April, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(4), 1301—1303 (1975) 1301

Formation of 9,9′:9′,9″-Terfluorenyl Isomers Using Metalated Fluorenes as Synthetic Intermediates

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(Received October 7, 1974)

Rotational isomers of 9,9′: 9′,9″-terfluorenyl were obtained by the addition of 9-lithiofluorene to 9,9′-bifluorenylidene (III). 2,7-Dibromo- (VI) and 2,7,2″,7″-tetrabromo-9,9′: 9′,9″-terfluorenyl (VIII) resulted from similar reactions of the corresponding bromo-derivatives. 9-Lithio-9,9′-bifluorenyl was treated with 9-bromo-9,9′-bifluorenyl to give 9,9′-bis(9,9′-bifluorenyl) (X), 9,9′: 9′,9″-terfluorenyl isomers (mp 293 °C (dec) (I) and mp 257 °C (dec) (II)), 9,9′-bifluorenyl (IX), III, and fluorenone. The isomerization of I by metallic potassium gave the other rotamer II, which decomposed into its components, IX, III, and fluorene (IV).

The formation of the stereoisomeric 9,9′: 9′,9″-terfluorenyl, mp 293 °C (dec) (I) and mp 257 °C (dec) (II), has been reported in the previous paper of this series.1) The conformations of I and II were proposed to be *s-cis,s-cis* and *s-cis,s-trans*, respectively.2) Both rotamers were produced simultaneously by the Michael reaction3) of 9,9′-bifluorenylidene (III)4) with fluorene (IV), by the reaction5) of 9-bromofluorene with methanolic potassium hydroxide in acetone, and by the reaction6) of 9-lithiofluorene with 9-bromo-9,9′-bifluorenyl.7)

The present investigation was undertaken in order to discover additional synthetic routes which gave 9,9′: 9′,9″-terfluorenyls through 9-lithiofluorenyl derivatives or other alkali metal compounds as active intermediates.

Results and Discussion

A possible route for the formation of both I and II was achieved by addition of 9-lithiofluorene to III in dry benzene. Similarly, 9-lithiofluorene was treated with 2,7-dibromo-9,9′-bifluorenylidene (V)8) to yield 2,7-dibromo-9,9′: 9′,9″-terfluorenyl (VI)8) as the main product, accompanied by a trace amount of 2′,7′-dibromo-9,9′: 9′,9″-terfluorenyl (VII).8) 2,7,2″7″-Tetrabromo-9,9′: 9′,9″-terfluorenyl (VIII)8) was obtained by the reaction of 2,7-dibromo-9-lithiofluorene with V.

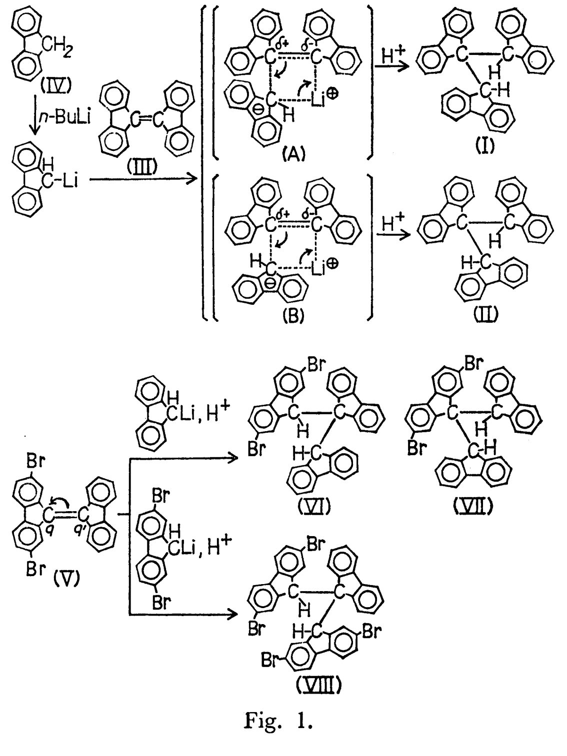

Fig. 1.

The formation of I and II by the reaction of 9-lithiofluorene with III could be expected to proceed through the four-center transition states (A) and (B), as shown in Fig. 1. The 9′-carbon is more electropositive than the 9-carbon in such a highly-polarized unsymmetrical ethylenic linkage as V owing to the electro-withdrawing effect of the two bromine atoms. This effect is brought out in the reaction of 9-lithiofluorene with V which gives a major product VI and a trace amount of VII.

The reaction of 9-lithio-9,9′-bifluorenyl with 9-bromo-9,9′-bifluorenyl yielded I, II, III, 9,9′-bifluorenyl (IX), 9,9′-bis(9,9′-bifluorenyl) (X),9) and fluorenone. When 9-bromo-9,9′-bifluorenyl was treated with a half mole equivalent of *n*-butyl lithium and the reaction mixture was immediately refluxed in xylene, 9-*n*-butyl-9,9′: 9′,9″-terfluorenyl (XI) was also isolated.

The formation of I and II can be attributed to the reaction of 9-bromo-9,9′-bifluorenyl with 9-lithiofluorene which may be generated by the metal-halogen interconversion reaction between 9-bromo-9,9′-bifluorenyl and *n*-butyl lithium.

It has been reported by Nasielski *et al.*9) that X was obtained by photo-reduction of III, however, no data on melting point, elementary analysis, molecular weight, *etc.*, were reported.

The structures of X and XI were confirmed from their mass spectral fragmentation patterns. The parent peak of X is small at *m*/*e* 658. The fragmentary ions *m*/*e* 493 (9,9′: 9′,9″-terfluorenyl cation, strong), 329 (9,9′-bifluorenyl cation, base peak), 328 (9,9′-bifluorenylidene ion, strong), and 165 (9-fluorenyl cation) originate from the simple cleavage of $C_{9-9'}$, $C_{9''-9'''}$, and/or $C_{9'-9''}$ bonds of the parent ion, X.

The mass spectrum of XI was as follows: the parent peak was small at *m*/*e* 550, and the fragment peaks were at *m*/*e* 493, 385 (9-*n*-butyl-9,9′-bifluorenyl cation, weak), 329, 328 (strong), 221 (9-*n*-butyl-9-fluorenyl cation, base peak), 191 (9-vinyl-9-fluorenyl cation), 179 (9-methyl-9-fluorenyl cation and/or 9,10-dihydrophenanthryl cation, strong), and 165 (very strong). The peaks at *m*/*e* 493, 329, 328, and 165 were identical with those of X.

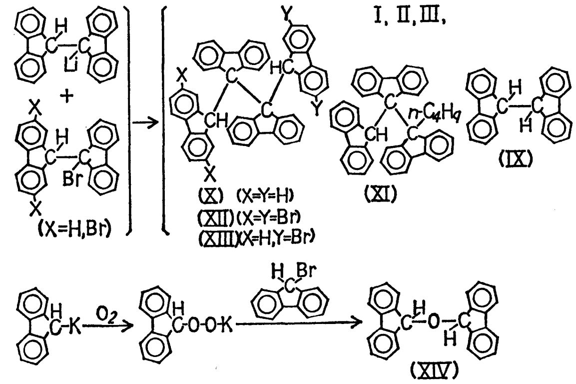

Fig. 2.

The IR spectrum of X closely resembled those of I and II.

An analogous reaction between 9-lithio-9,9′-bifluorenyl with 2,7,9′-tribromo-9,9′-bifluorenyl[10] yielded 9,9′-bis(2′,7′-dibromo-9,9′-bifluorenyl)(XII), 9-(2,7-dibromo-9-fluorenyl)-9,9′: 9′,9″-terfluorenyl (XIII), X, II, V, IX, III, 2,7-dibromofluorenone, and fluorenone. The IR spectra of XII and XIII were very similar to those of I, II, VIII, and X.

An attempt to synthesize X by the reaction of I, metallic potassium, and 9-bromofluorene was unsuccessful; however, isomeric II, IX, III, and di(9-fluorenyl) ether (XIV)[11] were isolated. Compound XIV was obtained by the reaction between 9-bromofluorene and metallic potassium, accompanied by II, IX, and III. The formation of II may result from the reaction of intermediate 9-potassio-9,9′-bifluorenyl with 9-bromofluorene.[6] The occurrence of XIV can be explained by the reaction of 9-bromofluorene with 9-fluorenylpotassium peroxide which could be formed by action of metallic potassium and 9-bromofluorene in the presence of contaminating oxygen in the nitrogen, as Fig. 2 shows.

I isomerized into II by reaction with metallic potassium; II was broken down into its components, IX, IV, and III by the same reaction.

These findings are analogous to the reaction[12] of I (or II) with lithium aluminum hydride, therefore, the isomerization presumably proceeds *via* intermediary 9-potassio-9,9′: 9′,9″-terfluorenyl.

Experimental

All the melting points are uncorrected.

The compounds were confirmed by mixed-melting-point determinations and by comparison of their IR spectra with those of authentic samples.

Mass, NMR, and IR spectra were recorded using Hitachi RMU-6E, JEOL JNM-C60-HL, and JASCO IR-G spectrometers.

All reactions were carried out under an atmosphere of dry nitrogen.

Reaction of 9-Lithiofluorene with 9,9-Bifluorenylidene (III): 9-Lithiofluorene was prepared in the usual way[13] by the reactions of *n*-butyl bromide (3.3 g in 20 ml of ether) with lithium chips (0.31 g) in ether (20 ml), and of the resulting mixture with IV (5.0 g) in benzene (45 ml). A solution of 6.56 g of III in 60 ml of benzene was added dropwise into the 9-lithiofluorene solution at 0 °C for 20 min, and the mixture was boiled.

After standing at room temperature, the reaction mixture was treated with 5% aqueous ammonium chloride, and the organic layer was dried over calcium chloride, and evaporated to dryness under reduced pressure.

The residue was purified by means of fractional recrystallization, alumina column chromatography, and vacuum sublimation: 1.25 g (13%) of I, mp 291—293 °C (dec) (benzene), 1.05 g (11%) of II, mp 255—257 °C (dec) (ethyl acetate), 0.20 g (2%) of fluorenone, mp 82—83 °C (ethanol), 2.13 g (32%) of III, mp 181—183 °C (cyclohexane), and 1.85 g (37%) of IV, mp 111—113 °C (ethanol), were isolated.

Reaction of 9-Lithiofluorene with 2,7-Dibromo-9,9′-bifluorenylidene (V): To the 9-lithiofluorene solution obtained from 2.3 g of IV in 25 ml of benzene, 6.7 g of V in benzene was added during a period of 35 min below 10 °C.

The reaction mixture was then worked-up as usual, the crude product afforded 6.55 g (73%) of VI, mp 285—286 °C (dec) (ethyl acetate), a trace amount of VII, mp 302—303 °C (dec) (benzene), and 0.12 g (2%) of V, mp 244—245 °C (ethyl acetate).

Reaction of 2,7-Dibromo-9-lithiofluorene[14] with V: 2,7-Dibromofluorene (4.5 g) was metalated to the corresponding 9-lithio-compound in the usual way, and then allowed to react with V (6.7 g) in benzene.

After the usual treatment, 2.34 g (21%) of VIII, mp 313—314 °C (dec) (benzene), a trace amount of 2,7-dibromofluorenone, mp 201—202 °C, 1.46 g (32%) of 2,7-dibromofluorene, mp 162—163 °C, and 3.29 g (49%) of V, mp 244—245 °C, were obtained.

Reaction of 9-Lithio-9,9′-bifluorenyl with 9-Bromo-9,9′-bifluorenyl. *a*): A solution of 4.1 g (10 mmol) of 9-bromo-9,9′-bifluorenyl in 70 ml of xylene was added dropwise to the *n*-butyl lithium solution obtained from 12.5 mmol of *n*-butyl bromide and 0.025 g. atom of lithium chips, while being stirred at 0—2 °C for 45 min, and the mixture was heated gradually to 135 °C. After cooling, 3.3 g (8 mmol) of 9-bromo-9,9′-bifluorenyl in 60 ml of xylene was added dropwise to the resulting solution at 5—10 °C for 30 min. The mixture was stirred for 24 hr at room temperature, and then was maintained at a boil for 30 min.

The resulting mixture was treated in the usual manner, and the residual part was chromatographed on alumina in benzene. Further elution and subsequent evaporation gave 0.016 g of X, mp 313—314 °C (dec) (pyridine). Found: C, 94.92; H, 5.06%. Calcd for $C_{52}H_{34}$: C, 94.80; H, 5.20%. Mass: *m/e* 658 (M^+), 493, 329, 328, and 165.

In addition, 0.13 g of I, mp 292—293 °C (dec) (ethyl acetate), 0.42 g of II, mp 256—257 °C (dec) (ethyl acetate), 0.10 g of IX, mp 244—245 °C (ethyl acetate), and 0.36 g of III, mp 182—183.5 °C (ethanol), were obtained from the benzene mother liquor.

By extraction with ethanol from the lower band on the column, 1.05 g of 9-hydroxy-9,9′-bifluorenyl, mp 193—195 °C (benzene), was isolated. Fluorenone (0.65 g), mp 82—83 °C (ethanol), was obtained from the upper yellow band.

b): To an *n*-butyl lithium solution (prepared from 0.08 g of lithium chips and 0.78 g (5.7 m mol) of *n*-butyl bromide in ether) was added slowly 4.1 g (10 m mol) of 9-bromo-9,9′-bifluorenyl in 45 ml of xylene at 3—7 °C, and then refluxed at 135 °C for 1 hr.

The solution was treated in the usual way, affording 0.43 g of X, mp 313—314 °C (dec) (pyridine), 0.08 g of XI, mp 280—281 °C (dec) (benzene), 0.01 g of I, mp 292—293 °C (dec) (benzene), 0.022 g of II, mp 256—257 °C (dec) (benzene), 0.86 g of III, mp 184—186 °C (cyclohexane), 0.01 g of IX, mp 244—245 °C (ethyl acetate), and 0.45 g of 9-hydroxy-9,9′-bifluorenyl, mp 193—195 °C (benzene). Found for XI: C, 93.85; H, 6.04%. Calcd for $C_{43}H_{34}$: C, 93.82; H, 6.18%. Mass: *m/e* 550 (M^+), 493, 385, 329, 328, 221, 191, 179, and 165.

The mother liquor was concentrated to dryness under reduced pressure, and the residue was steam distilled to give 0.021 g of oily products. The oil was confirmed to consist of fluorenone and a small amount (*ca.* 1%) of IV by comparing of their retention times on a gas chromatogram with those of authentic samples.

Reaction of 9-Lithio-9,9′-bifluorenyl with 2,7,9′-Tribromo-9,9′-bifluorenyl: A xylene (200 ml) solution containing 4.54 g of 2,7,9′-tribromo-9,9′-bifluorenyl was added to 9-lithio-9,9′-bifluorenyl (prepared from 4.09 g of 9-bromo-9,9′-bifluorenyl) solution while being stirred for 45 min at room temperature. The mixture was then continuously stirred for a period of 23 hr, and followed by refluxing for another 1 hr.

The reaction mixture was worked-up as usual and the following compounds were obtained: 0.70 g of XII, mp 295—296 °C (dec) (pyridine), 0.08 g of XIII, mp 292—294 °C (dec) (pyridine), 0.04 g of X, mp 313—314 °C (dec) (pyridine), 0.24 g of II, mp 254—256 °C (dec) (ethyl acetate), 1.36 g of V, mp 241—242 °C (ethyl acetate), 0.16 g of IX, mp 242—244 °C (ethyl acetate), 0.31 g of III, mp 183—185 °C (ethyl acetate), 0.03 g of 2,7-dibromofluorenone, mp 198—200 °C (ethanol), 0.23 g of fluorenone, mp 80—83 °C (ethanol), and 0.03 g of 9-hydroxy-9,9′-bifluorenyl, mp 193—194 °C (benzene). Found for XII: C, 64.29; H, 3.17%. Calcd for $C_{52}H_{30}Br_4$: C, 64.10; H, 3.10%. Found for XIII: C, 76.11; H, 3.89%. Calcd for $C_{52}H_{32}Br_2$: C, 76.48; H, 3.95%.

Reaction of 9,9′ : 9′,9″-Terfluorenyls with Potassium Metal and 9-Bromofluorene. *a*): A solution of 1.0 g of I and 0.1 g of potassium chips in 60 ml of tetrahydrofuran (THF) was refluxed for 3 hr. 9-Bromofluorene (1.25 g) in THF (20 ml) was added dropwise to the resulting mixture while it was stirred for 50 min at 5—10 °C. Then the reaction mixture was stirred for 13 hr at room temperature and refluxed briefly.

The mixture was decomposed with 10 ml of ethanol, then with dilute hydrochloric acid, and extracted with benzene. The organic layer was concentrated to give 0.66 g of I, mp 291—293 °C (dec) (ethyl acetate), 0.17 g of II, mp 255—257 °C (dec) (ethyl acetate), 0.04 g of IX, mp 243—245 °C (ethyl acetate), and 0.03 g of XIV, mp 227—228 °C (benzene).

Found for XIV: C, 90.24; H, 5.41%. Calcd for $C_{26}H_{18}O$: C, 90.15; H, 5.24%. Mass: *m/e* 346 (M^+), 181, 165, and 152. NMR (in 99% C_6D_6): δ 5.74 (2H, s) and 6.97—7.49 (16H, m) ppm.

The benzene mother liquor was chromatographed on an alumina column: 0.06 g of III, mp 183—184 °C (ethanol), and 0.03 g of fluorenone, mp 82—84 °C (ethanol), were separated.

b): II (1.0 g) was treated as in (a) to give 0.74 g of II, mp 255—257 °C (dec) (ethyl acetate), 0.03 g of IX, mp 243—245 °C (ethyl acetate), 0.06 g of XIV, mp 227—228 °C (benzene), 0.014 g of III, mp 181—183 °C (ethanol) and 0.15 g of fluorenone, mp 82—85 °C (ethanol).

Reaction of 9-Bromofluorene with Metallic Potassium: A mixture of 4.9 g of 9-bromofluorene and 0.78 g of potassium chips in 50 ml of THF was stirred at room temperature for 20 hr.

The reaction mixture was treated as usual and 0.57 g of II, mp 255—257 °C (dec) (ethyl acetate), 0.22 g of IX, mp 242—244 °C (ethyl acetate), 0.20 g of XIV, mp 226—228 °C (benzene), and 0.47 g of III, mp 184—186 °C (ethyl acetate), were isolated.

Reaction of I with Potassium: A solution of 1.0 g of I and 0.2 g of potassium chips in 70 ml of THF was refluxed for 3.5 hr.

After cooling, the resulting mixture was then worked-up as usual, and afforded 0.32 g of II, mp 256—257 °C (dec) (ethyl acetate). The mother liquor was evaporated to dryness under reduced pressure and sublimed *in vacuo* at 120 °C to give 0.10 g of IV, mp 111—113 °C (ethanol).

The residue from the sublimation gave 0.32 g of IX, mp 242—243 °C (ethyl acetate), and 0.03 g of III, mp 183—185 °C (ethyl acetate).

Reaction of II with Potassium: A solution of 1.0 g of II and 0.2 g of potassium chips in 70 ml of THF was refluxed for 20 hr and the mixture was treated as usual: 0.24 g of II, mp 256—257 °C (dec) (ethyl acetate), 0.35 g of IX, mp 242—243 °C (ethyl acetate), 0.02 g of III, mp 183—185 °C (ethanol), and 0.24 g of IV, mp 111—112.5 °C (ethanol), were obtained.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, which is acknowledged. The authors are grateful to Dr. Elizabeth K. Weisburger of the National Institutes of Health, U.S.A., for reading their manuscript.

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14) As we have already reported[8], the formation of 2,7-dibromo-9-lithiofluorene was confirmed as 2,7-dibromofluorene-9-carboxylic acid. However a misprint shows the melting point of the carboxylic acid as 208—209 °C instead of the correct value, 258—259 °C (dec).