

Fourfold Heck Reactions on the Tetraphenylmethane Tripod: Model Studies Towards Construction of Centrally Based Three Dimensional Networks

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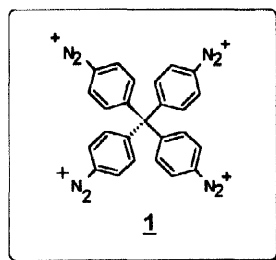
Received 10 October 1997; revised 2 December 1997; accepted 5 December 1997

Abstract: Fourfold Heck reaction on tetraphenylmethane provides a promising 'one-step' synthetic methodology for construction of centrally based three dimensional aromatic networks.

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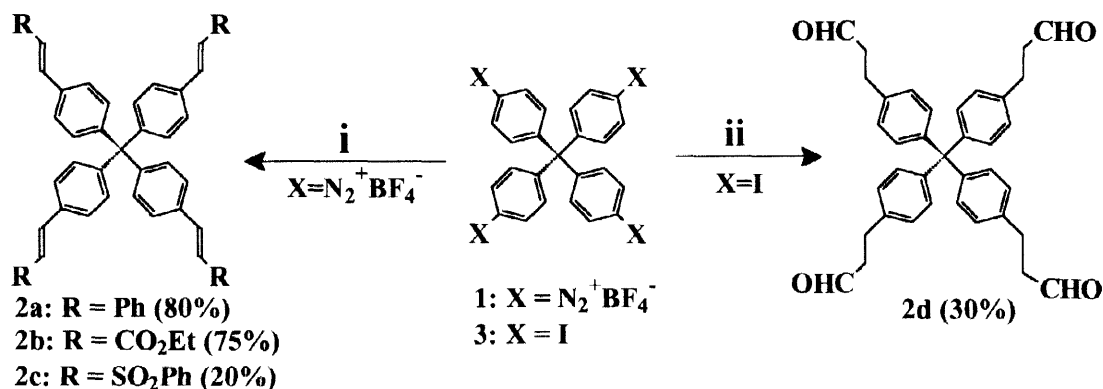
In recent years, much attention has been given to the synthesis of topologically interesting all-carbon networks.¹ Although linear and planar networks are common pursuits in this regard, limited effort has been directed towards construction of *centrally based three dimensional* carbon networks, perhaps due to difficulties in preparing the *tetrahedral* building blocks necessary for such regime. One such building block that have received some attention lately is tetraethynylmethane.² However, tetraethynylmethane is notoriously unstable and is available in small amounts after a lengthy synthetic sequence which considerably diminishes its synthetic appeal. In search of alternative building blocks, it occurred to us that tetraphenylmethane, a robust analog of tetraethynylmethane, could be a better choice for the *tetrahedral* core and envisioned a fourfold Heck reaction³ on its phenyl rings towards synthesis of *centrally based three dimensional* aromatic architectures. This Heck-reaction strategy was synthetically quite attractive since poly-Heck reactions (greater than twofold)⁴ on aromatic polyhalides not only provide a versatile, *one-step* synthesis of polysubstituted aromatics but is also an ideal recipe for network elaborations.

At the outset of this work, virtually nothing was known on fourfold C-C bond forming reactions on tetraphenylmethane, except for a couple of recent reports on Sonogashira-couplings with tetra(*p*-iodophenyl)methane.⁵ Although the latter could very well serve our present purpose, we decided to explore the corresponding *tetrakis*-diazonium salt **1** due to the superior Heck-reactivity of arenediazonium salts *vis-a-vis* aryl halides.⁶ While this study was in progress, Su and Menger⁷ reported a fourfold Stille-vinylation on tetra(*p*-iodophenyl)methane which prompted us to disclose our preliminary results in this Letter.



In the event, tetra(*p*-aminophenyl)methane, the precursor to **1**, was readily prepared from *p*-tritylaniline *via* suitable modifications of a literature procedure⁸ and was converted to the *tetrakis*-diazonium salt **1** through standard diazotization reaction (NaNO₂, conc. HCl, 0°, then NaBF₄). Fourfold Heck reaction on **1** was then carried out under our recently described aqueous-alcoholic reaction conditions (5% Pd(OAc)₂, EtOH-H₂O, 80°, 1h)^{6a} using 7-8 fold excess of styrene or ethyl acrylate as representative olefins which smoothly produced

the tetravinylated products **2a** and **2b** in 80 and 75% yields, respectively (**Scheme 1**).⁹ Phenyl vinyl sulfone also participated in this fourfold Heck reaction, but gave only poor yields (20%) of the tetrastaryl sulfone **2c**. Unfortunately, Heck reaction of **1** with allyl alcohol failed to produce the desired product **2d**. Since the latter was deemed essential for network propagation, for its synthesis, we took recourse to a fourfold Heck reaction on tetra(*p*-iodophenyl)methane **3**⁵ with excess allyl alcohol under Jeffery's PTC- conditions which then produced the highly sensitive tetraaldehyde **2d** in 30% isolated yield.



Scheme 1: i) 5% Pd(OAc)₂, EtOH-H₂O, CH₂=CHR, 80°, 1h; ii) 15% Pd(OAc)₂, allyl alcohol, TBAC, NaHCO₃, THF-DMF, RT, 48h.

In summary, we have shown that fourfold Heck reaction on tetraphenylmethane derived *tetrakis*-diazonium salt **1** or the tetraiodide **3** provides a novel synthetic prospect for the construction of *centrally based three dimensional aromatic architectures*. Extension of this methodology to higher generation network construction by this and other Pd-catalyzed regimen is currently under investigation.

Acknowledgements: Prof. G. Mehta is warmly thanked for some NMR spectra. Financial supports from CSIR (01/1371/EMR-II/95) and J.U. (JRF to S.K.S.) are gratefully acknowledged.

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- 9) Pd(OAc)₂ (6 mg) was added to a solution of **1** (0.20 g, 0.26 mmol) and ethyl acrylate (0.21 g, 2.10 mmol) in EtOH (10 ml)-H₂O (2 ml) and the solution heated under reflux for 1h. It was then filtered through celite, water (10 ml) added and extracted with CH₂Cl₂ (3x10 ml). Removal of solvent followed by recrystallization from aqueous EtOH gave **2b** (0.14 g, 75%) as a white solid: mp 188-190°C; IR (KBr) 2970, 1705, 1630, 1360, 1300, 1260, 1170, 1040 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) 1.38 (12H, t, J=7 Hz), 4.27 (8H, q, J=7 Hz), 6.40 (4H, d, J=16 Hz), 7.24 (8H, d, J=8 Hz), 7.47 (8H, d, J=8 Hz), 7.67 (4H, d, J=16 Hz).