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Tetrastyrylmethane

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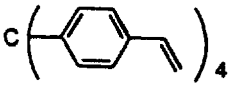
Abstract: The first synthesis of tetrastyrylmethane is reported.

This paper describes a synthesis of tetrakis(4-vinylphenyl)methane, i.e. tetrastyrylmethane or **TSM**. According to a Chemical Abstracts search from 1967 to the present,[1] the compound has until now not yet been reported. This is surprising since **TSM** would be expected to have interesting properties with regard to radical polymerizations. Although polymerization of **TSM** by itself would likely produce an infusable resin, low levels of the compound could be used advantageously as a cross-linking agent during polymerizations of styrene and other conjugated alkenes. As many as four distinct polymer chains could be interconnected at each **TSM** nucleus, an effect that might substantially alter the polymers relative to those made with the usual bidentate cross-linking agents.



TSM

Among tetradentate monomers, pentaerythritol is probably the most common.[2] Patents using pentaerythritol to fabricate condensation polymers, numbering well over a thousand, exemplify the potential utility of "super" cross-linkers such as **TSM**. Thus, polyesters composed of a diacid (e.g. adipate or phthalate) plus pentaerythritol with or without added ethylene glycol have been incorporated into electrical insulators, varnishes, plasticizers, surface coating etc.

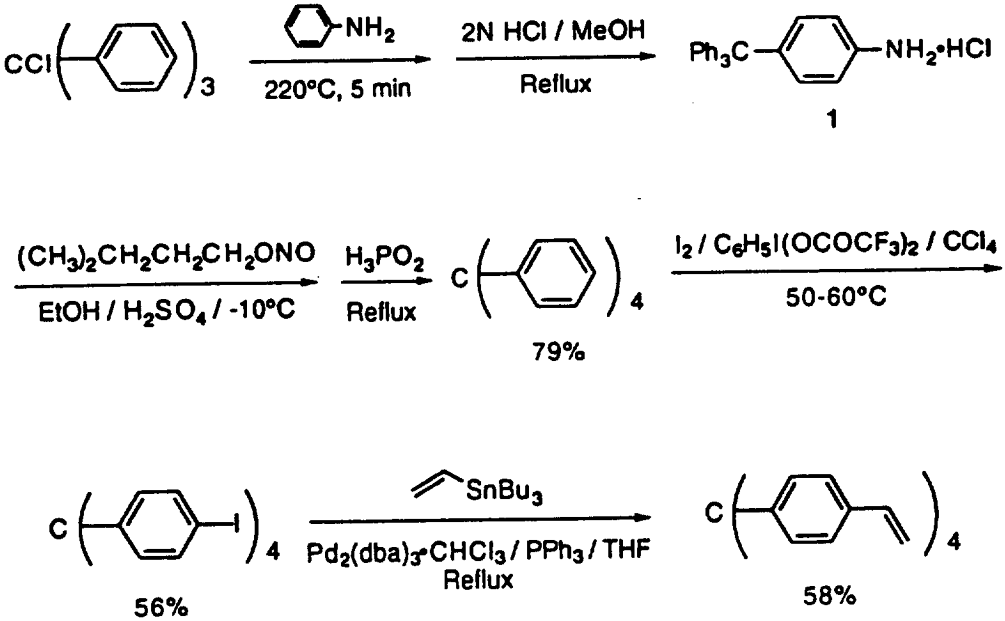
Pentaerythritol tetramethacrylate, a cross-linking agent that improves the impact resistence of poly(vinyl chloride),[3] serves a function similar to that expected for TSM.

The synthesis of TSM was accomplished according to Scheme 1 in 26% overall yield starting with commercially available triphenylmethyl chloride. Intermediates tetraphenylmethane and tetrakis (4-iodophenyl)methane are both known compounds.[4,5] Experimental details follow.

Experimental

Except for THF, which was dried over molecular sieves under argon, all chemicals were used as received.

Scheme 1



Tetraphenylmethane[4]

A mixture of triphenylmethyl chloride (28.5 g. 0.102 mol) and aniline (25.6 g, 0.274 mol) was heated at 220°C for 5 min and then cooled to 90°C. It was then treated with 2N hydrochloric acid (120 ml) and methanol (100 ml), and the resulting mixture was heated briefly at reflux. It was then cooled to room temperature and filtered to provide a gray solid, which was dissolved in a mixture of ethanol (250 ml) and concentrated sulfuric acid (30 ml). The resulting mixture was cooled to -10°C, stirred, and treated dropwise at - 10°C with isopentylnitrite (20 ml). The mixture was then stirred for 30 min, treated with 50% hypophosphorous acid (50 ml), and heated to reflux. The reaction mixture was cooled to room temperature and then filtered to provide an olive solid which was washed with ethanol and dried in vacuo. Crystallization from a mixed solvent of dioxane and ethanol gave tetraphenylmethane as a pale colored solid in 79% yield.

Tetrakis(4-iodophenyl)methane[5]

A suspension of tetraphenylmethane (7.52 g, 23.5 mmol), bis(trifluoroacetoxy) iodobenzene (23.5 g, 54.6 mmol), and iodine (12.4g, 49.8 mmol) in 150 ml of carbon tetrachloride was stirred at 50-60°C until the color of iodine disappeared. Carbon tetrachloride was removed by rotary evaporation. The residue was washed with ethanol and acetone and purified by recrystallization from THF to yield 10.9 g (56%) of tetrakis(4-iodophenyl)methane as a white crystalline solid.

Tris(dibenzylideneacetone)dipalladium(0) chloroform[6]

To a hot solution of dibenzylideneacetone (9.26 g, 39.5 mmol) and sodium acetate (7.83 g, 95.4 mmol) in methanol (250 ml) was added palladium dichloride (2.11 g, 11.9 mmol). The resulting mixture was stirred for 4 h around 50°C, to give a reddish purple precipitate, and allowed to cool to complete the precipitation. The precipitate was removed by filtration, washed successively with water and acetone and dried in vacuo. It was then dissolved in hot chloroform and then filtered to give a deep violet solution. When diethyl ether was added to the cooled solution, a deep purple crystalline solid precipitated. It was removed by filtration, washed with diethyl ether, and dried in vacuo. The complex Pd2(dba)3.CHCl3 was obtained in 50% yield, mp 122-122.5°(lit[6] mp 122-124°C).

Tetrakis(4-vinylphenyl)methane

In a 100 ml dry flask was placed a suspension of tetrakis(4-iodophenyl)methane (2.57 g, 3.12 mmol), tris(dibenzylideneacetone)dipalladium(0) chloroform[6] (0.226 g, 0.218 mmol), and triphenylphosphine (0.137 g. 0.521 mmol) in 45 ml of dry THF. Then vinyltributyltin (4.63 g, 14.6 mmol) was added. The resulting mixture was stirred and heated at reflux overnight. THF was removed by rotary evaporation, and the residue was dissolved in toluene to provide a solution which was further treated with saturated potassium fluoride in water for an hour. Filtration, separation of the organic phase, drying, and evaporation gave the crude product which was further purified by flash chromatography on silica gel using hexane and chloroform as eluent, followed by rinsing with hexane, to afford tetrakis(4vinylphenyl)methane in 58% yield, mp>310°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (8H, d, J=7.9 Hz), 7.21 (8H, d, J=7.9 Hz), 6.70 (4H, dd, J=17.5 Hz, 10.9 Hz), 5.70 (4H, d, J=17.5 Hz), 5.23 (4H, d, J=10.9 Hz). ^{13}C NMR (75 MH_Z; $CDCl_3$) δ 146.4, 136.6, 135.4, 131.3, 125.7, 114.0, 64.5. E.A. calcd for $C_{33}H_{28}$: C, 93.35; H, 6.65; Found: C, 92.71; H, 6.72. FAB MS: m/z 425.2272 (calcd for M + 1: 425.2269). The compound is stable in the dark.

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References and Notes

1. This included a sub-structure search for **TSM** bearing substituents at any site.
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