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# CONCERNING THE STABILITY OF 4,5,6,7,8-PENTAFLUORO-1-NAPHTHYLMAGNESIUM BROMIDE AND THE CORRESPONDING LITHIUM DERIVATIVE

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## SUMMARY

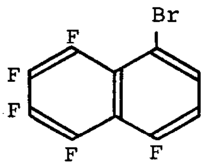
4,5,6,7,8-Pentafluoro-1-naphthylmagnesium bromide and the corresponding-lithium compound at elevated temperatures do not form a 1,8-dehydronaphthalyne intermediate (a 1,3-aryne) by loss of fluoride ion from C-8.

The formation of tetrafluorobenzyne as a reactive intermediate in the decomposition of pentafluorophenyllithium is well established and the decomposition of pentafluorophenylmagnesium bromide at elevated temperatures in tetrahydrofuran to give polymeric materials may also involve the same intermediate initially [1]. The aryne is highly electrophilic in character and acts as the 2π entity in Diels-Alder reactions with benzene and p-xylene [2]. Recently, the elimination of lithium fluoride from 1,3,4,5,6,7,8-heptafluoronaphthyllithium has been shown to give 3,4,5,6,7,8-hexafluoronaphthalyne as the intermediate by loss of fluorine at C-1, rather than the 2,3-naphthalyne by loss of fluorine at C-3 [3].

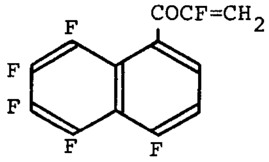
A route to 1-bromo-4,5,6,7,8-pentafluoronaphthalene (1) has recently become available and it was considered of interest to investigate the stability of the derived Grignard reagent and the lithium compound, since although no formation of the 1,2-naphthalyne could take place, the loss of fluorine at C-8 to give 2,3,4,5-tetrafluoro-1,8-dehydronaphthalene (a 1,3-

aryne) was a possible reaction path. Previously, 1,8-dehydronaphthalene a well documented 1,3-aryne generated by the oxidation of 1-aminonaphtho[1,8-de]triazine with lead tetraacetate, had been shown to react with benzene to give among the products 6b,10a-dihydrofluoranthene via an overall 1,2-cycloaddition reaction, and an isomer, 1-phenylnaphthalene. A similar reaction occurred with p-xylene [4].

The bromo compound (1) was readily obtained by a sequence of reactions starting from 1-fluorovinyl-4,5,6,7,8-pentafluoro-1-naphthyl ketone (2) [5] via oxidation with potassium permanganate in acetone to give the carboxylic acid (3) (75%). Treatment of the silver salt of (3) in carbon tetrachloride with bromine gave (1) in essentially quantitative yield.



(1)



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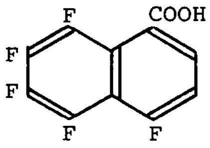
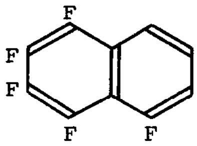


(3)

Compound (1) formed the Grignard reagent with magnesium which was quite stable at reflux temperature over 1 h. since on hydrolysis it gave 1,2,3,4,5-pentafluoronaphthalene (4) (97%). Reaction of (1) in benzene with one equivalent of n-butyllithium followed by heating the mixture under reflux for 3 h. failed to produce any detectable amount of material which resulted from reaction with the benzene. On working up the reaction, only compound (4) was isolated (7%), the residue being polymeric material. A similar result was obtained using the higher boiling point solvent p-xylene under reflux with the lithium compound over 1 h.



(4)

Consequently no 1,8-aryne is formed from 4,5,6,7,8-pentafluoro-1-naphthylmagnesium bromide in ether, and there is no positive evidence for the loss of lithium fluoride from the *peri*-position of 4,5,6,7,8-pentafluoro-1-naphthyllithium. The polymeric material formed from the lithium compound presumably arises via nucleophilic attack of the organometallic compound on β-fluorines in the naphthalene ring of a growing polynaphthylene molecule [6].

## EXPERIMENTAL

### Oxidation of 1-Fluorovinyl-4,5,6,7,8-pentafluoro-1-naphthyl ketone (2)

The vinyl ketone (2) (3.97 g) in dry acetone (10 ml) was added to a stirred solution of powdered potassium permanganate (7.5 g) in dry acetone (500 ml) at room temperature. The temperature rose rapidly and was maintained at 45-50° for 15 min. Water (100 ml) was added to the mixture, which was then decolourised with $SO_2$. The solution was acidified with sulphuric acid (25 ml, 1M), the acetone was removed by distillation in vacuo, and the crude product (2.7 g) was filtered, washed with water and dried. Recrystallisation of the product from benzene-petroleum ether [b.p. 60-80°] gave *4,5,6,7,8-pentafluoro-1-naphthoic acid (3)*, m.p. 177.5 - 178.5° (Found: C, 50.2; H, 0.9. $C_7H_3F_5O_2$ requires C, 50.4; H, 1.1%). $\upsilon_{max}$ 1710 $cm.^{-1}$ (C=O).

### 1-Bromo-4,5,6,7,8-Pentafluoronaphthalene (1)

The 1-naphthoic acid (3) (2.752 g) was treated with sodium hydroxide (125 ml, 0.101M) using phenolphthalein as indicator. The indicator was just decolourised with nitric acid (2M) and silver nitrate (150 ml, 0.1M) was added. The white precipitate was filtered, washed with water, then with ethanol and finally dried in vacuo at 90°/0.05 mm. A suspension of this silver salt (2.91 g) in carbon tetrachloride (40 ml) was treated at room temperature with bromine (1.27 g) which was immediately decolourised. The mixture was filtered, the solvent evaporated from the filtrate, and the residue (2.55 g) sublimed at 90°/ 0.05 mm and recrystallised from methanol to give 1-bromo-4,5,6,7,8-pentafluoronaphthalene (1), m.p. 79 - 79.5° (Found: C, 40.1; H, 0.4. $C_{10}H_2BrF_5$ requires C, 40.4; H, 0.7%).

## 1,2,3,4,5-Pentafluoronaphthalene (4)

The bromo compound (1) (0.161 g) in dry ether (5 ml) was added to magnesium turnings (0.81 g) in dry ether (10 ml). The mixture was heated under reflux for 1 h., acidified with sulphuric acid (1M) and the ether layer dried ($MgSO_4$). Evaporation of the solvent and sublimation of the residue in vacuo at 50°/0.05 mm gave the crude product (0.115 g) which was recrystallised from petroleum ether (b.p. 40 - 60°) to give 1,2,3,4,5-pentafluoronaphthalene (4) m.p. 70.5 - 71.0° (Found: C, 55.2; H, 1.2. $C_{10}H_3F_5$ requires C, 55.1; H, 1.4%).

## 4,5,6,7,8-Pentafluoro-1-naphthyllithium and its Decomposition in Aromatic Hydrocarbons

### (a) In benzene

The bromo compound (1) (0.201 g) in dry benzene (5 ml) was treated with n-butyllithium in hexane (0.43 ml, 1.57M) whereupon a white precipitate was formed. The mixture was heated under reflux for 3 h., diluted with ether and acidified. The ether layer was separated, dried ($MgSO_4$) and the solvent evaporated. Sublimation of the dark residue at 100°/0.01 mm gave only 1,2,3,4,5-pentafluoronaphthalene (4) (0.01 g).

### (b) In p-xylene

The bromo compound (1) (0.198 g) in dry p-xylene (5 ml) was treated with n-butyllithium in hexane (0.45 ml, 1.57M) and heated under reflux for 1 h. The mixture was worked up as in the previous experiment to give an oil (0.01 g) shown by mass spectroscopy to be a mixture of (4) and p-xylene.

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