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REACTION BETWEEN 3,3'-DIBROMO-4,4'-DIFLUOROBIPHENYL AND n-BUTYLLITHIUM

M. MARTÍNEZ DE BERTORELLO AND HÉCTOR E. BERTORELLO
Instituto de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba (República Argentina)

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SUMMARY

The reaction between 3,3'-dibromo-4,4'-difluorobiphenyl and n-butyllitium is described. The organolithium compound formed was carboxylated to give 4,4'-difluoro-3,3'-biphenyldicarboxylic acid in good yield. The formation of dehydroaromatic compounds by elimination of lithium fluoride is proposed on the basis of observed addition reactions with furan and autocondensation reactions which lead to macromolecules.

INTRODUCTION

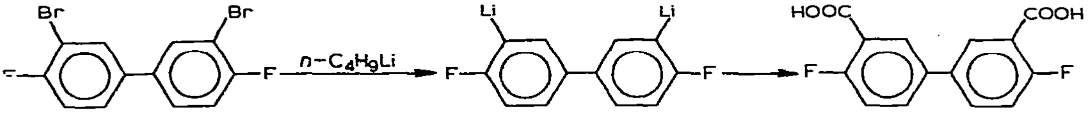
Wittig and Pohmer[1], succeeded in demonstrating the intermediacy of 1,2-dehydrobenzene (benzyne) during the decomposition of 2-fluorophenyllithium, trapping it with furan in a cycloaddition reaction of the Diels–Alder type. The formation of 3,3', 4,4'-didehydrobiphenyl, has been proposed[3] in the thermal decomposition of (4,4'-didiazonium)-3,3'-biphenyl-dicarboxylate and by electron impact of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride[4].

RESULTS AND DISCUSSION

In order to obtain 3,3',4,4'-didehydrobiphenyl in solution we have carried out some reactions between 3,3'-dibromo-4,4'-difluorobiphenyl and n-butyllitium.

3,3'-Dibromo-4,4'-difluorobiphenyl (I) was prepared by bis-diazotization of 4,4'-diamino-3,3'-dibromobiphenyl; the bis-diazonium fluoroborate obtained gave on thermal decomposition the product (I), m.p. 141–142°.

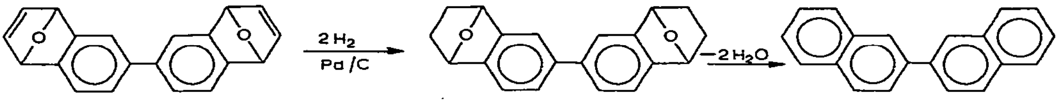
The halogen–metal transfer between one equivalent of (I) and two equivalents of n-butyllithium following the basic procedure used by Gilman[2] and Wittig[1] required 15 min at −78° and the concentration of the thermally unstable 4,4'-



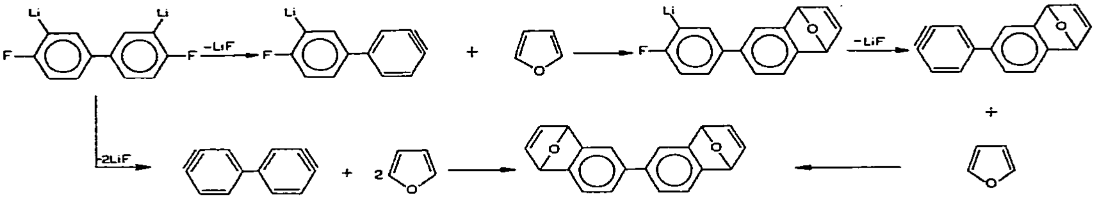
(I) (II) (III)

difluoro-3,3′-dilithiobiphenyl (II) was established by carboxylation to the diacid (III), m.p. 365–370° (98%). Shorter times and lower quantities of n-butyllithium gave mixtures with increased yield of monometallated product.

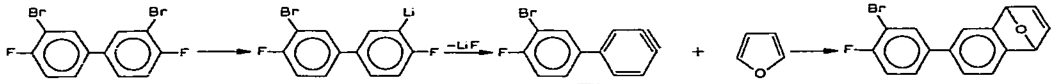
When the reaction between (I) and n-butyllithium was carried out in the presence of furan we isolated a product identified as 5,5′,8,8′-tetrahydro-5,8,5′,8′-diepoxy-2,2′-binaphthyl [(IV) 24%]. The structure of (IV) was proved by transformation to 2,2′-binaphthyl (V):



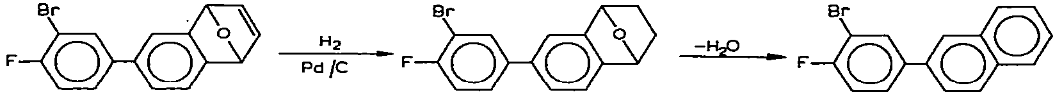
(IV) is believed to result from a Diels–Alder reaction of furan and a dehydroaromatic compound as shown below:



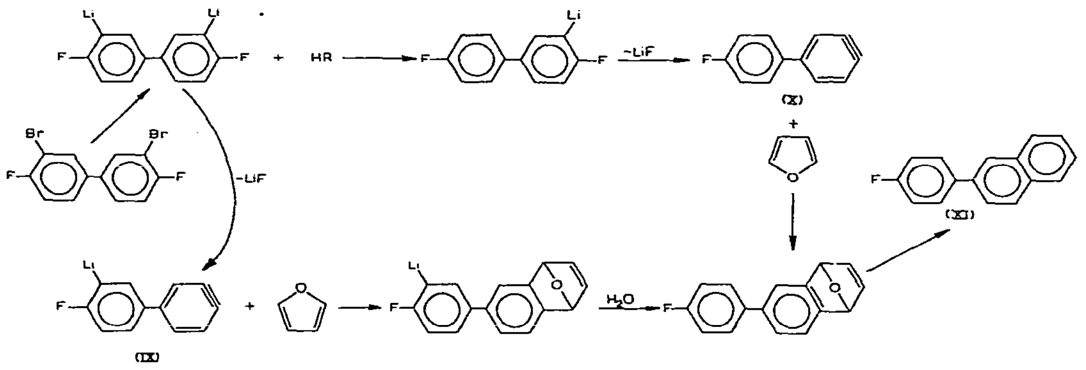
A second intermediate, the result of incomplete metallation, was present in the reaction mixture: 3-bromo-4-fluoro-3′,4′-dehydrobiphenyl, (VI), as could be inferred from the formation of 2-(3-bromo-4-fluorophenyl)-5,8-epoxy-5,8-dihydronaphthyl (VII) although in poor yield:



The structure of the latter compound was proved by its reduction and dehydration to 2-(3-bromo-4-fluorophenyl)-naphthalene (VIII) m.p. 102.5–103°:



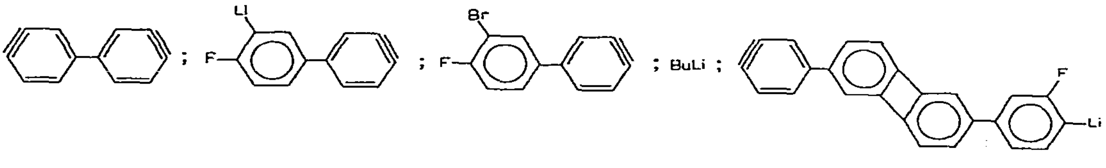
Also the isolation in low yield of 2-(4-fluorophenyl)-naphthalene (XI) in the reaction using furan (followed by hydrogenation and dehydration) could be indicative of the intermediate formation of 4-fluoro-3-lithio-3′,4′-dehydrobiphenyl (IX) or 4-fluoro-3′,4′-dehydrobiphenyl (X) according to the scheme shown below:



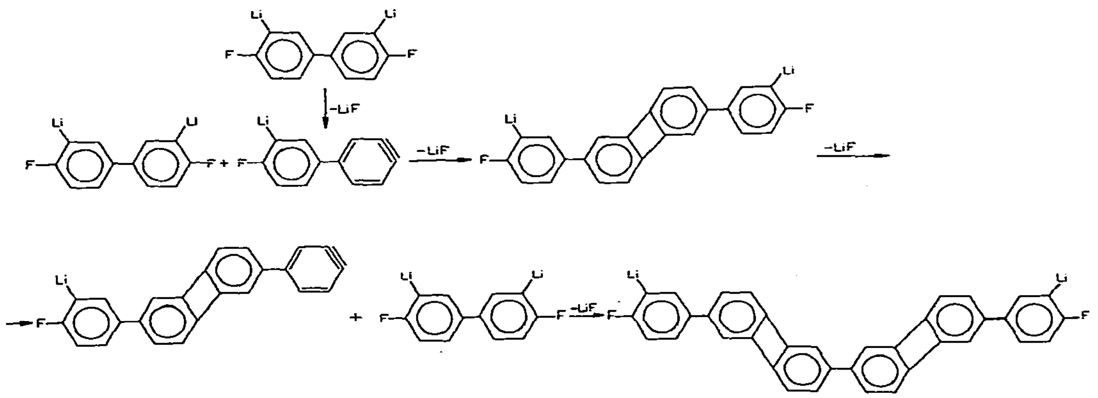
When the reaction between 3,3'-dibromo-4,4'-difluorobiphenyl and n-butyllithium was carried out in the absence of trapping agents, a mixture of polymers which were stable at high temperatures was obtained in almost quantitative yield. Fractionation of these polymers by extraction with different solvents, chromatography and precipitation gave, together with lithium fluoride, fractions with different elementary analyses, indicating an unequal elimination of bromine and fluorine.

These polymers were high-temperature resistant; thermogravimetric analyses conducted in an atmosphere of nitrogen showed only a 20% weight loss between temperatures of 400° and 900°. Thermogravimetric analyses in ambient air showed an 80% weight loss between temperatures of 400° and 500°.

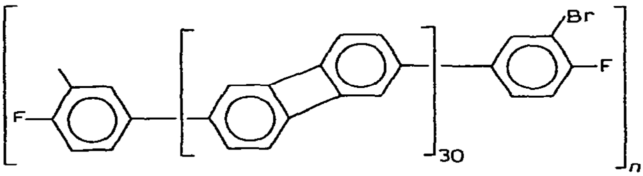
The process of polymerization could take place with the intervention of dehydroaromatic intermediates and organolithium compounds:

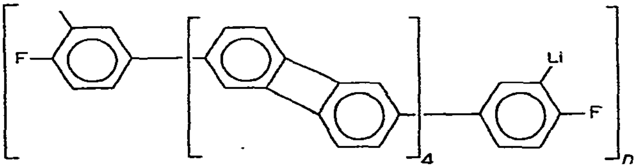


or it could take place without the intervention of 3,4,3',4'-didehydrobiphenyl in a stepwise process:



Some of the more plausible structures which these polymers could have, according to elementary analyses of the fractions obtained, are:





The biphenylenic structure was proposed on the basis of the results obtained on oxidation of the polymers, yielding principally trimellitic and biphenyltetracarboxylic acid, and by comparison with the results obtained previously by us[3]. IR spectra exhibited as a distinguishing feature absorption bands at 800, 1010, 1087, 1205, 1470 and 1587 cm^{-1}. Polymers obtained[3] in the thermal decomposition of 4,4'-didiazonium-3,3'-biphenyldicarboxylate, with polybiphenylenic structures showed bands at 800, 1010, 1265, 1470 and 1587 cm^{-1}.

Further studies on the characteristics and reactivity of these compounds are in progress.

EXPERIMENTAL

4,4'-Diamino-3,3'-dibromobiphenyl

This was obtained[5] by reduction of 2-nitrobromobenzene and rearrangement of the resulting 2,2'-dibromohydrazobenzene.

3,3'-Dibromo-4,4'-difluorobiphenyl

8.4 g (0.02 mole) of 3,3'-dibromo-4,4'-diaminobiphenyl suspended in 30 ml of hydrochloric acid was diazotized using 2.8 g (0.04 mole) of sodium nitrite dissolved in 16 ml of water. To the solution, separated by centrifugation, was added a cold solution of fluoroboric acid (2.720 g of boric acid dissolved in 8.44 g of 48 % hydrofluoric acid). The insoluble 3,3'-dibromo-4,4'-biphenylene-bis-diazonium fluoroborate obtained was dried, yielding 8.564 g (79 %) as a brown product. Its thermal decomposition yielded 4.910 g (89 %) of a product with m.p. 130–134° which was purified by sublimation and recrystallization from ethanol to give a white product, m.p. 142–143°.

This compound was characterized as 3,3'-dibromo-4,4'-difluorobiphenyl. (Found: C, 41.53; H, 1.87; F, 11.06; mol. wt. mass spectrometric, 348. Calcd.: C, 41.37; H, 1.74; F, 10.95 %; mol wt., 348.)

Reactions with organometallic compounds

All organometallic reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Solvents were purified and dried by conventional methods and distilled prior to use. Melting points are uncorrected. (VPC analyses were carried out on an General Electric Co F&M model 400 gas chromatograph using a 6 ft × 0.25 inch column, filled with silicone-rubber gum SE 30 and with helium gas carrier. The temperature was programmed at 10°/min). Mass spectrometric analyses were performed on an AEI MS-902 spectrometer at the Ohio State University (U.S.A.).

Preparation of 4,4′-difluoro-3,3′-dilithiobiphenyl and reaction with carbon dioxide

To a precooled (−78°), stirred solution of 10 mmole of n-butyllithium in 20 ml of dried ether and 10 ml of THF, a solution of 1.740 g (5 mmole) of 3,3′-dibromo-4,4′-difluorobiphenyl in 15 ml of THF was added dropwise, in 5 min. Dry carbon dioxide was bubbled through the organolithium reagent 15 min later and the mixture was then allowed to warm to room temperature with continued carbonation. The mixture was hydrolyzed with 20 ml of water, phase separated, and the organic layer extracted with dil NaOH. The cold, basic, aqueous layer was acidified with conc. HCl. The insoluble product was separated, yielding 1.360 g (98 %) of a white product, m.p. 360–364°. After repeated crystallization from acetic acid a white product m.p. 365–370° was obtained and identified as 4,4′-difluoro-3,3′-diphenyl dicarboxylic acid. (Found: C, 60.80; H, 2.54; F, 13.48; mol. wt. mass spectrometric, 278. $C_{14}H_8F_2O_4$ calcd.: C, 60.44; H, 2.89; F, 13.66 %; mol. wt., 278.)

The dimethyl ester was obtained by treating 0.278 g (1 mmole) of the product with diazomethane. After complete methylation, aspiration of the solvent yielded 0.290 g (98 %) of a white product m.p. 142–153°. By recrystallization from ethanol a product was obtained which was identified as 4,4′-difluoro-3,3′-biphenyldicarboxylic acid dimethyl ester, m.p. 151.5–153°. (Found: C, 62.50; H, 3.90; mol. wt. mass spectrometric, 306. $C_{16}H_{12}F_2O_4$ calcd.: C, 62.74; H, 3.95; F, 12.40; mol. wt. 306.)

Reaction with furan

To a precooled (−78°) stirred mixture of furan (15 ml), ether (10 ml), THF (10 ml) and n-butyllithium (10 mmole in 8 ml of diethyl ether was added in 5 min 1.740 g (5 mmole) of 3,3′-dibromo-4,4′-difluorobiphenyl dissolved in 15 ml of THF. The solution was stirred for 30 min and then allowed to warm to room temperature. The mixture was hydrolyzed with 10 ml of water, filtered from an insoluble portion, phase separated and extracted with benzene. The organic phase so obtained was dried over magnesium sulfate. Aspiration of the solvent yielded 1.383 g, of a solid yellow product (complex mixture according to thin-layer chromatographic analysis), with a decomposition temperature of 90°. Separation of the products was achieved by column chromatography on silica gel; 1.100 g of the crude product gave two principal fractions:

Fraction I. 509 mg, 46 % of the theoretical amount of diepoxide, eluted with chloroform/diethyl ether, was purified by repeated thin-layer chromatography on silicagel G using chloroform/acetone (21/1) as mobile phase, yielding 342 mg (24 %) of a yellow product, which decomposed at 140–150°, identified as 5,5′, 8,8′-tetrahydro-5,8,5′,8′-diepoxy-2,2′-dinaphthyl (IV). (Found: C, 84.13; H, 5.15; mol. wt. mass spectrometric, 286. $C_{20}H_{14}O_2$ calcd.: C, 83.90; H, 4.93 %; mol. wt., 286.)

Fraction II. 420 mg, eluted with benzene/chloroform, was resolved by thin-layer chromatography on silicagel G using chloroform/acetone (21/1) as elution mixture, by repeating assays into the compounds (3-bromo-4-fluorophenyl)-1,4-epoxynaphthalene and (4-fluorophenyl)-1,4-epoxynaphthalene, identified as the respective naphthalene derivatives in the following manner: 250 mg of fraction II was reduced with hydrogen at normal pressure using Pd/C as catalyst in two hours. The residue obtained, after filtration and elimination of the solvent was dehydrated in absolute methanol in the presence of hydrochloric acid. Two products were separated by fractional sublimation from the residue.

Product A with m.p. 103–103.8°, identified as (4-fluorophenyl)naphthalene. (Found: C, 86.60; H, 4.95; mol. wt. mass spectrometric, 222. $C_{16}H_{11}F$ calcd.: C, 86.46; H, 4.99; F, 8.55%; mol. wt., 222.)

Product B with m.p. 102.5–103° was identified as (3-bromo-4-fluorophenyl)-naphthalene. (Found: C, 64.87; H, 3.19; Br, 26.49; F, 6.36; mol. wt. mass spectrometric, 301. $C_{16}H_{10}BrF$ calcd.: C, 63.81; H, 3.35; Br, 26.53; F, 6.31%; mol. wt., 301.)

250 mg of the diepoxide (IV) obtained from fraction I, was also identified by reduction and dehydration, in the way indicated for fraction II, obtaining 2,2'-dinaphthyl, identical with a sample obtained acc. to the method of Chataway *et al.*[6].

Autocondensation reactions

To a precooled (−75°) stirred solution of 10 mmol of n-butyllithium, diethyl ether and THF was added a solution of 5 mmol of 3,3'-dibromo-4,4'-difluorobiphenyl and stirred for 30 min. The mixture was allowed to reach room temperature and finally boiled for some minutes. The yellow solid obtained after elimination of the solvent was repeatedly washed with cyclohexane and acetone. The crystalline residue obtained in this way, was extracted with a large amount of benzene and chromatographed on silica gel. One of the principal fractions obtained was repeatedly purified by solution in benzene and precipitation by cyclohexane, yielding 350 mg of a yellow product with a decomposition temperature of 450–500° and by analysis. [Found: C, 90.8; H, 4.7; Br, 1.7; F, 0.9. $(C_{372}H_{186}F_2Br)_n$ calcd.: C, 93.6; H, 3.6; Br, 1.68; F, 0.8%.)

The insoluble fraction in benzene was then washed with large amounts of hot xylene yielding 258 mg. After washing this yellow product with large amounts of water a yellow product was obtained. (Found: C, 88.0; H, 4.9; Br, 0; F, 4.5%.)

ACKNOWLEDGEMENTS

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