

Account / Revue

Reactions between aliphatic amines and [60]fullerene: a review

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Abstract

A review of [60]fullerene–aliphatic amine chemistry is presented. While a detailed understanding of the chemistry between [60]fullerene and aliphatic amines was slow to develop, steady progress on both synthetic and mechanistic fronts now enables the fullerene chemist to prepare a variety of well-defined aminated [60]fullerene structures in good to excellent yield. *To cite this article: G.P. Miller, C. R. Chimie 9 (2006).*

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1. Introduction

Soon after the discovery of a method to produce [60]fullerene in bulk quantities [1], scientists worldwide began exploring its fascinating chemistry. One of the very first reactions investigated was that between [60]fullerene and aliphatic amines [2]. Primary and secondary aliphatic amines add readily and repeatedly across [60]fullerene. Tertiary aliphatic amines were soon thereafter shown to undergo photocycloadditions across [60]fullerene [3]. Despite the potentially rich chemistry available via reaction with a wide range of aliphatic amine structures, a detailed understanding of the chemistry between aliphatic amines and [60]fullerene was slow to develop. This was due to the difficulty in char-

acterizing the frequently complex product mixtures as well as a poor understanding of the reaction mechanisms involved. Slowly but surely, these obstacles are lifting. Recent synthetic advances include conditions for the formation of well-defined tetraamino epoxide adducts in excellent yield [4]. Mechanistic insights include the realization that singlet oxygen plays a significant role in the photocycloaddition of tertiary amines [5], and perhaps in other reactions as well. Closely related to aliphatic amine additions are the reactions between [60]fullerene and aliphatic polyamines. At low temperatures, the chemistries involving polyamine are quite similar to their mono- and diamine counterparts. At elevated temperatures, however, polyamines have been shown to be useful reagents for the preparation of highly hydrogenated [60]fullerenes [6]. Diethylene triamine in particular is an effective hydrogenation reagent for the regioselective formation of C_{3v} C₆₀H₁₈ in excellent yield.

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2. Addition of primary and secondary aliphatic amines

Wudl et al. were the first to report the rich chemistry between [60]fullerene and aliphatic amines like *n*-propylamine, *n*-dodecylamine, *tert*-butylamine, and morpholine [2]. These and other primary and secondary aliphatic amines add readily and repeatedly across [60]fullerene producing complex reaction mixtures composed of numerous structures and isomers. Each amination reaction reportedly adds the elements R(R') N and H across a π -bond on [60]fullerene (Fig. 1). A number of regiochemistries are possible but available evidence (*vide infra*) suggests that hydroaminations prefer either a 1,2- or a 1,4-addition. The number of amine additions seems to be a function of the amine, the conditions of the experiment, and the solubility of the resulting products. Thus, products from the morpholine reaction precipitate from neat morpholine solution after approximately six additions [2,7] while smaller amines like *n*-propylamine add a dozen times without precipitation. Aqueous solutions of dimethylamine have been utilized to add approximately 10 equivalents of dimethylamine under biphasic conditions ($\text{H}_2\text{O}/\text{CHCl}_3$) without precipitation of product [8]. Unless oxygen is rigorously excluded, it will be incorporated into the product structures (*vide infra*).

Soon after the discovery of this potentially rich chemistry, a morpholine adduct of [60]fullerene with stated formula $\text{C}_{60}\text{H}_6(\text{morph})_6$ was reported to undergo multiple, rapid, nearly degenerate [1,5]-sigmatropic hy-

drogen shifts (i.e. 'globe-trotting' hydrogen) on the [60] fullerene surface [7] as judged by variable temperature NMR studies. This dynamic behavior, however, was later shown to be due to temperature and dilution dependent hydrogen bonding interactions between amine moieties on the fullerene surface and residual water, not globe-trotting hydrogen. Thus, Miller et al. demonstrated [8] that the NMR signals attributed to globe-trotting hydrogens could be completely removed upon the addition of 3 Å molecular sieves and returned again upon spiking samples with additional water. Moreover, dilution dependencies ruled out an intramolecular process.

While the complex product mixtures generated upon reacting [60]fullerene with excess primary or secondary aliphatic amine are problematic to characterize, Kampe et al. reported a simple method [9] for the generation of well-defined amine addition products using secondary diamines like *N,N'*-dimethylethylenediamine or piperazine (Fig. 2). The chemistry utilizes a modest excess of diamine and produces both mono- and bisadducts in overall 50–85% corrected yields (i.e. corrected for total quantity of [60]fullerene consumed). The bisadducts thus formed have been carefully isolated and characterized [9,10]. Butts and Jazdyk later demonstrated the photocycloaddition of substituted piperazines in good yield [11]. They demonstrated that substituted piperazines can be employed for the introduction of a large variety of additional functional groups including alcohol, ether, amide, and ester groups. Interestingly, the products of diamine addition, whether prepared by ther-

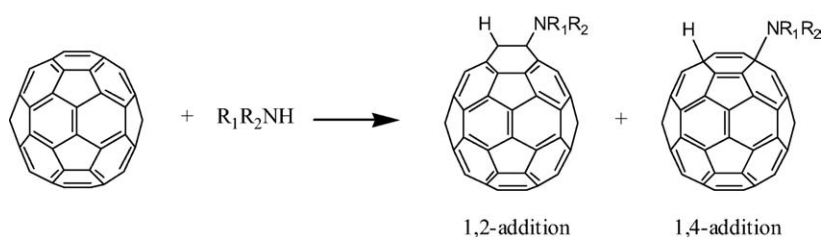


Fig. 1. Hydroamination of [60]fullerene with primary or secondary aliphatic amines.

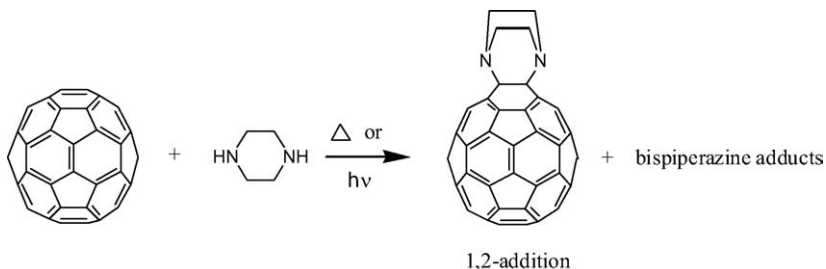


Fig. 2. A 1,2-addition of piperazine across [60]fullerene. See Refs. [9–11].

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