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Diinsertion of Fluorenylidene into a Sulfur-Sulfur Bond of Diaryl Disulfides

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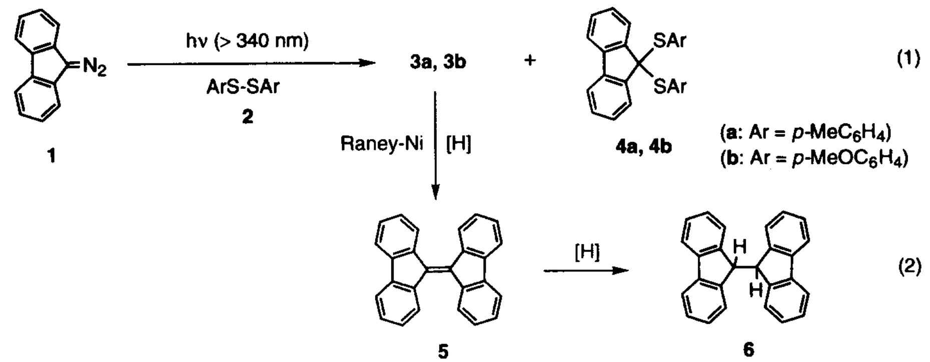
Abstract: Upon irradiation (>340 nm) of a benzene solution of diazofluorene with di-*p*-tolyl- or di-*p*-anisyl disulfide, the corresponding 9,9'-bis(arylmercapto)bifluorenyl was afforded in moderate to good yield accompanied by formation of 9,9'-bis(arylmercapto)fluorene. The major reaction pathway is considered to be a disulfur ylide formation followed by two times of successive Stevens rearrangement or by concerted electron redistribution *via* [2,3]sigmatropic rearrangement.© 1997 Elsevier Science Ltd.

Reactions of singlet carbenes with sulfides are one of the useful methodology for synthesizing sulfur ylides.[1] As an extension, the reaction of those with disulfides is an interesting approach to synthesize disulfur ylides. A study directing this conception has been less studied so far.[2] The major reactivity patterns which have been elucidated are carbene monoinsertion[3] into the S-S bond and desulfurization observed in sterically congested disulfides to give thioethers.[4] In the mechanistic viewpoints, the reactions of diphenylcarbene and fluorenylidene with sulfides and disulfides have been studied.[5] The results suggest that diphenylcarbene generally displays chemistry characteristic of the triplet state leading to the products (a thioether and a thioacetal) by a radical-like displacement mechanism. By contrast, triplet fluorenylidene is readily able to access the singlet manifold to give the same type of products by an ylide mechanism but the reaction of it with diaryl disulfide has been still unknown. Now we found the formation of 9,9'-bis(arylmercapto)bifluorenyl, namely a carbene diinsertion product between the S-S bond of the disulfide.

A benzene solution of 9-diazofluorene (**1**, 1.04×10^{-2} M) and di-*p*-tolyl disulfide (**2a**, 5.20×10^{-3} M) was irradiated under argon with a Xenon lamp (500 W) using a glass filter (>340 nm)[6] for 24 h. The resulting mixture was separated with column chromatography (silica gel) to give two products (**3a** and **4a**) (eq. 1). The minor product **4a** (yield, 1.4%) was determined as 9,9'-bis(*p*-tolylmercapto)fluorene by independent synthesis.[7] The structure of **3a** (yield, 52%) was determined unequivocally by single crystal X-ray crystallography[8] shown in Figure 1. Intriguing structural features of **3a**, 9,9'-bis(*p*-tolylmercapto)bifluorenyl,[9] are: 1) Relatively short distance (3.16 Å) between sulfur atoms shows close contact in both atoms with reference to the van der Waals radius of a sulfur atom (1.85 Å).[10] 2) Dihedral angle (51.0°) consisted of a central S-C-C-S framework shows a staggered structure of this compound which accommodates a favorable arrangement for lower repulsion between lone pair electrons of both sulfur atoms. The molecular structure of **3a** could be predicted also correctly by a semiempirical molecular orbital calculation[11] (a calculated dihedral angle of S(1)-C(1)-C(1)-S(1) of the energy-optimized **3a**: 49.6°). Based on the crystallographic and molecular modeling results, the molecular structure of **3a** is suggested to be that of a highly substituted ethane and the crystal structure is apparently the most energeti-



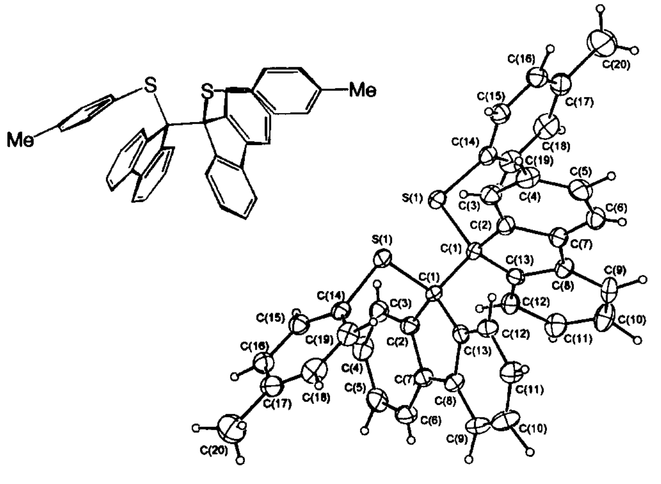


Fig. 1. ORTEP drawing of **3a** with atom labeling scheme.

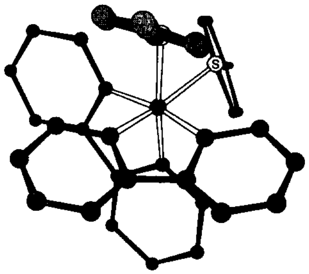


Fig. 2. Side view from the direction of the C(1)-C(1) axis of **3a** generated by a semiempirical molecular orbital calculation. Bonds are shaded except for the ones showing the ethane ligands. Hydrogens are omitted for clarity.

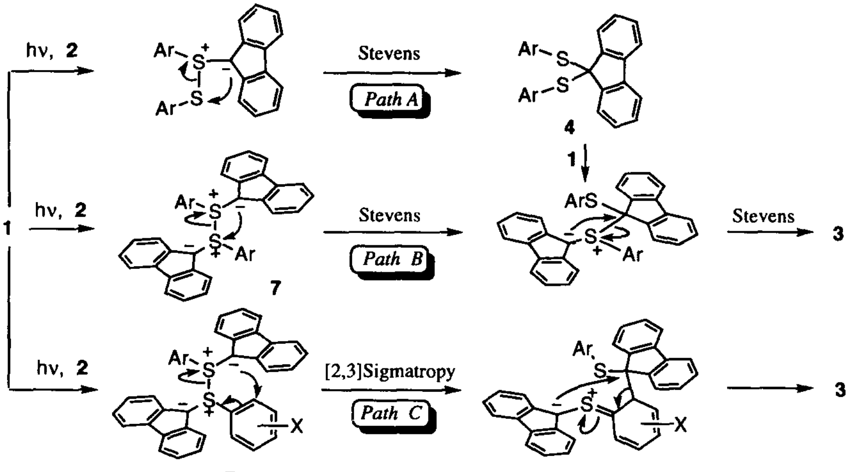
cally favored one (Figure 2). Hydrogenolysis of **3a** with Raney nickel gave 9,9'-bifluorene (**6**) quantitatively. When the reduction was done with the same catalyst with lower activity, bifluorenylidene (**5**) as well as **6** was obtained (eq. 2). Diazofluorene **1** and di-*p*-anisyl disulfide (**2b**) reacted in a similar way to give **3b**[12] in 43% and **4b** in 26% yields after chromatographic separation.[13] Formation of the carbene diinsertion products like **3** has been previously reported in only two examples as trace byproducts.[3a, 3c]

According to the EPR, laser flash photolysis and product studies on **1** with a variety of disulfides, Alberti *et al.* concluded that triplet fluorenylidene is a highly reactive carbene and forms ylides with great rapidity by facile intersystem crossing to the singlet state.[5] Likewise in our reaction, no effect of oxygen as a triplet quencher on the formation of **3a** was observed (runs 1 and 2 in Table 1) and when the photoreaction of **1** was examined in the presence of an equimolar mixture of **2a** and **2b**, **3a** and **3b** formed without any scrambling of *p*-tolyl and *p*-anisyl groups in **3**. These facts suggest that the photoreaction proceeds *via* a singlet state (a singlet fluorenylidene or a sulfur ylide). Moreover, although analogous photoreactions of diarydiazomethane were examined, no corresponding 9,9'-bifluorenyl was formed at all. Regarding the variation of disulfides, no 9,9'-bis(alkylmercapto)bifluorenyl was afforded with di-*n*-butyl and di-*t*-butyl disulfides and the experiments reproduced the results reported by Alberti *et al.*[5] Only the reactions with diaryl disulfides (aryl = phenyl, *p*-chlorophenyl, *p*-anisyl and *p*-tolyl) gave the fluorenylidene-diinsertion product into the S-S bond of them. One of the plausible intermediate (Scheme 1), a thioacetal **4** prepared independently[7] was subjected to the reaction with **1**, but **4** was recovered almost quantitatively (*Path A*). Another candidate of the intermediate, bifluorenylidene (**5**) was subjected to the reaction with **2a** (runs 3 and 4 in Table 1).[14] The reactivity of **5** was found to be *ca.* 1/7 of that of **1** (*Path D*, not shown in Scheme 1). *Paths A* and *D*, therefore, are minor reaction pathways, if any.[15] Based on the above experiments, we propose disulfur ylide formation followed by two times of successive Stevens rearrangement[16,17] (*Path B*) or by a concerted electron redistribution *via* [2,3]sigmatropic rearrangement[17] (*Path C*) to **3** shown in Scheme 1. The crystal structure of **3a** also suggests that face-to-face arrangement with ca. 50° of staggering of two fluorene moieties is auspicious of the concomitant formation of the S-ylide **7** by approaching fluorenylidenes to the sulfur atoms through the preexisting space of **2**[18] and subsequently, product **3** is formed by least motion of two fluorenylidene moieties of **7**. According to the experimental results that only diaryl disulfides **2** reacted with **1** to give **3** successfully, *Path C* is more suited as the actual reaction pathway. Under the present circumstances, elucidation of the detailed reaction mechanism awaits further studies.

Table 1. Photoreactions of **1** or **5** with **2a** in benzene.[a]

Run	Atmosphere	Recovery and Products (Yield/%)				
		1	**5**	**2a**	**3a**	9-Fluorenone
1[b]	Ar	79	-	85	15	-
2[b]	O_2	15	-	85	15	61
3[c]	Ar	-	98	98	2	-
4[c]	O_2	-	78	98	2	20

a) All reaction time was 40 min. Diazofluorene (**1**) (runs 1 and 2) or bifluorenylidene (**5**) (runs 3 and 4) with **2a** was irradiated with a Xe lamp (500 W) through a glass filter (Toshiba, UV-35, >340 nm) in a Pyrex test-tube. Product yields were estimated by ^{1}H NMR spectroscopy (400 MHz).
b) [**1**] = 1.0×10^{-3} M, [**2a**] = 5.0×10^{-4} M.
c) [**5**] = [**2a**] = 9.8×10^{-4} M.



Scheme 1

ACKNOWLEDGMENT

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6. Diazofluorene **1** only absorbs the incident light under the conditions.
7. (a) Evans, D. A.; Grimm, K. G.; Truesdale, L. K. *J. Am. Chem. Soc.* **1975**, *97*, 3229-3230. (b) Kuwajima, I.; Abe, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2183-2184. (c) Compound **4a**. Colorless needles; mp 140-142 °C (recrystallized from Et_2O); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 6.8 Hz), 7.16-7.29 (6H, m), 7.01 (4H, d, J = 8.1 Hz), 6.84 (4H, d, J = 8.1 Hz), 2.19 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.96, 139.17, 138.84, 136.37, 128.88, 128.25, 128.03, 127.05, 125.42, 119.77, 66.92, 21.23; MS (20 eV) m/z (%): 410 (M, 2), 287 ($M-C_6H_4Me$, 100), 165 (fluorene, 13), 123 (MeC_6H_4S, 12); Anal. Calcd for $C_{27}H_{22}S_2$: C,78.98; H 5.40%, found: C, 78.84; H, 5.44%.
8. Crystal data: $C_{40}H_{30}S_2$, M_w = 574.80, orthorhombic, space group, F_{ddd} (#70), crystal size 0.10 x 0.10 x 0.10 mm, a = 35.753(8), b = 37.922(8), c = 9.156(2) Å, V = 12415(5) Å^3, Z = 16, D_c = 1.23 g cm^{-3}, F (000) = 4831, R = 0.050, R_w = 0.041, 3360 reflections were collected.
9. Compound **3a**. Colorless needles; mp 253-254 °C (decomp.) (recrystallized from 50% $CHCl_3$-hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41(4H, brs), 7.05-7.09 (12H, m), 6.57 (4H, d, J = 7.8 Hz), 6.52 (4H, d, J = 7.8 Hz), 2.03 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.54, 140.80, 138.15, 136.15, 128.20, 127.78, 127.39, 126.84, 126.02, 118.60, 69.86, 21.01; MS (70 eV) m/z (%) 328 (bifluorenylidene, 72), 287 (M/2, 100), 246 (MeC_6H_4, 28), 196 (5), 180 (61), 165 (44), 123 (45), 91 (51); Anal. Calcd for $C_{40}H_{30}S_2$: C, 83.58; H, 5.26%, found: C, 83.57; H, 5.50%.
10. Emsley, J. *The Elements*; Oxford University Press: Oxford, 1997. In the ^1H NMR spectra of **3a** in benzene-d_6, the signal broadenings were observed at room temperature possibly due to a hindered rotation around the central C-C bond, suggesting that the interaction between S-S atoms are the one in both solid and liquid states.
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12. Compound **3b**. Colorless needles; mp 242-244 °C (decomp.) (recrystallized from 50% $CHCl_3$-hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (4H, brs), 7.02-7.20 (12H, m), 6.60 (4H, d, J = 8.8 Hz), 6.24 (4H, d, J = 8.8 Hz), 3.54 (6H, s); ^{13}C NMR(100 MHz, $CDCl_3$) δ 159.7, 145.6, 140.7, 137.9, 127.8, 127.3, 126.0, 121.1, 118.7, 112.9, 69.8, 54.9; MS (70 eV) m/z (%) 303 (M/2-H, 43), 165 ($M/2-MeOC_6H_4SH$, 100), 139 (M/2-fluorene, 79), 124 (SC_6H_4O, 18); Anal. Calcd for $C_{40}H_{30}O_2S_2$: C, 79.18; H, 4.98%, found: C, 79.16; H, 5.16%.
13. The corresponding thermal reactions did not proceed efficiently and the yields estimated by ^1H NMR (400 MHz, $CDCl_3$) of the reaction mixture were as follows: **3a** (*ca.* 3%), **4a** (11%), and **3b** (6%), **4b** (trace). The majority was recovered starting materials and others were bifuorenylidene and fluorenone azine.
14. Upon heating at the melting point of **3**, **3** was decomposed to **5** and **2** with a small amount of unidentified byproduct.[19] The fact suggests a possibility of a reversal reaction, the formation of disulfur substituted diaryl by addition of olefins and disulfides. Under the same conditions with the reactions of **1** and **2**, photoreaction of **5** with **2a** (2.62×10^{-3} M, each) for 1 week afforded **3a** in 46% yield in benzene.
15. Photo- and thermal reactions of 9-fluorenone azine with **2** were also examined but no supportive results were obtained. An arylsulfinyl radical cannot be generated under the reaction conditions.
16. In stricter sense, the mechanism of the Stevens rearrangement has been recognized as a homolytic dissociation-recombination process: Baldwin, J. E.; Erickson, W. F.; Hackler, R. E.; Scott, R. M.; *J. Chem. Soc., Chem. Commun.* **1970**, 576-578.
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18. The disulfide linkage of diaryl disulfides exists in a rigid non-planar conformation with a dihedral angle of *ca.* 90° between the Ar-S-S planes: Pappalardo, G. C.; Ronsisvalle, G. *Tetrahedron* **1972**, *28*, 4147-4154.
19. The corresponding photodecompositions of naphtho[1,8-*ef*][1,4]dithiepins have been reported: Fujii, T.; Takahashi, O.; Furukawa, N. *J. Org. Chem.* **1996**, *61*, 6233-6239.

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