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The Reduction of Fluorenone Azine with Lithium Aluminum Hydride

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Synopsis. The title reaction yielded fluorenone 9-fluorenylhydrazone and 9,9′-azo(9,9′-bifluorenyl), accompanied by some fragmentary compounds.

The reaction of azine with phenylmagnesium bromide has been reported to give the corresponding hydrazone.[1] The reduction of fluorenone azine (**1**) has yielded 9,9′-hydrazofluorene,[2] which is of interest for its possible use in benzidine-type rearrangements. The present paper will deal with the reduction of **1**, for which some interesting findings will be reported.

The hydrogenation of **1** with hydrazine hydrate in the presence of Ru on C yielded fluorenone 9-fluorenylhydrazone (**2**) (mp 177—178 °C), but not 9,9′-hydrazofluorene (mp 174—175 °C).[2] The acetylation of **2** afforded the corresponding *N*-acetyl compound (**3**). The UV absorption maximum of **2** was observed at a longer wavelength than that of benzophenone benzhydrylhydrazone.[3]

The reduction of **1** with lithium aluminum hydride (LAH) unexpectedly gave 9,9′-azo(9,9′-bifluorenyl) (**4**) accompanied by **2**, fluorenone hydrazone (**5**),[4] 9′-fluorenimine (**6**),[2] 9-fluorenamine (**7**),[4] fluorene (**8**), and 9,9′-bifluorene (**9**). The individual reactions of these products showed that **2** cleaved into **5** and **8**, and that **5** was converted to **7** *via* **6** under similar conditions.

It can be explained that the reduction of **1** yielded **2** and 9,9′-azofluorene (**2a**) through 1,2- and 1,4-addition respectively. The hydrogen atom on the 9-carbon of **2a** is very labile; therefore, the equilibrium between **2** and **2a** lies in the direction of the **2**.[1] The formation of **4** and **9** may be assumed by the generation of the 9-fluorenyl radical from **2a**. The addition of 9-fluorenyl radicals to **1** might form **4** under mild conditions.

Experimental

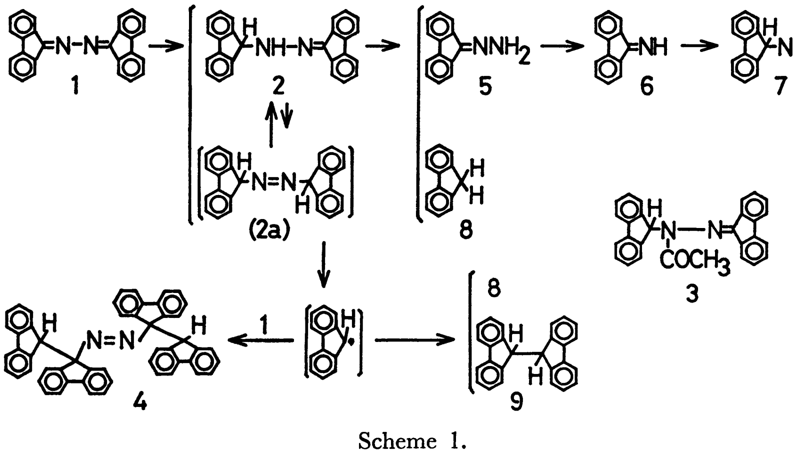
All the melting points are uncorrected. The instruments used in this experiment have been described elsewhere.[5]

*Hydrogenation of Azine **1**.* A solution of 3.56 g (10 mmol) of **1** and 12.8 ml of $H_2NNH_2\cdot H_2O$ (80%) in 180 ml of pyridine was stirred in the presence of 520 mg of Ru on C (5%) at 70 °C for a period of 3.5 h. Upon filtration, the filtrate was concentrated to a small volume and poured into H_2O. The precipitates were separated by alumina-column chromatography (benzene) and purified by recrystallization from benzene–EtOH (1: 1) to afford 2.86 g (80%) of **2** (mp 177—178 °C (dec)) and 0.16 g (4%) of **5** (mp 152—153 °C). UV_{max} of **2** (benzene), 350 nm (log ε 4.34); Raman spectrum, 2913 (CH), 3294 cm^{-1} (NH); NMR ($CDCl_3$) $\delta=5.86$ (1H, d, $J=9.0$ Hz), 6.67 (1H, d, disappeared by D_2O), 7.07—8.10 (16H, m); MS, *m/e*, 358 (M+), 356, 193, 180, 165. Found: C, 86.88; H, 5.18; N, 7.96%. Calcd for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06; N, 7.82%.

*Acetylation of Hydrazone **2**.* A mixture of 3.00 g (8.4 mmol) of **2** and 2.64 g of AcCl in 40 ml of benzene was stirred at room temperature for 10 h and then refluxed for an additional 2 h to give 2.91 g (87%) of **3**: mp 173.5—174.5 °C (dec); UV_{max} (isooctane) 378 nm (log ε 3.55); IR 1642 cm^{-1} (C=O); NMR ($CDCl_3$) $\delta=1.91$ (3H, s), 6.61—7.53 (16H, m), 7.97 (1H, s); MS, *m/e*, 400 (M+), 358, 324, 222, 179, 165. Found: C, 83.82; H, 5.10; N, 6.82%. Calcd for $C_{28}H_{20}N_2O$: C, 83.97; H, 5.03; N, 7.00%.

A solution of **3** (0.40 g; 1 mmol) in EtOH (40 ml) was refluxed with Zn dust (1.0 g) and $CaCl_2$ (0.40 g) in H_2O (3 ml) for 3.5 h to yield 0.22 g (49%) of *N*-9-fluorenylacetamide (mp 260—262 °C (lit,[4] mp 260—261 °C)) and 0.05 g (14%) of **7** (mp 60.5—62.0 °C).

*Reduction of Azine **1** with LAH.* *a)*: A suspension of 0.86 g (22.6 mmol) of LAH in 30 ml of THF was stirred, drop by drop, into a solution containing 5.00 g (14 mmol) of **1** in 200 ml of THF at room temperature for 10 min; the mixture



Scheme 1.

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was then refluxed for an additional 30 min. Upon cooling, the resulting mixture was decomposed with THF–H_2O and filtered. The filtrate was evaporated to dryness, and the residue was suspended in 50 ml of benzene and 50 ml of 4% hydrochloric acid.

The insoluble fraction was heated with the hydrochloric acid solution for 10 min and then collected. The precipitate was recrystallized from EtOH to give 0.05 g of fluorenone[6] (mp 83—84 °C). The filtrate was concentrated to a small volume to afford 0.96 g of hydrochloride of **7** (mp 220 °C (dec)).

The above-mentioned benzene solution was washed with H_2O, dried (Na_2SO_4), and chromatographed on alumina. The eluate yielded 0.86 g of **8** (mp 114—115 °C) and 0.18 g of **9** (mp 244—245 °C). Additionally, 1.40 g (28%) of **2** (mp 177—178 °C (dec)) and 0.08 g of **5** (mp 152—153 °C) were isolated from each band on the column.

b): A mixture of **1** (3.56 g; 10 mmol) and LAH (0.19 g; 5 mmol) in THF (280 ml) was stirred at room temperature for 4 h. By subsequent treatment similar to that described above, the resulting mixture afforded 0.47 g (14%) of **4**: mp 240—241 °C (dec); UV_{max} (benzene) 355 nm (log ε 4.22); IR 2923, 2852 cm^{-1} (CH); NMR ($CDCl_3$) δ=5.68 (1H, s), 6.89 (1H, s), 6.99—7.88 (32H, m). Found: C, 90.62; H, 4.92; N, 3.89%. Calcd for $C_{52}H_{34}N_2$: C, 90.93; H, 4.99; N, 4.08%.

Reduction of Azo Compound 4. A solution of **4** (0.500 g; 0.7 mmol) in AcOH (50 ml) was refluxed with Zn dust (1.0 g) for 1 h.

When worked-up in a manner like that described above, the mixture yielded 9-amino-9,9′-bifluorene (0.169 g, mp 179—181.5 °C (dec), lit,[7] mp 181 °C (dec)), a hydrochloride of **7** (0.131 g, mp 218 °C (dec)), **8** (0.012 g, mp 112—114 °C), and **9** (0.007 g, mp 242—243 °C). IR of 9-amino-9,9′-bifluorene, 3350 (NH), 2889 cm^{-1} (CH); NMR ($CDCl_3$) δ=2.04 (2H, s), 4.74 (1H, s), 6.85—7.75 (16H, m); MS, *m/e*, 345 (M^+), 180, 165.

References

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6) Imine **6** was converted quantitatively to fluorenone by hydrolyzing with dilute hydrochloric acid. The other compounds isolated by the same reaction were unchanged under these conditions.

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