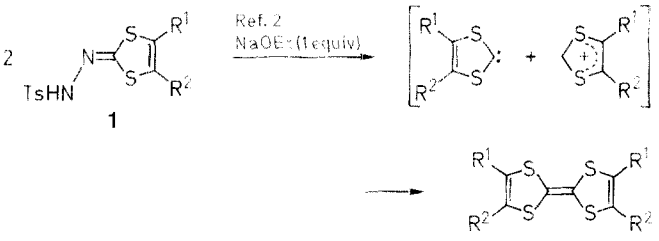
A Facile Synthesis of Substituted 2-Tosylhydrazono-1,3-dithioles

Shmuel Bittner,*[a] Alec Moradpour,*[b] Penina Krief[a]

[a] Department of Chemistry, Ben Gurion University of the Negev, Beer-Sheva 84120, Israel
[b] Laboratoire de Physique des Solides, UA2 du CNRS, Université de Paris-Sud, F-91405, Orsay, France

A new synthesis of 2-tosylhydrazono-1,3-dithioles is reported. These tetrathiafulvalene precursors are prepared by a one-pot reaction from potassium *N'*-tosylhydrazine-*N*-dithiocarboxylate and various α-haloketones.

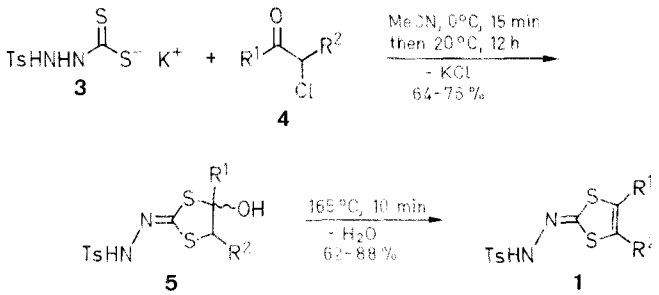
It was shown that 2-tosylhydrazono-1,3-dithioles **1** can be used as precursors of tetrathiafulvalenes **2**.[1] Thus, pyrolysis of the 1,3-benzenedithiol derivative in the presence of one equivalent of sodium ethoxide in diglyme at 180 °C, leads to dibenzotetrathiafulvalene.[2] It was postulated that the intermediate carbene formed (Scheme **A**) react in part with ethanol to form a 1,3-dithiolium salt. This salt couples with the carbene to produce the tetrathiafulvalene **2**.



Scheme **A**

The 1,3-dithioles **1** were previously prepared by *S*-methylation of 2-thioxo-1,3-dithiole derivatives followed by condensation with tosylhydrazide.[2] We now describe an alternative convenient method for the preparation of a variety of new compounds of type **1** under simple reaction conditions, and which can also be performed on a large scale.

Thus, when the potassium *N'*-tosylhydrazine-*N*-dithiocarboxylate (**3**)[3] was reacted with α-haloketones **4** in refluxing acetonitrile, the initial substitution step was followed by spontaneous cyclization to yield compounds **5**. In some cases (**4a, e**) the reaction did not stop at that stage but was followed by elimination of water, yielding the 2-tosylhydrazono-1,3-dithioles (**1a, 1e**). Both, the cyclization step and the water elimination, are probably acid-catalyzed by the tosylic N–H



1, 4, 5	R^1	R^2	1, 4, 5	R^1	R^2
a	CH_3	CH_3	**d**	$-(CH_2)_3-$	
b	Ph	H	**e**	$-(CH_2)_4-$	
c	Ph	Ph			

Scheme **B**

Table. Products **5b–d** and **1a–e** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula[a]	UV(CH_3OH)[b] λ_{max} (nm) (log ε)	IR (KBr)[c] ν (cm^{-1})	^{1}H-NMR[d] ($CDCl_3$/TMS) δ, J(Hz)	^{13}C-NMR[d] ($CDCl_3$/TMS) δ	MS[e] m/z (%)
5b	72	180–181 (MeCN)	$C_{16}H_{16}N_2O_3S_3$ (380.3)	–	3247, 3120, 1684, 1345, 1180, 695	2.47 (s, 3H); 3.63 (q, 2H, J = 11.7); 5.41 (s, 1H); 7.40 (m, 5H); 7.58 (q, 4H, J = 8.2); 7.87 (s, 1H)	–	–
5c	76[f]	145–146 (CH_2Cl_2)	$C_{22}H_{20}N_2O_3S_3$ (456.4)	–	3472, 3190, 1600, 1335, 1170, 698	2.47 (s, 3H); 4.48 (s, 1H); 5.12 (s, 1H); 4.82 (s, 1H); 5.29 (s, 1H); 6.78–7.92 (m, 14H); 8.22 (br s, 1H)	–	–
5d	64	164–165 (MeCN)	$C_{13}H_{16}N_2O_3S_3$ (344.3)	–	3456, 3198, 1596, 1330, 1170, 675	1.63 2.22 (m, 6H); 2.44 (s, 3H); 3.75 (m, 1H); 4.96 (br s, 1H); 7.58 (q, 4H, J = 7.1); 8.16 (s, 1H)	–	
1a	79	146–147 (MeOH)	$C_{12}H_{14}N_2O_2S_3$ (314.3)	334 (3.99)	3140, 1570, 1335, 1160, 1005, 670	2.17 (s, 3H); 2.38 (s, 3H); 2.43 (s, 3H); 7.45 (q, 4H, J = 8.3); 8.45 (s, 1H)	11.99; 12.83; 21.76; 114.23; 129.05; 129.88; 134.02; 135.46; 145.87; 183.77	314 (M^+, 41); 159 (100)
1b	62	165–166 (CH_2Cl_2)	$C_{16}H_{14}N_2O_2S_3$ (362.3)	328 (4.03)	3205, 1595, 1350, 1155, 660	2.38 (s, 3H); 5.29 (s, 1H); 7.33 (q, 4H, J = 8.3); 7.34–7.50 (m, 5H); 8.63 (s, 1H)	21.63; 105.44; 128.53; 129.40; 129.67; 134.41; 142.87; 145.35; 184.10	362 (M^+, 29); 134 (100)
1c	88	166–167 (MeOH)	$C_{22}H_{18}N_2O_2S_3$ (438.4)	340 (4.19)	3120, 1600, 1260, 1160, 695	2.35 (s, 3H); 7.19 (q, 4H, J = 8.2); 7.16 (m, 10H); 8.45 (s, 1H)	21.61; 122.03; 128.34; 128.45; 128.52; 128.65; 128.73; 129.40; 129.61; 131.09; 134.91; 137.49; 145.08; 185	438 (M^+, 9); 210 (100)
1d	72	147–148 (MeCN)	$C_{13}H_{14}N_2O_2S_3$ (326.3)	341 (3.99)	3260, 1595, 1350, 1165, 1160	2.44 (s, 3H); 2.51 (m, 2H); 2.77 (t, 2H, J = 7.1); 3.07 (t, 2H, J = 7.1); 7.31 (q, 4H, J = 8.1); 8.54 (s, 1H)	21.78; 25.76; 28.33; 121.20; 129.09; 130.00; 133.54; 145.41; 146.01; 183.81	326 (M^+, 14); 171 (100)
1e	84	164–165 (MeCN)	$C_{14}H_{16}N_2O_2S_3$ (340.3)	334 (3.98)	3190, 1597, 1352, 1170, 675	1.88 (m, 4H); 2.43 (s, 3H); 2.46 (br s, 2H); 2.82 (br s, 2H); 7.45 (q, 4H, J = 8.1); 8.38 (s, 1H)	21.65; 21.74; 22.64; 23.42; 24.26; 117.40; 129.88; 133.95; 137.96; 145.82; 184.05	340 (M^+, 26); 185 (100)

[a] Satisfactory microanalyses obtained: C ±0.22, H ±0.05, N ±0.09, S ±0.24.
[b] Recorded on a Bausch & Lomb Spectronic 2000.
[c] Recorded on a Perkin-Elmer 781 spectrophotometer.
[d] Recorded on a Bruker WP 200 SY spectrometer.
[e] Recorded on a Finnigan 4020 quadropole spectrometer.
[f] Obtained as a mixture of the *syn* and *anti* isomers.

moiety of the molecule (Scheme **B**). The isolated intermediates **5b–d** could be transformed to **1b–d** by short heating at 150–160°C.

The structures of **1a–e** and of **4b–d** were established with the help of spectral and analytical data (Table). All the intermediate compounds **5** and the asymmetrical product **1b** were obtained as mixtures of *syn* and *anti* geometrical isomers as was ascertained on the basis of their NMR data.

Melting points are uncorrected, measured with a Thomas–Hoover capillary apparatus. Reagents and quality solvents were used without further purification. The potassium salt of *N'*-tosylhydrazine-*N*-dithiocarboxylate (**3**) was prepared according to an earlier reported procedure.[3]

2-Tosylhydrazono-1,3-dithioles 1; General Procedure:
Potassium *N'*-tosylhydrazine-*N*-dithiocarboxylate (3.0 g, 10 mmol) is dissolved in MeCN (50 mL) under slight heating. To the cooled solution (0°C), the α-chloroketone **4** (10 mmol) dissolved in MeCN (10 mL) is added dropwise over a period of 15 min under Ar. The mixture is warmed to 20°C, then stirred for additional 12 h. The solvent is evaporated, H_2O (50 mL) is added, and the mixture extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases are dried ($MgSO_4$) and evaporated to give the crude products **1a, 1e**, which are purified by crystallization either from MeOH or MeCN (see Table). In all other cases, **1b–d**, the intermediate compounds **5b–d** are obtained at that stage. Compound **5** is heated without solvent for 10 min at 165°C under Ar until the gas evolution (H_2O) stops, and the melt gets a yellowish color. It is cooled and purified by recrystallization to yield **1b–d** (see Table).

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