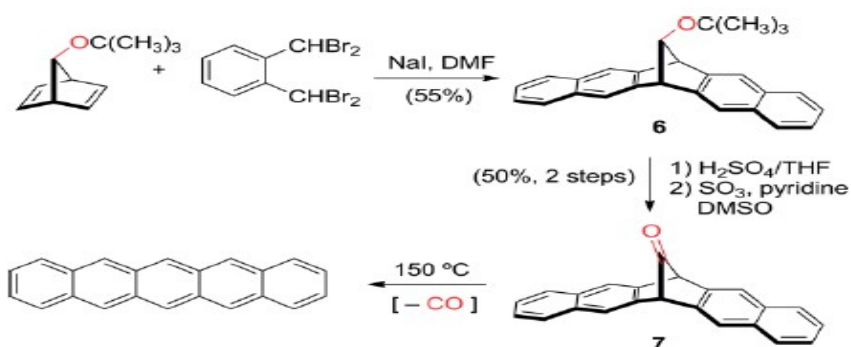


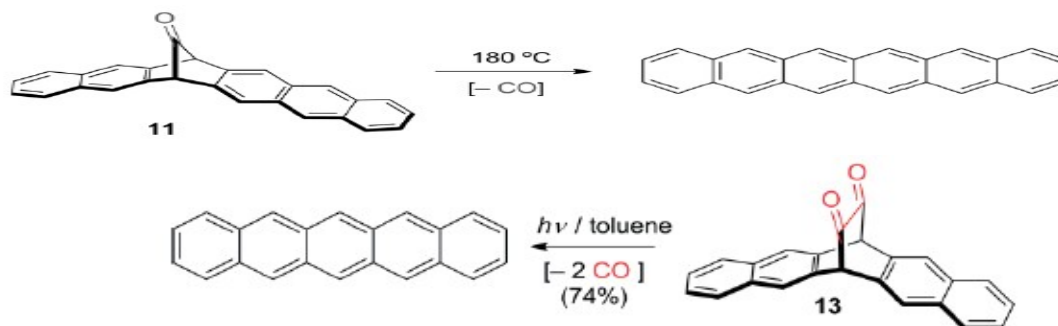
Reversible Diels-Alder Reactions of Acenes

By: Robert B. Login rloginconsulting.com

In a previous proposal, I reviewed the polymerization of some anthracene derivatives. I wondered about the higher acenes like pentacene etc, can they be vinylated and polymerized? But the instability of these acenes to attack by free radicals or environmental hazards like oxygen or UV would degrade said polymers after or before polymerization. Was there a way around this? I became aware that this type of question has been raised in the past.



Scheme 2. Synthesis of pentacene through cheletropic thermal decarbonylation.



The above are from the following excellent review and are just a few examples to make the point about interrupted acenes being stable. For example 13, 11 and 7 are relatively stable until converted to their acenes.

Dorel, R., & Echavarren, A. M. (2017). Strategies for the synthesis of higher acenes. *European journal of organic chemistry*, 2017(1), 14-24.

I also show this interrupted stability in a previous proposal concerning the use of the Bergman Cyclization as a method to produce interrupted acenes. Please see the pdf on my web page(<http://rloginconsulting.com/joomla/images/SiteFiles/Patents/BC%20polymers4.pdf>).

ABSTRACT: The synthesis of 2-vinylanthracene and 2-propenyl-2-anthracene and their polymerizations by free radical, anionic, cationic, and Ziegler techniques have been investigated. 2-Vinylanthracene and 2-propenyl-2-anthracene have been polymerized to high molecular weight polymers ($\overline{M}_n > 10^5$) by anionic addition type initiators. The polymerization reaction must be carried out with high purity monomer at low temperature ($< -40^\circ\text{C}$) to maximize molecular weight. Poly-2-vinylanthracene and poly-2-propenyl-2-anthracene are linear, soluble polymers with conventional vinyl structures. Both polymers undergo facile cross-linking and insolubilization in air/light. The cross-linking appears to result both from oxidation leading to free radicals and photodimerization of anthracene groups.

“Deliberate exposure of monomer to air/light for short periods (5-15 min) resulted in anomalous polymerizations (including total inhibition) and polymeric products. One feature of these vinylanthracene polymers which should be emphasized is their facile photo oxidation and photo cross-linking. The photo-dimerization of anthracenes is well known. In the polymers this reaction leads to rapid insolubilization and polymer handling and characterization requires considerable caution”

Stolka, M., Yanus, J. F., & Pearson, J. M. (1976). Polymerization of Vinylanthracene Monomers. 2. 2-Vinylanthracene and 2-Propenyl-2-anthracene. *Macromolecules*, 9(5), 710-714.

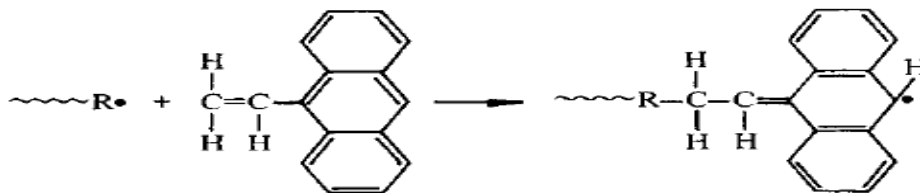
Stolka, M., Yanus, J. F., & Pearson, J. M. (1976). 1. Polymerization of Vinylanthracene Monomers. *Macromolecules*, 9(2), 374-376.

In this last reference, they couldn't FR polymerize 9-vinylanthracene.

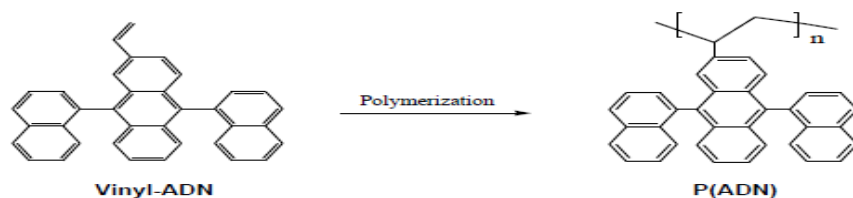
Stolka, M., Yanus, J. F., & Pearson, J. M. (1976). Polymerization of Vinylanthracene Monomers. 3. 1-and 9-Vinylanthracenes. *Macromolecules*, 9(5), 715-719.

“The synthesis of copolymers with anthracenyl groups has been studied by many researchers because of their potential applications as organic semiconductors, photoresist materials, and so on (1-3). However, the radical polymerization of monomers carrying anthracenyl groups is very slow. The propagating macroradicals are stabilized by formation of unreactive dibenzylic radicals which inhibit radical polymerization. Some metal halides such as alkylaluminum halides, stannic chloride, and boron trichloride are known to accelerate the free-radical copolymerization and produce alternating copolymers (3). However, few reports were published on the copolymerization of 9-vinylanthracene with polar vinyl monomers in the presence of metal halides. This paper describes the effect of the addition of ethylaluminum sesquichloride on radical copolymerization of 9-vinylanthracene (9-VA) with methyl methacrylate (MMA).”

“These results show that 9-vinylanthracene undergoes radical isomerization copolymerization with formation of polymer chains consisting mainly of 9-ethylidene-9,10-dihydroanthracene-derivative (its \cdot), as shown in Eq. (1).”



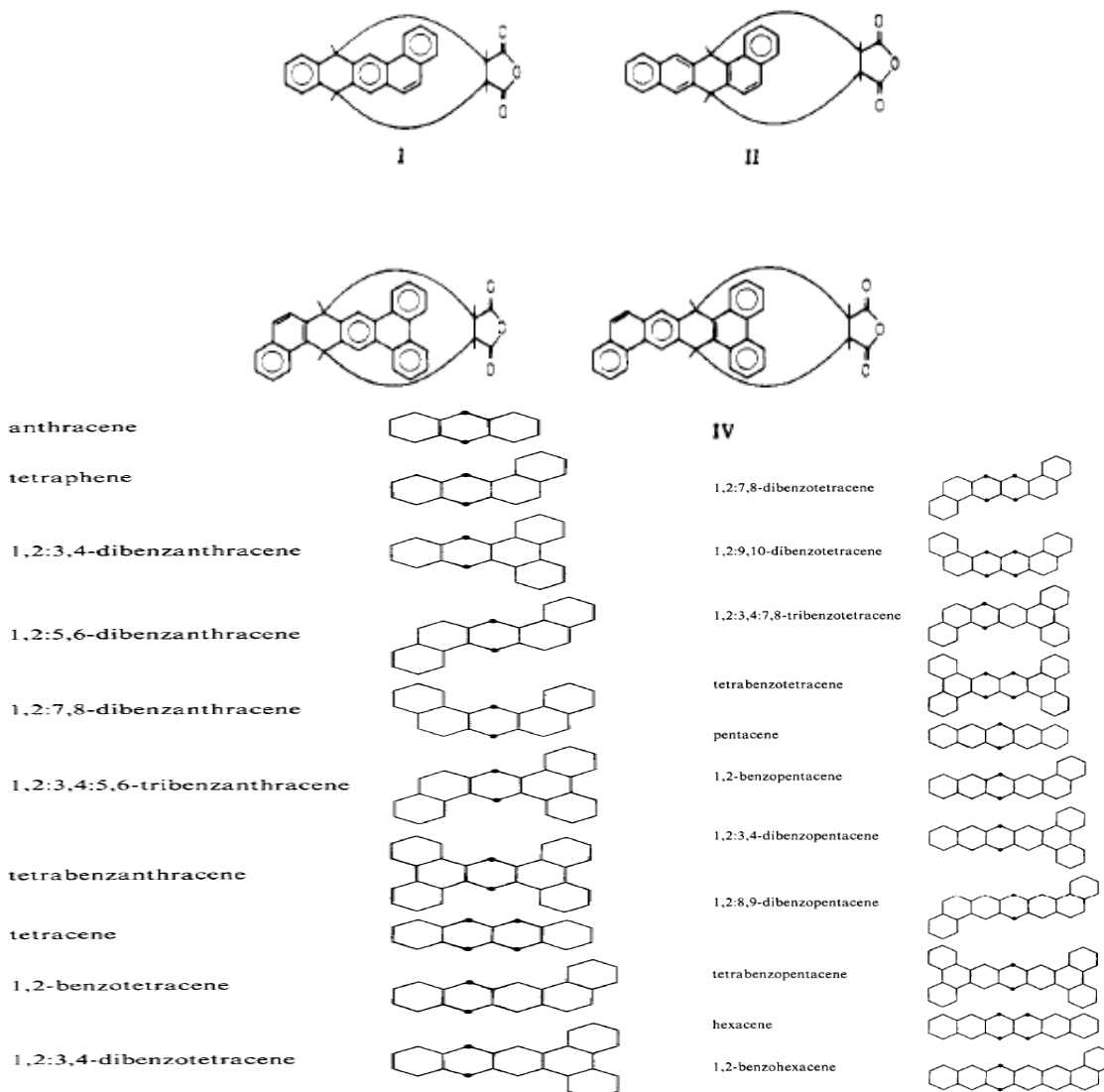
Takeuchi, K., Hanaoka, T. A., Arakawa, H., Matsuzaki, T., Sugi, Y., Takagi, S., & Doi, Y. (1989). Accelerated free radical copolymerization of 9-vinylanthracene with methyl methacrylate using ethylaluminum sesquichloride. *Die*



Scheme 2.1 Synthetic routes for the monomer Vinyl-ADN and its polymers.

Wang, J. (2013). Synthesis and characterization of conductive and soluble side-chain blue fluorescent polymers. This very interesting thesis shows that 2-vinylanthracene derivatives where the 9,10 positions are blocked can be easily FR polymerized.

Why not block the anthracene 9,10 positions with a Diels-Alder adduct? How about the higher acenes? Before getting into this, the first question is where does the DA reaction take place on various acenes?



The dots show where the dieneophiles would attach.

Although there are several methods of determining where the DA dieneophiles attach, the simplest is the Clar method which states that the attachment is where the resulting adduct has the largest number of complete aromatic rings. Anthracene for example is at the 9,10 positions because it is flanked by two complete sextet aromatic rings.

Biermann, D., & Schmidt, W. (1980). Diels-Alder reactivity of polycyclic aromatic hydrocarbons. 1. Acenes and benzologs. *Journal of the American Chemical Society*, 102(9), 3163-3173.

Solà, M. (2013). Forty years of Clar's aromatic π -sextet rule. *Frontiers in chemistry*, 1, 22.

The next thing is what dieneophile to use. What I want is one that is relatively easy to remove once it is no longer needed but stable enough to be employed for its intended application to interrupt the aromaticity. Anthracene is employed as an example.

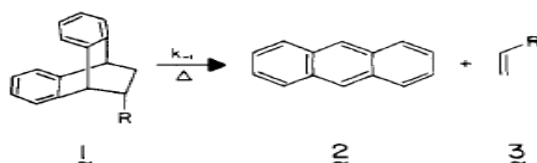


Figure 1.

Table I. First-Order Rate Constants of Retro-Diels-Alder Reactions at 250 °C in Diphenyl Ether

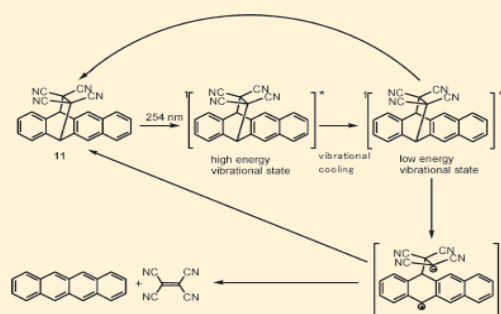
R	rel rate
H	1.00
Me	0.94
Et	0.90
<i>i</i> -Pr	0.80
<i>t</i> -Bu	0.73
Ph	123
SiMe ₃	16.2
CO ₂ H	139
CONH ₂	32.9
CO ₂ CH ₃	57.0
CN	75.9
COCH ₃	179
CHO	251
NO ₂	16.6
NH ₂	82.9
NHAc	13.8
NMe ₂	2480
NMe ₃ ⁺ TsO ⁻	1680
OAc	0.30
OH	1.34
OCH ₃	2.23
OSiMe ₃	2.26

Summary: The retro-Diels–Alder reaction of anthracene cycloadducts is influenced by dienophile substituents in the following ways: (1) electron-withdrawing groups increase the rate of the reaction; (2) strongly conjugating substituents make the reaction *much* faster than predicted by classical electron-withdrawing or -donating ability, in the best case by a factor of 3×10^6 , and (3) there is *no* observable steric effect, in contrast to literature statements to the contrary.

Nanjappan, P., & Czarnik, A. W. (1986). Reversal of electronic substituent effects in the retro-Diels-Alder reaction. A charge neutral analog of oxyanion-accelerated cycloreversion. *The Journal of Organic Chemistry*, 51(14), 2851-2853.

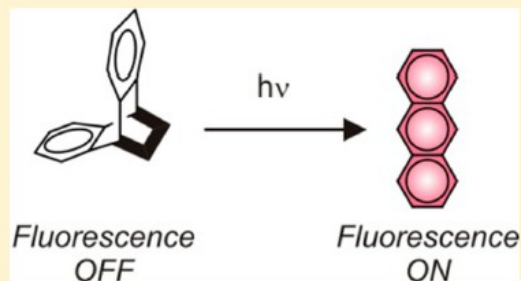
Chung, Y., Duerr, B. F., McKelvey, T. A., Nanjappan, P., & Czarnik, A. W. (1989). Structural effects controlling the rate of the retro-Diels-Alder reaction in anthracene cycloadducts. *The Journal of Organic Chemistry*, 54(5), 1018-1032.

ABSTRACT: Photo-retro-Diels–Alder (PrDA) reactions of a variety of Diels–Alder (DA) adducts were studied. Experimental results showed that the photoreactivity (quantum yield) depends on the electron-donating ability of the diene component and the electron-withdrawing ability of the dienophile component. The mechanism was studied by trapping the reaction intermediate, O_2 quenching, time-resolved absorption, and fluorescence spectroscopy. All the results support a mechanism that involves a charge-separated intermediate generated from a singlet excited state. The PrDA reaction may find applications in photoresponsive materials, photolithography, drug delivery, and mechanistic research.



Johns, V. K., Shi, Z., Dang, W., McInnis, M. D., Weng, Y., & Liao, Y. (2011). Photo Retro-Diels–Alder Reactions. *The Journal of Physical Chemistry A*, 115(28), 8093-8099.

ABSTRACT: Fifteen substituted maleimide cycloadducts of anthracene derivatives were synthesized in one or two steps from available precursors in yields ranging from 32 to 63%. They differ in the nature of the group on the maleimide nitrogen atom and of the substituents on the anthracene platform. In all instances, the introduction of a maleimide bridge across positions 9 and 10 of the anthracene skeleton isolates electronically its peripheral phenylene rings and suppresses its characteristic fluorescence. The cycloadducts with a 4-(dimethylamino)phenyl group on the maleimide nitrogen atom undergo retro-cycloaddition upon ultraviolet illumination with quantum yields ranging from 0.001 to 0.01. This structural transformation restores the aromatic character of the central ring of the oligoacene chromophore and activates its emission with fluorescence quantum yields ranging from 0.07 to 0.85. Thus, this particular choice of building blocks for the construction of photoresponsive compounds can translate into viable operating principles for fluorescence activation and, ultimately, lead to the realization of valuable photoactivatable fluorophores for imaging applications.



Thapaliya, E. R., Captain, B., & Raymo, F. M. (2014). Photoactivatable anthracenes. *The Journal of organic*

chemistry, 79(9), 3973-3981.

Although with a different end use or goal, the above references clearly illustrate the stabilized aromatic that can be safely handled only to be recovered by UV irradiation in its acene form.

The larger acenes are very unstable but they can be handled in their interrupted rDA derivatives. The rDA reaction is ideal for this application. I would employ dieneophiles such as methyl or ethylacrylate etc. to generate DA adducts that can be readily reversed by heat, vacuum, UV etc. to recover the acene. The idea is to formulate said polymeric DA adduct in a film with other ancillary ingredients and then to heat anneal the resulting film to free the acene. The acrylate would be a volatile byproduct and not interfere with the annealed films end use.

The idea interrupting the larger acenes with functionality that is then removed to produce the acene is not new.

Dorel, R., & Echavarren, A. M. (2017). Strategies for the synthesis of higher acenes. *European journal of organic chemistry*, 2017(1), 14-24.

Application of rDA in the final annealing step of organic electronic polymeric candidates is also not a new idea.

Liu, C., Xu, W., Guan, X., Yip, H. L., Gong, X., Huang, F., & Cao, Y. (2014). Synthesis of anthracene-based donor-acceptor copolymers with a thermally removable group for polymer solar cells. *Macromolecules*, 47(24), 8585-8593.

Freudenberg, J., Jänsch, D., Hinkel, F., & Bunz, U. H. (2018). Immobilization strategies for organic semiconducting conjugated polymers. *Chemical reviews*, 118(11), 5598-5689.

However, I see that this has been applied mostly to anthracene derivatives and not other higher acenes. Wouldn't higher polyvinyl acenes produce interesting applications!

So can you DA block an acene like anthracene in the 9,10 position while also substituted with a vinyl group at say the 2 position? Then after FR polymerization, then a rDA to obtain polymerized anthracene or in analogy, other acenes?

Thank you for reading this proposal.
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PS: remember that many acenes are carcinogenic/toxic and must be handled with caution!