

Xylylene Crosslinked Polymers

By: Robert B. Login rloginconsulting.com

Here in is described a proposed method of crosslinking unsaturated polymers or compounds that would retain the unbroken unsaturation by creating an aromatic link after crosslinking. This would be of interest for organic unsaturated compounds empolyed in organic photovoltaics, transistors, CO2 capture, H2 generation and so forth.

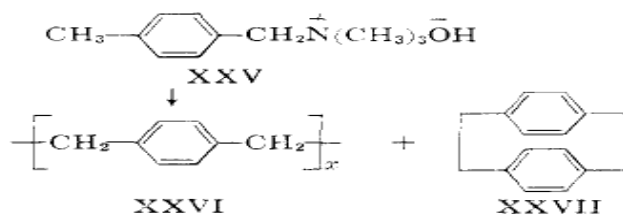
Winberg, early on developed a synthesis of [2,2]paracyclophanes by the Hofmann 1,6 elimination of (2-halo-4-methylbenzyl)trimethylammonium hydroxides.

“Synthesis of [2.2]Paracyclophane by Hofmann

Degradation.—Thermal decomposition of pmethylbenzyltrimethylammonium hydroxide (XXV) occurred at 60-100° under reduced pressure and gave, in addition to poly-[^]-xylylene

(XXVI) , small amount of [2.2]paracyclophane

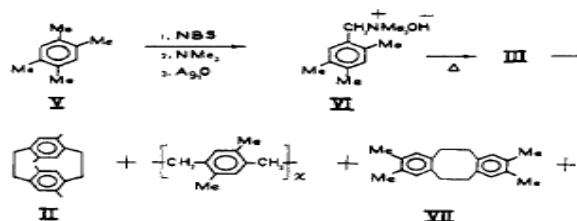
(XXVII) . The latter could be readily extracted from the reaction mixture with hot toluene.”



Synthesis

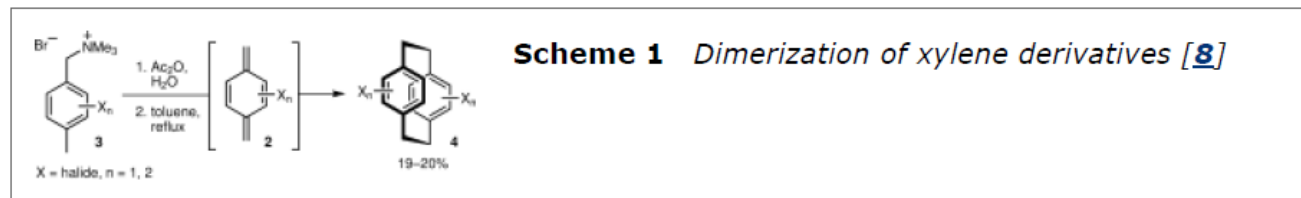
The Hofmann elimination route proved convenient for the preparation of large amounts of II (Scheme I).

Scheme I



Longone, D. T., & Chow, H. S. (1964). Paracyclophanes. IV. A Multilayered [2.2] Paracyclophane. *Journal of the American Chemical Society*, 86(18), 3898-3899.

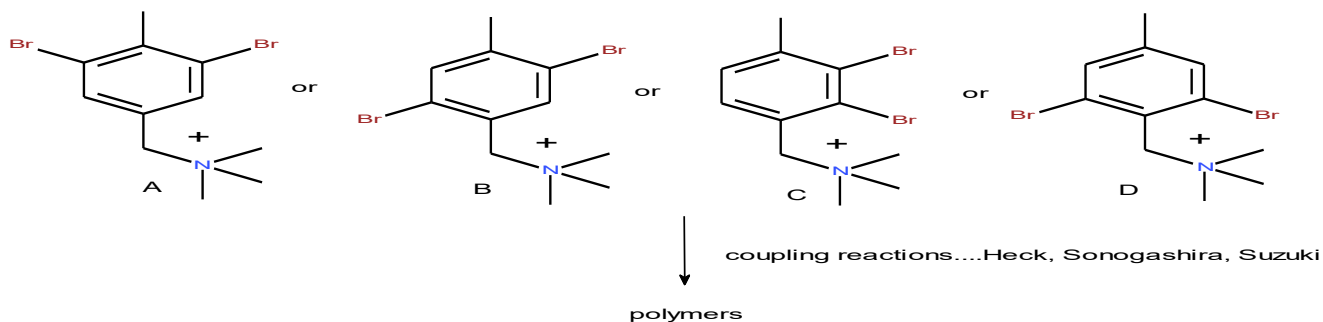
isomeric and polymeric mixtures. Chow demonstrated that xylene derivatives **3** can be selectively dimerized to substituted Pc derivatives **4** according to the Winberg cyclization (Scheme [1]). [8]



Chow, H. F., Low, K. H., & Wong, K. Y. (2005). An improved method for the regiospecific synthesis of polysubstituted [2,2] paracyclophanes. *Synlett*, 2005(14), 2130-2134.

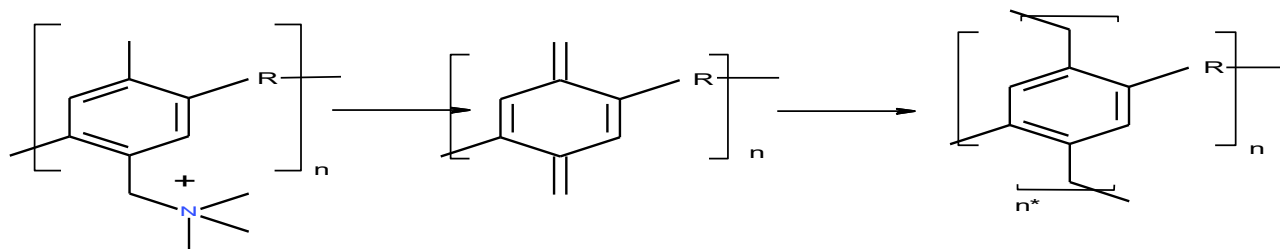
The above references indicate that the polymer is the major product, not the [2,2]paracyclophane. This fact permeates this chemistry as the goal has been to suppress this polymeric byproduct.

Nakano, T. (2014). *pi-stacked polymers and molecules*. Springer Verlag, Japan.



Scheme 1: Potential monomers for Winberg cyclization by 1,6 elimination(see page 196 of the Kakano book for details).

I propose that instead of synthesizing the [2,2]paracyclophane or polymer, the reaction is employed to crosslink conjugated polymers.



Scheme 2: As an example, polymerization of scheme 1B monomer is illustrated. The R unsaturated groups are the result of Pd based coupling reactions of which there are many possibilities. My idea is a unique method of crosslinking these polymers leaving the conjugation intact.

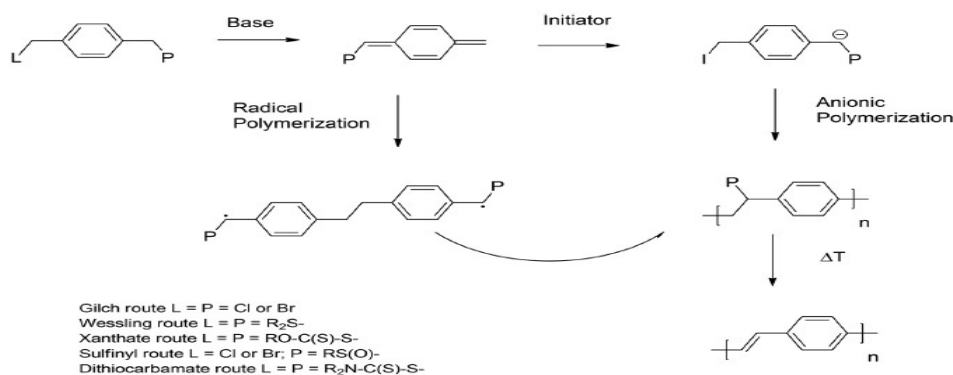
The Winberg cyclization results in the polymer or oligomer being the mayor product. Note that the hydroxide counterion is synthesized with Ag₂O but other workers have used strong ion-exchange to do the same substitution.

Otsubo, T., Mizogami, S., Otsubo, I., Tozuka, Z., Sakagami, A., Sakata, Y., & Misumi, S. (1973). Layered compounds. XV. synthesis and properties of multilayered cyclophanes. *Bulletin of the Chemical Society of Japan*, 46(11), 3519-3530.

Paradies, J. (2011). [2.2] Paracyclophane derivatives: synthesis and application in catalysis. *Synthesis*, 2011(23), 3749-3766.

Apparently, the formation of the xylylene diradical intermediate and then the crosslinking, can take place at reasonable temperatures such as 100C. Since it would be reasonable to assume that not all of the quat monomer would take part in the crosslinking reaction, the resulting crosslinked polymer would still be cationic and a gel.

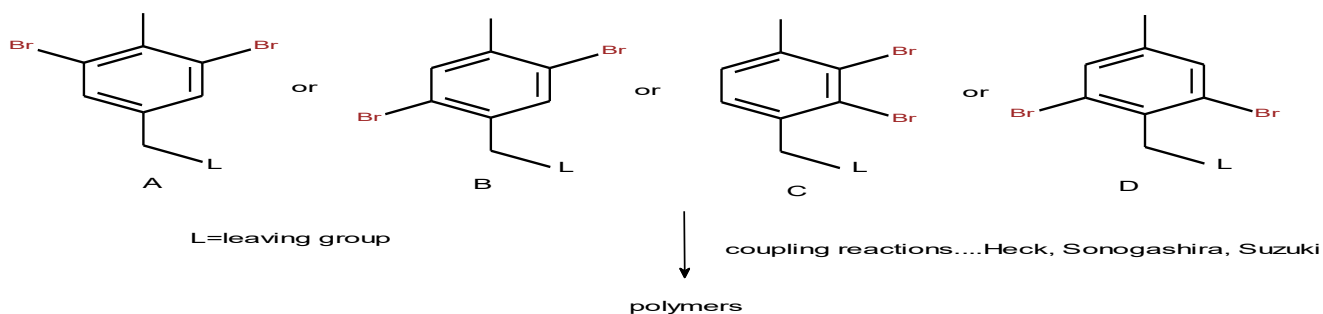
Can other monomers be devised that do not employ the Winberg Hofmann elimination quat but some other leaving group with the proviso that the para-xylylene monomer is monofunctionalized with a good non-polar leaving group. The Gilch reaction does this with a chloride replacing the quat.



Scheme 2 General scheme for the synthesis of PPVs using quinodimethane 'precursor' routes.

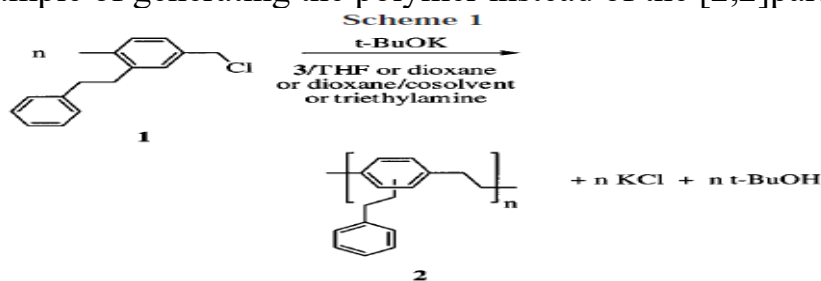
Zaquen, N., Lutsen, L., Vanderzande, D., & Junkers, T. (2016). Controlled/living polymerization towards functional poly (p-phenylene vinylene) materials. *Polymer Chemistry*, 7(7), 1355-1367.

In the above chart both L (leaving group) and P are both attached to the monomer. I propose that employing just L would work the same way as a replacement for the Winberg quat. So instead of the quat. hydroxide, something like a tosylate might work. The main requirement would be additional bromine substitution like in scheme 1 that can function in coupling reactions.

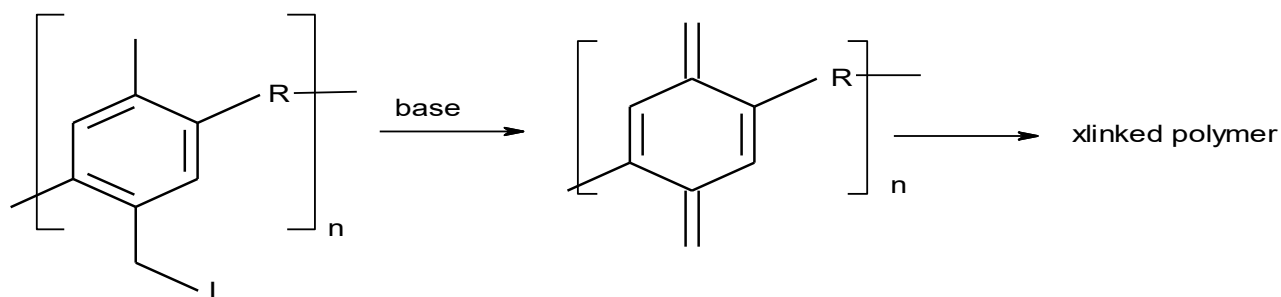


Scheme 3: The L leaving group is not defined but must not interfere with the coupling reactions.

Here is an example of generating the polymer instead of the [2,2]paracyclophane.

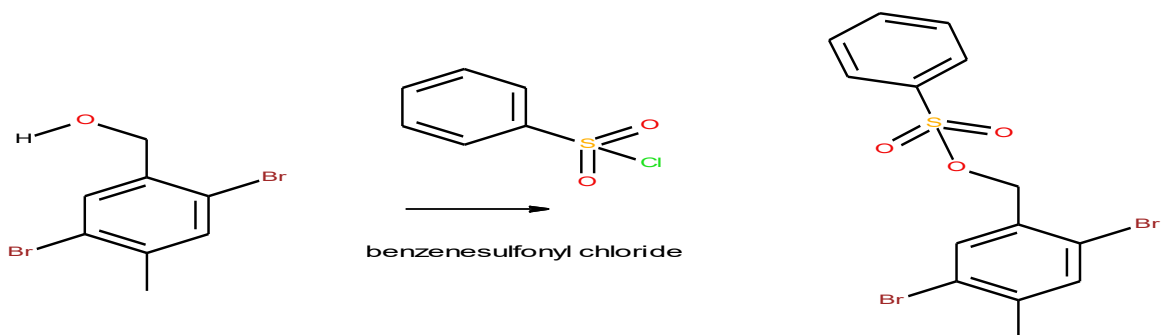


Brink-Spalink, F., & Greiner, A. (2002). Efficient Control on Molecular Weight in the Synthesis of Poly (p-xylylene)s via Gilch Polymerization. *Macromolecules*, 35(9), 3315-3317.



Scheme 4: This is the general idea but there are caveats such as can the R coupling polymer or group tolerate the base required to generate the xylylene crosslinker. There are many reviews of the coupling reactions employed to prepare these polymers. Coupling reactions such as the Stille, Heck, Suzuki are well known and reviewed many times.

However, I propose the following intermediate. It should be soluble in solvents such as toluene and if necessary more polar ones.



(2,5-dibromo-4-methyl-phenyl)methanol

Scheme 5: Proposed monomer example. The hydroxyl can also be converted to a variety of possible leaving groups such as various esters, for example. Some of the coupling reactions will leave these L(leaving) groups alone. See:

Parker and Marder, *Synthetic Methods in Organic Electronic and Photonic Materials; A Practical Guide*, 2015 Royal Soc. Of Chem.. Chap 5

Müllen, K., Reynolds, J. R., & Masuda, T. (Eds.). (2013). *Conjugated polymers: a practical guide to synthesis*. Royal Society of Chemistry.

Leclerc, M., & Morin, J. F. (Eds.). (2010). *Design and synthesis of conjugated polymers*. John Wiley & Sons.

Thank you for reading these proposals.

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