

Studies in the Pyrene Series¹

V. 3-Pyrenyl-lithium

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All attempts to make 3-bromo- or 3-iodopyrene react with magnesium to form a Grignard reagent have been unsuccessful. Only the iodine compound reacts slowly, the result of this reaction being dipyrenyl^{1a}. Yet, in order to utilize the great reactivity of organo-metallic compounds in pyrene chemistry, experiments were carried out to synthesize 3-pyrenyl-lithium. This compound is readily formed, when 3-bromopyrene in an ether-benzene solution is treated with phenyl-lithium. The pyrenyl-lithium partly separates from the solution as yellow crystals. Subsequent carbonation gave pyrene-3-carboxylic acid in yields indicating at least a 75 % conversion of the bromopyrene into pyrenyl-lithium.

The slight solubility of pyrenyl-lithium makes it easy to isolate this compound in a pure state, before it is brought into reaction with other substances.

The amount of pyrenyl-lithium, that separates as crystals, may be estimated as the difference between the equivalents of phenyl-lithium used and the equivalents of aryl-lithium remaining in the solution, by pouring the mother liquor into water and titrating the lithium hydroxide with hydrochloric acid (methyl red as an indicator). The results so obtained are in good accordance with the amounts of pyrene found on hydrolysis of the crystalline pyrenyl-lithium. In some cases the yield of crystalline pyrenyl-lithium were as high as 85 %.

In its reactivity and mode of reaction 3-pyrenyl-lithium behaves as an ordinary organo-lithium compound. As mentioned above, treatment with carbon dioxide yields the corresponding carboxylic acid. With ketones pyrenyl-lithium reacts readily to give carbinols. As an example 3-benzoylpyrene yielded 3,3'-dipyrenyl-phenyl-carbinol, which is formed, too, from dipyrenyl ketone and phenyl-lithium thus demonstrating the structure of the

dipyrenyl ketone, the synthesis of which is described, to be 3,3'. In the same way benzophenone yielded 3-pyrenyl-diphenyl-carbinol, identical with the carbinol obtained from 3-benzoyl-pyrene and phenyl-magnesium bromide ².

Of special interest is the reaction between pyrenyl-lithium and alkyl halides, because of the difficulty of the direct monoalkylation of pyrene in the Friedel-Crafts reaction ^{1b}. Both of these reactions will be the subjects of subsequent papers. Here, to show the applicability of the present method, the preparation of methyl- and ethylpyrene is described.

With mercuric chloride pyrenyl-lithium gives dipyrenyl-mercury, and with iodine iodopyrene is formed in good yield, making this route to the iodine compound an alternative to the diazotization method ^{1a}.

EXPERIMENTAL

3-Pyrenyl-lithium

In a typical experiment 5.6 g (0.02 mole) of 3-bromopyrene, dissolved in 10–15 ml of dry benzene and diluted with 20–30 ml of dry ether, were placed in a Schlenk tube, the sidearms of which were both fitted with a stopcock. 0.022 Mole of a phenyl-lithium solution was measured from a burette flask into the tube, which was then allowed to stand for about six hours at room temperature. All operations were carried out in a nitrogen atmosphere. The 3-pyrenyl-lithium crystallized in yellow needles forming clusters adhering to the walls of the tube. The clear solution was decanted and hydrolyzed (the crystals were washed twice with dry ether, which was added to the main portion). Titration of the aqueous layer showed that 0.0112 mole of aryl-lithium had remained in solution, while 0.0108 mole had disappeared. From the ether layer 1.3 g of pyrene was isolated. The yellow crystals on hydrolysis yielded 1.6 g of pyrene corresponding to 0.008 mole of pyrenyl-lithium, in accordance with 0.0086 mole as found on titrating the aqueous layer, but only 74 % of the amount expected from the first titration. The total yield of crude pyrene corresponds to a 72 % yield of pyrenyl-lithium. The pyrene formed was identified (m. p., mixed m. p. and picrate) with an authentic sample.

If desired, the pyrenyl-lithium may be obtained as a more finely dispersed precipitate by shaking the reaction tube, when crystallization starts. This is convenient in cases, where a reagent reacts slowly with the lithium compound.

Pyrene-3-carboxylic acid

Phenyl-lithium was prepared from 0.4 g of rasped lithium and 3.45 g (0.022 mole) of bromobenzene in 50 ml of dry ether. The phenyl-lithium solution was filtered, in a nitrogen atmosphere, into a Schlenk tube and after addition of 5 g (0.018 mole) of 3-bromopyrene in 15 ml of benzene and 20 ml of ether left for 16 hours. The yellow crystals and the mother liquor were carbonated separately with solid carbon dioxide. Water was added and 2.2 g and 1.1 g, respectively, of pyrene-3-carboxylic acid were isolated from the water layers, representing a total yield of 75 %, based on bromopyrene. From the ether layers 0.2 g of pyrene and 0.8 g of impure bromopyrene, respectively, were isolated.

The pyrene undoubtedly was formed from unreacted pyrenyl-lithium, thus rising the yield of this compound to 80 %. The acid was found to be identical with that obtained in the usual way by oxydation of 3-acetyl-pyrene³. M. p. and mixed m. p. 273–274°; ethyl ester, m. p. and mixed m. p. 63°.

Phenyl-3,3'-dipyrenyl-carbinol

3-Pyrenyl-lithium was prepared from 10 g (0.036 mole) of 3-bromopyrene and 0.045 mole of phenyl-lithium. Decantation and titration of the mother liquor indicated a 78 % yield (0.028 mole) of crystalline pyrenyl-lithium. On addition of 7 g (0.023 mole) of 3-benzoylpyrene³ dissolved in an ether-benzene mixture (2:1) the pyrenyllithium readily dissolved. The tube was left overnight at room temperature, when a yellowish crystalline complex of one mole of carbinol and one mole of ether had separated. Solution and crystals were poured into acidified water and extracted with ether. After evaporation of the ether 8 g of the complex crystallized. It could be recrystallized from benzene-ether (1:3). By rapid heating the m. p. is about 210°, dec.

$C_{39}H_{24}O, C_4H_{10}O$	Calc.	C 88.7	H 5.84	Mol. wt. 582.6 = 2 · 291.3
	Found	» 88.1	» 5.91	» » (benzene) 282

The ether molecule cannot be removed from the complex by heating for three hours at 100°, but heating at 140° for four hours removed it completely. 1.107 g lost 0.149 in weight, corresponding to 0.141 g as calculated for one mole of ether. The ether free carbinol has no definite m. p. but decomposes at about 270°.

$C_{39}H_{24}O$	Calc.	C 92.1	H 4.75
	Found	» 91.5	» 4.75

The same carbinol was prepared from dipyrenyl ketone (4.3 g; 0.01 mole) and phenyl-lithium (0.0125 mole). Yield 3.4 g of the carbinol-ether complex.

Found	C 88.1	H 5.93
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The solubility of the carbinol in glacial acetic acid is very slight and the solution is nearly colourless. On heating, however, to the boiling point the colour distinctly turns green, indicating formation of the ionized acetate. On cooling the colour disappears. Addition of concentrated mineral acids develops the usual³ intensely green halochromic colour.

Phenyl-dipyrenyl-methyl chloride. Phenyl-dipyrenyl-carbinol (1 g of the ether complex) was dissolved in 15 ml of dry benzene and 4 ml of acetyl chloride were added. In a few minutes the chloride began to separate (0.75 g) as a yellowish green solid. It could not be recrystallized because of the poor solubility and non-stability at elevated temperatures. Drying at 100° for 2–3 hours causes blackening. By treatment of the chloride, suspended in dry benzene and with exclusion of the air, with molecular silver the phenyl-dipyrenyl-methyl radical was formed as indicated by a brownish-red colour

which, on exposure to the air, turned pale yellow. Further experiments on this free radical have not yet been made.

$C_{39}H_{23}Cl$ Calc. Cl 6.73 Found Cl 6.60

3,3'-Dipyrenyl ketone. 20.2 g (0.1 mole) of pyrene and 35 g of aluminium bromide were dissolved in 200 ml of tetrachloroethane. A solution of 7 g of carbonyl chloride in 50 ml of tetrachloroethane was added, with stirring, in the course of 20 minutes. After two hours at room temperature and one hour at 50° the reaction product was poured on ice and hydrochloric acid. The organic layer, after washing, was diluted with 400 ml of ether, when a yellow precipitate (2.7 g) appeared (I). M. p. after recrystallization from 1,2,4-trichlorobenzene 340° (355° corr.). I undoubtedly is dipyrenoyl-pyrene, $C_{16}H_9 \cdot CO \cdot C_{16}H_9 \cdot CO \cdot C_{16}H_9$, and probably, because of the high m. p., the 3,8-compound.

$C_{50}H_{26}O_2$ Calc. C 91.2 H 3.98
Found » 90.5 » 4.01

To the filtrate from I 600 ml of ether were added, and another yellow precipitate (3.4 g) was formed (II), which proved to be the dipyrenyl ketone; m. p. upon crystallization from xylene 232°.

$C_{33}H_{18}O$ Calc. C 92.1 H 4.19
Found » 91.3 » 4.16

From the filtrate from II 5 g of unchanged pyrene were isolated besides another crop of II, crude product 6.0 g, recrystallized 2.4 g, m. p. 231–232°.

Dipyrenyl ketone was also prepared from pyrene (30 g) and oxalyl chloride (15 g) in carbon disulfide (120 ml) with aluminium chloride (22 g). The mixture was refluxed for 6.5 hours and then poured on ice and hydrochloric acid. The yellow solid formed was extracted several times with carbon tetrachloride to remove unchanged pyrene (13 g), and the residue recrystallized from 300 ml of xylene. Yield 12.5 g, m. p. 231°. Repeated recrystallization yielded 10.5 g, m. p. 234–235°.

Alkylation

*3-Methyl-pyrene*³. This compound was prepared from 0.025 mole of crystalline 3-pyrenyl-lithium and 5 g (0.035 mole) of methyl iodide in 25 ml of dry ether. The pyrenyl-lithium rapidly dissolved with considerable evolution of heat. After 15 minutes the clear solution was poured into water. The aqueous layer by titration was found to contain 0.003 mole of lithium hydroxide and 0.0224 mole of lithium iodide, indicating a nearly complete reaction. The ether layer, on evaporation, left 4.0 g of methyl-pyrene, m. p. 70.5–71.5°, or 83 %, based on pyrenyl-lithium. In another experiment 0.025 mole of pyrenyl-lithium and 7.0 g (0.05 mole) of methyl iodide yielded 5 g of crude methyl-pyrene or 4.5 g recrystallized from ethanol.

*3-Ethyl-pyrene*³ was prepared in the same way from 0.03 mole of pyrenyl-lithium and 7.3 g (0.047 mole) of ethyl iodide, yielding 5.1 g (77.3 %) of crude ethyl-pyrene, recrystallized from ethanol 4 g, m. p. 91°.

3-Iodopyrene

7.0 g (0.055 atom) of finely powdered iodine were added to 0.025 mole of crystalline 3-pyrenyl-lithium suspended in 25 ml of dry ether. In a vigorous reaction the pyrenyl-lithium dissolved. After 30 minutes the solution was poured into water. The ether layer was separated and washed free from iodine with a solution of sodium thiosulfate and dried over calcium chloride and decolorized with Norite. After evaporation of the solvent 4.6 g of crude iodopyrene, m. p. 81–82°, remained (56 %). Recrystallized from ethanol-ethyl acetate-glacial acetic acid (4 : 1 : $\frac{1}{2}$) it melted at 85°; mixed m. p. with iodopyrene (m.p. 87°) from 3-aminopyrene^{1a}, the same.

3,3'-Dipyrenyl-mercury

To 0.029 mole of pyrenyl-lithium suspended in ether were added 4 g of finely powdered mercuric chloride (0.015 mole). After the initial vigorous reaction the tube was shaken for 12 hours. The mixture was poured into water and the solid was filtered off and washed several times with water, ethanol and, finally, with ether. 7 g (80.4 %) of a greyish white powder was obtained. The dipyrenyl-mercury has no definite m. p.

$C_{32}H_{18}Hg$ Calc. Hg 33.2 Found Hg 33.3

SUMMARY

3-Pyrenyl-lithium has been prepared by the action of phenyl-lithium on 3-bromopyrene, and its characteristics as a starting-point for syntheses in various directions have been elucidated.

REFERENCES

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