Nanotube Synthesis

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One-Step Conversion of Aromatic Hydrocarbon Bay Regions into Unsubstituted Benzene Rings: A Reagent for the Low-Temperature, Metal-Free Growth of Single-Chirality Carbon Nanotubes**

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In principle, the Diels–Alder cycloaddition of acetylene to a bay region on the rim of a suitable cylindrical hydrocarbon template, and subsequent loss of two hydrogen atoms, could serve as the basis for an iterative reaction sequence leading to the controlled chemical synthesis of either armchair or chiral single-walled nanotubes (SWNTs) of predefined diameter and (n,m) index (Figure 1).[1,2] The lack of intervention required at intermediate stages would make "growing" carbon nanotubes in this manner conceptually akin to a metal-free living polymerization.[3]

As our research group has recently demonstrated, Diels–Alder cycloaddition reactions in the bay regions of polycyclic aromatic hydrocarbons (PAHs) that resemble strips of nanotube sidewalls can occur readily at temperatures below 150 °C, provided that a sufficiently reactive dienophile is used.[1] With acetylenedicarboxylic ester as the dienophile, the highly exothermic aromatization of each newly formed six-membered ring occurs spontaneously by loss of the two original bay region hydrogen atoms (see Figure 1), even in the absence of oxidizing agents.[4,5] For the growth of nanotubes from hydrocarbon templates as envisioned here, however, each Diels–Alder cycloaddition/rearomatization cycle must leave a new unsubstituted benzene ring (i.e. a new ring bearing only hydrogen atoms). Unfortunately, the parent acetylene molecule, C_2H_2, behaves poorly as a dienophile in Diels–Alder reactions, even when presented with far more reactive dienes.[6] We are especially pleased, therefore, to report our finding that the direct conversion of aromatic hydrocarbon bay regions into new unsubstituted benzene rings can be achieved in one operation by the action of nitroethylene, a potent dienophile that serves as a "masked acetylene" in this demanding new context.

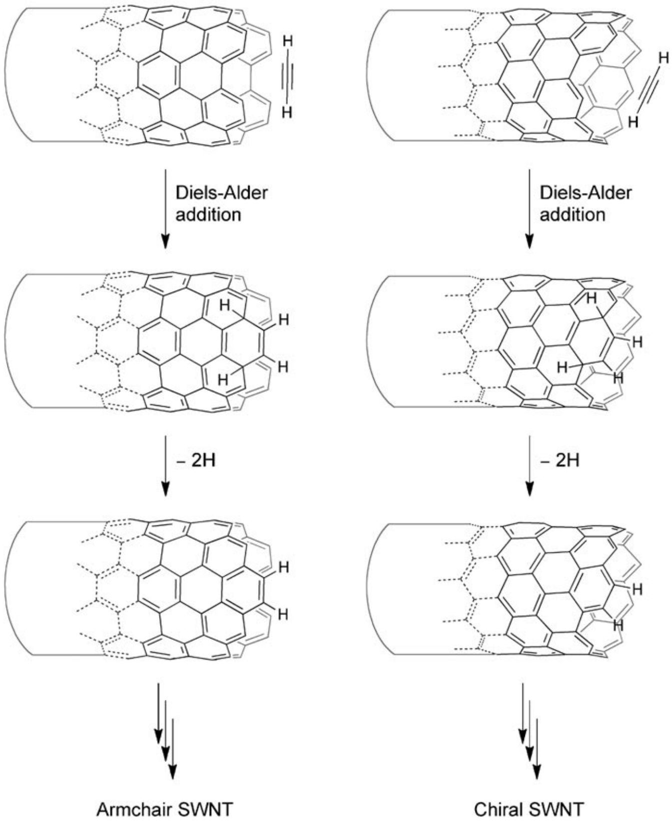

Figure 1. Proposed application of the Diels–Alder reaction to chemical syntheses of uniform single-walled nanotubes (SWNTs).

Nitroethylene can be obtained in the pure state (yellow liquid, b.p. = 98.5 °C), but it polymerizes readily;[7] consequently, it is often generated in situ from 2-nitroethanol by dehydration with phthalic anhydride.[8] We have recently introduced 7,14-dimesitylbisanthene (**1**) as a soluble model compound that has bay regions with reactivity comparable to that predicted for bay regions on the rims of hydrogen-terminated carbon nanotubes.[1] Heating hydrocarbon **1** in toluene with an excess of nitroethanol and phthalic anhydride (1:1, 135 °C, 24 h) gave the doubly benzannulated hydrocarbon, 7,14-dimesitylovalene (**2**), in a yield of 84 % for the isolated product (Scheme 1 a). Both bay regions are converted into new unsubstituted benzene rings in a single operation. Even perylene (**3**), a notoriously sluggish Diels–Alder reaction partner,[1] was converted into benzo[*ghi*]perylene (**4**) by nitroethylene, albeit much more slowly (Scheme 1 b).[9,10] Freshly prepared nitroethylene can also be used to convert **1** into **2**, although no advantage was gained (see the Supporting Information).[11]

The concept of using masked acetylenes to add the elements of C_2H_2 in Diels–Alder reactions is not new. Most of

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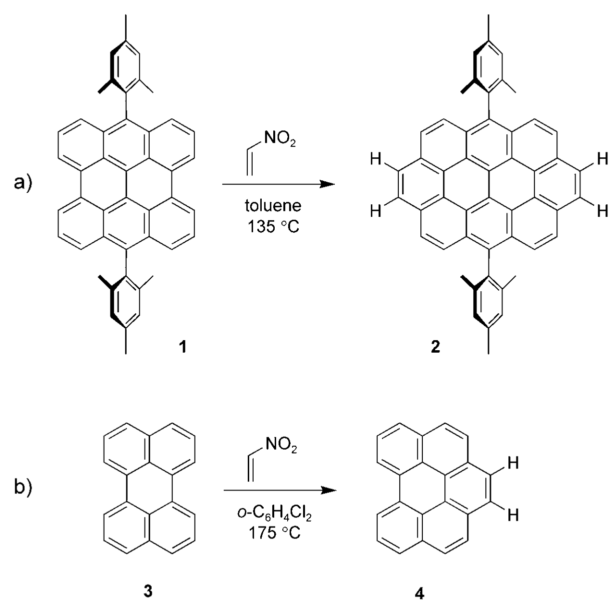


Scheme 1. One-step conversion of aromatic hydrocarbon bay regions into new unsubstituted benzene rings by nitroethylene, generated in situ from 2-nitroethanol by dehydration with phthalic anhydride.

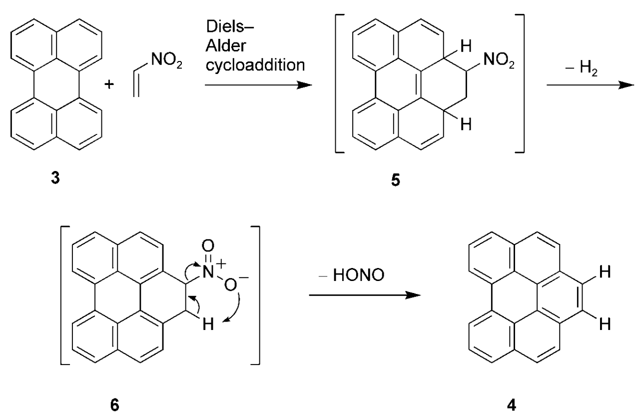
the reagents that have been introduced for this purpose, however, require that a separate reaction be performed on the initial cycloadduct to strip away everything but the desired C_2H_2 unit.[12] Unfortunately, two-stage protocols preclude the use of such acetylene equivalents as feedstock for growing carbon nanotubes by the polymerization strategy outlined in Figure 1.

Among the many masked acetylenes now available, there is only one that does not suffer the drawback of a mandatory intervention. Cleverly designed by Paquette et al. in 1978,[13] phenyl vinyl sulfoxide adds in Diels–Alder fashion to normal 1,3-dienes, and the initial cycloadducts then fragment under the reaction conditions by a thermal *syn* elimination of the sulfoxide to unmask the final product of net C_2H_2 addition. Our hopes for this reagent were quickly dashed, however, by the discovery that phenyl vinyl sulfoxide polymerizes/decomposes faster than it adds to perylene (**3**) in Diels–Alder fashion when the two are heated together neat at 155 °C ($<10\,\%$ cycloaddition in 4 days, see the Supporting Information). The sulfoxide functional group, unfortunately, does not activate this dienophile enough to enable such a difficult cycloaddition. Vinyl selenoxides are even worse dienophiles.[14]

With the more reactive bisanthene **1**, phenyl vinyl sulfoxide did add and then spontaneously fragmented to yield the doubly benzannulated product **2**; however, the reaction was far slower, much less clean, and less efficient than with nitroethylene (see supporting information). Fluoroalkyl vinyl sulfoxides exhibit modestly greater dienophilicity than phenyl vinyl sulfoxide, as predicted by theory, but the fluoroalkyl groups retard the subsequent sulfoxide elimination.[15] We were led to examine nitroethylene by calculations that predict a $>10\,000$-fold rate increase for its Diels–Alder cycloaddition to perylene (**3**) at 135 °C, relative to that for phenyl vinyl sulfoxide ($\Delta E_a = 8.8\ \text{kcal mol}^{-1}$, B3LYP/6-31G*; see the Supporting Information).

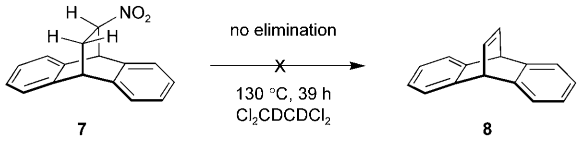
In qualitative agreement with this calculated difference in reactivity, we have observed that diphenylisobenzofuran reacted with nitroethylene and gave the Diels–Alder adduct with a half-life of about 80 seconds at room temperature, whereas the reaction with phenyl vinyl sulfoxide at the same concentrations proceeded with a half-life of about 65 minutes at 100 °C. As an indication of where nitroethylene falls on the reactivity scale with respect to more familiar dienophiles, the same reaction with dimethyl acetylenedicarboxylate proceeds with a half-life of about 50 minutes at room temperature (see the Supporting Information).

How does nitroethylene bring about these direct benzannulations? The overall process actually involves three distinct steps (Scheme 2). The potency of nitroethylene as a dienophile facilitates the first step, but that is only the beginning. Thermal [4+2] cycloreversion reactions of dihydrogen are rare but well documented,[5] so the rearomatization step (**5**→**6**) is not unexpected. The final loss of HONO, on the other hand, (**6**→**4**) deserves an explanation. Thermal *syn* eliminations of the sort suggested in Scheme 2 (**6**→**4**) resemble those of sulfoxides and amine oxides (Cope eliminations), but nitroalkanes do not ordinarily fall apart in this manner at 135 °C. Nonetheless, we anticipated this fragmentation on the grounds that **6** is no ordinary nitroalkane, because 1) the C–H bond being cleaved is benzylic and thereby weak, 2) the C–N bond being cleaved is benzylic and thereby also weak, and 3) the transition state energy for fragmentation should be lowered by the aromatic stabilization of the incipient benzene ring. None of these three factors comes into play until after loss of the two bay region hydrogen atoms. Accordingly, though unproven, it seems likely that the steps occur in the order shown.



Scheme 2. Proposed mechanism for bay region benzannulation.

Actually, most Diels–Alder adducts of nitroethylene are thermally stable and retain the nitro group (e.g. **7** in Scheme 3). The reaction of anthracene with phenyl vinyl sulfoxide continues all the way to dibenzobarrelene (**8**),[13] but the corresponding reaction of nitroethylene stops at **7**. Thus, under normal circumstances, nitroethylene does not behave as a masked acetylene.[16]



Scheme 3. Without benzylic activation of the C–N bond and/or the *syn* C–H bond, thermal loss of HNO_2 is not normally observed.

In summary, we have found that nitroethylene, though not a universal masked acetylene, is uniquely suited for the one-step conversion of reactive aromatic hydrocarbon bay regions into new unsubstituted benzene rings. The challenge now is to design and prepare cylindrical hydrocarbon templates that will be suitable for growth by the "masked acetylene" cycloaddition/rearomatization strategy. Strain effects and electronic considerations will determine the suitability of potential templates. Diels–Alder cycloadditions are expected to be difficult on cycloparaphenylenes,[1e,f,g] for example (cf. biphenyl). Consequently, such short nanotube sections probably cannot be extended by this chemistry, even with nitroethylene. On the other hand strain energy considerations predict that the bay regions of large diameter hydrocarbon templates will undergo Diels–Alder cycloadditions more readily than those of smaller diameter templates. It is our hope that the prospect for low-temperature, metal-free growth of single walled carbon nanotubes of predefined diameter and (n,m) index by the use of nitroethylene as a polymerization feedstock will intensify the quest for suitable hydrocarbon templates.[17]

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[17] Regardless of whether the template is obtained by total synthesis, by fullerene surgery, or from a nanotube prepared another way, the rim must be hydrogen-terminated for this growth strategy to work.