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Synthesis of New Surfactants Mono and Bipolar Derived from 1,2,4-Triazole-5-thione

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ABSTRACT

3-Phenyl-1,2,4-triazole-5-thione (PTS) and 3-methyl-1,2,4-triazole-5-thione (MTS) are prepared in two steps. The first is a condensation of the thiosemicarbazide with the benzoyl chloride and the acetyl chloride for the PTS and MTS respectively in pyridinic medium. This step leads to the formation of 1-benzoylthiosemicarbazide and 1-acetylthiosemicarbazide. The 1-acetylthiosemicarbazide is also prepared with a new method consisted of a simple solvolysis the thiosemicarbazide in acetic

4189

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acid for 4 hr. The second is the intramolecular cyclization in methanol with the presence of the sodium methalate leads to the formation of the PTS and the MTS in good yields. The alkylation of MTS and PTS under the conditions of solid–liquid phase transfer catalysis (PTC) allowed us to synthesize some new mono and bipolar surfactants compounds derived from 1,2,4-triazole-5-thione in good yields.

Key Words: 1,2,4-Triazole-5-thione; Intramolecular cyclization; Alkylation; PTC; Surfactant.

INTRODUCTION

Heterocyclic compounds present various applications especially in pharmacology^[1-3] and metal surface treatments.^[4] Many studies have shown that triazole derivatives have useful corrosion inhibition effects.^[5-8] In our laboratory we have shown that 3-methyl-1,2,4-triazole-5-thione (1) and 3-phenyl-1,2,4-triazole-5-thione (2) were found to have a marked inhibiting effect of brass corrosion in the neutral medium.^[9,10]

Because 1,2,4-triazole-5-thione surfactants monopolar, bipolar and bicatenar are interesting from synthetic and applied points of view; we developed a method to prepare new triazole derivatives of general formula (Scheme 1).

RESULTS AND DISCUSSION

This study describes the synthesis of monopolar, bipolar, and bicatenar surfactants of 1,2,4-triazole-5-thione derivatives.

1,2,4-Triazole-5-thione is not commercially available so we prepared it by using Jones's method described elswhere,^[11] as shown in Scheme 2.

The yields were about 60%. The special conditions for this reaction are presented in the experimental section.

In our laboratory, we developed a new method of synthesis of the 1-acetylthiosemicarbazide by heating thiosemicarbazide and acetic acid during 4 hr (Scheme 3).

The intramolecular cyclization in ethanol and in the presence of sodium leads to the formation of the MTS in 80%.

Our method appears very interesting compared to the one described in the literature.^[11] In fact it is a soft and short method.

The products **1** and **2** have been purified and characterized by infrared (IR), ¹H NMR, and ¹³C NMR spectra.



Scheme 1. Synthetic compounds.

To investigate chemical behavior of compounds 1 and 2, they were reacted with some alkyl bromide using PTC method, which gave isolated monopolar surfactants (1a, 1b, 1c, and 1d) and (2a, 2b, 2c, and 2d) respectively. The examination of the ¹H NMR and ¹³C NMR spectra of the products showed formation of the monopolar surfactants derived from 1,2,4-triazole-5- thione.

The compounds 1a-c have been found as corrosion inhibitor of carbon steel in acidic medium.^[12] We have shown that compound 1c was the best inhibitor and its efficiency increases with increasing immersion time.

Furthermore, it was interesting to examine the behavior of compounds 1 and 2 with some 1,n-dibromoalkane, which leads to give the bis alkylation form 1e and 1f in good yield. These compounds obtained were identified by ¹H NMR, IR, mass spectra, and microanalysis data.

It is remarkable that the NH group in 3-methylalkylthio-1,2,4,-triazole can be alkylated. To obtain a bicatenar surfactant compound, we have reacted **1d** with n-dodecylbromide in DMF using PTC solid-liquid



Scheme 2. Synthetic method to obtain the compounds 1 and 2.

method for 24 hr leads to a mixture of two isomerization products **1g** (50%) and **1h** (50%) in accord with usual 1,3-hydrogen transfer in the 1,2,4-triazole derivatives. Paper chromatography was tried with various solvents, and the best results were obtained with n-hexane–ethylacetate mixtures (80:20), the Rf values are $R_{1g} = 0,77$ and $R_{1h} = 0,56$. The structures of the products have been characterized by ¹H NMR, ¹³C NMR, and mass spectra. All the synthesized surfactants compounds are summarized in Scheme 4.

The correct structures assignment of **1g** and **1h** were made especially by analysis of ¹³C NMR spectra. On the basis of the ¹H NMR data, one cannot distinguish between these isomers. on the other hand the analysis of their ¹³C NMR spectra shows that the one of the compound **1g** presents two signals to 11.91 ppm and to 14.19 ppm correspondent to the methyl groups, whereas one of the compound **1h** presents only one signal to 14.1 ppm correspondent to the three methyl groups. It can be interpreted by steric effect caused by the presence of the alkyl chain close to the methyl group in position 3 of the cycle. To confirm these two structures, the mass spectra under electronic impact reveals the presence of a peak at m/z = 224 in the spectra assigned to the compound **1g** which corresponds to the CH₃-C = N⁺-N-(CH₂)₁₁-CH₃

$$\begin{array}{ccc} H_2 N - NH - C - NH_2 & \xrightarrow{CH_3 CO_2 H} & CH_3 \cdot C - NH - NH - C - NH_2 \\ \parallel & & & & \\ S & & & & & \\ S & & & & & \\ \end{array}$$

Scheme 3. Synthetic method to obtain 1-acetylthiosemicarbazide.



Scheme 4. Synthetic method to obtain the compounds 1_{a-d} , 2_{a-d} , and 1_{e-h} .

fragment. The non-existence of this fragment in the structure **1h** confirms the results gotten on the basis of the 13 C NMR spectra.

EXPERIMENTAL

- 1. Melting point: Melting points (MP) were obtained on a Kofler Prolabo apparatus.
- Nuclear magnetic resonance (NMR): ¹H NMR spectra were recorded on a Varian EM 360 at 60 MHz with TMS as internal standard. ¹³C NMR data were recorded at 75.469 MHz by using a Bruker AC 200 WB spectrophotometer. In the description of spectra, letters m, s, and t mean, respectively, multiplet, singulet and triplet.
- IR Spectra: Perkin-Elmer 577 spectrometer was used to record IR spectra.
- 4. Mass spectra were recorded on a Nermag R10-10 instrument: Chemical Ionization (DCI/NH₃).
- All columns chromatography were carried out by using merck of silica gel 60 (0.063–0.200 mm)

GENERAL METHOD TO OBTAIN 1,2,4-TRIAZOLE-5-THIONE (1, 2)

1-Alkyl (ou 1-aryl) Thiosemicarbazide

a) Our method ($R = CH_3$)

Twenty milliliters of acetic acid, which contained 4.55 g (50 mmol) of colorless thiosemicarbazide was refluxed on a steam bath for 4 hr. The acetic acid was removed by evaporation. The 1-acetylhiosemicarbazide was obtained and recrystallized from water (yield, 70%), ¹H NMR (200 MHz, DMSO d6) δ : 9.72(s,H); 9.16(s,H); 7.84(s,H); 7.71(s,H); 1.8(S,3H). ¹³C NMR(50 MHz, DMSO d6): 181.70, 168.82, 20.77.

b) $R = CH_3$ or C_6H_5

1-Acetylhiosemicarbazide (or 1-benzoylthiosemicarbazide) was prepared by the addition of 2.355 g (30 mmol) of acetyl chloride (or benzoylchloride) to a stirred suspension of 2.7 g (30 mmol) of thiosemicarbazide and 30 mL of dry pyridine. The temperature was maintained between -5 and 0°C throughout the addition. After standing at room temperature for 24 hr most of the pyridine was removed by evaporation under reduced pressure.

3-Methyl-1,2,4-triazole-5-thione

To effect cyclization to 3-methyl-1,2,4-triazole-5-thione, the 1-acetylthiosemicarbazide was dissolved in 40 mL of ethanol and 3.24 g (60 mmol) of sodium was added. The mixture was heated for 24 hr on the steam bath, and then the solvent was removed by evaporation under reduced pressure. This residue was dissolved in 6 mL of water and 6 mL of concentrated hydrochloric acid. A precipitated solid was washed with water and dried air, the sample was recrystalized from water, the yield was 80%, mp > 264°C. IR (KBr, cm⁻¹): 1607($\nu_{C=N}$), 1108($\nu_{c=S}$), 3450(ν_{NH}). ¹H NMR (60 MHz, DMSO d₆) δ : 13.80 (s, 2H), 2.37 (s, 3H). ¹³C NMR (75 MHz, DMSO d₆) δ : 156.70, 148.75, 12.72.

3-Phenyl-1,2,4-triazole-5-thione (2)

1-Benzoylthiosemicarbazide was dissolved in 18 mL of methanol, and 3,24 g (60 mol) of sodium methylate was added. The mixture was heated for

Synthesis of New Surfactants

24 hr in the steam bath, and then the solvent was removed by evaporation under reduced pressure. This residue was dissolved in 6 mL of water and 6 mL of concentrated hydrochloric acid. A precipitated solid was recrystalized from water, the yield was 53%, mp > 264°C. IR (KBr, cm⁻¹): 1628 ($\nu_{C=N}$), 1070($\nu_{c=S}$), 3066 (ν_{N-H}). ¹H NMR (60 MHz, DMSO d₆) δ : 14.50 (s, 2H), 8.67–7.50 (m, 5H). ¹³C NMR (75 MHz, DMSO d₆) δ : 181.92, 165.77, 132.36, 131.69, 128.10, and 127.76.

GENERAL METHOD FOR OBTAINING MONOCATENAR SURFACTANTS

S-Alkylthio-1,2,4-triazole (1a, 1b, 1c, 1d)

A mixture of 3-methyl-1,2,4-triazole-5-thione (0.575 g, 5 mmol), alkyl bromide (5 mmol), potassium carbonate (K_2CO_3) (0.759 g, 5.5 mmol), tetrabutylammonium bromide (BABA) (0.161 g, 0.5 mmol) in 25 mL of DMF was stirred at room temperature for 24 hr. The resulted solution was filtered through a filter paper, and then the solvent was removed by evaporation under reduced pressure and the obtained product was recrystallized from ethanol.

S-Alkylthio-1,2,4-triazole (2a, 2b, 2c, and 2d)

By the same procedure used above, 3-phenyl-1,2,4-triazole-5-thione was condensed by different alkyl bromide to obtain the corresponding monocatenar surfactants **2a**, **2b**, **2c**, and **2d**. The products were purified by using a column chromatography on silica gel eluting with n-hexane–ethyl acetate (80:20).

The ¹H NMR, IR spectra, and physical characteristics of isolated products 1_{a-d} and 2_{a-d} are summarized in Tables 1 and 2.

GENERAL METHOD FOR OBTAINING BIPOLAR SURFACTANTS 1e, 1f

1,n-bis[5-(1,2,4-triazoly1)thio]alkane **1e** and **1f** were prepared from a solution of 1,15 g, (10 mmol) of 3-methyl-1,2,4-triazole-5thione, 30 mL of DMF, 5 mmol of 1,n-dibromoalkane (n = 10,12), 2,76 g, (20 mmol)of K₂CO₃ and 0,322 g, (1 mmol) of BTBA. The mixture was stirred at room temperature for 24 hr. The resulted solution is filtered through a filter paper, and then the

		IR (KBr)				
Products	δ(CH ₃)	$\delta(C_6H_5)$	$\delta(\operatorname{CH}_{2}\alpha(S))$	$\delta((CH_2)n-CH_3)$	$v_{C=S}$	$v_{ m NH}$
1a	2.70 (s)	—	3.20 (t)	[0.66–2.10] (m)	—	3438
1b	2.67 (s)	—	3.30 (t)	[0.67–2.10] (m)	—	3428
1c	2.67 (s)		3.27 (t)	[0.67–2.07] (m)	_	3448
1d	2.67 (s)		3.30 (t)	[0.67–2.07] (m)	_	3458
2a		[7.43–8.63] (m)	3.30 (t)	[0.63–2.06] (m)	—	3458
2b	—	[7.50–8.66] (m)	3.30 (t)	[0.60-2.08] (m)	_	3438
2c	—	[7.53–8.56] (m)	3.26 (t)	[0.66-2.00] (m)	—	3465
2d	—	[7.57–8.57] (m)	3.30 (t)	[0.70–2.08] (m)	—	3448

Table 1. Data of ¹H NMR and IR of S-alkylthio-1,2,4-triazole $(1_{a-d} \text{ and } 2_{a-d})$.

 $\label{eq:table 2. Physical characteristics of isolated products (1_{a-d} \mbox{ and } 2_{a-d}).$

Products	MP (°C)	Yield (%)	$\frac{\left(M+1\right)^{+}}{\left(m/z\right)}$	Analysis				
					%C	%H	%N	%S
1a	98	51	256	Calc.:	61.06	9.78	16.43	12.52
				Tr.:	61.08	10.29	16.85	12.97
1b	85	52	270	Calc.:	62.34	10.02	15.58	11.87
				Tr.:	62.34	10.68	15.76	12.04
1c	102	59	284	Calc.:	63.55	10.31	14.82	11.31
				Tr.:	62.32	10.77	14.81	11.42
1d	92	72	298	Calc.:	64.54	10.42	14.12	10.76
				Tr.:	62.33	10.76	13.96	10.65
2a	73	65	318	Calc.:	68.02	8.50	13.22	10.08
				Tr.:	68.10	8.95	13.65	10.25
2b	88	60	332	Calc.:	68.76	8.75	12.67	9.65
				Tr.:	68.72	9.20	13.06	9.94
2c	75	75	346	Calc.:	69.51	9.04	12.16	9.28
				Tr.:	69.43	9.56	12.49	9.46
2d	80	89	360	Calc.:	70.09	9.18	11.68	8.90
				Tr.:	70.25	9.76	12.15	9.05

	1	IR (KBr)			
Products	δ(CH ₃)	$\delta(\operatorname{CH}_2 \alpha(S))$	$\delta((CH_2)n)$	$v_{\rm C=S}$	$v_{ m NH}$
le lf	2.92 (s) 2.52 (s)	3.48 (t) 3.16 (t)	[1.00-2.20] (m) [0.95-2.00] (m)		3416 3421

Table 3. Data ¹H NMR and IR spectra of 1,n-bis[5-(1,2,4-triazolyl) thio] alkane **1e** and **1f**.

Table 4. Physical characteristics of the bipolar surfactants 1e and 1f.

Products		Yield (%)	$\begin{array}{c} \left(M+1\right)^+ \\ \left(m/z\right) \end{array}$	Analysis				
	MP (°C)				%C	%H	%N	%S
1e	164	72	369	Calc.:	52.17 51.73	7.61 8.01	22.83 22.08	17.39 16.86
1f	163	72	397	Calc.: Tr.:	54.54 53.90	8.08 8.33	21.21 20.89	16.16 15.87

solvent was removed by evaporation under reduced pressure. A sample was recrystallized from ethanol. The products have been characterized by ¹H NMR, IR, mass, and microanalysis data. The characteristics of the products are presented in Tables 3 and 4.

SYNTHESIS OF BICATENAR SURFACTANTS 1g, 1h

A mixture of 5-dodecylthio-3-methyl-1,2,4-triazole 1,415 g, (5 mol), K_2CO_3 (1,38 g, 10 mmol), tetrabutylammoniumbromide (0,161 g, 0,5 mmol) and (1,245 g, 5 mmol) of dodecylbromide in 30 mL of DMF was stirred at room temperature for 24 hr. The solvent was evaporated. The residue was separated by column chromatography (silica gel -n-hexane/ethyl acetate (80:20)) to give the **1g** (50%, liquid) and **1h** (50%, mp < 50°C).

1g: ¹H NMR (60 MHz, CDCl₃) δ : 4.20 (t,2H), 3,37 (t,2H), 2,47 (s,3H), [0,66–2,07] (m, nH). ¹³C NMR (75 MHz, CDCl₃) δ : 158.89, 152.56, 48.45, [32.19–22.71], 14.18 (2CH₃), 11.90 (1CH₃). Mass: (M + 2)^{+•} = 454,3; [CH₃–C = N–N–(CH₂)₁₁–CH₃]^{+•} = 224.

1h: ¹H NMR (60 MHz, CDCl₃) δ : 4.20 (t,2H), 3,20 (t,2H), 2,50 (s,3H), [0,6–2,17] (m, nH). ¹³C NMR (75 MHz, CDCl₃) δ : 160.30, 151.47, 48.32, [33.61–22.68], 14.07 (3CH₃). Mass: M^{+•} = 452.5.

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