chloric acid and the mixture warmed (80°) and stirred under reflux until a clear solution resulted (about 15 min.). A solution of morpholine hydrochloride (0.60 mole) in 160 ml. of water was then added and the flask contents cooled to below 10°. Then 30 g. of 95% sodium cyanide (0.60 mole) in 100 ml. of water was slowly introduced below the surface of the cooled, stirred solution. The flask was immersed in the cooling bath so that the liquid level was well below the surface of the bath. After 2 hr. in the cold, a solution of 24 g. (0.60 mole) of sodium hydroxide in 60 ml. of water was added. The mixture was stirred in the cold for an additional hour and then filtered. The white solid was collected, washed with cold water several times, and air dried. The yield of α-morpholinoacrylonitrile, m.p. 62.5–63.5° after recrystallization from 30–60° petroleum ether, was 40 g. (58%).

Anal. Calcd. for $C_7H_{10}N_2O$: C, 60.85; H, 7.30; N, 20.28. Found: C, 61.50; H, 7.15; N, 20.09.

High Polymer Research Laboratory
Industrial Rayon Corp.
Cleveland, Ohio

A New Method for the Preparation of Formamidine

Keijiro Odo, Eiichi Ichikawa, Kozo Shirai and Kiichiro Sugino

Received April 23, 1957

The formation of formamidine as an intermediate was first reported by Odo and Sugino by the electrolytic reduction of cyanamide in 8% $(NH_4)_2SO_4$ catholyte at a tin cathode.[1]

$$NH_2CN + 2H \longrightarrow NH_2\cdot CH{=}NH$$

Further study on the mechanism of this electrode reaction showed that the first step in the reduction of cyanamide to formamidine seems to be favored by carrying it out catalytically over palladium rather than electrochemically. The yield is almost quantitative. It was surprising to us that this simple method had not been previously reported.

EXPERIMENTAL[2]

Twenty grams of palladium-charcoal catalyst[3] (containing 1.4% Pd) in 200 cc. water was placed in a reduction bottle provided with two separatory funnels and with a stream of hydrogen flowing through it to exclude air. The bottle was first shaken to reduce the catalyst completely. To it, there was added 100 cc. of 12% H_2SO_4 (or 100 cc. of 9% HCl) from one funnel. Then, from the other funnel, an aqueous solution of 11 g. of freshly prepared cyanamide (purity 97% as silver cyanamide) in 100 cc. water was added portion-wise (1.5 cc. at intervals of 3 min.) for 3 hr. with shaking at room temperature, while the hydrogen continued to be taken up. The reduction was complete about 10 min. after the last portion had been added at which time 5.8 l. (0.25 mole, 100% of theoretical) of hydrogen had been absorbed.

After the reduction, the mixture was filtered and the filtrate was combined with catalyst washings. The resulting solution was adjusted to pH 4.8–5.0 by adding a small amount of Amberlite 1R4B and was evaporated to dryness below 60° under diminished pressure. The crystals of formamidine sulfate (or hydrochloride) separated. After recrystallization from methanol, 22.5 g. of pure formamidine sulfate (or 18.8 g. hydrochloride) was obtained, m.p. 156–158° (hydrochloride, 76–78°), yield 95% (hydrochloride, 92%).

Anal. of the sulfate. Calcd. for $CH_4N_2\cdot{}^1/_2H_2SO_4$: N, 30.11. Found: N, 29.82.

Laboratory of Organic Electrochemistry
Department of Chemical Engineering
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo, Japan

---

[1] K. Odo, K. Sugino, *J. Electrochem. Soc.*, **104**, 160 (1957).

[2] All melting points are uncorrected.

[3] This catalyst consisted of activated charcoal with absorbed Pd, prepared according to the procedure of Wieland, *Ber.*, **45**, 484 (1912).

Metalation of Aryl Fluorides in Tetrahydrofuran

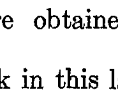
Henry Gilman and Theodore S. Soddy

Received March 25, 1957

The metalation of fluorobenzene with phenyllithium at 0° in diethyl ether by Wittig and coworkers gave products which indicated that o-fluorophenyllithium was one of the intermediates.[1–3] Under the conditions that were employed, however, o-fluorophenyllithium was too reactive to be successfully detected by the formation of derivatives as such.

Later work demonstrated that the o-fluorophenyllithium gave rise to the more reactive "benzyne" intermediate which was indirectly responsible for products that were obtained such as triphenylene.[4–7]

More recent work in this laboratory has shown that o-fluorophenyllithium can be obtained in excellent yields from o-fluorobromobenzene and n-butyllithium at -60° by means of the halogen-metal interconversion reaction.[6] Evidence was also obtained for the formation of the "benzyne" intermediate by the isolation of 1,4-dihydronaphthalene-1,4-endoxide (I) when the o-fluorophenyllithium was permitted to warm to room temperature in the



I

---

[1] G. Wittig, G. Pieper, and G. Fuhrmann, *Ber.*, **73** 1193 (1940).

[2] G. Wittig and W. Merkel, *Ber.*, **75**, 1491 (1942).

[3] G. Wittig, *Naturwiss.*, **30**, 696 (1942).

[4] G. Wittig and L. Pohmer, *Angew. Chem.*, **67**, 348 (1955).

[5] G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

[6] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **78**, 2217 (1956).

[7] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **79**, 2625 (1957).

TABLE I

PHYSICAL CONSTANTS AND RELATED DATA FOR ACIDS FROM ARYL FLUORIDES

Compound	Yield, %	M.P., °C.	Neutral Equivalent		Fluorine	
			Calcd.	Found	Calcd.	Found
o-Fluorobenzoic acid	60.0	123–124				
5-Methyl-2-fluorobenzoic acid	58.0	159–160	154	156, 159	12.33	12.45, 12.68
3-Methyl-2-fluorobenzoic acid	2.6	109–110	154	154, 155	12.33	12.10, 12.18
1-Fluoro-2-naphthoic acid	30.0	193–194	190	187, 187	9.99	9.97, 9.81

presence of furan.[7] The same adduct was isolated when o-fluorobromobenzene was shaken for 4 days at 25° with lithium amalgam in furan.[5]

When n-butyllithium which was prepared in tetrahydrofuran[8] was added to fluorobenzene at −40°, no reaction was noted, but on warming to −25° a very vigorous reaction occurred, and a small amount of triphenylene was isolated. In order to avoid this almost uncontrollable reaction, the temperature of the reaction mixture was maintained between −50 and −60° for 7 hr. On carbonation o-fluorobenzoic acid was obtained in a crude yield of 60%. By employing these conditions, the metalation of the following aryl fluorides was effected in the same manner (Table I).

EXPERIMENTAL[9]

The following reaction under method A for the metalation of fluorobenzene is described in detail, and this general procedure was employed for the metalation of the other aryl fluorides.

Fluorobenzene and n-butyllithium in tetrahydrofuran a −50°. Method A. Into a 3-necked, 500-ml., round-bottomed flask was introduced 9.6 g. (0.1 mole) of fluorobenzene in 100 ml. of tetrahydrofuran.[10] To this slowly stirred solution, which was cooled to −50° by means of a Dry Ice–acetone bath, was added over a period of 5 min. 0.1 mole of n-butyllithium in 55 ml. of tetrahydrofuran.[11] The reaction mixture was stirred at this temperature for 7 hr. and carbonated by pouring jet-wise onto a Dry Ice–ether slurry. The basic extract was acidified to yield 9 g. (60% of crude o-fluorobenzoic acid which melted between 110–116°. On crystallization from water, the m.p. was 123–124°. A mixed melting point with an authentic specimen was undepressed.

In two other preparations which were carried out as described above except that the times were 3 and 12 hours, respectively, the yields of crude o-fluorobenzoic acid were 36 and 33%. When p-fluorotoluene was treated in the same manner for a period of 3 or 12 hr., the yields of 5-methyl-2-fluorobenzoic acid were 20 and 33%, respectively.

Method B. To a stirred solution of 0.1 mole of n-butyllithium in 75 ml. of tetrahydrofuran, was added 9.6 g. (0.1 mole) of fluorobenzene. The temperature was kept at −40° for 35 min. and when no reaction was noted, the temperature was permitted to rise to −25°. At this point a vigorous reaction took place, and the temperature rose to 12°. The color of the reaction mixture was brown. The reaction mixture was carbonated and worked up in the preceding manner. No acid was obtained from the basic extract, but from the neutral layer 0.6 g. of triphenylene was isolated. The m.p. was 193–194° on crystallization from 1-propanol. A mixed m.p. with an authentic specimen was undepressed.

THE DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

---

[8] This solvent was employed because its base strength is greater than that of diethyl ether; H. C. Brown and R. M. Adams, *J. Am. Chem. Soc.*, **64**, 2557 (1942).

[9] All melting points are uncorrected, and all reactions were carried out in a dry, oxygen-free atmosphere.

[10] The tetrahydrofuran was dried and purified by first shaking with sodium hydroxide pellets, refluxing over sodium metal for several hours, and finally distilling, immediately before use, from lithium aluminum hydride.

[11] H. Gilman and B. Gaj, *J. Org. Chem.*, 22, 447 (1957).

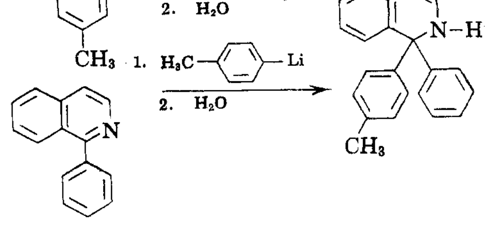
Reaction of Phenyl- and p-Tolyllithium with 1-Arylisoquinolines

HENRY GILMAN AND THEODORE SODDY

Received April 9, 1956

In the course of an investigation in this laboratory which involved the preparation of some 1-substituted isoquinolines, there arose the desirability of studying the addition of aryllithium reagents to 1-arylisoquinolines.

In an earlier investigation,[1] the addition of phenyl- and p-tolyllithium to 2-p-tolylquinoline and 2-phenylquinoline, respectively, was found to yield the identical compound, 2-phenyl-2-(p-tolyl)-1,2-dihydroquinoline which resulted from the attack at the azomethine linkage. At that time, also, there was an attempt made to prepare 1-phenyl-1-(p-tolyl)-1,2-dihydroisoquinoline by treating 1-p-tolyl- and 1-phenylisoquinoline with



---

[1] H. Gilman and G. C. Gainer, *J. Am. Chem. Soc.*, 69, 877 (1947).