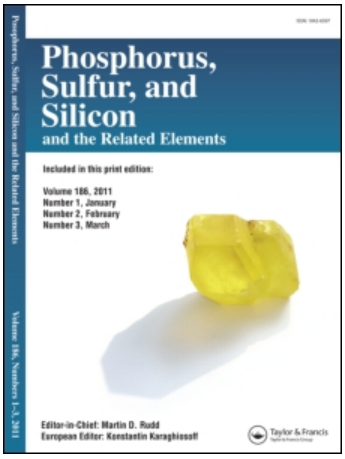

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REACTIONS OF DICHLOROMETHANE WITH THIOANIONS. 2. FORMATION OF 5-ALKYL-1,3,5-DITHIAZINANES, 3,5-DIALKYL-1,3,5-THIADIAZINANES, AND 1,3,5-TRIALKYL-1,3,5-TRIAZINANES BY REACTION OF DICHLOROMETHANE WITH SODIUM SULFIDE AND MONOALKYLAMINES

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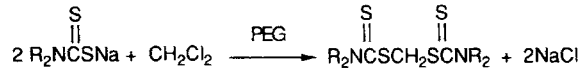
The reaction of dichloromethane with sodium sulfide and monoalkylamines, catalyzed by polyethyleneglycol 1,500, is studied. A mixture of 5-alkyl-1,3,5-dithiazinane, 3,5-dialkyl-1,3,5-thiadiazinane, and 1,3,5-trialkyl-1,3,5-triazinane is obtained. The proportion of these heterocycles depends on the amine structure and the presence of sodium hydroxide.

Key words: 5-Alkyl-1,3,5-dithiazinanes, 3,5-dialkyl-1,3,5-thiadiazinanes, dichloromethane double substitution, polyethyleneglycol as catalyst.

The formation of disubstituted methanes by reaction of dichloromethane with different nucleophiles is a well established chemical transformation. Recently we have published the preparation of bis(N,N-dialkylthiocarbamoylthio) methanes[1] (**2**) by reaction of sodium N,N-dialkyldithiocarbamates (**1**) with dichloromethane catalyzed by polyethyleneglycol (PEG) 1,500.



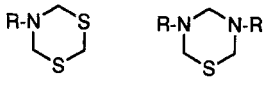
1 **2**

The possible intermediate $R_2NCS_2CH_2Cl$ of this reaction was not found, so this assumed species must be very reactive. In a similar way to the formation of compounds **2**, the method to produce bis(O-alkyldithiocarbonate) methanes $[(ROCS_2)_2CH_2]$ has been patented.[2]

It is also known that amines, nucleophiles different from thioanions, may react with dichloromethane affording aminals even without catalyst. In the formation of aminals from secondary amines $[(R_2N)_2CH_2]$ the monosubstituted intermediate has been detected.[3]

On the basis of these reactions of dichloromethane we considered the possibility of the formation of methylene products supporting two different substituents by reaction of dichloromethane with a mixture of a monoalkylamine and the bivalent

sulfide anion. These possible mixed disubstituted methanes would be linear or cyclic azathioacetals. Six membered heterocycles which contain methylene groups, N, and S atoms are the 5-alkyl-1,3,5-dithiazinanes (**3**) and 3,5,-dialkyl-1,3,5-thiadiazinanes (**4**).



3 **4**

Heterocyles **3** have been synthesized[4] by reaction of formaldehyde 37% in water with monoalkylamine, or its hydrochloride, and sodium sulfide nonahydrate or sodium hydrosulfide at 20–25°C for 13–30 h.

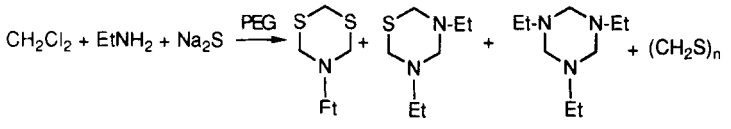
$$HCHO + RNH_2 + Na_2S \text{ (or NaHS)} \rightarrow \mathbf{3}$$

In a similar way[4] heterocycles **4** were prepared by passing hydrogen sulfide into aqueous 37% formaldehyde followed by addition of this solution to the amine at 0–5°C and kept for 36 h.

$$HCHO + H_2S + RNH_2 \rightarrow \mathbf{4}$$

Selective formation of these heterocycles is difficult due to the similar conditions used to prepare them. As can be expected hetrocycles **3** and **4** are not very stable and compounds **4** decompose easily.

Considering the previously mentioned information we decided to study the behavior of dichloromethane in the presence of a mixture of sodium sulfide and a monoalkylamine. When the mixture of aqueous 70% ethylamine and sodium sulfide, in different molar rations, was stirred with dichloromethane, as reagent and solvent, at 40°C for 24 h in the presence of 5% molar PEG 1,500 on the basis of Na_2S, a mixture of 5-ethyl-1,3,5-dithiazinane (**3a**), 3,5-diethyl-1,3,5-thiadiazinane (**4a**), 1,3,5-triethyl-1,3,5-triazinane (**5a**) and polymethylenesulfide was formed.



3a **4a** **5a**

Taking into account that aminolysis of CH_2Cl_2 affords HCl, sodium hydroxide was added in some assays. In one assay no PEG was used. After a fast acidic extraction and separation of PEG the crude product was weighted and analyzed by ^{1}H-NMR. In these extractions small quantities of polymethylenesulfide appear in the water-dichloromethane interphase. This polymer was not quantified. The performed assays appear in Table I.

The result of these reactions indicates that the **3a**, **4a** and **5a** proportion is very sensitive to the ethylamine and sodium sulfide molar ratio (assays 1–5); sodium hydroxide increases ethylamine conversion (assays 4 and 5) and PEG 1,500 only catalyses the Na_2S conversion (assays 6–8).

On the basis of these results we studied the formation of 1,3,5-thiazinanes **3** and

TABLE I

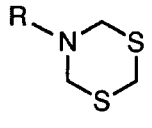
Assays of CH_2Cl_2, Na_2S and $EtNH_2$ in the reaction

Assay Nr	$EtNH_2$ (mol)	Na_2S (mol)	NaOH (mol)	Weight[a] (g)	Conversion[b] $EtNH_2$(%)	Conversion[b] Na_2S(%)	**3a** %	**4a** %	**5a** %
1	0.8	0.4	0	20.4	-	48	56	31	13
2	0.8	0.4	0.4	24.9	-	38	21	54	25
3	1.6	0.4	0	24.2	-	48	45	32	23
4	0.2	0.4	0	9.3	47	-	47	47	6
5	0.2	0.4	0.4	13.9	85	-	23	57	20
6	0.8	0	0	1.2	3	-	0	0	100
7	0.8	0	0.4	1.5	4	-	0	0	100
8	0	0.4	0	5.8	-	31	-[c]	-[c]	-[c]
9[d]	0.8	0.4	0.4	3.5	-	1	-	-	-

a) Weight of **3a** + **4a** + **5a** mixture. b) According to limiting reagent and on the basis of **3a** + **4a** + **5a**. c) $(CH_2S)n$ is only produced. d) Without PEG.

TABLE II

Formation of heterocycles **3**, **4** and **5**



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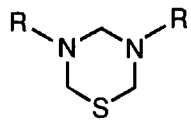

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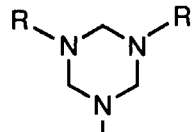

5

Assay[a] Nr.	Products **3,4,5** R		Conversion Na_2S(%) NaOH	no NaOH	Relative proportion (%) **3** NaOH	no NOH	**4** NaOH	no NaOH	**5** NaOH	no NaOH
1,2	Et	a	38	48	21	56	54	31	25	13
10	n-Pr	b	33	50	17	60	21	22	62	18
11	i-Pr	c	19	66	28	97	-	-	72	3
12	n-Bu	d	19	50	12	55	12	23	76	22
13	i-Bu	e	15	44	16	65	16	26	68	9
14	t-Bu	f	3	29	100	100	-	-	-	-

a) Molar ratio: $RNH_2/Na_2S/NaOH/PEG$ = 0.8:0.4:0.4:0.02. Temp.: 40°C. Time: 24 h.

4 using different monoalkylamines with low lipophylic character. We selected the conditions used in assay 1 of Table I since they give a reasonable Na_2S conversion and a moderate yield of 5-ethyl-1,3,5-dithiazinane (**3a**) whose parent compounds are interesting to us.[5] All the assays were performed with and without NaOH in order to study the influence of NaOH on the Na_2S conversion and the yield of product **3**. Aniline was also tested as a representative primary aromatic amine. The results are shown in Table II which includes the data of assays 1 and 2 for comparison.

TABLE III

^1H- and ^{13}C-NMR spectra[a] of heterocycles **3**, **4** and **5** d (ppm)

Products 3,4,5 R		3 SCH_2S $^1H^b$	3 SCH_2S ^{13}C	3 SCH_2N $^1H^b$	3 SCH_2N ^{13}C	4 SCH_2N $^1H^b$	4 SCH_2N ^{13}C	4 NCH_2N $^1H^b$	4 NCH_2N ^{13}C	5 NCH_2N $^1H^b$	5 NCH_2N ^{13}C
Et	a	4.10	33.99	4.45	57.66	4.27	55.97	3.90	72.99	3.33	73.90
n-Pr	b	4.11	34.06	4.44	58.35	4.27	55.53	3.90	72.97	3.31	74.45
i-Pr	c	4.14	33.92	4.52	56.42	-	-	-	-	3.50	68.24
n-Bu	d	4.11	34.03	4.44	58.30	4.27	56.55	3.88	73.88	3.30	74.73
i-Bu	e	4.11	34.07	4.41	57.15	4.27	57.22	3.88	74.77	3.27	75.30
t-Bu	f	4.26	35.15	4.62	55.66	-	-	-	-	-	-

a) $CDCl_3$ at 35°C, b) Broad singlet.

In all of these reactions polymethylene sulfide was detected in low quantities. It is believed that the possible cyclic trimethylene sulfide, 1,3,5-trithiane, was also formed. Aniline did not react at all, probably due to its lower basicity. Table II shows that sodium hydroxide decreases the Na_2S conversion (assays 10–14), and without NaOH the isopropylamine gave almost exclusively 3-isopropyl-1,3,5-dithiazinane (**3c**) (assay 11). This product and 3-tertbutyl-1,3,5-dithiazinane (**3f**), formed exclusively according to assay 14, arises from the amines with steric hindrance on the nitrogen atom.

As noted, the proportion of each heterocycle in the mixtures of crude reaction products were analyzed by NMR spectrometry. Table III shows the ^1H and ^{13}C spectra of products **3**, **4** and **5** which were separated as described in the experimental section. Proton signals of the SCH_2S group were used to evaluate the proportion of **3**, those of NCH_2S for **4**, and those of NCH_2N for **5** in the mixture. As can be seen the common groups NCH_2S in **3** and **4**, and NCH_2N in **4** and **5** show different proton chemical shifts.

The ring methylene proton signals of hetrocycles **3**, **4** and **5** are rather broad signals due to a slow interconversion between the two chair forms. The N-alkyl group of compounds **3** ring is in the preferred axial position according to ^1H-NMR studies.[4] This fact has then been confirmed by ^{13}C-NMR.[6] Heterocycles **4** probably also exist largely with one or two axial N-alkyl groups.[4]

Heterocycles **3**, **4** and **5** decomposed easily so no satisfactory elemental analysis could be obtained. However the ^1H-NMR data of compounds **3** and **4** are in good agreement with those of A. R. Katritzky.[4] Moreover the ion molecular mass spectra of compounds **4a** and **4b** correspond to their molecular formulas.

EXPERIMENTAL

IR spectra were obtained on a Perkin-Elmer model 1310 spectrophotometer, ^1H and ^{13}C-NMR spectra were recorded on a Bruker AC-200 apparatus. Mass spectra were determined on a VB-12-250 spectrometer. Only a few satisfactory elemental analyses could be obtained.

Reaction of dichloromethane with sodium sulfide and ethylamine

A solution of sodium sulfide nonahydrate (0.4 mol) in water (100 mL) was mixed successively with solutions of 70% wt% ethylamine (0.2, 0.8 and 1.6 mol) in water, and a solution of polyethyleneglycol, average Mn ca. 1,500 (0.002 mol) in dichloromethane (200 mL) in a round bottom flask fitted with two coiled condensers, a latex balloon on the top of the upper condenser (to retain volatile ethylamine) and a magnetic stirrer. The mixture was heated on a water bath for 24 h at 40°C. The product was filtered by suction through a Whatmann filter paper to collect polymethylene sulfide which was in the interphase of water and dichloromethane. The solid was washed with additional dichloromethane. The two-layer filtrate was separated and the aqueous layer washed with dichloromethane to extract residual products. The combined organic layers and extracts were rapidly treated with cold 10% hydrochloric acid in order to extract the basic products and leave aside polyethyleneglycol in dichloromethane which is a better solvent than water for this polymer. This acidic aqueous layer was treated with 20% water NaOH solution in order to reach a basic pH. The basic organic products were extracted with 68–70°C light petroleum which does not solubilize polyethyleneglycol. The solution was dried with magnesium sulfate and the evaporation of the light petroleum left a residue composed of a mixture of **3a**, **4a** and **5a**, which was analyzed by NMR spectrometry. A portion of this hetrocyclic mixture was separated by preparative thin layer chromatography using silica gel (Merck, art 7747) and ethyl acetate as eluent.

Reaction of dichloromethane with sodium sulfide

Sodium sulfide nonahydrate (0.4 mol) in water (100 mL) was stirred with a solution of polyethyleneglycol 1,500 (0.02 mol) in dichloromethane (200 mL) at 40°C for 24 h. The formed solid product was collected by filtration through a Whatmann filter paper and dried. It melted at 205–220°C, was insoluble in common organic solvents and its IR spectrum was almost identical[7] to that of 1,3,5-trithiane. Since the m.p. of 1,3,5-trithiane is c.a. 215° and that of $(CH_2S)n$ is 160–220° depending on preparation,[8] the obtained solid should be a mixture of polymethylenesulfide and the oligomer 1,3,5-trithiane.

Reaction of dichloromethane with sodium sulfide and amines

A solution of sodium sulfide nonahydrate (0.4 mol) in water (100 mL) and 0.8 mol of n-propyl-, i-propyl-, n-butyl, i-butyl, and tert-butylamine was stirred with a solution of polyethylene glycol 1,500 (0.02 mol) in dichloromethane (200 mL) in the same apparatus and conditions as used for ethylamine. The mixture of the formed heterocycles was purified and separated in a similar way but using mixtures of the following eluents for the different amines, in parenthesis. Ethyl acetate-dichloromethane 1:2 (propyl- and isopropylamine), dichloromethane (butylamine), and benzene (isobutylamine).

Physical properties of **3**

3-Ethyl-1,3,5-dithiazinane (**3a**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 4.45 (b.s., 4H, SCH_2N); 4.10 (b.s., 2H, SCH_2S), 3.07 (q, 2H, CH_2) 1.08 (t, 3H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 57.66, 42.77, 33.99, 12.37; IR (neat) 1280, 1090, 960, 690 cm^{-1}.
Anal. Calcd. for $C_5H_{11}S_2N$: C, 40.23, H. 7.43. Found: C, 40.47, H, 7.32

3-Propyl-1,3,5-dithiazinane (**3b**): colorless crystals; m.p. 30–31°C, ^{1}H-NMR ($CDCl_3$) δ 4.44 (b.s., 4H, SCH_2N), 4.11 (b.s., 2H, SCH_2S), 2.97 (t, 2H, CH_2), 1.47 (m, 2H, CH_2), 0.93 (t, 2H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 58.35, 50.73, 34.06, 20.27, 11.68; IR (neat) 1285, 1080, 970, 695 cm^{-1}.

3-Isopropyl-1,3,5-dithiazinane (**3c**): white crystals; m.p. 33–35°C, ^{1}H-NMR ($CDCl_3$) δ 4.52 (b.s., 4H, SCH_2N), 4.14 (b.s., 2H, SCH_2S), 3.77 (m, 1H, CH), 1.15 (d, 6H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 56.42, 45.10, 33.92, 20.74; IR (neat) 1283, 1040, 963, 895, 735 cm^{-1}.
Anal. Calc. for $C_6H_{13}NS_2$: C, 44.13, H, 8.02. Found: C, 44.51, H, 8.72

3-Butyl-1,3,5-dithiazinane (**3d**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 4.44 (b.s., 4H, SCH_2N), 4.11 (b.s., 2H, SCH_2S), 3.01 (t, 2H, CH_2), 1.49–1.27 (m, 4H, CH_2CH_2), 0.93 (t, 3H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 58.30, 48.48, 34.03, 29.16, 20.35. 13.99; IR (neat) 1293, 1100, 970, 698 cm^{-1}.

3-Isobutyl-1,3,5-dithiazinane (**3e**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 4.41 (b.s., 4H, SCH_2N), 4.11 (b.s. 2H, SCH_2S), 2.78 (d, 2H, CH_2), 1.68 (m, 1H, CH), 0.91 (d, 6H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 59.04, 57.15, 34.07, 25.84, 20.55; IR (neat) 1282, 1102, 980, 697 cm^{-1}.

3-Terbutyl-1,3,5-dithiazinane (**3f**): white crystals; m.p. 42–45°C; ^{1}H-NMR ($CDCl_3$) δ 4.62 (b.s., 4H, SCH_2N), 4.26 (b.s., 2H, SCH_2S), 1.35 (s, 9H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 55.66, 54.30, 35.11, 29.81; IR (neat) 1282, 1202, 1062, 960, 690 cm^{-1}.
Anal. Calcd. for $C_7H_{15}NS_2$: C, 47.41, H, 8.56. Found: C, 47.61, H, 9.00

Physical properties of **4**

3,5-Diethyl-1,3,5-thiadiazinane (**4a**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 4.27 (b.s., 4H, SCH_2N), 3.90 (b.s., 2H, NCH_2N), 2.88 (q, 4H, CH_2), 1.05 (t, 6H, CH); ^{13}C-NMR ($CDCl_3$) δ 72.99, 55.97, 46.75, 13.45; IR (neat) 1455, 1258, 1233, 1075, 940, 78 cm^{-1}; MS m/z 160 ($M^{+\cdot}$)

3,5-Dipropyl-1,3,5-thiadiazinane (**4b**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 4.27 (b.s., 4H, SCH_2N), 3.90 (b.s., 2H, NCH_2N), 2.78 (t, 4H, CH_2), 1.43 (m, 4H, CH_2), 0.89 (t, 6H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 72.97, 55.53, 53.69, 20.38, 10.70; IR (neat) 1460, 1250, 1210, 1080, 950, 740 cm^{-1}; MS m/z 188 ($M^{+\cdot}$).

3,5-Dibutyl-1,3,5-thiadiazinane (**4d**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 4.27 (b.s., 4H, SCH_2N), 3.88 (b.s., 2H, NCH_2N) 2.82 (t, 4H, CH_2), 1.47–1.22 (m, 8H, CH_2CH_2), 0.91 (t, 6H, CH_3); ^{13}C-NMR δ 73.88, 56.55, 52.45, 30.34, 20.35, 13.94; IR (neat) 1460, 1278, 1258, 1090, 940, 845 cm^{-1}.

3,5-Diisobutyl-1,3,5-thiadiazinane ((**4e**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 4.27 (b.s., 4H, SCH_2N), 3.88 (b.s., 3H, NCH_2N), 2.60 (d, 4H, CH_2), 1.63 (m, 2H, CH), 0.87 (d, 12H, CH_3). ^{13}C-NMR ($CDCl_3$) δ 74.77, 60.96, 57.22, 26.67, 20.61; IR (neat) 1470, 1285, 1255, 1095, 1015, 720 cm^{-1}.

Physical properties of **5**

1,3,5-Triethyl-1,3,5-triazinane (**5a**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 3.33 (b.s., 6H, NCH_2N), 2.49 (q, 6H, CH_2), 1.08 (t, 9H, CH_3). ^{13}C-NMR ($CDCl_3$) δ 73.90, 46.60, 12.78; IR (neat) 1478, 1380, 1215, 1150, 1020, 920 cm^{-1}.

1,3,5-Tripropyl-1,3,5-triazinane (**5b**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 3.31 (b.s., 6H, NCH_2N), 2.37 (t, 6H, CH_2), 1.48 (m, 6H, CH_2), 0.90 (t, 9H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 74.45, 54.47, 20.51, 11.65; IR (neat) 1463, 1378, 1203, 1120, 1010, 940 cm^{-1}.

1,3,5-Triisopropyl-1,3,5-triazinane (**5c**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 3.50 (b.s., 6H, NH_2N): 2.85 (m, 3H, CH), 1.07 (d, 18H, CH_3). ^{13}C-NMR ($CDCl_3$) δ 68.24, 49.47, 19.63; IR (neat) 1470, 1390, 1218, 1170, 1010, 895 cm^{-1}.

1,3,5-Tributyl-1,3,5-triazinane (**5d**); colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 3.30 (b.s., 6H, NCH_2N), 2.40 (t, 6H, CH_2), 1.49–1.27 (m, 12H, CH_2CH_2), 0.91 (t, 9H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 74.73, 52.57, 29.77, 20.69, 14.06; IR (neat) 1470, 1275, 1195, 1110, 1015, 920 cm^{-1}.

1,3,5-Triisobutyl-1,3,5-triazinane (**5e**): colorless liquid; ^{1}H-NMR ($CDCl_3$) δ 3.27 (b.s., 6H, NCH_2N), 2.20 (d, 6H, CH_2), 1.69 (m, 3H, CH), 0.90 (d, 18H, CH_3); ^{13}C-NMR ($CDCl_3$) δ 75.30, 60.98, 26.37, 20.94; IR (neat) 1475, 1390, 1215, 1120, 1025, 935 cm^{-1}.

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