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SYNTHESIS OF SOME ETHYNYLTRIFLUOROMETHYLFURANS AND THEIR POLYMERIZATION

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SUMMARY

Some trifluoromethyl group substituted ethynylfurans were prepared according to the method of Okuhara. However, dichlorofluorovinylation of lithiated 2,3-bis(trifluoromethyl)-furan did not undergo so smoothly because of the electron-withdrawing trifluoromethyl groups and the initially substituted dichlorofluorovinyl group. Thermal, γ-ray induced, or oxidation polymerizations were investigated, and 1,4-diethynyl-2,3-bis(trifluoromethyl)furan thermally polymerized to give an insoluble polymer in a violent exothermal reaction.

INTRODUCTION

As a part of our continuing interest in the chemistry of fluorine-containing ethynyl compounds [1], we describe here the first synthesis dealing with the hitherto unknown trifluoromethyl group substituted ethynylfurans and their polymerizations.

RESULTS AND DISCUSSION

As previously reported by Okuhara [2], lithiated furan reacts with 1,1-dichloro-2,2-difluoroethylene (1) to afford good yields of dichlorofluorovinylfurans, which are useful as precursors for ethynylfurans by treatment with n-butyllithium.

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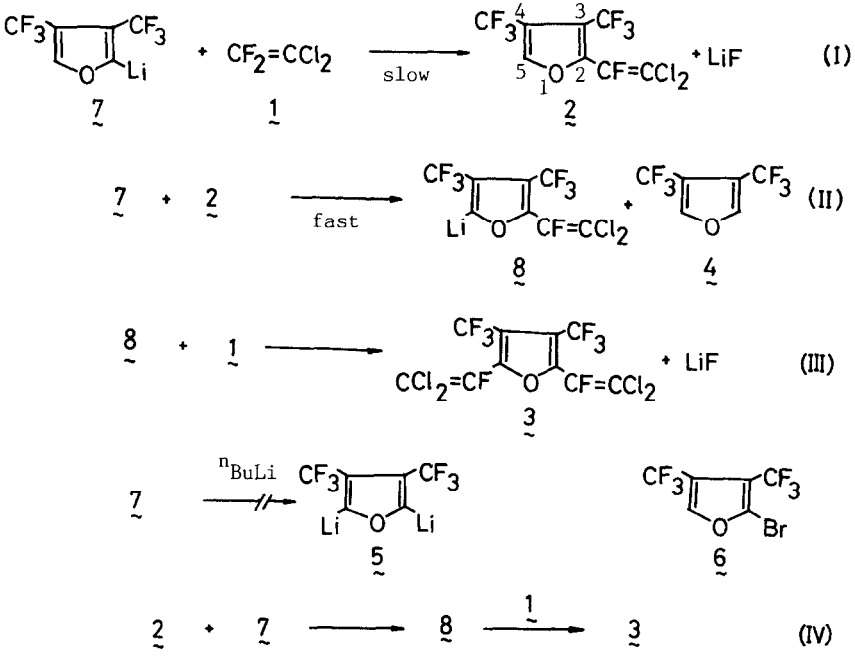
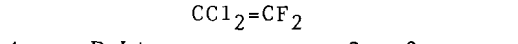
However, in the case of the trifluoromethylfurans, different results were obtained, as shown in Table I. Thus, it is interesting that the product ratio of 2-(2,2-dichloro-1-fluorovinyl)-3,4-bis(trifluoromethyl)furan (2) to 2,5-bis(2,2-dichloro-1-fluorovinyl)-3,4-bis(trifluoromethyl)furan (3) was larger at higher reactant ratio of 1 to 3,4-bis(trifluoromethyl)furan (4). It is obvious that 3 was not derived from dilithiofuran 5 because quenching of the lithiated furan with Br_2 gave only 2-bromo-3,4-bis(trifluoromethyl)furan 6, bromination product of monolithio derivative 7 which formed directly by the equimolar reaction of the furan 4 with n-butyllithium in ether at -30°C. The lithium exchange reaction of 7 and 2 (eq. II) is considerably faster than the reaction of 7 with 1 (eq. I). In fact, the reaction of 2 with 3-fold excess of 7 followed by addition of 1 (equimolar to 2) yielded only bis-olefin 3 (eq. IV), and the yields of 3 changed almost parallel with the recovery of 4 (Table I).



Therefore, when the molar ratio of 1 to the lithiofuran 7 is low, 2, which firstly formed in the reaction (I), changes

TABLE I

Yield Ratios (2 : 3) in Various Conditions

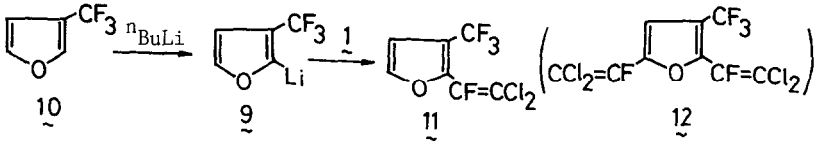


Run	4 mmol	^{n}BuLi mmol	1 mmol	Molar ratio 4 : 1	Yield (%)[c] 2	3	Ratio 2 : 3	Recovery (%)[c] 4
1[a]	49	52	147	1 : 3.0	2	24	1 : 12	28
2[b]	25	26	34	1 : 1.4	4	28	1 : 7	33
3[b]	49	57	300	1 : 6.1	23	15	1.5 : 1	24
4[a]	98	112	850	1 : 8.7	30	5	6.0 : 1	17

[a]The usual addition method. [b]The inverse addition method. [c]Calculated by GLC.

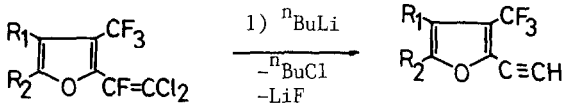
quickly to deprotonated 8 that reacts with 1 to afford 3. If the ratio of 1 to 7 is large as in the inverse addition method, the ratio of 3 to 2 is less than in the usual addition one (see run 1 and 2 in Table I). When the ratio of 1 to 7 is substantially high, the reaction (I) is relatively faster than the reaction (II) even in the usual addition method. This can be confirmed from the comparison between run 3 and 4. The above phenomenon may be caused by the increase in C-H acidity of the C-5 position of 2 affected by the electronegativity of the trifluoromethyl group at the adjacent position, and the dichlorofluorovinyl group in the C-1 position.

On the contrary, 2-lithio-3-trifluoromethylfuran (9) which was prepared from 3-trifluoromethyl furan (10) with n-butyllithium in ether gave only mono-dichlorofluorovinyl product 11 (51 %), and no bis-substitution product 12. This is consistent with the expected decrease of C-H acidity from 2 to 11.



10 9 11 12

Treatment of the compounds 2, 3 and 11 with n-butyllithium gave the desired ethynylfurans 13 (74%), 14 (67%) and 15 (48%), respectively.



	R_1	R_2		R_1	R_2
2;	CF_3	H	13;	CF_3	H
3;	CF_3	$-CF=CCl_2$	14;	CF_3	$-C\equiv CH$
11;	H	H	15;	H	H

The thermal and γ-ray induced polymerizations of 13 and 15 gave oligomers of roughly 2000 molecular weight, comparable with those of phenylacetylene [3]. The rate of thermal oligomerization of 13 increased along with the increase in tempera-

ture, as estimated from the conversion; 28 % at 70°C for 480 h, 27 % at 100°C for 105 h, 36 % at 150°C. The rate of oligomerization of 15 was nearly equal to that of 13 (conversion of 15; 23 % at 70°C for 480 h). In the γ-ray induced oligomerization of 13, conversion was 46 % for 1.4×10^6 rad at room temperature. On the other hand, the rate of thermal polymerization of 14 was ten times larger than those of oligomerization of 13 and 15, where 14 became glassy at 70°C for 53 h and the conversion was 30 %. The rate of polymerization of 14 above 100°C was so fast that the ampoule exploded; for instance, such an explosion occurred at 100°C. Such higher exotherm was probably caused by the presence of the two ethynyl groups in the furan 14 of which polymerization would give a net polymer. Therefore, it was better to polymerize 14 in two steps. Acetylene 14 was polymerized firstly at 70°C and then above 100°C. After the polymerization at 150°C for 170 h, the conversion became 80 %, but no polymerization proceeded further for longer time. This means that the maximum conversion is 80 % at 150°C. In the polymerization at 300°C, the maximum conversion was 93 %. It is conceivable that the residual ethynyl groups were locked in the net of the polymer chains and unable to migrate. It is noticed that there were no IR absorptions assignable to -C≡CH in the polymer formed from the oxidation polymerization of 14.The decomposition temperature of the polymer formed in the oxidation polymerization of 14 was 280°C in both nitrogen atmosphere and in air, which was nearly equal to those of poly(diethynylbenzene) and poly(diethynylpyrrole) [4]. The decomposition temperature of the polymer formed in the thermal polymerization of 14 (for 53 h at 70°C and then for 170 h at 150°C) was 370°C in nitrogen and 336°C in air.

EXPERIMENTAL

IR spectra were recorded on a Hitachi 285H. Mass spectra were recorded on a Shimazu GC-MS 7000. ^{1}H- and ^{19}F- NMR spectra were recorded on a Hitachi R-22 at 90 MHz and on a Hitachi R-20B at 56.45 MHz, respectively. Chemical shifts were re-

ported in parts per million in downfields (δ) from $SiMe_4$ as an internal standard for ^1H and from CF_3COOH as an external standard for ^{19}F, respectively.

3-Trifluoromethylfuran (10) and 3,4-bis(trifluoromethyl)furan (4) were prepared by the methods reported previously [5]. n-Butyllithium and 1 were also prepared by the methods reported [2,6]. All reactions of n-butyllithium were conducted under nitrogen atmosphere, with use of sodium-dried ether.

2-(2,2-Dichloro-1-fluorovinyl)-3,4-bis(trifluoromethyl)-furan (2) and 2,5-bis(2,2-dichloro-1-fluorovinyl)-3,4-bis(trifluoromethyl)furan (3)

(a) The usual addition method: n-Butyllithium ethereal solution (1.6 mol/l, 70 ml, 112 mmol) was added dropwise to a stirred solution of 4 (20.1 g, 98 mmol) in ether (100 ml) at -30 – -35°C in 7 min, and the resulting mixture was stirred at the same temperature for 1.5 h. Then, 1 (25 ml, 282 mmol) was added to the mixture in one portion. After a vigorous boiling subsided, an additional 1 (50 ml) was added and the mixture was kept stirring at room temperature for 2 h. The mixture was poured into ice water containing HCl. The organic layer was separated, washed with aq. $NaHCO_3$ and water, dried with anhydrous Na_2SO_4, and distilled to obtain 2 (9.5 g, 30 %) and 3 (2.1 g, 5.0 %). 2: bp. 90-1°C (50 mmHg); n_D^{20} 1.4165; d_4^{20} 1.696; IR (neat film) 1008 cm^{-1}; ^1H NMR (CCl_4) 7.97 (-CH=); ^{19}F 20.04 (CF_3 in C-3), 19.26 (CF_3 in C-4), -20.82 (-CF=); MS m/z rel. intensity (%) 316 (98, M^+), 297 (24), 288 (20), 281 (100).

Anal. Calcd for $C_8HCl_2F_7O$: C, 30.31; H, 0.32.
Found: C, 30.15; H, 0.40.

3: bp. 115-20°C (40 mmHg); n_D^{20} 1.4621; d_4^{20} 1.786; IR 1016 cm^{-1}; ^{19}F NMR (CCl_4) 19.54 (CF_3), 21.81 (-CF=); MS m/z (%) 434 (11, M^+), 432 (49), 430 (100), 428 (77), 397 (10), 395 (29), 393 (30), 366 (17), 364 (18).

Anal. Calcd for $C_{10}Cl_4F_8O$: C, 27.94. Found C, 27.84.

(b) The inverse addition method: To ice-cooled 1 (27 ml, 300 mmol), a mixture prepared with 4 (10.0 g, 49 mmol) and

n-butyllithium ethereal solution (57 mmol, 1.6 mol/l, 37 ml) in ether (85 ml) was added dropwise in 15 min, and the resulting mixture was kept stirring at 0°C for 2.5 h. Work-up as above yielded 2 (3.6 g, 23 %) and 3 (3.1 g, 15 %).

2-(2,2-Dichloro-1-fluorovinyl)-3-trifluoromethyl-furan (11)

n-Butyllithium ethereal solution (1.6 mol/l, 27 ml, 43 mmol) was added to a stirred mixture of 10 (5.0 g, 37 mmol) and ether (30 ml) at -30 – -40°C in 11 min, and the mixture was kept stirring for 30 min. Then, 1 was added to the stirred mixture in one portion. After a vigorous boiling subsided, 1 (6.0 ml) was further added. The resulting mixture was kept stirring at room temperature for 30 min. Work-up as above gave 11 (4.7 g, 51 %): bp 83-5°C (40 mmHg); n_D^{20} 1.4600; d_4^{20} 1.600; IR (neat film) 1000 cm^{-1}, ^1H NMR (CCl_4) 7.54 (-O-CH=), 6.68 (-C-CH=); ^{19}F 20.00 (CF_3), -24.33 (-CF=); MS m/z (%) 248 (100, M^+), 229 (10), 219 (23), 213 (82).

Anal. Calcd for $C_7H_2Cl_2F_4O$; C, 33.77; H, 0.81.
Found; C, 33.59; H, 0.77.

2-Ethynyl-3,4-bis(trifluoromethyl)furan (13)

n-Butyllithium ethereal solution (1.6 mol/l, 145 ml, 232 mmol) was added dropwise to a stirred mixture of 2 (22.3 g, 70 mmol) and ether (100 ml) at -45 – -50°C in 20 min and the mixture was kept stirring at the same temperature for 30 min. Work-up as above gave acetylene13 (11,9 g, 74 %): bp 84-6°C (160 mmHg); n_D^{20} 1.3885; d_4^{20} 1.348; IR (neat film) 3320, 2138, 1008 cm^{-1}; ^1H NMR (CCl_4) 3.61 (-C≡CH), 7.73 (-CH=); ^{19}F 20.14 (CF_3 in C-3), 18.90 (CF_3 in C-4); MS m/z (%) 228 (85, M^+), 209 (98), 199 (100), 159 (85).

Anal. Calcd for $C_8H_2F_6O$ C, 42.13; H, 0.88.
Found; C, 41.91; H, 0.91.

2,5-Bis(ethynyl)-3,4-bis(trifluoromethyl)furan (14)

From 3 (19.2 g, 45 mmol) and n-butyllithium (220mmol), acetylene 14 was obtained as similar as above; 7.5 g, 67 %: bp 47-8°C (9 mmHg); n_D^{20} 1.4336; d_4^{20} 1.430; IR (neat film) 3308,

2130, 1008 cm^{-1}; ^1H NMR (CCl_4) 3.60 (-C≡CH); ^{19}F 19.89 (CF_3); MS m/z (%) 252 (100, M^+), 333 (18), 199 (29).

Anal. Calcd for $C_{10}H_2F_6O$; C, 47.64; H, 0.80.
Found; C, 47.52; H, 0.75.

2-Ethynyl-3-trifluoromethylfuran (15)

Furan 11 (21.2 g, 85 mmol) and n-butyllithium (248 mmol) gave 15 as similar as above; 6.5 g, 48 %: bp 80-2°C (300 mmHg); n_D^{20} 1.4240; d_4^{20} 1.301; IR (neat film) 3308, 2118, 995 cm^{-1}; ^1H NMR (CCl_4) 3.59 (-C≡CH), 7.37 (-O-CH=), 6.56 (-C-CH=); ^{19}F 19.40 (CF_3); MS m/z (%) 160 (100, M^+), 141 (21), 131 (35).

Anal. Calcd for $C_7H_3F_3O$; C, 52.52; H, 1.89.
Found; C, 52.23; H, 1.30.

Polymerization.

In the thermal and γ-ray induced polymerizations, the monomer in an ampoule was degassed by a successive freezing and melting procedure, and the ampoule was sealed under vacuum (ca. 10^{-3} mmHg). The thermal polymerizations were carried out by maintaining the ampoule at given temperature for given time (see text). The γ-ray induced polymerizations were carried out at 2.9×10^5 rad/h at room temperature.

Oxidation polymerization of 14 To a mixture of 14 (1.0 g, 4.0 mmol), CuCl (0.10 g, 1.0 mmol) and tetramethylene diamine (0.12 g, 1.4 mmol) in acetone (10 ml) was bubbled O_2 at room temperature for 30 min to afford the polymer (55 % yield).

In the oligomerizations of 13 and 15, the conversions and the molecular weights were estimated by a Toyo Soda HLC-8024A GPC, where the calibration curve for polystyrene was used to calculate the molecular weights. In the polymerization of 14, the conversions were estimated by a IR absorption at 3308 cm^{-1}, since the polymer of 14 was insoluble in organic solvents. Thermal analyses were carried out by a Seiko Instrument & Electronics Ltd. TG 20 type.

Acetylenes 13 and 15 hardly polymerized with the catalyst generated by UV irradiation to $W(CO)_6$ in CCl_4 [1].

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