Hexadecarboxylative Synthesis of Hexaazatriphenylene

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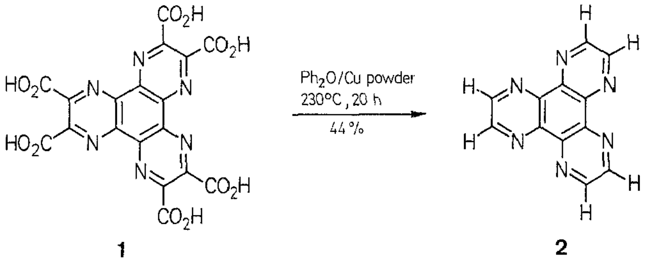
Thermal decarboxylation of hexaazatriphenylene hexacarboxylic acid (**1**) in diphenyl ether (230 °C for 20 h) with added copper powder affords the parent heterocycle, hexaazatriphenylene, in 44 % yield after filtration through an alumina plug.

Hexaazatriphenylene (**2**; abbreviated HAT) is a highly symmetrical heterocycle first synthesized by Nasielski-Hinkens *et al.* that has been used to prepare polynuclear chromium carbonyl complexes.[1] This ligand, while of potential utility in the synthesis of other polynuclear complexes, has not until recently become readily accessible. The original synthesis[1] is on the order of ten steps long. A shorter route was conceived by Kohne and Praefcke as proceeding from a triple condensation of glyoxal with the known hexaaminobenzene (HAB), but this reaction lead to HAT in only very low yield (related hexaalkyl derivatives could be obtained in good to excellent yield however).[2] Most recently, Rogers has reported that this reaction can be accomplished in good yield by using a modification of this procedure.[3] This most recent paper prompts us to describe our own method for the synthesis of HAT at this time. While the method described using HAB as starting material is a valuable one, it does suffer from the disadvantage that the immediate precursor to HAB, namely 1,3,5-triamino-2,4,6-trinitrobenzene, is a military explosive and potentially subject to detonation. Under some circumstances, this may be an unacceptable drawback.



1 **2**

We now report that HAT may be prepared *via* the hexadecarboxylation of HAT$(COOH)_6$ (**1**), a compound whose synthesis we have reported *via* a three-step sequence.[4] Thermal decarboxylations of heterocyclic α-carboxylic acids have long been reported as preparatively useful in, for example, the pyrazine series: the mono-, di-, tri-, and tetracarboxylic acid derivatives of 1,4-pyrazine all afford pyrazine itself under appropriate conditions.[5] While a variety of conditions have been employed for this general reaction (e.g., heating in dibutyl phthalate, glacial acetic acid, or other solvents) and examined by us, the decarboxylation of hexaacid **1** occurs best in diphenyl ether with added copper powder. Heating under these conditions at 230 °C for 20 h in an inert atmosphere affords HAT in 44 % yield after filtration through an alumina plug. The resulting solid sample is identical to HAT prepared as previously described in every respect, and is of analytical purity.

This route, which is four steps from commercially available precursors, does not involve the intermediacy of potentially explosive precursors and may be preferable to that reported recently[3] in some situations.

1,4,5,8,9,12-Hexaazatriphenylene (2):

A mixture of hexaazatriphenylene hexacarboxylic acid[4] (**1**; 1.0 g, 4.2 mmol), copper powder (0.2 g), and freshly distilled diphenyl ether (25 mL) is stirred at 230 °C for 20 h under a dry nitrogen atmosphere. The reaction is then cooled and filtered, and the solid is washed with hexane (3 × 50 mL) to remove adsorbed diphenyl ether. The crude solid sample is added to the top of a short column of neutral alumina and eluted with $CHCl_3$. The single band is collected and the solvent evaporated to afford **2** as a light yellow solid; yield: 210 mg (44 %) mp > 360 °C (Lit.[1] mp > 350 °C).

The product is identical to an authentic sample[3] in all respects.

$C_{12}H_6N_6$	calc.	C 61.53	H 2.58	N 35.88
(234.2)	found	61.20	2.68	35.77

Funding for this work via a grant from the Army Research Office is acknowledged with gratitude.

Received: 15 April 1987; revised: 13 July 1987

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