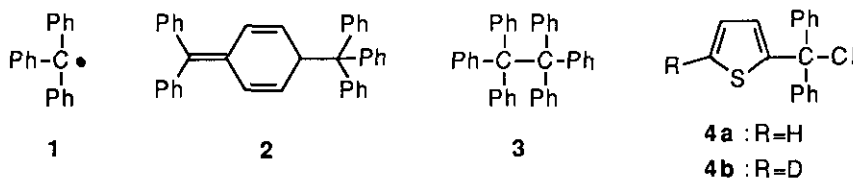


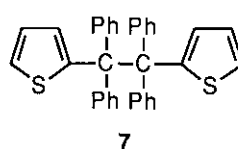
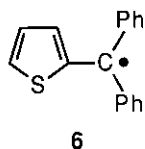
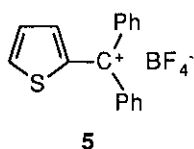
FORMATION OF TWO DIMERS FROM DIPHENYL-2-THIENYLMETHYL RADICALS AND THEIR STRUCTURE

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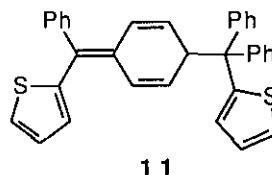
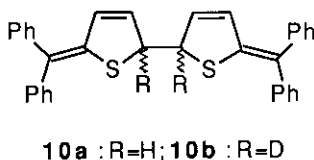
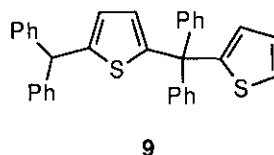
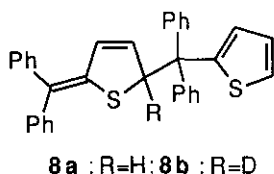
Abstract—Diphenyl-2-thienylmethyl radical dimerizes in solution at room temperature to give 2-(diphenylmethylene)-5-(diphenyl-2-thienylmethyl)-2,5-dihydrothiophene and a small amount of 5,5'-bis(diphenylmethylene)-2,2',5,5'-tetrahydro-2,2'-bithiophene.

Although the chemistry of triphenylmethyl radical (1) has been a matter of extensive investigation, its heterocyclic analogs, in which one or more phenyl groups are replaced by heteroaromatic groups, have received only scanty attention. In 1968 the dimer of 1 was determined to be the quinoid compound (2) but not hexaphenylethane (3).¹ As early as 1929 Minnis claimed that the red color developed during the reduction of diphenyl-2-thienylmethyl chloride (4a) with metallic silver in benzene was due to diphenyl-2-thienylmethyl radical (6),² whilst in 1955 Chu and Weisman reported that the radical (6) generated by reduction of 4a with silver amalgam dimerized at room temperature to give 1,1,2,2-tetraphenyl-1,2-di-2-thienylethane (7), its structure being elucidated by the conventional methods of those days.³ We report that the radical (6) dimerizes to give 2-(diphenylmethylene)-5-(diphenyl-2-thienylmethyl)-2,5-dihydrothiophene (8a) along with a small amount of 5,5'-bis(diphenylmethylene)-2,2',5,5'-tetrahydro-2,2'-bithiophene (10a).





Treatment of **4a** with silver amalgam in benzene at room temperature for 24 h afforded a red mixture as previously reported,^{2,3} from which the dimer (**8a**) was isolated in good yield as an unstable reddish glassy solid.⁴ Treatment of the reaction mixture with potassium *t*-butoxide brought about the aromatization of **8a** to give **9⁵** in 75% yield. The ¹H-nmr spectrum of **8a** showed a typical absorption due to an allylic system and the ¹³C-nmr revealed the presence of one methine (δ 65.2) and one quaternary (δ 60.3) carbons in addition to sp^2 carbons. The molecular ion peak was observed at m/z 498 in the mass spectrum (FAB).⁶



Interestingly, when **4a** was treated with zinc in benzene at room temperature for 24 h, the symmetrical dimer (**10a**) was formed in a small amount in addition to the unsymmetrical dimer (**8a**); the ratio of **8a** to **10a** determined by ¹H-nmr analysis is 20:1.⁷ The dimer (**10a**) thus formed was a diastereomeric mixture of 2:1 from which the major diastereomer⁸ could be isolated in pure form by column chromatography. The formation of **10a** in small amounts was also observed on reduction of **4a** with mercury in benzene at room temperature for 24 h and on reduction of the carbenium salt (**5**) with zinc in dimethoxyethane at room temperature for 17 h. When the chloride (**4b**), in which the hydrogen of 5-position of 2-thienyl is replaced by deuterium, was reduced with zinc, the methine proton signals of the resulting

dimers (**8b**) and (**10b**) disappeared. This shows that the dimerization to **8** and **10** occurs at the 5-position but not the 3-position of the thiophene ring.⁹

Heating a 10:1 mixture of **8a** and **10a** in deuteriochloroform at 63 °C for 45 h under nitrogen afforded a 6:1 mixture of **8a** and **10a** [diastereomeric ratio of **10a** also changed from 2:1 to 0.7:1]. The pure one diastereomer of **10a** also isomerized to give a 1.2:1 mixture of **8a** and **10a**, when heated at 61 °C for 21 h in deuteriochloroform. These observations show that the dimers thermally dissociate into the radical (**6**).

The dimers (**8a**) and (**10a**) are fairly stable toward oxygen in contrast to the dimer (**2**) which rapidly absorbs molecular oxygen to give bis(triphenylmethyl) peroxide.¹⁰ Throughout this work no formation of such dimers as **7** and **11** was observed.

REFERENCES AND NOTES

1. H. Lankamp, W. T. Nauta, and C. MacLean, Tetrahedron Lett., **1968**, 249.
2. W. Minnis, J. Am. Chem. Soc., 1929, **51**, 2143.
3. T. L. Chu and T. J. Weismann, J. Am. Chem. Soc., 1955, **77**, 2189.
4. **8a**: ¹H-Nmr (CDCl₃) δ 6.10 (triplet-like, *J*=1.8 Hz, 1H), 6.14 (br s, 1H), 6.26 (br d, *J*=5.4 Hz, 1H), 6.87-6.96 (m, 4H), and 7.13-7.34 (m, 19H). We were unable to obtain the compound having the melting point (114 °C) reported by Chu and Weisman;³ our compound does not show a clear melting point.
5. **9**: mp 163 °C (hexane); ¹H-nmr (CDCl₃) δ 5.56 (s, 1H), 6.48 (d, *J*=3.5 Hz, 1H), 6.66 (d, *J*=3.5 Hz, 1H), 6.85 (dd, *J*=3.7, 1.1 Hz, 1H), 6.95 (dd, *J*=3.7, 5.0 Hz, 1H), and 7.18-7.29 (m, 21H); ¹³C-nmr (CDCl₃) δ 52.15 (d), 59.43 (s), 124.76 (d), 125.68 (d), 126.17 (d), 126.60 (d), 127.02 (d), 127.46 (d), 128.34 (d), 128.36 (d), 128.80 (d), 128.80 (d), 129.76 (d), 143.52 (s), 146.69 (s), 146.92 (s), 151.25 (s), and 152.61 (s); ms *m/z* 498 (M⁺, 100), 421 (94), 331 (50), and 249 (10). Anal. Calcd for C₃₄H₂₆S₂: C, 81.89; H, 5.25. Found: C, 81.92; H, 5.33.
6. M. Barber, D. Bell, M. Eckersley, M. Morris, and L. Tetler, Rap. Comm. Mass Spectrom., 1988, **2**, 18.
7. A ¹H-nmr analysis shows that dimer formation occurs nearly quantitatively. However, the instability of the dimers made it difficult to determine the isolated yields of **8a** and **10a**.

8. Isolated pure one diastereomer of **10a**: ^1H -Nmr (CDCl_3) δ 4.60 (s, 2H), 6.15 (td, $J=6.2$, 1.3 Hz, 2H), 6.55 (d, $J=6.2$ Hz, 2H), and 7.14-7.39 (m, 20H). In the ^{13}C -nmr spectrum, only methine carbon (δ 61.9) was observed in the aliphatic region. Ms (FAB) m/z 498.
9. We have recently reported a similar dimerization of tri-2-thienylmethyl radical: J. Nakayama, A. Ishii, Y. Yamada, M. Sugino, and M. Hoshino, Tetrahedron Lett., 1990, **31**, 2627.
10. J. M. McBride, Tetrahedron, 1974, **30**, 2009.

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