# A Novel Synthesis of 9,9'-Bifluorenylidene

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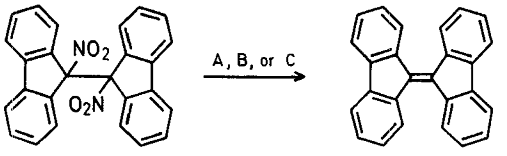
9,9'-Bifluorenylidene (**2**) was usually prepared from 9-bromofluorene[1], or 9,9-dichlorofluorene[2]. No methods for the synthesis of **2** from 9,9'-dinitro-9,9'-bifluorenyl (**1**) have been described. The present communication describes the preparation of **2** by the denitration of **1** with tin(II) chloride dihydrate, or anhydrous tin(II) chloride, or tin(II) alkoxide.

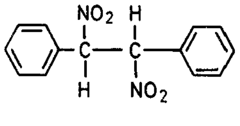


**1** **2**

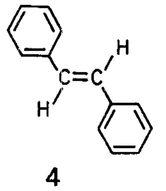
Method A: $SnCl_2$; 98% yield;
Method B: $SnCl_2 \cdot 2H_2O$; 95% yield;
Method C: $Sn(OR)_2$; R = $CH_3$, $C_2H_5$; 96% yield.

Compound **1** was conveniently prepared from 9-bromo-9-nitrofluorene and the potassium salt of 9-nitrofluorene in satisfactory yields. The methods reported for its preparation all afford the mixture of **1** with fluorenone, from which the separation is cumbersome, and yields are low[3]. Compound **1** was smoothly converted into **2** by refluxing with tin(II) chloride dihydrate, or anhydrous tin(II) chloride, or tin(II) alkoxide in ethanol for a short time. In this method, it is necessary to use a fourfold molar quantity of the tin(II) compound.

The I.R., U.V., and N.M.R. spectra of **2** thus prepared were identical with those of the authentic sample (m.p. 188–190°) which was prepared from 9-bromofluorene according to the method of Fuson and Porter[1], and furthermore, **2** was converted into 9,9'-bifluorenyl (m.p. 242–243°, lit.[4] 243–244°) on treatment with zinc dust and aqueous ammonia in ethanol. This method could also be applied for the preparation of an alkene such as *trans*-stilbene (**4**) from the corresponding *vic*-dinitro compound **3** (*dl*-1,2-dinitro-1,2-diphenylethane).



**3**



**4**

Several attempts to obtain an aliphatic alkene such as 2,3-dimethyl-2-butene and 1,1'-bicyclohexylidene by treating the corresponding aliphatic *vic*-dinitro compounds (2,3-dimethyl-2,3-dinitrobutane and 1,1'-dinitrobicyclohexyl, respectively) failed under these conditions. This method therefore seems to be applicable only to the synthesis of aromatic alkenes from the corresponding aromatic *vic*-dinitro compounds from which intermediary radicals – stabilized by the aromatic rings – could be formed by the denitration. The following procedure is typical.

**9,9'-Dinitro-9,9'-bifluorenyl (1):**
9-Bromo-9-nitrofluorene[5] (1.45 g, 5 mmol) in dimethyl sulfoxide (5 ml) is added to the potassium salt of 9-nitrofluorene[6] (1.25 g, 5 mmol) suspended in dimethyl sulfoxide (10 ml) and the mixture is maintained at room temperature for 2 h under a nitrogen atmosphere, and is then was poured into ice/water. The precipitate was collected by filtration, dried, and recrystallized from benzene; yield: 1.87 g (89%); m.p. 175° (lit.[3] m.p. 181–182°).

**9,9'-Bifluorenylidene (2):**
A mixture of **1** (1.05 g, 2.5 mmol), tin(II) chloride dihydrate (2.26 g, 10 mmol) and 99.5% ethanol (30 ml) was heated to reflux for 1 h. The color of the reaction mixture turned red and precipitates formed. After removal of a large portion of the ethanol from the mixture by evaporation in vacuo, water was added to the residue. The precipitate, thus formed, was collected by

iltration and recrystallized from ethanol; yield: 0.78 g (98%); n.p. 182–183°.

H-N.M.R. ($CDCl_3$, TMS): $\delta=7.12$ (m, 8H), 7.61 (d, 4H), 8.31 pm (d, 4H).

J.V. (dioxan): $\lambda_{max}=458$ (log $\varepsilon=4.37$), 272 nm (4.59).

*rans*-**Stilbene (4)**:

\ mixture of **3**[7] (1.37 g, 5 mmol), anhydrous tin(II) chloride 3.79 g, 20 mmol), and 99.5% ethanol (30 ml) was refluxed for l h. After removal of a large portion of the ethanol, the residue vas diluted with water, the product isolated by filtration, and ecrystallization from ethanol to give pure **4**; yield: 0.86 g (96%); n.p. 123–124° (lit.[8] m.p. 123–124°).

Received: December 10, 1974
(Revised form: March 10, 1975)

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