyllithium (31 mmol, 19 ml) was added to a cooled stirred suspension of **12a** (3.36 g, 11.5 mmol) in ether (60 ml) over a period of 12 min below −58 °C. After addition of chlorotrimethylsilane (6 g, 55 mmol) at −5 °C, the resulting mixture was stirred for 1.5 h without cooling. Hydrolysis, workup, and solvent evaporation afforded a crystalline residue, from which 2.65 g (mp 82.5—83.5 °C) of **17a** was obtained by digestion with ethanol followed by filtration. From the filtrate, less pure **17a** (mp 79—81 °C. 0.36 g; total 95%) was recovered. Recrystallization from ethanol afforded the analytical sample (mp 82.5—83.5 °C). MS *m/e* (rel intensity), 276 (M, 100), 261 (M−CH$_3$, 51).

The same compound was obtained in 95% yield from **20a** by the same procedure, its identity being confirmed by undepressed mixed melting point.

*1,4-Bis[*p*-(trimethylsilylethynyl)phenyl]-1,3-butadiyne (16c).* An acetone (10 ml) solution of crude **15c**$^{29)}$ obtained from **12c** (2.00 g, 7.0 mmol) by treatment with butyllithium (19 mmol) was added to an oxygen-bubbled solution of *N,N,N′,-N′*-tetramethylethylenediamine (0.12 g) and copper(I) chloride (0.10 g) in acetone (20 ml). The resulting mixture, which became a crystalline slurry in a few minutes, was stirred for 39 min with continued oxygen bubbling and treated with a mixture of ether (*ca.* 150 ml) and aqueous hydrochloric acid. Crystals of **16c** remaining insoluble even after addition of benzene (50 ml) followed by shaking of the total mixture were filtered off (dried 0.28 g, mp 231—232 °C). An additional amount (0.79 g) of crystals of **16c** was obtained from the organic layer after washing (with aqueous hydrochloric acid and then with water), drying, and concentration, with increase in the total isolated yield of **16c** to 78% (based on **12a**). A mixture (0.20 g, 15%) of **15c** and **16c** recovered from the mother liquor is excluded from the above yield. Recrystallization from benzene afforded the analytical sample (mp 231—232 °C). MS *m/e* (rel intensity), 394 (M, 100), 279 (M−CH$_3$, 94). The corresponding thiophene and furan derivatives (**16a** and **16b**) were much more soluble in organic solvents than **16c**; most of the acetone was removed by evaporation before similar work-up.

2,5-Bis(2,2-dichloro-1-fluoroethenyl)thiophene (20a). Ethereal butyllithium (300 mmol, 180 ml) was added (exothermic) to a stirred solution of thiophene (8.41 g, 100 mmol) in ether (100 ml) in a 500 ml four-necked flask equipped with a thermometer, a dropping funnel, and a Dimroth condenser. The solution was refluxed for 12 h to give a slurry. Compound **1** (51 g, 380 mmol) was added over a period of 43 min, during which time the internal temperature was kept below −50 °C by cooling with Dry Ice-acetone. Circulation of ice water through the Dimroth condenser was initiated, and the dropping funnel was replaced by an additional condenser, two condensers being necessary to control the excessive exothermicity. The cooling bath was replaced with a vacant bath vessel, which was filled with ice water to the necks of the flask as soon as the internal temperature reached 0 °C. The temperature rose slowly up to 20 °C but very rapidly to refluxing temperature (30—32 °C) from 20 °C. After vigorous boiling subsided, the cooling bath and the additional condenser were removed, the mixture was heated to reflux for 2 h, and poured onto a mixture of crushed ice and concd hydrochloric acid (30 ml). The ether layer was separated, washed (with water and with aq NaHCO$_3$), dried, and 95% of the solution was evaporated to leave a crystalline residue. Digestion with ethanol followed by filtration afforded **20a** (14.50 g). Fractional distillation of the filtrate with a short Vigreux column gave an additional amount (4.51 g) of **20a** (bp 130—132 °C/2 mmHg), increasing its total yield to 64%, besides an approximately 1:1 mixture (3.02 g, in three fractions) of **4a** (7% yield) and **21a** (7% yield). The analytical sample of **20a**, mp 85—86 °C, obtained from a distilled sample by recrystallization from ethanol, was colorless. MS *m/e* (rel intensity), 308 (M, 100), 273 (M−Cl, 6), 238 (M−2Cl, 32). A pure sample of **21a** was obtained by preparative GC. MS *m/e* (rel intensity), 230 (M, 100), 195 (M−Cl, 30), 160 (M−2Cl, 42). By a similar procedure with an externally heated refluxing time of 2 h for lithiation of thiophene using 2.4 equivalents of butyllithium, **4a** and **20a** were isolated 31 and 35% yields, respectively.

2,5-Diethynylthiophene (23a). Ethereal butyllithium (20 mmol, 12 ml) was added below −58 °C over a period of 10 min to a cooled stirred slurry of **20a** (1.00 g, 3.2 mmol) in ether (50 ml). The resulting mixture was allowed to warm to −10 °C and poured onto a mixture of concd hydrochloric acid (4 ml) and crushed ice. The whole mixture was shaken, the ether layer separated, washed (with water and with aq sodium hydrogencarbonate), and dried (Na$_2$-

SO_4). The oil (0.57 g; *caution*[30]) obtained after brief rotary evaporation was dissolved in ethanol (20 ml), and a solution of silver nitrate (2.00 g) in water (2 ml) was added giving a bright yellow precipitate, which was filtered off and washed with ethanol and with ether. The precipitate was stirred in ether (100 ml). An aqueous solution (15 ml) containing 3 ml of concd hydrochloric acid was added, the ether layer separated (after complete conversion of the precipitate), then washed (aq hydrochloric acid, water, and aq sodium hydrogencarbonate), dried and evaporated (up to 45 °C bath temp) to give **23a** as an oil (0.37 g, 87%). IR and ^{1}H NMR examination indicated the presence of ether (2%), the yield of **23a** being 85%. Pure **23a** was obtained by further evaporation.

Aqueous potassium hydroxide (a 0.08g pellet dissolved in 2 ml of water) was added to a solution of **17a** (1.00 g, 3.6 mmol) in methanol (50 ml) stirred in a bath kept at 20 °C. After 20 min, the resulting solution was shaken with a mixture of ether (100 ml) and water (100 ml). Crude **23a** was obtained from the ether layer and purified by conversion *via* the disilver diacetylide. Regenerated **23a** (0.42 g) contained 3% of ether (yield of **23a**: 85%). A 0.20 g portion of this sample was further evaporated to give 0.18 g of pure **23a** (79% from **17a**). MS *m/e* (rel intensity), 132 (M, 100), 82 ($M-C_4H_2$, 16), 69 ($M-C_5H_3$, 23), 63 (C_5H_3, 11); IR (neat),[31] 3290 [1], 3100 [2], 3090 sh [2], 2590 w, 2106 [3], 1784 [4], 1620 [5], 1518 [6], 1513 sh [6], 1442 [7], 1340 br [8], 1235 sh, 1219, 1152, 1138, 1034 [9], 813 [10], 705, 676 sh [11], 670 [11], 608 [12], 548, 495, 442 cm^{-1} [13].

2,5-Diethynylfuran (23b). MS *m/e* (rel intensity), 116 (M, 100), 88 ($M-CO$, 12), 63 (C_5H_3, 13), 62 (C_5H_2, 13), 53 ($M-C_5H_3$, 10); IR (neat),[31] 3290 [1], 3146 [2], 3110 w [2], 2692 w, 2107 [3], 1730 [4], 1600 [5], 1570 [6], 1565 sh [6], 1497 [7], 1380 br [8], 1347, 1310, 1214, 1200, 1022 [9], 965, 800 [10], 688 [11], 670 sh [11], 604 [12], 453 cm^{-1} [13].

1-Ethynyl-4-(1,3-butadiynyl)benzene (26c). Compound **10c** (1.00 g, 3.1 mmol each time) was treated with butyllithium or propyllithium (20 mmol) below −50 °C in order to find an appropriate isolation procedure for **26c**, an unstable compound. The ether solution obtained after work-up from each run was dried (Na_2SO_4) and subjected to rotary evaporation to leave a crystalline residue (0.5—0.6 g, corresponding to 109—130% yield of **26c**). All samples showed ^{1}H NMR signals at the alkyl hydrogen region, impurities not being completely removable by continued evaporation. Digestion with cold ethanol (or methanol) followed by filtration afforded pure **26c**, the yields being less than 50% even after combining the crystals obtained by cooling the filtrates to −20 °C. Conversion into the disilver diacetylide led to the highest isolated yield of pure **26c**. Thus the crude sample obtained from a butyllithium run was dissolved in ethanol (25 ml), and a solution of silver nitrate (2.00 g) in water (2 ml) was added to give a pale yellow precipitate, which was filtered off, washed, and treated with aqueous hydrochloric acid as in the case of **23a**. The sample of regenerated **26c** (0.36 g, 79%) showed no ^{1}H NMR signal other than three single peaks (2.52, 3.20, 7.47 ppm) in 1:1:4 relative intensities. The crystals of **26c** first appearing on the inside wall of the flask upon evaporation of every worked-up solution were nearly white, indicating that **26c** is stable in ether. However, the crystals turned rapidly to beige and to brown black. The compound showed no melting point and turned dark with rise in temperature. Cooling to or below −20 °C was neccessary for storage even for a short time (*e.g.* 2 h). The spectroscopic data of freshly prepared samples are as follows. MS *m/e* (rel intensity), 150 (M, 100), all other peaks (<7); IR (KBr), 3295 sh(w), 3275 sh, 3270, 2205, 1920, 1670, 1505 sh, 1497, 1403, 1378 w, 1269, 1258, 1109, 1020, 838, 711, 679, 668, 641, 636 sh, 548, 508, 451 cm^{-1}. The KBr discs of IR measurement turned black in one day upon standing in the dark at room temperature. The IR spectrum at this stage was nearly the same as the spectrum obtained after several months. Notable spectral changes were: (1) broadening and decrease in intensity of the 3270, 1403, 1109, 1020, 838, 668, 641, and 548 cm^{-1} bands, (2) disappearance of 2205, 1920, 1670, 1378, 1269, 1258, 711, 679, 508, and 451 cm^{-1} bands, and (3) replacement of the bands at 711—636 cm^{-1} by two broad bands (of decreased intensity) at 650 and 618 cm^{-1}.

*5-[*p*-(Carboxyethynyl)phenyl]-2,4-pentadiynoic Acid (27c).* Compound **10c** (1.00 g, 3.1 mmol) was treated with butyllithium as above, several pieces of Dry Ice (*ca.* 10 g) being added to the resulting active mixture. After stirring for 1.5 h water was added, the whole mixture shaken, filtered, the aqueous layer separated, washed with ether, and acidified with aqueous hydrochloric acid. The resulting faintly yellow crystalline precipitate was filtered off and dried (0.62 g, 85% yield of **27c**) over calcium chloride in a vacuum desiccator. Recrystallization of a portion of the sample from a small amount of methanol by cooling to −20 °C gave a colorless analytical sample showing no melting point and turning dark above *ca.* 190 °C. Recrystallization from water was inappropriate. Heating the compound in boiling water appeared to induce decarboxylation, the product (not purely isolated) suspected to be $HO_2CC{\equiv}CC_6H_4C{\equiv}C{-}C{\equiv}CH$. (The analytical samples of **24a** and **24b** were obtained by recrystallization from acetone and from water, respectively.)

1-(Trimethylsilylethynyl)-4-(4-trimethylsilyl-1,3-butadiynyl)benzene (28c). Compound **10c** (2.00 g, 6.1 mmol) was treated with butyllithium (40 mmol), and the resulting active mixture with chlorotrimethylsilane. From the crystalline mixture obtained after work-up, **28c** (1.45 g, 81%; mp 107.5—108.5 °C) was obtained by digestion with methanol followed by filtration. The filtrate upon standing for one week, precipitated crystals (0.21 g, mp *ca.* 75—97 °C), which were found to be a mixture (*ca.* 3:2) of **28c** and a compound whose mass spectroscopic molecular weight is greater than that of **28c** by 130 [$(CH_3)_3SiC_4H_9$]. The latter seems to have the structure **30c**.

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6) In the reaction of **1** with organolithium compounds (RLi), the proportion of the Cl-Li exchange to the sum of the exchange and substitution varies widely depending on the nature of R. It is suggested that the smaller the extent of delocalization of the negative charge in the reagent, the higher the proportion of the exchange (Ref. 1). The word "delocalization" may be replaced by "stabilization."

7) The isolated yield of **4b** was improved to 76% from the yield (53%) reported in Ref. 1. The major difference in reaction conditions is that the refluxing time for lithiation of furan with butyllithium was extended from 1 h (used after standing overnight) to 4 h (used at once). Compound **4b**, though turning intensely colored and then darkend on exposure to air, remained colorless when stored at −20 °C in an ampule filled with nitrogen.

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21) Compound **11a** in a sealed NMR tube as a 20% benzene solution decomposed almost completely in several years whereas compound **11c** under the same conditions showed no sign of decomposition. See Experimental for exothermic decomposition of **11a**.

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27) None of the peaks due to ^{37}Cl-containing species is given. Such a peak is not taken as a base peak (intensity 100) even if it is the strongest (*e.g.*, *m/e* 310 in the case of **20a**).

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29) This compound was previously reported: V. D. Ermakova, M. G. Chauser, J. S. Nesterova, and M. I. Cherkoshin, *Tesisy Dokl. Vses, Konf. Khim. Stsetilena*, 5th, 1975, 505; *Chem. Abstr.*, **88**, 153350r (1978).

30) In an earlier experiment of the same scale, such an oil (crude **23a**) was further evaporated, and GC examination of the resulting oil (0.30 g, not pure according to IR) was attempted. As soon as the needle of the microsyringe was inserted into the injection port (*ca.* 250 °C), the content (1 μl+needle volume) decomposed with ignition. Although crude samples of lower **23a** content (and solutions of **23a** in ether) were injectable, a considerable decomposition of **23a** was apparent in its low sensitivity.

31) The figures in square brackets indicate the correspondence of frequencies of **23a** and **23b** suggested from comparative inspection of the two spectra (aside from rigorous assignments of frequencies).