Derivatives of Fluorene. 35. Hydrazine-Hydrate and Raney-Nickel Reduction of Nitrofluorenones to Aminofluoren-9-ols

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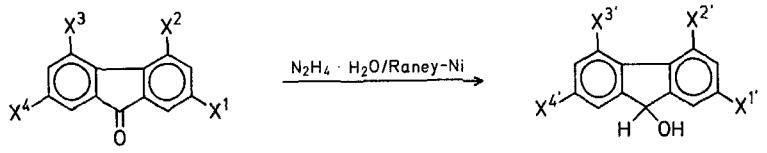
Reduction with hydrazine hydrate in hot ethanol using Raney nickel as catalyst is a very convenient method for the preparation of aromatic amines from the corresponding nitro compounds[1]. Carbonyl groups are generally unaffected in this reaction. However, by employing a large excess of hydrazine hydrate (~100 molar equivalents) and a considerable amount of the catalyst, nitrofluorenones are reduced to aminofluoren-9-ols in good yields (Table 1). Under the same conditions, 2-aminofluorenone is also reduced to 2-aminofluoren-9-ol. Carbonyl reduction seems to be related to the specific configuration of the fluorenone

molecule, since the related nitro-ketones, 3- and 4-nitrobenzophenone, give only amino-ketones in this reduction, with only a trace of the corresponding aminophenyl phenyl carbinol being detected in the case of the 3-nitro isomer.



1a $X^1 = -NO_2$, $X^2 = X^3 = X^4 = H$
b $X^1 = X^4 = Cl$, $X^2 = -NO_2$, $X^3 = H$
c $X^1 = X^2 = X^4 = Cl$, $X^3 = -NO_2$
d $X^1 = X^4 = -NO_2$, $X^2 = X^3 = H$
e $X^1 = -NH_2$, $X^2 = X^3 = X^4 = H$

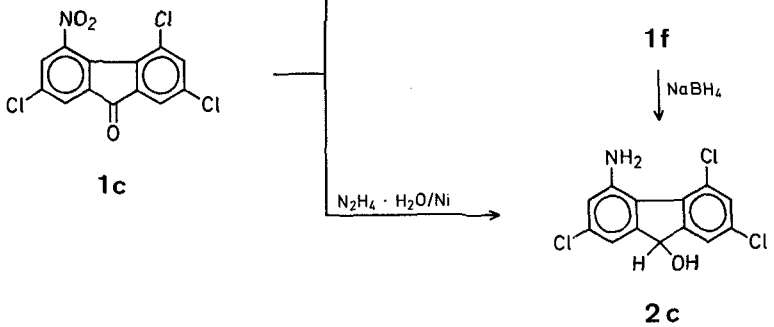
2a $X^{1'} = -NH_2$, $X^{2'} = X^{3'} = X^{4'} = H$
b $X^{1'} = X^{4'} = Cl$, $X^{2'} = -NH_2$, $X^{3'} = H$
c $X^{1'} = X^{2'} = X^{4'} = Cl$, $X^{3'} = -NH_2$
d $X^{1'} = X^{4'} = -NH_2$, $X^{2'} = X^{3'} = H$
e = **2a**

Table 1. Aminofluoren-9-ols from the Reduction of Nitrofluorenones with Hydrazine Hydrate and Raney Nickel (**1**→**2**)

Product	Yield %	m.p.[a]
2a	78 (75[b])	199.5–200°[c]
2b	*78*	*205–206.5°*[d]
2c	67[e]	231–232°
2d	50	216–217°[f]

[a] Melting points were taken on a Fisher-Johns block and are corrected to standards.
[b] From 2-aminofluorenone.
[c] Ref.[5], m.p. 200°.
[d] Ref.[2], m.p. 206–207°.
[e] $C_{13}H_8Cl_3NO$ (300.56) calc. C 51.95 H 2.68 N 4.66; found 51.87 2.84 4.85. The analyses were performed by Alfred Bernhardt, D-5251 Elbach, West-Germany.
[f] Ref.[6], m.p. 216°.

Compound **1c** is prepared from 2,4,7-trichlorofluorene[2,3] by nitration to 5-nitro-2,4,7-trichlorofluorene[3] followed by dichromate oxidation. Reduction of **1c** with tin(II)-chloride/hydrochloric acid gives 5-amino-2,4,7-trichlorofluorenone (**1f**).



The products were identified by mixture melting points, by T.L.C. comparison, and by reduction of the aminofluorenones with sodium borohydride in methanol[4].

Aminofluoren-9-ols (2a–d) from Nitrofluorenones (1a–d):
The nitrofluorenone (0.02 mol) was dissolved in boiling 95% ethanol (1–1.5 l) (2 l per 0.005 mol of **1d**). The hot solution was mixed with 85% hydrazine hydrate (50 ml) and Raney nickel[7] (1 g, wet weight), and heated on the steam bath for 30 min. After addition of a second portion (50 ml) of hydrazine hydrate, the mixture was heated on the steam bath for another 30 min and filtered hot. The filtrate was concentrated, diluted with water, and the aminofluoren-9-ol was collected by filtration and recrystalled from ethanol, ethanol/water, or benzene.

2-Aminofluoren-9-ol (2a) from 2-Aminofluorenone (1e):
Compound **1e** (3.9 g, 0.02 mol) was mixed with 95% ethanol (1 l), 85% hydrazine hydrate (50 ml), and Raney nickel (~1 g, wet). The mixture was heated on a steam bath for 30 min, and filtered. Concentration and work up as above gave the product.

5-Nitro-2,4,7-trichlorofluorenone (1c):
5-Nitro-2,4,7-trichlorofluorene[8] [47 g, 0.15 mol; prepared by nitration of 2,4,7-trichlorofluorene with nitric acid (d 1.42) and sulfuric acid in acetic acid; m.p. 253–254° (Ref.[3], m.p. 253°)] was suspended in hot acetic acid (2.5 l). To the stirred boiling suspension, sodium dichromate dihydrate (250 g) was added portionwise over a period of 15 min. After 1 hr of boiling, the reaction mixture was diluted with water. The product was recrystallized from 95% ethanol; yield: 44.8 g (91%); m.p. 145.5–146.5°.

$C_{13}H_4Cl_3NO_3$ (328.54) calc. C 47.52 H 1.23 N 4.27; found 47.50 1.39 4.17

5-Amino-2,4,7-trichlorofluorenone (1f):
Compound **1c** (32.9 g, 0.1 mol) was mixed with tin(II)-chloride dihydrate (400 g) by grinding. The mixture was then heated with stirring in conc. hydrochloric acid (1.5 l) and 95% ethanol (0.4 l) to a gentle boiling, and continuously boiled for 15 min, and

cooled. The reaction mixture was treated with 8% aqueous sodium hydroxide (12 l) and the product was collected by filtration and recrystallized from toluene; yield: 25.8 g (86%); violet needles, m.p. 252–253°.

$C_{13}H_6Cl_3NO$	calc.	C 52.30	H 2.26	N 4.70
(298.55)	found	52.27	2.14	4.82

Supported by a grant (CA-01744) from the National Cancer Institute.

The authors thank Carol-Ann Cole for running the T.L.C. and for the preparation of 2,4,7-trichlorofluorene.

Received: November 26, 1971

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[8] Schidlo and Sieglitz reported this compound as 5(?)-nitro-2,4,7-trichlorofluorene, see Ref.[3]. We have substantiated the position of the nitro group by reducing and dechlorinating this compound with hydrazine hydrate and palladium on charcoal to 4-amino-fluorene, by a procedure described in H.-L. PAN, T. L. FLETCHER, J. Heterocyclic Chem. **7**, 597 (1970).