An Efficient Synthesis of Triphenylene

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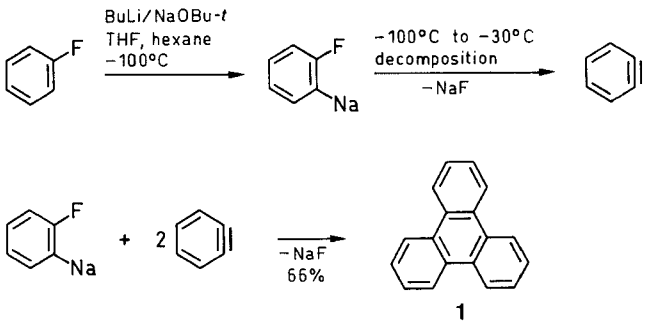
Triphenylene (**1**) has been obtained in 66% yield by decomposition of 1-fluoro-2-sodiobenzene. The corresponding *ortho*-lithio, potassio and caesio compounds gave mainly other, unidentified products.

Triphenylene (**1**) can be obtained by ring closure or dehydrogenation of polycyclic compounds. Yields are often high but a serious draw-back of these syntheses is that the precursors are not simply available.[1] Another synthetic principle involves the decomposition of (in situ prepared) *ortho*-metalated halobenzenes.[2] Triphenylene can be synthesized in reasonable yields from the readily available *o*-bromoiodobenzene and lithium, but the results are variable and dependent on a number of factors.[3] Wittig and Knauss[4] obtained **1** in 20% yield from the reaction of *o*-bromofluorobenzene with magnesium in tetrahydrofuran. Heaney et al.[5] reported a yield as high as 85% for the same conversion, but our results were comparable with those of Wittig and Knauss.

In a previous communication we reported on the facile *ortho*-metalation of fluorobenzene with equimolar mixtures of butyllithium and potassium *tert*-butoxide in tetrahydrofuran.[6] During a study on the decomposition of *o*-fluorolithiobenzene and analogues with a heavier alkali metal we noticed that sodiated fluorobenzene decomposed more easily than the other metal derivatives. Analysis of the resulting mixture revealed that appreciable amounts of **1** were present in the product, whereas in the other cases only minor amounts were formed.



Scheme 1

The isolated yield of **1** appeared to depend strongly upon the rate at which the temperature was allowed to rise, after in the region above −40 °C the decomposition had become clearly observable by the heating effect. Moderate yields were obtained when by efficient cooling the temperature was allowed to rise to over 0 °C over periods of 15 to 30 minutes. More than 60% yield could be obtained by quickly immersing the reaction flask completely in a bath with liquid nitrogen as soon as (at ca. −30 °C) the temperature had begun to rise very fast: nevertheless the temperature rose within a few seconds to ca. 20 °C. The fast decomposition of the metalated fluorobenzene may give rise to a high concentration of benzyne and hence to a high yield of **1**.

Triphenylene (1):
In a 500 mL three-necked round-bottomed flask, equipped with a mechanical stirrer, thermometer and dropping-funnel (in combination with gas-inlet and -outlet, respectively) a solution of BuLi (0.10 mol) in hexane (63 mL, 1.6 molar solution) was cooled to below −50 °C. Fluorobenzene (11.5 g, 0.12 mol) was added and the mixture was further cooled with liquid N_2 to −100 °C. Then a solution of NaOBu-*t* (9.6 g, 0.10 mol) in THF (100 mL) was added over a few min with efficient stirring while maintaining the temperature between −90 °C and −100 °C. The temperature of the light-yellow, clear mixture was allowed to rise to −30 °C within 10 min (occasional cooling may be neccessary). At this point when a strongly exothermic reaction was observed the flask was *promptly* immersed completely in a bath with liquid N_2 (when no cooling is applied, the temperature may rise to over 60 °C and part of the mixture may be splashed out of the flask due to the rapid evolution of butane). The temperature rose over a few seconds to 20 °C. The black slurry was then treated with ice (100 mL) and, after separation of the layers, extraction with Et_2O (3 × 50 mL) was carried out. The combined organic fractions were dried ($MgSO_4$) and subsequently concentrated in vacuo. Crystallization of the remaining solid from CCl_4 gave triphenylene (**1**) as white needles: 5.0 g (66%); mp 189–191 °C, Lit.[4,5] 189–191 °C; NMR spectroscopy on a Bruker AC300 spectrometer in CS_2/C_6D_6 (10%).

^{1}H NMR: δ = 7.45 (6 H, dd, J = 9.6, 3.3), 8.41 (6 H, dd, J = 9.5, 3.4).

^{13}C NMR: δ = 123.7, 127.5, 130.1.

NMR data are in accordance with literature.[7]

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