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General and Facile Synthesis of 2-Substituted Tropothiones

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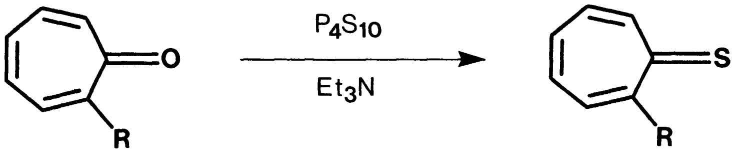
Several tropothiones having an electron-donating group at the C-2 position have been synthesized by direct thiocarbonylation of the corresponding tropones in polar solvents. The products are characterized by IR, UV-visible, and ^1H NMR spectroscopies.

We have recently reported that tropothione (**1a**, R = H) exists as 'reactive crystals' where **1a** undergoes cyclodimerisation spontaneously in the crystalline state below the melting point, representing the first case of nontopochemically controlled reaction.[1)] The compound **1a** is isolated at low temperatures as an unstable crystalline material (mp 21 °C, $\underline{t}_{1/2}^{0\ °C}$ ca. 1 h).[1,2)] The instability of **1a** has precluded its investigation for a long period. In connection with the parent **1a**,[2,3)] we need to prepare its stable derivatives which can be handled at room temperature.

In this paper we would like to report a general and facile synthetic procedure to obtain a variety of substituted tropothiones by the introduction of an electron-donating group (R: Me, Ph, NH_2, NHMe, OH, OMe, and SMe) at the C-2 position resulting in appreciable resonance stabilization over the ring. These tropothiones **1d-h** correspond to tropones **2d-h** which are well-known as 'active troponoid compounds'.[4)]

In order to prepare **1b-h** by direct sulfurization of the corresponding tropones (**2b-h**), we sought an efficient catalyst, solvent, and reaction conditions which enabled the reaction to proceed smoothly. After several unsuccessful attempts according to the previously reported method on the



(2) (1)

R: a, H; b, Me; c, Ph; d, NH_2; e, NHMe; f, OH; g, OMe; h, SMe

Table 1. Synthesis of Tropothiones

R	Compound	Condition			Yield[a)]	Mp	Property
		Solvent	Temp/°C	Time	%	θ_m/°C	
H	**1a**[b)]	CCl_4	10	30 min	98	20-21	red needles
Me	**1b**	CH_2Cl_2	0	1 h	94	38-39	red needles
Ph	**1c**	CH_2Cl_2	0	1 h	62	—	red oil
NH_2	**1d**	CH_3CN	20	3 h	63	137-138[c)]	orange needles
NHMe	**1e**	CH_2Cl_2	0	1 h	75	66-67[d)]	orange needles
OH	**1f**	CH_3CN	20	1 h	86	54-55[e)]	orange plates
OMe	**1g**	CH_2Cl_2	0	40 min	96	74-75	red prisms
SMe	**1h**	CH_3CN	0	30 min	82	75-76	red prisms

a) Yield of isolated product. b) Ref. 2. c) Ref. 7.
d) Refs. 7 and 9. e) Ref. 8.

preparation of **1a** from tropone[5)] (**2a**) with phosphorous decasulfide (P_4S_{10}) and triethylamine (Et_3N) in nonpolar solvents (benzene or carbon tetrachloride),[2)] a modification of the reported procedure using a polar solvent, dichloromethane or acetonitrile was found to give satisfactory yields.[6)] When the reaction were carried out in non-polar solvents, the starting tropones were recovered unchanged or the yields diminished significantly. We have also found that homogeneity and molarities of the reagent and catalyst are important in this synthetic reaction. We have used a homogeneous solution of P_4S_{10} and Et_3N in the molar ratio of 1:4. Thus, treatment of **2b-h** under the above conditions gave the desired tropothiones (**1b-h**). Table 1 summarizes the experimental results. Most of these tropothiones thus obtained are thermally stable except **1b,c** which do not possess heteroatom substituents. They decompose gradually at 0 °C, though **1b** has a sharp melting point.

The dipole moments of **1e,g** and **2e** were measured in benzene at 20.0 ± 0.1 °C.[10)] Table 2 summarizes the results with the reported values for **1a,f** and **2a,f,g**. The results indicate the polar nature of the molecules, in sharp contrast to those of the parent **1a** and **2a**, suggesting that the degree of polarization for **1** is larger than those for the corresponding **2**. The delocalization of electrons of tropothiones increases by methylamino, hydroxy, and methoxy group.

Table 2. Dipole Moments of Tropothiones and Tropones

R	Compound	μ/D	Compound	μ/D
H	**1a**	3.88[a)]	**2a**	4.17,[b)]4.30[c)]
NHMe	**1e**	4.73	**2e**	3.36
OH	**1f**	4.36[d)]	**2f**	3.53[d)]
OMe	**1g**	5.10	**2g**	4.72[b)]

a) Ref. 2. b) Ref. 11.
c) Ref. 12. d) Ref. 13.

Table 3. UV-visible and IR Spectral Data of Tropothiones

R	Compound	λ_{max} (MeOH) nm (log ε)			$\nu_{C=S}$[a]	ν_{X-H}[a]
H	**1a**[b]	225 (3.97)	253 (4.02)	381 (4.21)	1087	
Me	**1b**	227 (4.02)	261 (4.10)	387 (4.18)	1055	
Ph	**1c**	228 (4.44)[c]	252 (4.30)	388 (4.01)	1103	
NH_2	**1d**	236 (4.06)	276 (4.43)	444 (4.26)	1069	3470, 3198
NHMe	**1e**	240 (4.03)	284 (4.40)	456 (4.16)	1042	3080
OH	**1f**	234 (4.13)	266 (4.22)	418 (4.10)	1095	2742
OMe	**1g**	238 (4.10)	271 (4.22)	412 (4.22)	1049	
SMe	**1h**	226 (4.04)	304 (4.35)	428 (4.05)	1059	

a) cm^{-1} (CCl_4). b) Ref. 2. c) Shoulder.

Table 4. ^1H NMR (90 MHz, $CDCl_3$, Me_4Si) Spectra of Tropothiones[a]

R	Compound	H-7	H-3 — 6[b]	Substituent
H	**1a**[c]	8.02 (dm, *J* 12.5 Hz)	7.04,[d] 6.80[e]	————
Me	**1b**	8.28 (dm, *J* 11.7 Hz)	7.46 - 6.66[f]	2.52 (s, Me)
Ph	**1c**	8.21 (dm, *J* 11.8 Hz)	7.16 - 6.73	7.66-7.23 (m, Ph)
NH_2	**1d**	8.66 (complex m)	7.33 - 6.85	7.40 (br s, NH_2)
NHMe	**1e**	8.70 (complex m)	7.56 - 6.64	9.16,[g] 3.22[h]
OH	**1f**	8.57 (complex m)	7.62 - 6.96	9.95 (br s, OH)
OMe	**1g**	8.51 (dm, *J* 11.6 Hz)	7.13 - 6.60	4.04 (s, OMe)
SMe	**1h**	8.31 (dm, *J* 11.4 Hz)	7.37 - 6.61	2.48 (s, SMe)

a) Chemical shifts are represented in δ unit. b) Complex multiplet. c) Ref. 3 (400-MHz data). d) H-4,5. e) H-3,6. f) Separated into two parts at δ 7.46 (d, 1 H, $J_{3,4}$ = 9.0 Hz, H-3) and δ 7.06-6.66 (m, 3 H, H-4-6). g) Br s, NH. h) D, NHMe, $J_{NH,Me}$ = 5.4 Hz.

Tables 3 and 4 summarize the spectral data[14] obtained for **1b**-**h** on UV-vis, IR, and ^1H NMR along with those[2] of **1a** for comparison. The IR spectra of these tropothiones are characterized by the very strong broad absorption at around 1040 - 1100 cm^{-1} due to the C=S stretching vibration. UV-visible spectra of **1b**-**h** show characteristic three π-π^* transitions. The noteworthy feature in the ^1H NMR spectra (Table 4) of the tropothiones is that the H-7 protons resonate by far downfield from other ring protons due to strong C=S bond anisotropy.[15] This differs remarkably from those of the corresponding tropones (**2b**-**h**). Three derivatives **1d**-**f** are further stabilized with intramolecular hydrogen bonding whose IR spectra appear at around 3000 cm^{-1}. These absorptions shift to 2596 and 2368, 2300, and 2083 cm^{-1} for **1d**, **1e**, and **1f**, respectively, by addition of D_2O (ν_{X-H}/ν_{X-D}

= 1.32 - 1.35; X: N or O). **1d,e** and **1g,h** were hydrolyzed with potassium hydroxide in ethanol to afford **1f**.

As described above, we have succeeded in developing a general synthetic method to tropothiones. Considering availability of starting materials and experimental simplicity obviously superior to those in the reported methods$^{7-9)}$ for the synthesis of **1d,e** and **1f**, the explored scheme is promising as a practical synthetic route to these tropothiones.

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