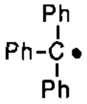
FORMATION OF TWO DIMERS FROM DIPHENYL-2-THIENYLMETHYL RADICALS AND THEIR STRUCTURE

Akihiko Ishii, Motoaki Sugino, Juzo Nakayama,* and Masamatsu Hoshino
Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

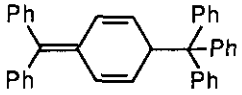
Abstract–Diphenyl-2-thienylmethyl radical dimerizes in solution at room temperature to give 2-(diphenylmethylene)-5-(diphenyl-2-thienylmethyl)-2,5-dihydrothiophene and a small amount of 5,5'-bis(diphenylmethylene)-2,2',5,5'-tetrahydro-2,2'-bithiophene.

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**).

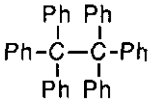


$Ph_3C\bullet$

1

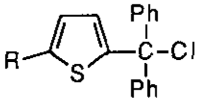


2

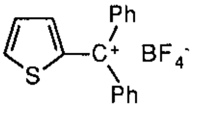


Ph_3C-CPh_3

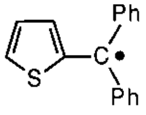
3



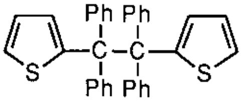
4a : R=H
4b : R=D



5

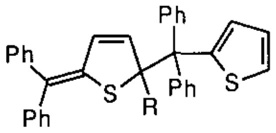


6

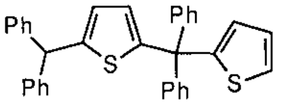


7

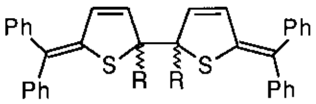
Treatment of **4a** with silver amalgam in benzene at room temperature for 24 h afforded a red mixture as previously reported,[2,3] from which the dimer(**8a**)was isolated in good yield as an unstable reddish glassy solid.[4] Treatment of the reaction mixture with potassium *t*-butoxide brought about the aromatization of **8a** to give **9**[5] in 75% yield. The ^{1}H-nmr spectrum of **8a** showed a typical absorption due to an allylic system and the ^{13}C-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]



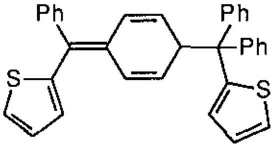
8a : R=H; **8b** : R=D



9



10a : R=H; **10b** : R=D



11

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 ^{1}H-nmr analysis is 20:1.[7] The dimer (**10a**) thus formed was a diastereomeric mixture of 2:1 from which the major diastereomer[8] 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**: ^{1}H-Nmr ($CDCl_3$) 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); ^{1}H-nmr ($CDCl_3$) 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); ^{13}C-nmr ($CDCl_3$) 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 $C_{34}H_{26}S_2$: 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 ^{1}H-nmr analysis shows that dimer formation occurs nearly quantatively. 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**: ^{1}H-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.

Received, 14th September, 1990