Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

SYNTHESIS OF 1,2-DILITHIOTETRAFLUOROBENZENE

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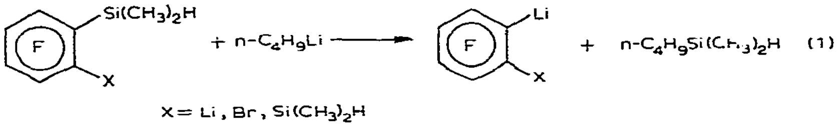
(Received June 19th, 1969; in revised form August 20th, 1969)

In our previous studies on the synthesis of polyfluoroaryllithium compounds, we have reported[1] the dimetalation of 1,4- and 1,2-dihydrotetrafluorobenzene to yield the 1,4-dilithiotetrafluorobenzene and 1,2-dilithiotetrafluorobenzene (I). We have also shown[2] that lithium–bromine (or iodine) interconversion reactions are much faster and more efficient than lithium–hydrogen interconversion reactions (metalation) in polyfluoroaromatic compounds. Thus it was not too surprising to find that two equivalents of n-butyllithium reacted nearly quantitatively with 1,4-dibromotetrafluorobenzene to yield 1,4-dilithiotetrafluorobenzene within a few minutes. However, attempts to prepare 1,2-dilithiotetrafluorobenzene in a similar manner (in THF or diethyl ether) proved to be different in degree of interconversion. The reaction between two equivalents of n-butyllithium and 1,2-dibromotetrafluorobenzene (II) yielded a mixture of 1,2-dilithiotetrafluorobenzene and 1-lithio-2-bromotetrafluorobenzene (III) as indicated by hydrolysis of such reaction mixtures, which gave both 1,2,3,4-tetrafluorobenzene (IV) and 1-bromo-2,3,4,5-tetrafluorobenzene (V). Unsuccessful attempts to prepare pure 1,2-dilithiotetrafluorobenzene by similar procedures were recently described by Cohen and Massey[3]. We would now like to report some further studies on the preparation of organolithium intermediates derived from 1,2-dibromotetrafluorobenzene.

Although a 2/1 mole ratio of n-butyllithium to 1,2-dibromotetrafluorobenzene was insufficient to cause complete interconversion, we have found that a 20% mole excess (2.4/1) of n-butyllithium converted the 1,2-dibromotetrafluorobenzene to the 1,2-dilithiotetrafluorobenzene in 95–97% yields. The resulting organometallic reaction mixture (VI), of course still contained the excess n-butyllithium. For some applications as an intermediate, this mixture of organometallic compounds may find utility. However, in certain other reactions the excess n-butyllithium present is detrimental and introduces complications.

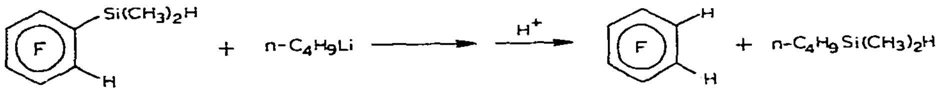
Hydrolysis of the reaction mixture (VI) produces excellent yields of 1,2,3,4-tetrafluorobenzene (>95%). Carbonation of the reaction mixture yields tetrafluorophthalic acid (90%). The excess n-butyllithium in the reaction mixture had no effect on these reactions. Alkylation of the reaction mixture with dimethylchlorosilane, however, produced a complex mixture (at least seven products) which by VPC and mass spectral analysis of the various products indicated that the excess n-butyllithium had reacted further with the initially formed silylated products. The excess n-butyllithium could possibly react with the Si–H bond to yield a Si–C_4H_9 compound. Alkylations of Si–H bond have been previously reported[4]. The excess n-butyllithium could also cleave the polyfluorophenyl–Si bond as reported previously by Gilman and Fearon[5].



(1)

Although the reaction products were not characterized unequivocally, VPC and mass spectral analysis indicated the following type products could be present in the mixture: (M^+ found experimentally) $C_6F_4H_2$ (150), $C_4H_9Si(CH_3)_2H$ (116), $HC_6F_4Si(CH_3)_2H$ (208), $C_6F_4[Si(CH_3)_2H]_2$ (266), $HC_6F_4Si(CH_3)_2C_4H_9$ (264), and $BrC_6F_4Si(CH_3)_2H$ (286).

To further substantiate the cleavage of a polyfluorophenyl–Si bond by n-butyllithium, 1-(dimethylsilyl)-2,3,4,5-tetrafluorobenzene (VII) was allowed to react with n-butyllithium under similar conditions as described in eqn. (1).



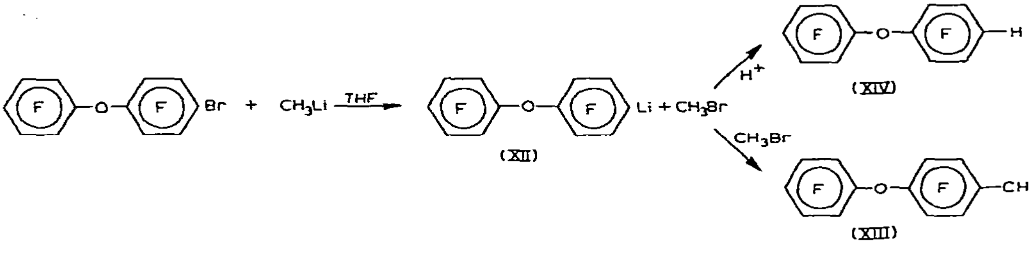
(2)

(VII) (VIII) (IX)

The two principal products (VIII) and (IX) produced in this reaction lend further support to the cleavage of a polyfluorophenyl–Si bond by n-butyllithium.

The 1,2-dilithiotetrafluorobenzene (VI) prepared as described above is a very unstable organometallic and must be reacted at −70°. Although the rate and mode of decomposition have not been studied, it has been our experience through qualitative observations that it is considerably less stable than pentafluorophenyllithium[6].

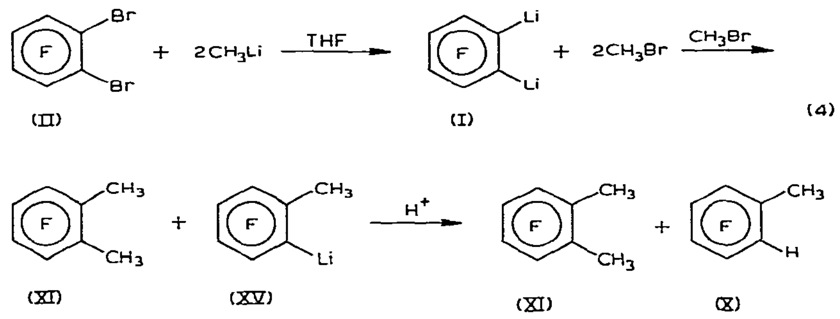
When methyllithium (2/1 mole ratio, in diethyl ether) was used in place of n-butyllithium in the preparation of (I), the results were quite similar in that incomplete metal–halogen interconversion was observed. One difference between the reactions was noted however in that a small quantity of 2,3,4,5-tetrafluorotoluene (X) was formed. Use of methyllithium in tetrahydrofuran, however, indicated a dramatic difference due to solvent effect. Complete conversion of the dibromo compound (II) (using exactly 2/1 mole ratio) was observed. The only products of the reaction were 3,4,5,6-tetrafluoro-*o*-xylene (XI) and 2,3,4,5-tetrafluorotoluene (X). We previously[7] have encountered alkylated products instead of metalated products when methyl-



(XII) (XIV) (XIII) (3)

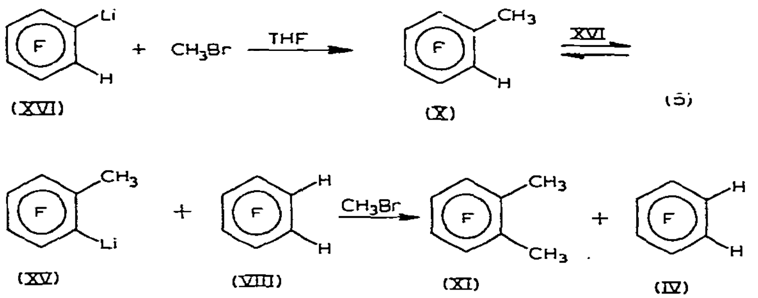
lithium was used in metal–halogen reactions. For example, it has been shown that 4-bromononafluorodiphenyl ether and methyllithium (THF) yield the alkylated product instead of the expected lithiated compound.

If a sample of the reaction mixture is withdrawn during the early stages of the metal–halogen interconversion, hydrolysis and VPC analysis of this sample indicated, beside the principal alkylated product (XIII), some 4-hydrononafluorodiphenyl ether (XIV). With further reaction time, the transient organolithium intermediate (XII), reacts further with the methyl bromide to yield the methylated product (XIII) exclusively. In this example, the rate of reaction between (XII) and CH_3Br is slow enough so that the intermediate (XII) can be identified through its hydrolysis product (XIV). In the reaction between methyllithium (THF) and 1,2-dibromotetrafluorobenzene we envision a similar reaction.



(4)

The reaction rates for both metal–halogen interconversion and reaction of the organolithium intermediates with methyl bromide must be extremely fast. An aliquot sample of the reaction mixture, after one minute reaction time, indicated only alkylated products. To further substantiate this mechanism by which alkylated products are formed, methyl bromide was added slowly to a THF solution of 2,3,4,5-tetrafluorophenyllithium (XVI)[8] (prepared from 1,2,3,4-tetrafluorobenzene and n-butyllithium). Two alkylated products were formed, (X) and (XI) in a 4/1 ratio (VPC area ratio). Since equivalent quantities of methyl bromide and the organolithium (XVI), were used it was surprising to note the relatively high yield of the dimethylated product (XI). Both products could arise by the route described in eqn. (5).



(5)

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* We have observed previously[9] disubstituted products from monoorganolithium compounds. For example, 2-bromo-3,4,5,6-tetrafluorophenyllithium on carbonation yields some tetrafluorophthalic acid besides the expected 2-bromo-3,4,5,6-tetrafluorobenzoic acid.

Since the methyl bromide was added slowly to the organolithium intermediate (XVI), there was sufficient time for equilibration between (X) and (XVI) to have occurred prior to reaction with methyl bromide*.

Although thus far we (as well as others[3]) have been unable to prepare pure 1,2-dilithiotetrafluorobenzene (in the absence of another organolithium compound), our reagent mixture (VI) contains only a single polyfluoroaryllithium species and has demonstrated considerable synthetic utility.

EXPERIMENTAL

All organometallic reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. VPC analyses were carried out on an F&M model 700 gas chromatograph. A 6 ft. column of Apiezon L, 10% on Chromosorb W, was used. Nuclear magnetic resonance spectra were carried out using a Varian 56–60 spectrometer. Chemical shifts are reported in ppm from fluorotrichloromethane (^{19}F NMR) or tetramethylsilane (^{1}H NMR) as internal standards. Mass spectrometer analyses were performed on a CEC 21–104.

Preparation of 1,2-*dilithiotetrafluorobenzene* (*I*)

n-Butyllithium (0.039 mole, 25 ml of a hexane solution) was added over 10 min to a precooled (−70°) stirred solution of 1,2-dibromotetrafluorobenzene (0.0162 mole, 5.00 g) dissolved in 100 ml of anhydrous diethyl ether and n-decane (2.44 g) as an internal VPC standard. Twenty min later, the reaction mixture was hydrolyzed with 40 ml of 6 *N* HCl, warmed to room temperature, phase separated, aqueous layer extracted with additional diethyl ether and the organic layers combined and dried over magnesium sulfate. VPC analysis of the diethyl ether indicated the solvent peak, 1,2,3,4-tetrafluorobenzene (IV) (94%), n-bromobutane (97%), n-decane (internal standard) and 1-bromo-2,3,4,5-tetrafluorobenzene (V) (7%).

When the above reaction was carried out in a 2/1 molar ratio (n-BuLi/$C_6F_4Br_2$), the hydrolysis products of the reaction mixture indicated 1,2,3,4-tetrafluorobenzene (IV) and 1-bromo-2,3,4,5-tetrafluorobenzene (V) in a 4/1 area ratio.

Carbonation of 1,2-*dilithiotetrafluorobenzene*

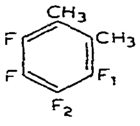
Carbon dioxide was bubbled through 1,2-dilithiotetrafluorobenzene (prepared as described above) for a period of 30 min. The reaction mixture was hydrolyzed with 60 ml of 6 *N* HCl, phase separated and the aqueous layer extracted with diethyl ether. The combined ether layers were extracted with 6 *N* NaOH, the base extract was acidified with 6 *N* HCl and extracted with diethyl ether. To the dried ($MgSO_4$) diethyl ether was added diazomethane in order to convert all carboxylic compounds to their methyl esters. VPC analysis of the diethyl ether solution of the mixed esters indicated the following products; dimethyl tetrafluorophthalate (90%) and two minor components, methyl 2-bromo-3,4,5,6-tetrafluorobenzoate (~8%) and methyl 2,3,4,5-tetrafluorobenzoate (~2%).

Reaction of methyllithium with 1,2-*dibromotetrafluorobenzene*

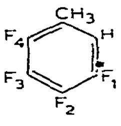
Methyllithium (0.0242 mole, 20 ml of a diethyl ether solution) was added over 7 min to a precooled (−70°) stirred solution of 1,2-dibromotetrafluorobenzene

(0.0121 mole, 3.73 g) dissolved in 125 ml of tetrahydrofuran and n-dodecane (1.81 g) as an internal VPC standard. Fifteen min later, the reaction mixture was hydrolyzed with 40 ml of 6 *N* HCl, warmed to room temperature, extracted with diethyl ether, and dried over magnesium sulfate. VPC analysis of this diethyl ether solution indicated two products (XI) and (X) in a 8/1 VPC area ratio. Product (XI) (82% yield) was characterized as 3,4,5,6-tetrafluoro-*o*-xylene. (Found: C, 53.59; H, 3.34. $C_8H_6F_4$ calcd.: C, 53.94; H, 3.40%.) Mass spectrometer analysis; found: *m/e*, 178; calcd.: 178. NMR analysis, ^1H ($CDCl_3$ solvent, TMS standard) CH_3, 2.16 ppm (multiplet). ^{19}F ($CDCl_3$ solvent, $CFCl_3$ standard) $F_1 + 144.5$ ppm (multiplet, 1); $F_2 + 162$ ppm (multiplet, 1) $J(F_1-F_2) + 20$ Hz.

Product (X) was characterized as 2,3,4,5-tetrafluorotoluene. (Found: C, 50.90; H, 2.43. $C_7H_4F_4$ calcd.: C, 51.23; H, 2.46%.) Mass spectrometer analysis; found: *m/e*, 164; calcd.: 164. NMR analysis; ^1H (CCl_4 solvent, TMS standard) CH_3, 2.28 ppm (multiplet, 3); Ar–H, 6.77 (multiplet, 1). $J(\text{ArH}-F_1) = 11$ Hz, $J(\text{ArH}-F_2) = 8$ Hz, $J(\text{ArH}-F_3) = 2$ Hz. ^{19}F (CCl_4 solvent, $CFCl_3$ standard) $F_1 + 141.8$ ppm (multiplet, 1); $F_2 + 161.3$ ppm (multiplet, 1); $F_3 + 158.3$ ppm (multiplet, 1); $F_4 + 143.8$ ppm (multiplet, 1). $J(F_1-F_2) = 20$ Hz; $J(F_1-F_3) = 1.8$ Hz; $J(F_1-F_4) = 13$ Hz; $J(F_2-F_3) = 18$ Hz; $J(F_2-F_4) = < 2$ Hz; $J(F_3-F_4) = 19$ Hz.



(XI)



(X)

When the above reaction was carried out in diethyl ether as the principal solvent, the VPC analysis of the hydrolysis products of the reaction mixture were 1,2,3,4-tetrafluorobenzene (IV) and 1-bromo-2,3,4,5-tetrafluorobenzene (V) in a 6/1 area ratio. A trace of 2,3,4,5-tetrafluorotoluene (X) was also found.

Reaction of methyl bromide with 1,2,3,4-tetrafluorophenyllithium

1,2,3,4-Tetrafluorophenyllithium[8] (XVI) was prepared by the addition of n-butyllithium (0.10 mole, 63 ml of a hexane solution) to a precooled (−70°) THF (200 ml) solution of 1,2,3,4-tetrafluorobenzene (0.10 mole, 15.0 g). Methyl bromide (0.10 mole, 9.5 g) was slowly (5 min) bubbled through the reaction mixture. Fifteen min later, the reaction mixture was hydrolyzed with 80 ml of 6 *N* HCl, warmed to room temperature, extracted with diethyl ether, phase separated and dried ($MgSO_4$). VPC analysis of the reaction mixture indicated only 2 products, (X) and (XI) (4/1 area ratio). The products were separated on a spinning band column, (X), b.p. 40°/32 mm, (XI), b.p. 66°/31 mm. Both compounds were characterized by VPC retention time and NMR analysis and shown to be identical with previously characterized compounds (see above experiment).

Reaction of n-butyllithium with (2,3,4,5-tetrafluorophenyl)dimethylsilane[8]

n-Butyllithium (0.01 mole, 6.2 ml of a hexane solution) was added (1 min) to a precooled (−70°) THF (20 ml) solution of 1-(dimethylsilyl)-2,3,4,5-tetrafluorobenzene (VII) (0.01 mole, 2.10 g) and n-decane (1.81 g) as an internal standard. After 15 min

Color Test IIA was negative indicating the absence of any n-butyllithium. The reaction mixture was hydrolyzed with 40 ml of 6 *N* HCl, warmed to room temperature, extracted with diethyl ether, phase separated and dried ($MgSO_4$). VPC analysis indicated 2 products 1,2,3,4-tetrafluorobenzene (VIII) and n-butyldimethylsilane (IX). Compound (VIII), mass spectrometer analysis; found: *m/e* 150, calcd.: 150. Compound (IX), mass spectrometer analysis; found: *m/e* 116, calcd.: 116. Both compounds were further characterized by comparing their VPC retention times and ^1H NMR spectra with those of authentic samples.

Reaction of 1,2-*dilithiotetrafluorobenzene with dimethylchlorosilane*

Dimethylchlorosilane (15.4 g, 0.163 mole) was added over 8 min to a (−70°) diethyl ether solution (200 ml) of 1,2-dilithiotetrafluorobenzene prepared as described above from 1,2-dibromotetrafluorobenzene (20.0 g, 0.065 mole) and n-butyllithium (0.163 mole, 105 ml of a hexane solution). The reaction mixture was stirred at −70° for an additional 30 min, allowed to warm to room temperature and hydrolyzed with 100 ml of 3 *N* HCl, phase separated and dried ($MgSO_4$). The solvent was removed by distillation using a spinning band column. The remaining material was analyzed by VPC. A complex mixture of seven products was present. A VPC-mass spectral analysis of this mixture suggested the following possible compounds: $C_6F_4H_2$ (mol. wt. 150), $C_4H_9Si(CH_3)_2H$ (mol. wt. 116), C_4H_9Br (mol. wt. 137), $HC_6F_4Si(CH_3)_2H$ (mol. wt. 208), $C_6F_4[Si(CH_3)_2H]_2$ (mol. wt. 266), $HC_6F_4Si(CH_3)_2C_4H_9$ (mol. wt. 286). No detailed characterization of the above compounds have been made other than VPC and mass spectral molecular weight analysis.

ACKNOWLEDGEMENT

The authors wish to thank D. S. Dyer of the Air Force Materials Laboratory for his interpretation of the NMR spectra.

REFERENCES

1 R. J. Harper, E. J. Soloski and C. Tamborski, *J. Org. Chem.*, 29 (1964) 2385.
2 C. Tamborski and E. J. Soloski, *J. Org. Chem.*, 31 (1966) 743.
3 (a) S. C. Cohen and A. G. Massey, *Chem. Ind. (London)*, (1968) 252;
(b) S. C. Cohen and A. G. Massey, *J. Organometal. Chem.*, 10 (1967) 471.
4 V. Bažant, V. Chvalovský and J. Rathouský, *Organosilicon Compounds*, Prague, Czechoslovakia, 1965, p. 120.
5 F. W. G. Fearon and H. Gilman, *J. Organometal. Chem.*, 10 (1967) 409.
6 P. L. Coe, R. Stevens and J. C. Tatlow, *J. Chem. Soc.*, (1962) 3227.
7 R. J. De Pasquale and C. Tamborski, *J. Organometal. Chem.*, 13 (1968) 273.
8 C. Tamborski and E. J. Soloski, *J. Organometal. Chem.*, 17 (1969) 185.
9 C. Tamborski and E. J. Soloski, *J. Organometal. Chem.*, 10 (1967) 385.