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The Reaction of Thiocumulenes with Fulvene

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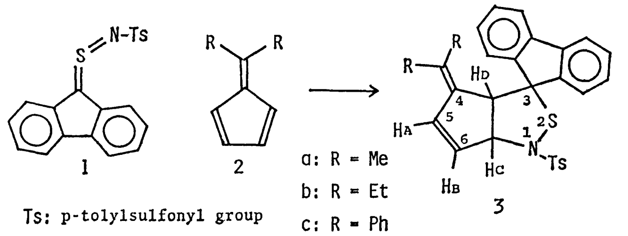
Synopsis. *S*-(9-Fluorenylidene)-*N*-(*p*-tolylsulfonyl)-sulfimide and bis(*p*-tolylsulfonyl)sulfur diimide reacted as 1,3-dipoles with fulvenes to form (2+3)cycloadducts.

Thiocumulenes add readily to a great variety of multiple bond compounds, giving rise to stable or unstable cycloadducts. *N*-Sulfinylamines (R–N=S=O), sulfur diimides (R–N=S=N–R′), thione *S*-oxides (RR′C=S=O), and sulfimides (RR′C=S=N–R″) react as 2π-components with acyclic dienes to give stable (2+4)-cycloadducts.$^{1-4)}$ In the reaction with cyclopentadiene, thione *S*-oxides react also as 2π-components,$^{3)}$ whereas sulfimides react as 1,3-dipoles to give (2+3)cycloadducts.$^{4)}$ The (2+4)adduct of cyclopentadiene and *N*-sulfinylbenzenesulfonamide can be isolated only at low temperatures, but decomposes into its components at room temperature.$^{5)}$ Accordingly we took an interest in the reactions of these thiocumulenes with fulvene because fulvene is one of the model compounds which undergo periselective cycloaddition reactions.$^{6)}$

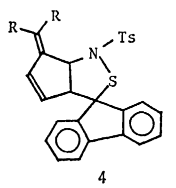
The reaction of sulfimide (**1**) with dimethylfulvene (**2a**) under mild conditions produced a single adduct **3a** in nearly quantitative yield. The mass spectra and the elemental analyses suggested that the product was a 1:1-adduct. The IR spectrum showed the presence of νC=C absorption at 1670 cm^{-1} and the absence of any strong νS=N absorption band in the region of 900—1000 cm^{-1}. The ^{1}H NMR spectrum displayed three methyls as singlets at δ 0.57, 1.49 and 2.47 (Ts) and two olefinic and two methine protons (δ 6.59 (H_A, dd), 5.96—5.76 (H_B, H_C, m), 4.04 (H_D, d)). The chemical shifts of H_A-H_D and the coupling constants (J_{AB}=5.3, J_{AC}=1.9, J_{CD}=7.0 Hz) determined by spin-decoupling measurements centered at H_A, H_{B-C}, and H_D are consistent with structure **3** or **4** rather than with **5** or **6**, indicating that H_A and H_B are vicinal olefinic protons and that H_C and H_D are vicinal *cis*-methine protons. In the two methyls of the fulvene moiety, the resonance for the inside methyl group (δ 0.57) appeared at a higher field than that of the outside methyl group (δ 1.49) due to the shielding effect exerted by the diamagnetic anisotropy of the adjacent fluorenylidene ring. This excludes the possibility of the regioisomer **4**. The structure **3** was also supported by the ^{13}C NMR spectroscopy (see Experimental). Treatment of **1** with **2b** and **2c** also gave (2+3)cycloadducts (**3b** and **3c**) in fairly good yields.



1 2 3

a: R = Me
b: R = Et
c: R = Ph

Ts: p-tolylsulfonyl group



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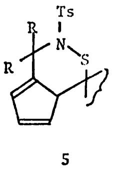

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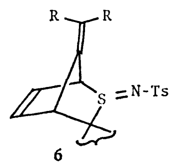

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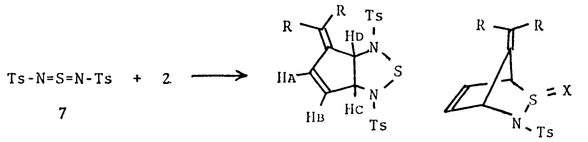
When the mixture of bis(*p*-tolylsulfonyl)sulfur diimide (**7**) and **2a** in 1,2-dichloroethane was stirred for a day at room temperature, a minor cycloadduct (**8a**) was obtained together with a major polymeric black tar and *p*-toluenesulfonamide, which might be derived from **7** (the unreacted **7** or **9**) during the column chromatography operation.$^{7)}$ The IR spectrum of the adduct showed νC=C at 1660 cm^{-1}. In the ^{1}H NMR spectrum, four sets of methyl protons were observed, at δ 1.80, 1.83, 2.42 and 2.44, as singlets. Obviously the two methyls of higher field were those of the substituents at C-6 of the fulvene, and the others arose from the megnetically unequivalent *p*-tolylsulfonyl groups. The four resonances at δ 6.56 (dd, H_A, J_{AB}=5.8, J_{AC}=1.0 Hz), 5.69 (dt, H_D, J_{CD}=6.0, J_{BD}=1.0 Hz), 5.38 (d of m, H_B, J_{AB}=5.8 Hz), and 5.23 (d of m, H_C, J_{CD}=6.0, J_{AC}=1.0 Hz) were assigned to the protons attached to the fulvene frame in **8a** by means of spin-decoupling measurements. These coupling patterns exclude the other peri-isomeric cycloadducts such as the Diels-Alder type (2+4)cycloadduct **9a**. The treatment of **2a** with *N*-sulfinyl-*p*-toluenesulfonamide (**10**) also gave **8a** in a low yield (6%), along with the major decomposed products. Partial conversion of **10** into **7** can account for this anomalous result.$^{8)}$ As in the reaction between *N*-sulfinylbenzenesulfonamide and cyclopentadiene,$^{5)}$ it has been considered that **7** and **10** can also interact with **2** to give (2+4)-cycloadducts (**9**, **11**), but the adducts would be unstable and decomposed under the reaction conditions.



7 8

a: R = Me, b: R = Et, c: R = Ph

9: X=NTs, 11: X=O

Reactions of 9-fluorenethione *S*-oxide or 9-xanthenethione *S*-oxide with **2** were unsuccessful, and only decomposed products were formed.$^{9)}$

In summary, the thiocumulenes$^{10)}$ (**1**, **7**) with the preferential 1,3-dipolar nature were found to react with **2** to give the stable (2+3)cycloadducts regio- and siteselectively, whereas the dienophilic thiocumulenes$^{10)}$ (**10** and thione *S*-oxide) underwent only decomposition reactions, presumably *via* unstable (2+4)cycloadducts.

Experimental

Reaction of Sulfimide (1) with Fulvenes (2). To a partially suspended solution of **1** (914 mg, 2.5 mmol) in dry 1,2-dichloroethane (30 ml) was added a solution (10 ml) of dimethylfulvene (**2a**) (318 mg, 3 mmol) with stirring at temperature 0—5 °C under a nitrogen atmosphere. The red suspension of **1** gradually disappeared and the solution turned orange-yellow within 1 h. After the reaction mixture was stirred overnight at room temperature, the solvent was evaporated and the residue was recrystallized from benzene–hexane to give spiro[fluorene-9,3′-1′,2′,3′,3′a,4′,6′a-hexahydro-4′-isopropylidene-1′-(*p*-tolylsulfonyl)-2′-thia-1′-azapentalene] (**3a**) as colorless needles (99% yield). None of the other adducts was obtained from the reaction mixture by a chromatography, and the excess of the fulvene was recovered. The adduct **3b** was obtained by a similar treatment and column chromatography (silica gel, benzene and/or dichloromethane). The reaction of **1** with diphenylfulvene (**2c**) was carried out at a temperature of *ca.* 30 °C for 3 h. After the mixture was stirred overnight at room temperature, the solvent was evaporated and the residue was subjected to a column chromatography (silica gel, benzene) to give **3c** as colorless crystals (benzene–hexane, 87%).

3a: 99% yield; mp 210—211 °C; IR (KBr) 1670 cm^{-1} (C=C); ^{1}H NMR δ 0.57, 1.49 (s, CH$_3$), 2.47 (s, CH$_3$(Ts)), 4.04 (d, H_D, $J_{CD}=7.0$ Hz), 5.76—5.96 (m, H_B, H_C), 6.59 (dd, H_A, $J_{AB}=5.3$, $J_{AC}=1.9$ Hz), 7.00—7.92 (m, 12H, arom); ^{13}C NMR δ 20.2 ,21.6 (q, CH$_3$), 21.7 (q, CH$_3$(Ts)), 59.2 (d, C-5), 72.3 (s, C-4), 77.0 (d, C-1); MS *m/e* 471 (30, M$^+$). Found: C, 71.35; H, 5.44; N, 2.97%. Calcd for $C_{28}H_{25}NO_2S_2$: C, 71.32; H, 5.34; N, 2.97%.

3b: 74% yield; mp 166—167 °C; IR (KBr) 1660 cm^{-1} (C=C); ^{1}H NMR δ 0.26 (t, CH$_3$ (inside Et)), 0.64 (t, CH$_3$ (outside Et)), 0.7—1.3 (m, CH$_2$ (inside Et)), 1.7—2.1 (m, CH$_2$ (outside Et)), 2.49 (s, CH$_3$ (Ts)), 4.07 (d, H_D, $J_{CD}=$ 7.0 Hz), 5.80—5.96 (m, H_B, H_C), 6.61 (dd, H_A, $J_{AB}=5.3$, $J_{AC}=2.0$ Hz), 7.03—7.96 (m, 12H, arom); ^{13}C NMR δ 11.4, 13.1 (q, CH$_3$), 21.6 (s, CH$_3$(Ts)), 23.6 25.7 (t, CH$_2$), 58.7 (d, C-5), 72.4 (s, C-4), 76.8 (d, C-1); MS *m/e* 499 (33, M$^+$). Found: C, 72.22; H, 5.90; N, 2.76%. Calcd for $C_{30}H_{29}NO_2S_2$: C, 72.13; H, 5.85; N, 2.80%.

3c: 87% yield; mp 215—216 °C; IR (KBr) 1660 cm^{-1} (C=C); ^{1}H NMR δ 2.45 (s, CH$_3$(Ts)), 4.66 (d, H_D, $J_{CD}=$ 6.8 Hz), 5.89 (ddd, H_C, $J_{CD}=6.8$, $J_{AC}=2.1$, $J_{BC}=2.1$ Hz), 6.07 (dd, H_B, $J_{AB}=5.7$, $J_{BC}=2.1$ Hz), 6.14—6.30 (m, 2H, arom), 6.46—6.70 (m, H_A, 3H-arom), 6.77—7.03 (m, 12H, arom); MS *m/e* 595 (39, M$^+$). Found: C, 76.67; H, 5.03; N, 2.27%. Calcd for $C_{38}H_{29}NO_2S_2$: C, 76.62; H, 4.91; N, 2.35%.

*Reaction of Sulfur Diimide (**7**) with Fulvene (**2**).* The sulfur diimide (**7**) was prepared from *N*-sulfinyl-*p*-toluenesulfonamide (**10**) by the method in the literature.[2,8] A freshly prepared sulfur diimide (**7**) (1.15 g, 3.11 mmol) in a 1,2-dichloroethane solution (15 ml) was dropwise added over a period of 1.5 h to a solution of **2a** in 1,2-dichloroethane (10 ml) with stirring at a temperature of −10—−15 °C. After being stirred overnight at room temperature, the solvent was evaporated and the residue was subjected to column chromatography twice (silica gel, benzene and dichloromethane) to give crude **8a**, which was recrystallized from benzene–ligroin. Consequent elution with methanol gave *p*-toluenesulfonamide (0.69 g, 65%).

8a: Colorless crystals (14% yield); mp 179—180 °C; IR (KBr) 1660 (weak, C=C); ^{1}H NMR δ 1.80, 1.83 (s, CH$_3$), 2.42, 2.44 (s, CH$_3$(Ts)), 5.23 (d of m, H_C, $J_{CD}=6.0$, $J_{AC}=1.0$ Hz), 5.38 (d of m, H_B, $J_{AB}=5.8$ Hz), 5.69 (dt, H_B, $J_{CD}=$ 6.0 Hz), 6.56 (dd, H_A, $J_{AB}=5.8$, $J_{AC}=1.0$ Hz), 7.20—7.88 (m, 8H, arom); ^{13}C NMR δ 20.9, 22.0 (q, CH$_3$), 21.6, 21.7 (q, CH$_3$(Ts)), 70.0, 72.0 (d, C-1, C-5); MS *m/e* 476 (7, M$^+$). Found: C, 55.59; H, 5.10; N, 5.77; S, 20.06%. Calcd for $C_{22}H_{24}N_2O_4S_3$: C, 55.44; H, 5.08; N, 5.88; S, 20.18%.

8b: Colorless crystals (12% yield); mp 129—131 °C; IR (KBr) 1655 cm^{-1} (weak, C=C); ^{1}H NMR δ 0.88, 0.96 (t, CH$_3$), 1.9—2.5 (m, 4H, CH$_2$), 2.42 ,2.45 (s, CH$_3$(Ts)), 5.19 (ddd, H_C, $J_{CD}=6.0$, $J_{BC}=2.4$, $J_{AC}=1.0$ Hz), 5.44 (dd, H_B, $J_{AB}=6.0$, $J_{BC}=2.4$ Hz), 5.69 (d, H_D, $J_{CD}=6.0$ Hz), 6.54 (dd, H_A, $J_{AB}=6.0$, $J_{AC}=1.0$ Hz), 7.2—7.9 (m, 8H, arom); ^{13}C NMR δ 13.0 ,13.6 (q, CH$_3$), 21.6, 21.7 (q, CH$_3$ (Ts)), 24.6, 25.6 (t, CH$_2$), 70.3, 71.5 (d, C-1, C-5); MS *m/e* 504 (5, M$^+$). Found: C, 57.13; H, 5.76; N, 5.38; S, 18.92%. Calcd for $C_{24}H_{28}N_2O_4S_3$: C, 57.12; H, 5.59; N, 5.55; S, 19.06%.

8c: Colorless crystals (27% yield); mp 209—210 °C; IR (Nujol) 1670 cm^{-1} (weak, C=C); ^{1}H NMR δ 2.36 ,2.42 (s, CH$_3$ (Ts)), 5.29 (ddd, H_C, $J_{CD}=6.0$, $J_{BC}=2.5$, $J_{AC}=0.8$ Hz), 5.65 (dd, H_B, $J_{AB}=5.8$, $J_{BC}=2.5$ Hz), 6.31 (d, H_D, $J_{CD}=6.0$ Hz), 6.49 (dd, H_A, $J_{AB}=5.8$, $J_{AC}=0.8$ Hz), 6.9—7.8 (m, 18H, atom); ^{13}C NMR δ 21.6 (q, CH$_3$ (Ts)), 70.0, 71.7 (d, C-1, C-5); MS *m/e* 600 (2, M$^+$). Found: C, 64.01; H, 4.69; N, 4.67; S, 15.98%. Calcd for $C_{32}H_{28}N_2O_4S_3$: C, 63.98; H, 4.70; N, 4.66; S, 16.01%.

Reaction of N-*Sulfinyl*-p-*toluenesulfonamide (**10**) with Dimethylfulvene (**2a**).* To a solution of **10** (1.09 g, 5 mmol) in 1,2-dichloroethane (20 ml) was added dropwise a solution of **2a** (0.53 g, 5 mmol) in 1,2-dichloroethane (15 ml) with stirring at 0 °C. The reaction mixture was stirred for 4 h and gradually became darker. After removal of the solvent, the residue was chromatographed (silica gel, benzene, dichloromethane and methanol) to give 72 mg (6%) of **8a**, 20 mg of unidentified material, 0.7 g (82%) of *p*-toluenesulfonamide, and a black tar. The **8a** was identified by comparisons of the IR and NMR spectra with those of the previously mentioned **8a**.

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6) a) K. N. Houk, J. K. George, and R. E. Duke, Jr., *Tetrahedron*, **30**, 523 (1974); b) K. N. Houk and L. J. Luskus, *J. Org. Chem.*, **38**, 3836 (1973); c) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," Wiley, London (1976).

7) On the contrary, a (2+3) adduct between **7** and cyclopentadiene was quantitatively obtained (92%; mp 189—191 °C).

8) W. Wucherpfenning and G. Kresze, *Tetrahedron Lett.*, **1966**, 1671. *N*-Sulfinylarenesulfonamides easily produce the corresponding sulfur diimides even by the action of a catalytic weak base such as pyridine.

9) Zwanenburg *et al.* reported that the reaction of thione S-oxides with cyclopentadiene and acyclic dienes yielded Diels-Alder type (2+4)cycloadducts, which were relatively unstable (Ref. 3).

10) According to the proposal by Inagaki and Okazaki, the order of 1,3-dipolar nature is as follows:

$$>\!CSN- \; > \; -NSN- \; > \; >\!CSO \; > \; -NSO.$$

Y. Inagaki and R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **36**, 1 (1978).