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Tetrakis(2-thienyl)allene and 1,1,3,3-Tetrakis(2-thienyl)allyl Cation, an Electron-rich Reactive Tetraarylallene and a Remarkably Stable Tetraaryl-substituted Allyl Cation

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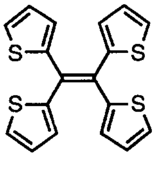
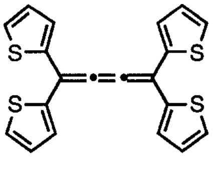
Abstract: Tetrakis(2-thienyl)allene was synthesized as an acid-sensitive tetraarylallene by dehydration of the corresponding tetrathienylallyl alcohol with anhydrous copper(II) sulfate. This electron-rich allene forms a remarkably stable tetrathienylallyl cation by protonation, undergoes Diels-Alder reaction with tetracyanoethylene, and is capable of tetrafold lithiation and functionalization.

Key words: Allenes; Carbonium ions; Cycloadditions; Lithiation

While tetrakis(2-thienyl)-ethene and -butatriene, **1** and **2**, have been synthesized recently, 1,1,3,3-tetrakis(2-thienyl)-1,2-propadiene (tetrathienylallene: TTA) **3** has remained unknown.[1,2] In view of electron-donating property of 2-thienyl group, **3** would be an electron-rich allene and form 1,1,3,3-tetrakis(2-thienyl)allyl cation **4** (TTAC) as a considerably stable allyl cation upon protonation. In addition, possible lithiation and functionalization of the 2-thienyl groups would make **3** a potential building block for novel conjugated molecules containing allene moieties. As a part of our studies on novel conjugated molecules based on thiophene chemistry,[2,3] we have synthesized **3** to examine its properties and synthetic utility. Here we report the synthesis and properties of **3** and **4**.



1



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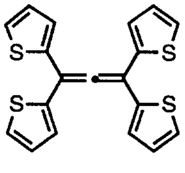

3

Tetraaryl-substituted allenes have been synthesized by either acid-catalyzed dehydration of the corresponding allyl alcohols[4,5] or base-induced dehydrohalogenation of 2-halogenopropenes.[6] We here employed the dehydration procedure for the synthesis of **3** because of short synthetic steps. However, initial attempts of acid-catalyzed dehydration of allyl alcohol **7**, prepared from dithienyl ketone **5** through **6** (Scheme 1), did not give successful

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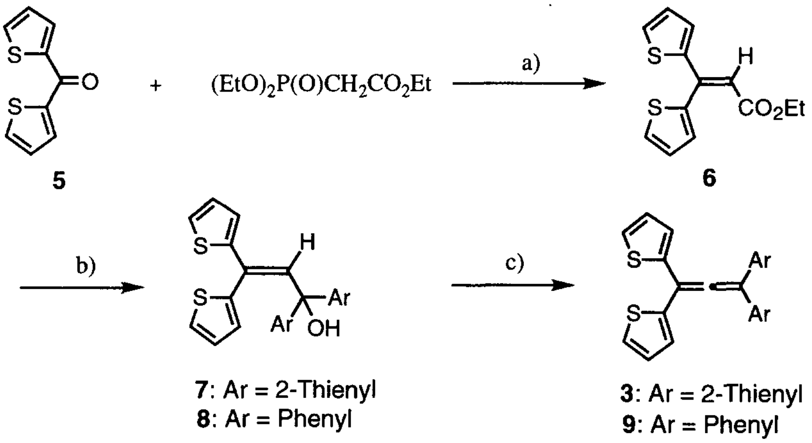
results: while treatment of **7** with *p*-toluenesufonic acid in benzene or ethyl acetate at room temperature for two days afforded TTA **3**[7] in poor yields of about 5%, heating the mixtures led to decomposition of both **3** and **7** to suggest the acid-sensitive nature of **3**. Attempted dehydration of **7** with phosphoryl chloride or methanesulfonyl chloride in pyridine also failed, yielding **3** in only trace amount. The most successful result (62% yield) was obtained by heating of **7** with anhydrous copper(II) sulfate[8](10 molar equiv.) in THF at reflux for 3 h. This procedure was also successful for the preparation of 1,1-diphenyl-3,3-bis(2-thienyl)allene **9**[9] (72% from allyl alcohol **8**).

Scheme 1



Reagents and conditions (for **3**): a) NaH/benzene, reflux, 1 d, 92%; b) 2-thienyllithium /THF, 0 °C - r.t., 70% ; c) anhyd. $CuSO_4$ (10 molar eq.)/THF, reflux, 3 h, 62%.

TTA **3** is a pale yellow crystalline substance, stable at solid state and in neutral solutions, but sensitive to acids.[10] Upon gradual addition of trifluoroacetic acid (TFA) in dichloromethane, the pale yellow solution of **3** turned to greenish forming TTAC **4** which exhibits strong visible absorptions at 456, 525, and 637 nm (Scheme 2 and Figure 1). As low as 1% (v/v) concentration of TFA is nearly enough for full spectral change at the UV spectral concentration (10^{-5} M). TTAC **4** is significantly stable surviving for a few days in the solution at room temperature in contrast to much lower stability of 1,1,3,3-tetraphenylallyl cation (due to intramolecular cyclization[5,11]). In our experiment, tetraphenylallene needed more than 5% (v/v) of TFA for sufficient protonation, and the absorptions of tetraphenylallyl cation (λ_{max} = 399, 473, and 578 nm in TFA-CH_2Cl_2) disappeared in about 1 h. ^{1}H NMR spectrum[12] of **4** at 30 °C (Figure 2) shows the thienyl protons at 0.53 ppm lower field in average than those of **3** (δ_{av} 7.79 vs. 7.26) in consonant with the monocation structure. The ^{1}H NMR observation of four equivalent thienyl groups instead of two kinds in **4** is suggestive of easy bond rotation of the carbon-carbon bonds in the allyl cation part around room temperature.[13]

TTA **3** smoothly reacted with tetracyanoethylene (TCNE) in benzene at room temperature to form, in good yield, the Diels-Alder adduct **10**[14] in which one of the thienyl groups takes part (Scheme 2). Under the similar condition, diphenyldithienylallene **8** yielded regioselective adduct **11**[14], indicating higher reactivity of the diene at the thienyl side than the diene at the phenyl side.

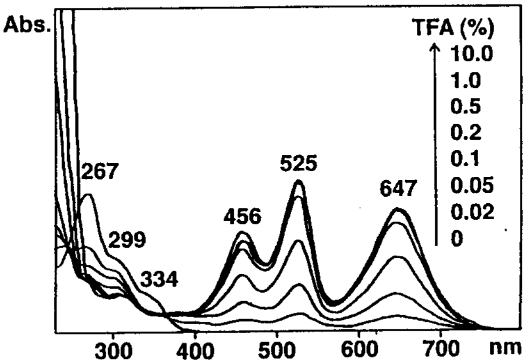


Figure 1. UV-vis spectral change of TTA **3** upon gradual addition of CF_3COOH in CH_2Cl_2.

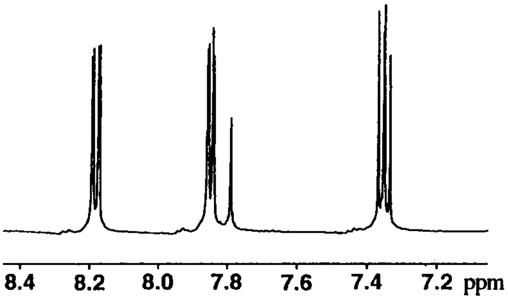
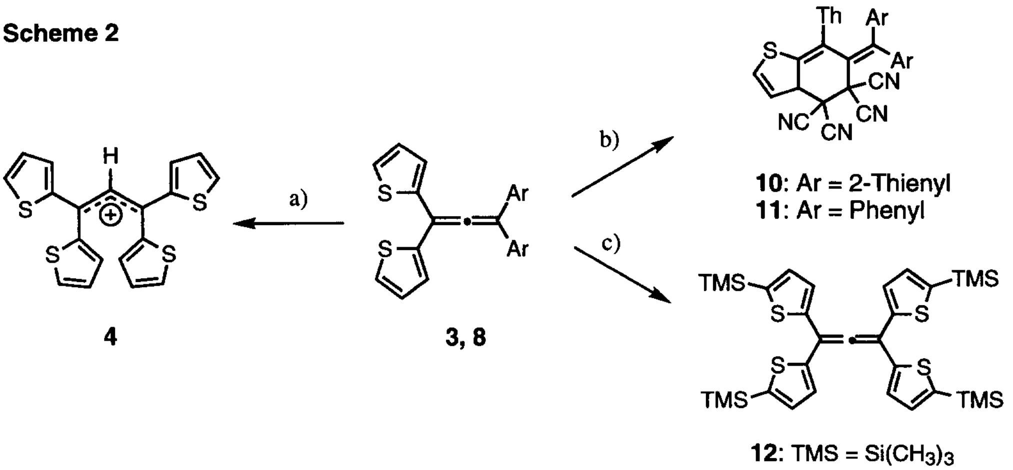


Figure 2. ^1H NMR spectrum of TTAC **4** in CD_2Cl_2-TFA at 30 °C.

Scheme 2



Reagents and conditions: a) CF_3COOH/CH_2Cl_2; b) TCNE/benzene, rt, 72% (**10**), 55% (**11**); c) i) 4.4 eq. n-BuLi/THF, -78 °C, 30 min, ii) 6 eq. $(CH_3)_3SiCl$, -78-0 °C, 1 h, 91%.

In view of ready metallation of thiophene at 2 (5)-position(s) and stabilizing effects of 2-thienyl group on both carbocations and carbanions,[3] it is an interesting question whether strong bases effect selective metallation of 5-position of the thienyl groups or preferentially add to the sp carbon of TTA **3** to form 1,1,3,3-tetrathienylallyl anions. In fact, treatment of **3** with n-BuLi (4.4 equiv.) in THF at -78 °C followed by addition of excess chlorotrimethylsilane afforded tetra-silylated compound **12**[15] in high yield (Scheme 2). This successful tetrafold lithiation of **3** should allow the syntheses of novel conjugated systems containing tetrathienylallene moiety.

Further studies and synthetic application of **3** and **8** are in progress.

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7. mp 109-110 °C; ^{1}H NMR (270 MHz, acetone-d_6) δ 7.12 (4H, dd, J = 3.8, 5.2 Hz), 7.34 (4H, dd, 1.3,.3.8 Hz), 7.51 (4H, dd, 1.3, 5.2 Hz) (δ 7.10, 7.32, 7.36 respectively in CD_2Cl_2); ^{13}C NMR (67.8 MHz, acetone-d_6) δ 103.98, 127.28, 127.73, 128.56, 138.64, 206.32 (spC); UV (log ε) λ_{max} 267 (4.47), 299 (sh, 4.21), 334 nm (sh, 3.93).
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9. mp 105-106 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.04 (m, 2H), 7.26 (m, 4H), 7.34 (m, 6H), 7.46 (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 102.36, 113.66, 125.20, 126.13, 127.50, 127.87, 128.57, 128.74, 135.96, 138.92, 208.20 (spC); UV (log ε) λ_{max} 259 nm (4.39).
10. X-Ray analysis on a single crystal of **3** confirmed the allene structure, although disorder at the thienyl group did not allow to give exact bond angles and lengths.
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12. ^{1}H NMR (270 MHz, CD_2Cl_2-TFA) δ 7.35 (4H, dd, J = 4.0, 5.0 Hz), 7.79 (1H, s), 7.85 (4H, dd, 1.3, 4.0 Hz), 8.18 (4H, dd, 1.3, 5.0 Hz).
13. The ^{1}H NMR spectrum remained essentially unchanged down to -40 °C except only slight broadening, and further studies on the dynamic process of **4** are undergoing.
14. **10**: yellow needles, mp 178-179 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.39 (1H, dd, J = 1.7, 3.0 Hz), 6.16 (1H, dd, 3.0, 6.3 Hz), 6.77 (1H, dd, 3.9, 5.0 Hz), 6.84 (1H, dd, 3.9, 5.0 Hz), 6.88 (1H, dd, 1.1, 3.9 Hz), 6.92 (1H, dd, 1.1, 3.9 Hz), 6.95 (1H, dd, 1.7, 6.3 Hz), 7.17 (1H, dd, 1.1, 5.0 Hz), 7.24 (1H, dd, 3.6, 5.2 Hz), 7.30 (1H, dd, 1.1, 5.0 Hz), 7.71 (1H, dd, 1.1, 5.2 Hz), 7.81 (1H, dd, 1.1, 3.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 41.25, 50.57, 57.23, and 22 signals for sp^2 (18) sp (4) carbons between δ 108.80-142.91.

    11: pale yellow needles; mp 173-174 °C (decomp.); ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.48 (1H, dd, J = 1.7, 3.0 Hz), 6.12 (1H, dd, 3.0, 6.0 Hz), 6.68 (2H, m), 6.89 (3H, m), 7.07 (4H, m), 7.50 (5H, m).
15. Pale yellow prisms; mp 46-47 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.31 (36H, s), 7.18 (4H, d, J = 3.6 Hz), 7.37 (4H, d, 3.6 Hz); ^{13}C NMR (67.8 MHz, acetone-d_6) δ 0.00, 102.81, 128.00, 134.40, 141.35, 143.58, 208.81.