PHOTOCHEMICAL SYNTHESIS AND ELECTROCHEMICAL BEHAVIOR OF TRIPHENYLENO[4,5-*bcd*]THIOPHENE AND TRIPHENYLENO[4,5-*bcd*]-SELENOPHENE DERIVATIVES

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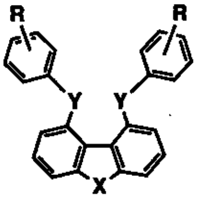
Abstract - Photolysis of 1,9-bis(arylthio)dibenzothiophene afforded triphenyleno-[4,5-*bcd*]thiophene and tribenzo[*bc,e,hi*][2,7]dithiaazulene derivatives. Deuterium tracer experiment revealed that this reaction proceeded intramolecularly.

Recently, we have reported that sterically congested 1,9-bis(phenylthio)dibenzothiophene (**1a**) and 1,9-bis(phenylseleno)dibenzoselenophene (**1b**) were prepared by the simple ligand coupling reaction of corresponding 4,6-disubstituted thianthrene-5-oxide and selenanthrene-5-oxide with *n*-butyllithium or phenyllithium and they gave new dithia and diselena dications on treatment with concentrated H_2SO_4.[1,2] In the course of this study, we have succeeded in preparation of hitherto unknown dibenzo[*bc,fg*][1,4]dithiapentalene from the photolysis of 1,9-bis(methylthio)dibenzothiophene.[3,4] In contrast to the methylthio derivative, we have found that the photolysis of 1,9-bis(arylthio)dibenzothiophene (**1**) proceeds *via* concomitant desulfurization and ring contraction reactions to give triphenyleno[4,5-*bcd*]thiophene (**2**) and tribenzo[*bc,e,hi*][2,7]dithiaazulene (**3**) derivatives. Conventional procedures for preparation of triphenylenothiophene require expensive triphenylene[5] as a starting material and therefore a few reports have been presented with respect to the studies on the chemical properties of triphenylenothiophene derivatives. In this paper we wish to report a new convenient preparation of polyaromatic compounds (**2**) and (**3**) together with their electrochemical properties.

Irradiation of **1a** was carried out with a 400 W high pressure mercury lamp in benzene under argon for 12 h, and after the usual work-up **2a** (72%) and **3a** (26%) were obtained. The photodecomposition reactions of selenium analogs (**1b**) and (**1c**) were carried out in the similar manner to give **2b** as the sole product in 81% and 77% yields, respectively (Table 1).[6]

This paper is dedicated to Prof. Edward C. Taylor on the occasion of his 70th birthday.



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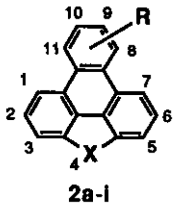

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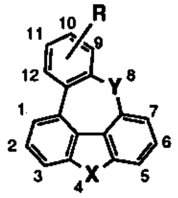

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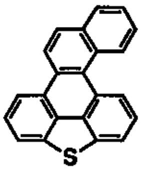

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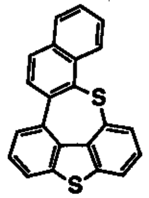

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Table 1. Photolysis of Compounds (**1**) in Benzene.

Sub.	X	Y	R	Product	Yield(%)	Product	Yield(%)
1a	S	S	H	**2a**	72	**3a**	26
1b	Se	Se	H	**2b**	81	**3b**	0
1c	Se	S	H	**2b**	77	**3b**	0
1d	S	S	*o*-D[a]	**2d** (8-D)	75 (*d*=45%)	**3d** (9-D)	22 (*d*=46%)
1e	Se	S	*o*-D[a]	**2e** (8-D)	62 (*d*=52%)	**3e** (9-D)	0
1f	S	S	*o*-CH_3	**2f** (8-CH_3)	69	**3f** (9-CH_3)	24
1g	S	S	*p*-CH_3	**2g** (9-CH_3)	67	**3g** (11-CH_3)	30
1h	S	S	*m*-CH_3	**2f+2g**	54[b]	-[c]	-
1i	S	S	*p*-Cl	**2i** (9-Cl)	81	**3i** (11-Cl)	11
1j[d]	S	S	-	**2j**	13	**3j**	3

[a] Deuterium contents (*d*) are 99% in both the phenylthio groups; [b] 2f:2g=1:1; [c] Complex mixture; [d] 1,9-Bis(2-naphthylthio)dibenzothiophene.

In order to know whether the benzene ring condensed to the products (**2**) and (**3**) comes from the phenylthio or phenylseleno substituents or from the solvent, the photolysis was carried out using the following two ways, namely the reaction of **1c** in *p*-xylene and that of *o*-monodeuterated compounds (**1d,e**) in benzene. When **1c** was photolyzed in *p*-xylene, no incorporation of *p*-xylene was observed in the product. Furthermore, 1,9-bis(*o*-monodeuterated phenylthio)dibenzothiophene (**1d**) (*d*=99%) was photolyzed similarly as described above to give 8-deuterated triphenylenothiophene (**2d**) (75%, *d*=45%) and 9-deuterated tribenzodithiaazulene (**3d**) (22%, *d*=46%), while 8-deuterated triphenylenoselenophene (**2e**) was obtained (62%, *d*=52%) in the photolysis of compound (**1e**).[7] Similarly, the photolysis of other arylthio derivatives (**1f-j**) produced the corresponding triphenylenothiophene (**2f-j**) and tribenzodithiaazulene (**3f-j**) derivatives (Table 1).[8] On the other hand, the photolysis of 1- phenylthio dibenzothiophene did not proceed at all under the similar reaction conditions. These results seem to reveal that a strong interaction between the two sulfur or selenium atoms of compound (**1**) should be essentially required to initiate the photolytic reactions and the reaction may proceed *via* the concomitant desulfurization or deselenization and the intramolecular cyclization to give compounds (**2**) and (**3**).

Furthermore, since photolysis of *m*-tolylthio derivative (**1h**) gave a 1:1 mixture of **2f** and **2g** (54%), these cyclizations of tolyl derivatives seem not to be influenced by the steric hindrance of methyl group. Thus the present photolysis reactions provide possibilities for regiospecific preparation of substituted triphenylenothiophenes from compound (**1**).

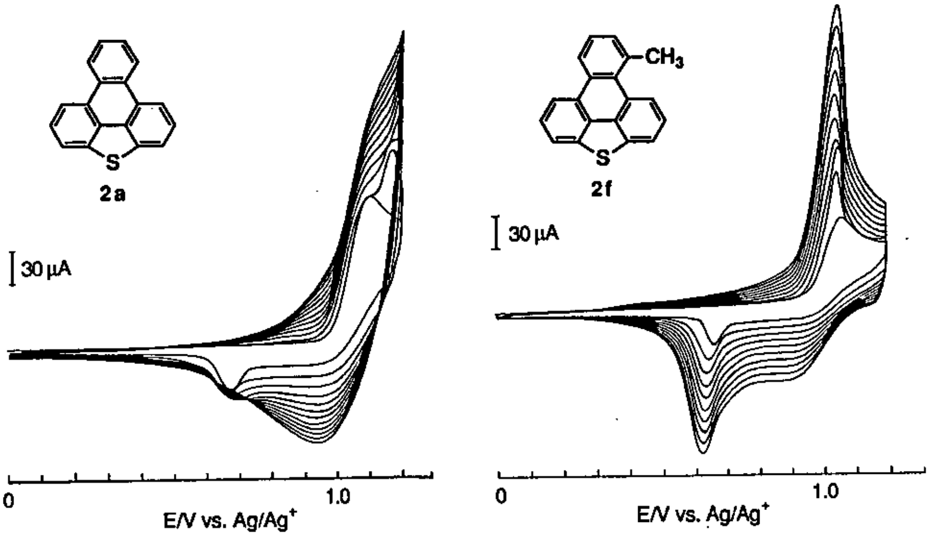

Figure 1. The Cyclic Voltammograms of Compounds (**2a**) and (**2f**) with Repeated Scan in CH_3CN (0.1 M $NaClO_4$); **2a** (2.0 mM), 12 Times; **2f** (0.9 mM), 10 Times.

Since the compounds (**2**) and (**3**) are considered to be effective electron donor molecules which may serve as electroconducting materials, the oxidation potentials of **2** and **3** were determined with cyclic voltammetry in CH_3CN at 20 °C. The cyclic voltammograms were irreversible for all compounds, and their peak potentials (E_p vs Ag/0.01 M $AgNO_3$; scan rate: 200 mV/s) are as follows: **2a** (1.11 V), **2b** (0.99 V), **2f** (1.08 V), **2g** (1.09 V) and **3a** (1.11 V). Interestingly, however, the intensity of the electric currency of triphenylenothiophene derivatives (**2a**), (**2f**) and (**2g**) increases gradually with repeated scannings of electric potential between 0 to 1.20 V (Figure 1). These results imply that new polythiophene derivatives are produced on the electrode surface.[3,9] Further investigations for synthetic application and electrochemical properties of triphenylenothiophene derivatives are in progress in this laboratory.

ACKNOWLEDGMENT

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6. **2b**: mp 184-185 °C; ^{1}H-nmr (270 MHz, $CDCl_3$) δ 8.77-8.70 (m, 2H, 8,11-H), 8.53 (d, J=7.8 Hz, 2H, 1,7-H), 8.11 (d, J=7.8 Hz, 2H, 3,5-H), 7.81 (t, J=7.8 Hz, 2H, 2,6-H), 7.79-7.71 (m, 2H, 9,10-H); ^{77}Se-nmr (51 MHz, $CDCl_3$) δ 458.1; ms (m/z) 306 (M^+); Anal. Calcd for $C_{18}H_{10}Se$: C, 70.83; H, 3.30. Found; C, 70.71; H, 3.23.
7. When tribenzodithiaazulene (**3a**) was photolyzed under the similar conditions, both desulfurization and ring contraction reaction did not occur and the starting **3a** was recovered quantitatively suggesting that **2a** was obtained directly from **1a** and not via **3a**.
8. **2f**: mp 169 °C; ^{1}H-nmr (500 MHz, $CDCl_3$) δ 8.74 (d, J=7.9 Hz, 1H), 8.68 (d, J=7.7 Hz, 1H), 8.44 (d, J=7.9 Hz, 1H), 8.06 (d, J=7.7 Hz, 1H), 8.03 (d, J=7.7 Hz, 1H), 7.83 (t, J=7.9 Hz, 2H), 7.61 (t, J=7.7 Hz, 1H), 7.56 (d, J=7.7 Hz, 1H), 3.20 (s, 3H, CH_3); ms (m/z) 272 (M^+); Anal. Calcd for $C_{19}H_{12}S$: C, 83.79; H, 4.44. Found: C, 83.56; H, 4.58; **3f**: ^{1}H-nmr (270 MHz, $CDCl_3$) δ 7.88 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H), 7.78 (dd, J_1=7.8 Hz, J_2=1.1 Hz, 1H), 7.75 (dd, J_1=7.6 Hz, J_2=1.1 Hz, 1H), 7.60 (t, J=7.8 Hz, 1H), 7.55 (dd, J_1=7.6 Hz, J_2=1.1 Hz, 1H), 7.43 (t, J=7.6 Hz, 1H), 7.33 (dd, J_1=7.8 Hz, J_2=1.4 Hz, 1H), 7.25 (t, J=7.8 Hz, 1H), 7.14 (dd, J_1=7.8 Hz, J_2=1.4 Hz, 1H), 2.75 (s, 3H, CH_3); Found: m/z 304.0384. Calcd for $C_{19}H_{12}S_2$: M, 304.0380.
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