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Regioselective Synthesis and Polymerization of Substituted *o*-Trimethylsilylphenylacetylenes

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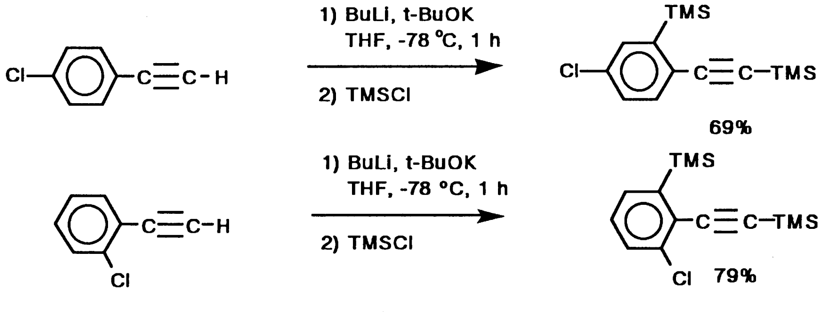
Substituted *o*-trimethylsilylphenylacetylenes were synthesized by *o*-metalation of phenylacetylenes with complex reagent of butyllithium and *t*-BuOK, and were polymerized in the presence of a tungsten catalyst giving deeply colored poly(arylacetylene)s. Relationship between the structure of monomers and polymers was examined.

Directed metalation of aromatic nuclei with organometallic reagents is a useful transformation in organic synthesis, and various directing groups have been devised for this purpose. Ethynyl group has also been known to possess directing ability, and reactions of phenylacetylene and 1-naphthylacetylene were reported.1) Since most directing group has contained heteroatoms, the effect of ethynyl group is interesting. Recently, *o*-trimethylsilylphenylacetylene synthesized by this reaction was reported to give a high molecular weight conjugated polyacetylene when polymerized with W or Mo catalyst.2) It therefore seemed worthwhile to study the metalation and silylation of phenylacetylenes with various substituents, and our results are shown here. Phenylacetylenes obtained were polymerized with a tungsten catalyst, and the relationship between the structure of monomers and polymers was also examined.



Scheme 1.

At first, silylation of chrolophenylacetylenes was examined (Scheme 1). Since the original procedures1) did not give the *o*-silylated product here, a modified method was employed. Lithium acetylide of 4-chrolophenylacetylene was treated with 5 equivalents of butyllithium and *t*-BuOK at -78 °C for 1h followed by excess TMSCl, and the expected product was obtained in good yield.3) Reaction of 2-chrolo derivative proceeded similarly, while 3-chrolo derivative resulted in decomposition presumably *via* a benzyne. Under the same reaction conditions 4- and 3-methylphenylacetylene were also silylated at the aromatic ring (Scheme 2).

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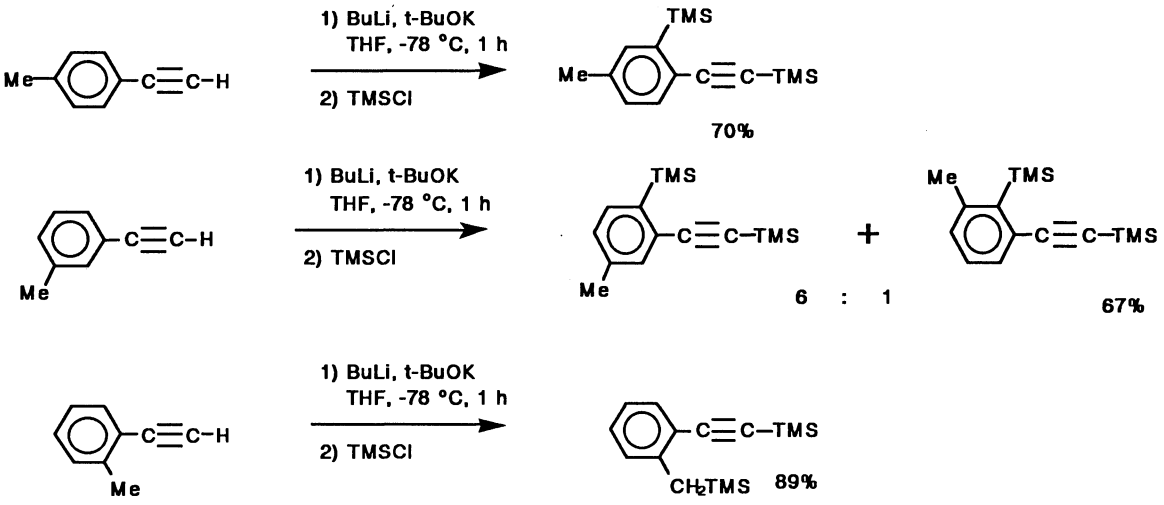
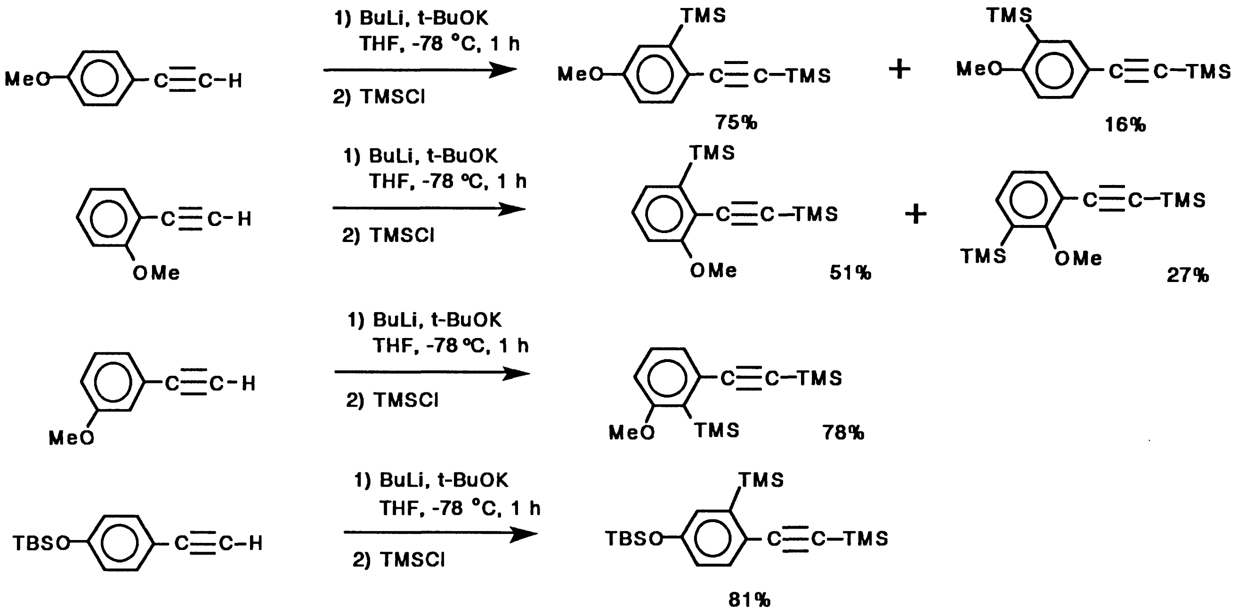
Metalation proceeded predominantly at the less hindered site in the latter case. The reaction of 2-methylphenylacetylene, however, resulted in benzylic metalation.



Scheme 2.

Alkoxyphenylacetylenes were also effected with the metalating reagents (Scheme 3). As shown by the example of 4- and 2-methoxyphenylacetylene, metalation was directed preferentially by ethynyl group. When phenolic hydroxy group was protected as *t*-butyldimethylsilyl (TBS) ether, silylation took place exclusively at *o*-position of ethynyl group. 3-Methoxyphenylacetylene was selectively metalated at the position between the two functional groups.

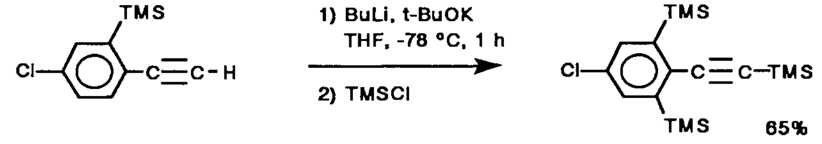


Scheme 3.

Above results indicate that ethynyl group, or more precisely metalated ethynyl group, functions as a stronger directing group in the aromatic metalation compared with chloride or methoxy group. The reaction occurred between two directing groups in the cases of 3-methoxyphenylacetylene and, presumably, 3-

chlorophenylacetylene, while the steric factor played an important role in the reaction of 3-methylphenylacetylene.

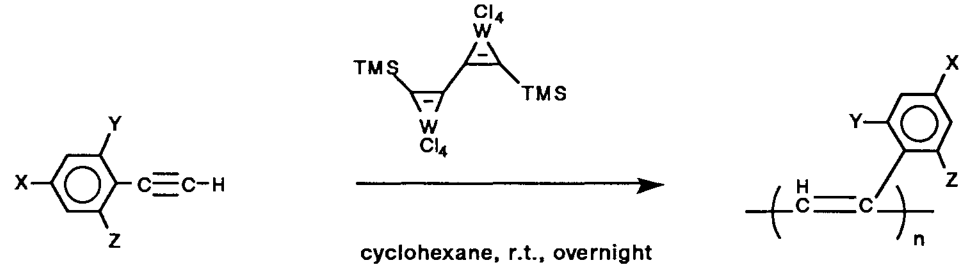
As shown in Scheme 4, two TMS groups could be introduced by repeating the metalation and silylation process.



Scheme 4.

A typical silylation reaction is as follows: Under a nitrogen atmosphere, a hexane solution (0.38 ml) of butyllithium (0.38 ml, 0.6 mmol) was added to a THF (2 ml) solution of 4-chlorophenylacetylene (78 mg, 0.5 mmol) at -78 °C. The mixture was stirred for 10 min, and THF-hexane (2 and 1.3 ml) solution of *t*-BuOK (224 mg, 2 mmol) and butyllithium (2 mmol) prepared at -78 °C was added. Stirring was continued for 2 h at the temperature, and TMSCl (0.5 ml) was added. The mixture was warmed to 10 °C for 2 h, and saturated aqueous NH_4Cl was added. A standard workup gave (4-chloro-2-trimethylsilylphenylethynyl)trimethylsilane (97 mg, 69%). H-NMR ($CDCl_3$) δ 0.26 (9H,s), 0.38 (9H,s), 7.1-7.3 (3H,m). IR (neat) 2160, 840 cm^{-1}. Anal. Calcd for $C_{14}H_{21}ClSi_2$: C; 59.88, H; 7.53 %. Found: C; 59.61, H; 7.56 %.

Table 1. Polymerization of Substituted Phenylacetylenes



Ar	Yield / %	MW_n (x 10^{-3})[a]	Color of Powder	UV λmax / nm in $CHCl_3$
4-ClC_6H_4	quant.	100	red	442
4-Cl-2-$TMSC_6H_3$	quant.	**610**	purple	542
4-MeC_6H_4	90	10	brown	b)
4-Me-2-$TMSC_6H_3$	85	**340**	purple	564
4-MeO-2-$TMSC_6H_3$	quant.	18	purple	526
4-TBSO-2-$TMSC_6H_3$	90	**920**	red	496
2-ClC_6H_4	90	**250**	red	460
2-Cl-6-$TMSC_6H_3$	35	**180**	purple	535

a) Determined by GPC method with polystyrene standard employing THF as the eluent. Bold line indicates the ability to form self-standing film. b) No distinct absorption maxima observed.

Ethynyl TMS group could be removed by treating with KOH or K_2CO_3 in refluxing methanol,4) and resulted terminal acetylenes were subjected to the polymerization with a tungsten-alkyne complex (Table 1).5) The experiments showed several interesting features of this reaction concerning the relationship between the structure of monomers and polymers. Introduction of *o*-TMS group generally gave higher molecular and weight and wider conjugated polymers. However, severe steric hindrance of 2,6-disubstituted phenylacetylene lowered the yield of the polymer. Although *p*-methoxyphenylacetylene did not give high molecular weight product, a deeply colored substance with MWn 920×10^3 was obtained from a TBSoxyphenylacetylene. Self-standing film could be formed by casting method for polymers of high molecular weight ($>100 \times 10^3$). A typical polymerization reaction is as follows: Under a nitrogen atmosphere, a mixture of 4-chloro-2-trimethylsilylphenylacetylene (153 mg, 0.73 mmol), tungsten-alkyne complex (34 mg, 0.04 mmol) in cyclohexane (0.5 ml) was stirred for 12 h at r.t. The reaction was quenched by adding chloroform and a small amount of methanol, and the mixture was stirred for 2 h. Insoluble inorganic materials were removed by filtration, and solvents were evaporated *in vacuo.* The polymer (151 mg, 98 %) was precipitated by adding hexane to the residue.

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References

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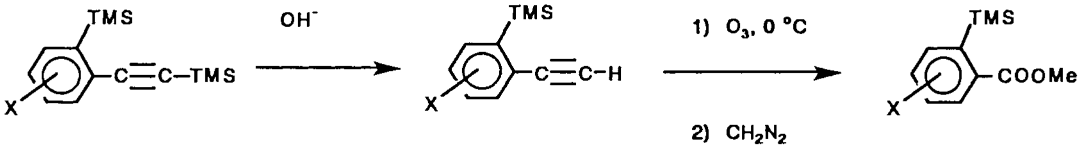
2) T. Masuda, T. Hamano, K. Tsuchihara, and T. Higashimura, *Macromolecules*, **23**, 1374 (1990).

3) Removal of acetylenic TMS group followed by ozonolysis and methylation gave methyl benzoate derivatives (Scheme 5). Silylated sites were determined here.



Scheme 5.

4) Since selective desilylation of ethynyl TMS group from 4-TBSoxy-2-TMSphenylacetylene derivatives was unsuccessful, both silyl group was removed by alkaline treatment, and then TBS protecting group was introduced at phenol moiety.

5) K. Stahl and K. Dehnicke, *J. Organomet. Chem.*, **316**, 85 (1986). Several other organotungsten (IV) compounds were also screened since W(IV) species has been considered to be a responsible for the polymerization. The alkyne complex used here was relatively insensitive to air and possessed high catalytic activity. Catalysts examined include WCl_4, $WCl_4(PPh_3)_2$, WCl_4-diphenylacetylene complex, and $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$.

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