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GRIGNARD PREPARATION OF FLUORENE-2-CARBOXYLIC ACID (I)

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GRIGNARD PREPARATION OF FLUORENE-2-CARBOXYLIC ACID (1)

D. C. Morrison

October 19, 1951

Berkeley, California

GRIGNARD PREPARATION OF FLUORENE-2-CARBOXYLIC ACID (1)

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October 17, 1951

In connection with work on incorporation of isotopic elements into the fluorene molecule, the preparation of a Grignard reagent from 2-bromofluorene was studied. Under certain conditions this was found to be moderately successful and carbonation of the resulting reagent furnished the 2-carboxylic acid. Miller and Bachman (2) failed to detect appreciable amounts of this Grignard but these authors did not examine the possibility of entrainment for the preparation. The use of ethyl bromide as entrainer enables the aryl bromide to undergo some reaction with the magnesium.

The reaction was carried out at ether reflux temperature and under these conditions very little, if any, interaction with the 9-position (methylene group) took place. The identity of the acid was confirmed by permanganate oxidation of a portion to fluorenone-2-carboxylic acid.

Some evidence was obtained that the Grignard could be coupled by cupric chloride to a bifluoryl. From this reaction, a very sparingly soluble pale yellowish substance melting about 300 was isolated which, however, was difficult to burn and gave carbon value 1.8% too low.

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- (2) Miller and Bachman, J. Am. Chem. Soc., 57 766 (1935).

EXPERIMENTAL

The 2-bromofluorene was obtained by the method of Thurston and Shriner (3). The preparation was studied in two ways, varying the time of reaction and the amount of ethyl bromide employed.

A mixture of 0.5 g. of 2-bromofluorene with 0.5 ml. of ethyl bromide in 50 ml. of ether was reacted with excess magnesium (about 5 g.) until quiet. A solution of 4.5 g. of 2-bromofluorene and 1.5 ml. of ethyl bromide in 100 ml. of ether was then added slowly during one-half hour. Twenty ml. of benzene was also added during this time. The resulting orange-brown solution was refluxed overnight (16.5 hours) and then carbonated while still warm with an excess of dry ice. The mixture was hydrolyzed with dilute hydrochloric acid and the organic layer removed and washed with water. It was extracted with 3 portions of dilute sodium carbonate solution and the extracts combined and acidified. This caused precipitation of the acid as a cream colored powder. After filtering, washing, and drying it weighed 750 mg. (17.5%). It was recrystallized from acetone-water and from ether, m.p. 260-267° C. with some sublimation and darkening.

In another run, 5 g. of 2-bromofluorene with excess magnesium in 100 ml. of ether were treated dropwise during 1 hour with 20 ml. of ethyl bromide dissolved in 100 ml. of ether. The solution was refluxed one-half hour and then carbonated and processed as before. The yield of acid was 900 mg. or 21%. From the filtrate from the acid precipitation, on standing overnight, 50 mg. of a white acid m.p. 216-221° C. were formed. This was not identified but did not decompose on boiling its alkaline solution or on melting.

The large excess of ethyl bromide was employed in an effort to secure greater utilization of the bromofluorene. Some of the latter may be recovered from

(3) Thurston and Shriner, J. Am. Chem. Soc., 57 2163 (1935).

the neutral reaction products.

A portion of the acid was oxidized in aqueous alkaline solution by an excess of permanganate by heating several hours on the steam bath. The permanganate was destroyed by oxalic acid, and the solution filtered from MnO_2 . Acidification furnished the fluorenone-2-carboxylic acid which was recrystallized from ether. It had m.p. about $330^{\circ} C.$ with much sublimation and some decomposition.

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