Polymer Bulletin 16, 27-33 (1986)

Polymer Bulletin

Characterization of the organolithium intermediates in polymerization reaction of 4,4'-difluorodiphenyl sulfone

M.C. Briñón, M.M. de Bertorello, and H.E. Bertorello

Departamentos de Química Orgánica y Farmacia, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Suc. 16 – C.C. 61, RA-5016-Córdoba, Argentina

SUMMARY

The mechanism of the polymerization of 4,4'-difluorodiphenyl sulfone with n-BuLi does not follow the way previously proposed by us for other diphenyl derivatives (1-4). Metallation occurs principally in the ortho position of the sulfone group and cyclization reactions also take place. The different intermediates formed were characterized by gas chromatography and mass spectrometry. More than eighteen compounds were identified as lithiated monomers which were able to participate in the polymerization process.

INTRODUCTION

A number of aromatic polymers formed by reactions of biphenyl derivatives and n-butyllithium (1-4) have been found to have attractive properties, including excellent thermal stability and unusual resistance to common solvents. A mechanism of reaction with the intervention of organolithium and/or dehydroaromatic intermediates leading to biphenylidenic structures (ladder polymers) has been proposed by us (1-4). We have recently focused our attention on the preparation of polymers derived from 4,4'-difluorodiphenyl sulfone (DFDS, I) (5,6).

This work describes the application of GC-MS to the separation and identification of trimethylsilyl derivatives formed by quenching the lithiated products of DFDS (I) with trimethylsilyl chloride, in order to characterize the probable organolithium intermediates which participate in the polymerization reaction.

EXPERIMENTAL

4,4'-difluorodiphenyl sulfone (Pierce Chemical Company) and trimethylsilyl chloride (C.Erba) were used without further purification. n-Butyl bromide (Fluka), diethyl ether and tetrahydrofuran (THF) were analytical reagent grade and were purified and dried by conventional methods and distilled before use.

All organometallic reactions were carried out in an atmosphere of dry, oxigen-free nitrogen. Solutions of n-butyllithium in diethyl ether were prepared by the metal-halogen exchange reaction between n-butyl bromide and lithium metal(7). The analysis of n-butyllithium was determinded by the Gilman's double titration method(8).

All mass spectra were recorded on a Finnigan model 3300 F-100 quadrupole mass spectrometer. Data was collected and processed with an INCOS data system using a Nova III computer. Sample introduction was accomplished by means of a Finnigan model 9500 gas chromatograph directly interfaced to the mass spectrometer by a SE30 glass capillary column. Helium was used as the carrier gas with a flow rate of 40 ml/min. The oven temperature was programmed from 110 to 260º C at a rate of 6º C/min.

2,2'-dibromo-4,4'-difluorodiphenyl sulfone (II)

4,4'-DFDS(I) (0,509 g, 0.002 mol) in 22,5 ml, of Et_2O: THF (1:2) was metallated with 0.0045 mol of n-BuLi at -60º C in 2 hs. To the cooled reaction mixture, 1 ml of bromine and traces of copper bromine were added, then allowed to reach room temperature. After 48 hs. the mixture was hydrolyzed and the phases separated. The obtained product was recrystallizated from ethanol giving a white product (yield 47%) m.p. 160-161º C. The ^{1}H-NMR (acetone-d6); δ=6.8-7.4 (m, 2); δ=7.9-8.2 (m, 1). Analysis; Found: C, 35.21%; H, 1.9%; calculated for $C_{12}H_6Br_2F_2SO_2$: C, 34.97%; H, 1.47%, M+, m/z (%): 414(48), 412(90), 410(46), 239(9), 237(9), 223(M^+, 100), 222(11), 221 (100), 191(24), 189(24), 188(32), 175(35), 174(10) and 173(36). ir (KBr pellet) cm^{-1}: 1335 and 1160 ($-SO_2-$), 1115 (C-F); 855 (1,2,4-trisubstituted aromatic ring).

2,2'-dicarboxy-4,4'-difluorodiphenyl sulfone

The above organometallic mixture was carbonated by bubbling in carbon dioxide 5 min; and the reaction mixture was slowly allowed to warm to room temperature with continued carbonation. The mixture was hydrolyzed with 10 ml of water, the phases separated, and the aqueous layer acidified with HCl. The insoluble product (80% yield) was recrystallizated from water; m.p. 224-227ºC. Analysis; Found: C, 49.01%; H, 2.63%. Calculated for $C_{14}H_8O_6SF_2$: C, 49.13%; H, 2.35%. ^{1}H-NMR (DMSO-d_6 and TMS as standard): δ =7.6 (m, 2H), δ=8.20 (m, 1H). i.r. (KBr pellet) cm^{-1}: 1725 (Ar-COOH); 1335 ($-SO_2-$); 1220 (C=O); 1160 ($-SO_2-$); 1115 (C-F); 855 (1,2,3-trisubstituted aromatic ring).

2,2'-dicarbomethoxy-4,4'-difluorodiphenyl sulfone (III)

The carboxylic acids were treated with an ethereal solution of diazomethane and the obtained esters (yield 78%) were recrystallizated from ethanol, m.p. 87-88º C. Analysis; Found: C, 51.89%; H, 3.74%. Calculated for $C_{16}H_{12}O_6F_2S$: C, 51.47%; H, 3.26%. ^{1}H-NMR (Cl_3CD with TMS as standart): δ = 3.81 (s, 3H), δ = 7.22(m, 2H), δ = 8.08(m, 1H). M^+, m/z(%): 370(10%); 339(10); 305(20); 248(30) and 247(M^+, 100). ir(KBr pellet) cm^{-1}: 1775 and 1650(C=O); 1610 (COO^-); 1442($COOCH_3$); 1335 and 1182(SO_2); 1110(CF); 830, 810,(trisubstituted aromatic ring).

Reaction with Trimethylsilyl Chloride:

4,4'-DFDS (I) (0.254 g, 0.001 mol) in 20 ml of Et_2O-THF (1:20) was metallated with n-BuLi (0.010 mol) at -80º C for 10 hs. Then 1.5 ml (0.010 mol) of Me_3SiCl was added and the mixture was allowed to warm to room temperature before being refluxed for two hours. Upon cooling, the solution was hydrolyzed with water (10 ml) and the phases separated. The organic layer provided 395 mg of a yellow oily residue. The reaction mixture was analyzed by GC-MS, and the results are shown in Table 1.

Polymer Synthesis:

The above organometallic mixture was allowed to warm up to room temperature and then refluxed for two hours. The mixture was hydrolyzed with 10 ml of water and the phases separated. The organic layer yielded a solid product which was extracted in a soxhlet with benzene, chloroform, acetone, ethanol and water succesively. The insoluble product was a brown solid which was infusible until 452º C. Analysis; Found: C, 62.46%; H, 3.96%; F, 6.70%. Calculated for $C_{60}H_{37}F_4S_5O_9$, C, 63.20%; H, 3.25%; F, 6.68%.

Benzene extraction: The dry residue (yield 35%) was recrystallized from ethanol; m.p. 146-147º C and identified as 2,8-difluorodibenzothiophene(X). ^{1}H-NMR (Cl_4 C, TMS as an internal reference); aromatic protons; $\delta = 7.07$ (1H, m) and $\delta = 7.57$ (2H, m). Analysis; Found: C, 65.3%; H, 2.90%. Calculated for $C_{12}H_6F_2S$; C, 65.48%; H, 2.72%. M^+, m/z (%): 220(M^+, 100); 188(9); 176(3); 175(14); 157(3). ir(KBr pellet) cm^{-1}: 1220 (C=S); 880 and 810 (aromatic 1,2,4-trisubstitution).

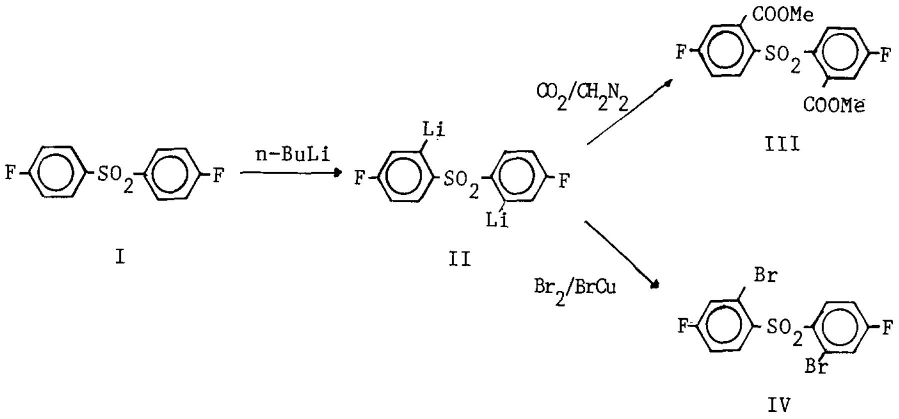
Isothermal aging of the polymer: The brown powder submitted to temperatures of 300º C showed the following loss of weight:

- In a nitrogen atmosphere: 1h, 9%; 2h, 9%; 3h 9%.
- In an air atmosphere: 0.5h, 9.13%; 1h, 13.35%; 2h, 13.83%; 3h, 18.02%; 4h, 20.73%; 6h, 25.68%; 13h, 33.83%.

RESULTS AND DISCUSSION

In order to better understand the polymerization mechanism, we needed to identify the different organolithium intermediates formed by increasing time and temperature which afterwards yielded polymeric material. The lithiation of DFDS(I) with n-BuLi (1:2) in ether-tetrahydrofuran (1:20) at -60º C, 2h, occurs mainly ortho to the sulfone group leading to 2,2'-dilithio-4,4'-difluorodiphenyl sulfone (II) (Scheme 1).

Scheme 1



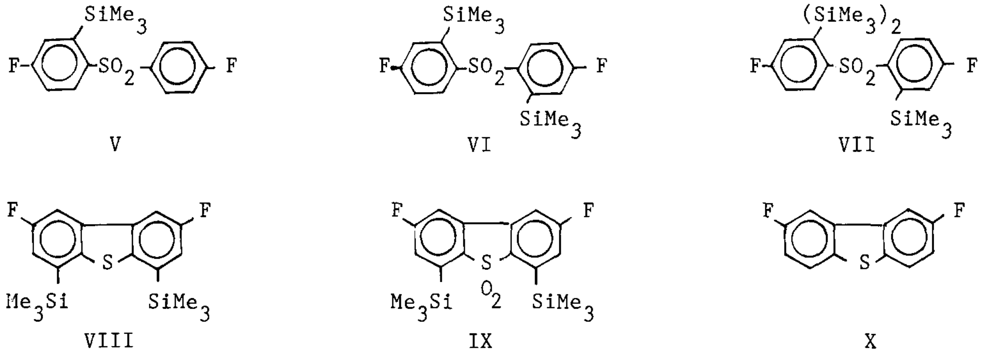
When the organolithium mixture was quenched with trimethylsilyl chloride and after gradual temperature increase to 40º C (4hs.); mono-(V); bis-(VI) and tris-trimethylsilyl (VII) derivatives were formed. 2,8-difluoro-4,6-ditrimethylsilyl-dibenzothiophene (VIII) and 2,8-difluoro-4,6-ditrimethylsilyl-dibenzothiophene-5,5-dioxide (IX) were also present in the reaction mixture. (Scheme 2).

Compounds V-IX were purified by column chromatography and identified by ^{1}H-NMR and MS.

When the organolithium mixture was allowed to warm to 45º C, 4hs, prior to water hydrolysis, a cyclodehydration occurs leading quantitatively to 2,8-difluorodibenzothiophene (X).

Longer times (10 hs.) and higher quantities of n-BuLi (1:10) gave a complex reaction mixture of organolithium intermediates which was quenched with trimethylsilyl chloride. The reconstructed ion chromatogram of the reaction (SE 30 glass capillary column) showed a mixture of at least 20 compounds. Through a combined GC-MS analysis, we could separate and identify this complex mixture.

Scheme 2

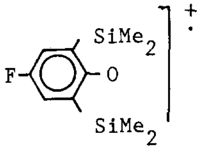


In Table 1 we have listed the relative abundance, molecular weight and molecular formula for each of these components. As we can see, the use of this combined technique, permitted also the identification of minor and trace compounds in the mixture of trimethylsilyl constituents.

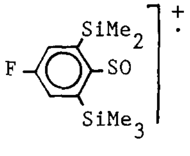
Under conditions where 1% of the starting material was recovered (Table 1), the dominant product in the reaction mixture was the tris-trimethylsilyl derivative (VII) of the original sulfone (peak 10, 27% and peak 11, 19%). The bis-trimethylsilyl derivative (VI) accounted for another 19% of the reaction mixture. All the products resulting from cyclization of the original sulfone to dibenzothiophene derivatives (Table 1) accounted for 23% of the total product mixture.

This cyclization reaction proceeds as an intramolecular cyclodehydration of the original lithiated sulfone (II) by loss of lithium hydride (9-11) due to elevated temperature. Subsequent reduction of sulfone to sulfide occurs.

Mass spectra of the tris-trimethylsilyl derivative VII gave fragment ions at m/z 225 and m/z 272 which require the presence of two-trimethylsilyl groups attached to the same aromatic ring.



m/z 225



m/z 272

The same ion, m/z 255, was observed for the bis-trimethylsilyl (peak 5, 3%) and tetrakis-trimethylsilyl derivatives (peaks 13 and 16 respectively). It indicates that both of these compounds must have two-trimethylsilyl groups on each ring. The bis-trimethylsilyl derivative (peak 8) gave a fragment ion at m/z 291 which corresponds to loss of m/z 92 (FSiMe$_3$) from the base peak. This peak indicates the occurrence of ortho-fluorine metallation in this compounds (yield 0.9%), which indicates that metallation adjacent to the sulfone is favored over metallation adjacent to the fluorine, as would be expected.

Table 1. GC-MS analysis of the metallation of 4,4'-difluorodiphenyl sulfone, after treatment of the reaction mixture with Me_3SiCl.

Peak[a]	BP[b](MI)[c]	Probable structure	Molecular F.	Yield %
1	220(220)	2,8-DFDBT[d]	$C_{12}H_6SF_2$	0.11
2	143(254)	4,4'-DFDS[e]	$C_{12}H_8SO_2F_2$	1.01
3	277(292)	2,8-DFDBT-4-$SiMe_3$	$C_{15}H_{14}SSiF_2$	3.9
4	311(326)	4,4'-DFDS-2-$SiMe_3$	$C_{15}H_{16}SO_2SiF_2$	0.1
5	383(398)	4,4'-DFDS-2,6-$(SiMe_3)_2$	$C_{18}H_{24}SO_2Si_2F_2$	3.1
6	309(324)	2,8-DFDBT-4-$SiMe_3$-5,5-O_2	$C_{15}H_{14}SO_2SiF_2$	6.1
7	383(398)	4,4'-DFDS-2,2'-$(SiMe_3)_2$	$C_{18}H_{24}SO_2Si_2F_2$	19.05
8	383(398)	Isomer of 7		0.93
9	349(364)	2,8-DFDBT-4,6-$(SiMe_3)_2$	$C_{18}H_{22}SSi_2F_2$	1.5
10	73(470)	4,4'-DFDS-$(SiMe_3)_3$	$C_{21}H_{32}SO_2Si_3F_2$	26.7
11	73(470)	Isomer of 10		19.11
12	381(396)	2,8-DFDBT-4,6-$(SiMe_3)_2$-5,5-O_2	$C_{18}H_{22}SO_2Si_2F_2$	10.39
13	272(542)	4,4'-DFDS-$(SiMe_3)_4$	$C_{24}H_{40}SO_2Si_4F_2$	1.03
14	455(470)	4,4'-DFDS-$(SiMe_3)_3$	$C_{21}H_{32}SO_2Si_3F_2$	0.18
15	363(378)	N.I.[f]		1.31
16	272(542)	4,4'-DFDS-$(SiMe_3)_4$	$C_{24}H_{40}SO_2Si_4F_2$	1.02
17	381(396)	Isomer of 12		0.71
18	453(468)	2,8-DFDBT-$(SiMe_3)_3$-5,5-O_2	$C_{21}H_{30}SO_2Si_3F_2$	0.38
19	421(435)	2,8-DFDBT-$(SiMe_3)_3$	$C_{21}H_{30}SSi_3F_2$	0.32
20	493	N.I.		0.9

a) Gas chromatographic peak; b) Base peak; c) Molecular ion; d) Difluorodibenzothiophene; e) Difluorodiphenyl sulfone; f) Not identified.

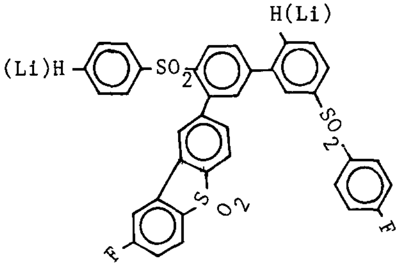
When the reaction mixture (substrate:n-BuLi, 1:10, 10 hs) was allowed to warm up and refluxed for two hours before work up, two principal products were obtained: a polymer (77.0%) exhibiting high temperature resistance and 2,8-difluorodibenzothiophene (X, 13%). The structure of the latter was elucidated by mass spectrometry, ir, elemental analysis and ^{1}H-NMR.

The mass spectrum resulting from the acetone extract of the solid residue has shown two peaks at m/z 684 and m/z 488 respectively which indicate the presence of trimeric and dimeric species (Scheme 3).

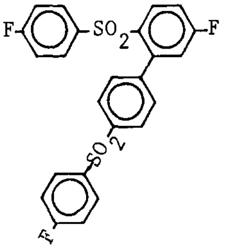
CONCLUSIONS

It is remarkable that metallation-silylation of 4,4'-difluorodiphenyl sulfone with n-butyllithium in ether-tetrahydrofuran produced only 0.2% of products corresponding to mono-metallation under conditions that allowed for isolation of 1% of starting sulfone. The fact that the tetra-metallated derivatives exceeded the abundance of the mono-metallated derivatives by more than an order of magnitude under these reaction conditions indicates that metallation at a second site of the starting compound is somehow favored over the mono-metallation reaction. It suggest that mono-metallation is a kinetically controlled process while polymetallation is thermodynamically favored.

Scheme 3



m/z 684

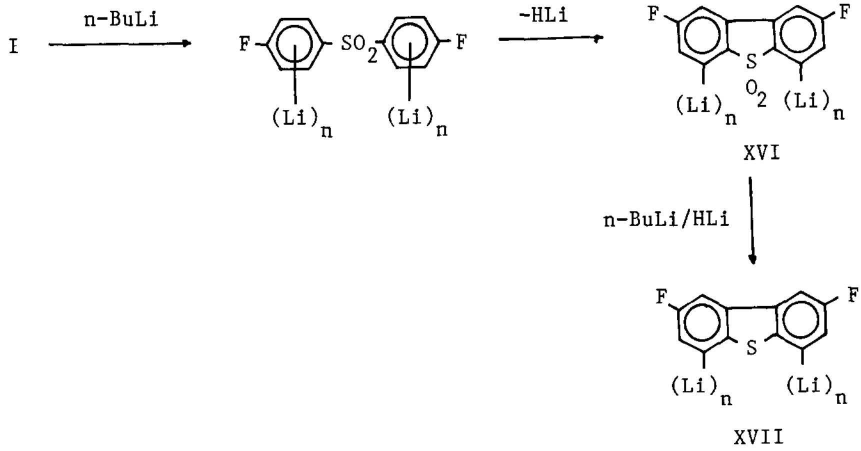


m/z 488

The fact that compound VI was the most abundant of the bis-dimethylsilyl derivatives indicates that metallation on an adjacent ring is favored over metallation in the same ring.

According to the different organolithium intermediates formed, it is expected that many nucleophilic displacement reactions take place leading to various polymers, as those proposed in Scheme 4, and, as in the formation of some perfluoro-polyphenylenes (12).

Scheme 4



$$XV + XVI + XVII \longrightarrow POLYMER$$

It is difficult to visualise for the present reaction a mechanism such as proposed by us for other biphenylic compounds (1-4) involving the intervention of dehydroaromatic species, since the metallation occurs principally at the ortho-position to the sulfone group.

ACKNOWLEDGEMENTS

We thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Secretaría de Ciencia y Técnica (SECYT) de la República Argentina for financial support. We thank Dr. R.A. Dougherty for useful discussions and comments on the manuscript.

REFERENCES

1- M.M. de Bertorello and H.E. Bertorello, J. Organometal. Chem., 23, 285 (1970).
2- R.A. Contigiani, M.M. de Bertorello and H.E. Bertorello, J. Organometal. Chem., 32, 7 (1971).
3- R.A. Contigiani and H.E. Bertorello, Rev. Latinoam. Quím., 3/4, 163 (1973).
4- J.R. de la Fuente, M.M. de Bertorello and H.E. Bertorello, Polymer Bulletin, 13, 557 (1985).
5- M.C. Briñón, L. Alassia, M.M. de Bertorello and H.E. Bertorello. II Sempol, october, 27-31 (1980). Río de Janeiro, Brasil.
6- M.C. Briñón, M.M. de Bertorello and H.E. Bertorello. Proceeding of the Third International Meeting of Polymer Science and Technology, 224, Nov. 1981, La Plata, Argentina.
7- R.G. Jones and H. Gilman, Org. Reactions, 6, 339 (1975).
8- H. Gilman and F.K. Cartledge, J. Organometal. Chem., 2, 447 (1964).
9- M.C. Briñón, M.M. de Bertorello and H.E. Bertorello, Anal. Asoc. Quím. Argent. 69, 247 (1981). Chem. Abst. 96: 6504w (1982).
10- M.C. Briñón, M.M. de Bertorello and H.E. Bertorello. Anal. Asoc. Quím. Argent., 71, 571 (1983).
11- R.W. Hoffmann "Dehydrobenzene and Cycloalkynes", Academic Press, N. York 65 (1967).
12- D.D. Callander, P.L. Col and J.C. Tatlow. Tetrahedron, 22, 419 (1966).

Accepted June 12, 1986

K