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Article



Irada B. Hajiyeva

Azerbaijan University of Architecture and Construction
 1073, Baku, 11, A. Sultanov street,

Institute of Chemistry of Additives named after Academician A.M.Quliyev
 ANAS 1029, Baku, Boyukshor highway, quarter 2062

irada70@yahoo.com

**THE CONDENSATION PRODUCT OF CHLOROACETAMIDE WITH
 FORMALDEHYDE AND THE PREPARATION OF N, N'-
 OXYDIMETHYLENE AND N, N'-
 METHYLENEBISALKYLXANTOGENATO ACETAMIDES BASED ON
 THEM**

Abstract: *N*-methylolchloroacetamide, *N,N'*-oxymethylenebischloroacetamide and *N,N'*-methylenebischloroacetamide were synthesized, which has got different reactive capability and were reacted with alkaline salts of alkyl xanthogenic acids. Optimal conditions for the synthesis of *N, N'*-oxydimethylene- and *N, N'*-methylenebisalkylxanthogenatoacetamides, whose structure has been studied by IR and NMR spectroscopy methods and are uniquely consistent with the formulas attributed to them. The structure of all synthesized compounds was proved by studying their physicochemical properties, including the determination of refractive indices (n_{D}^{20}), specific gravity (d_{4}^{20}) and the calculation on their basis of molecular refraction. With their subsequent comparison, elemental composition and IR spectroscopy. The IR-spectrums of absorption were taken with the SPECORD-751R IR spectrophotometer, made by Karl-Zeis (GDR) firm, using prisms KBr in the 4000-400 cm^{-1} region. Absorption bands (most characteristic): stretching vibrations of the C-H bond 2928-2856 cm^{-1} , stretching vibrations of the N-H 3384-3192 cm^{-1} bond, stretching vibrations of the C = O 1648 cm^{-1} carbonyl group, and an intense absorption band of 768 and 556 cm^{-1} C-Cl bonds correspond to functional bonds and groups of synthesized compounds, which confirms their structure. The structure of the compounds was also confirmed by 1H NMR and ^{13}C NMR spectra, taken in a solution of dimethyl sulfoxide (DMSO d_6). NMR spectra were recorded on "Bruker AC300" spectrometer with operating frequency of 300.13 MHz and 75.47 MHz.

Key words: xanthogenic acids, chloroacetamide, condensation, *N*- chloroacetamide, *N,N'*-methylenebischloroacetamide.

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Introduction

Studies carried out in the field of petrochemical synthesis show that chemical compounds that have sulfur, nitrogen atoms and various functional groups in the molecule improve both lubricating and biocidal properties of oils [1,2]. Therefore, the synthesis of new sulfur- and nitrogen-containing compounds is of great interest in science.

The aim of this work is the synthesis of new compounds containing, along with a xanthogen group, an amide group, enhancing the biological activity of the compounds, which was confirmed earlier by our works [3,4,5]. In the present article, the results of studies on the synthesis of *N,N'*-oxydimethylenebisalkylxanthogenatoacetamides and *N,N'*-methylenebisalkylxanthogenacetamides.

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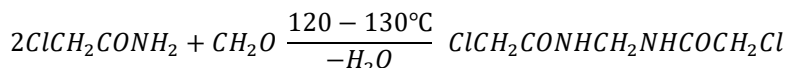
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Material and Methods

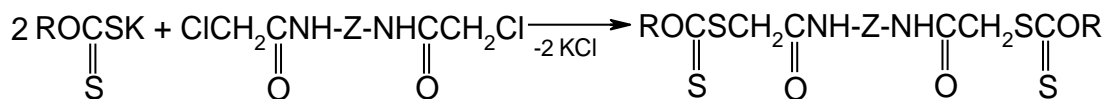
The key compound of this work is chloroacetamide, since new compounds of N,N'-oxydimethylene and N,N'-methylenebisalkylxanthatoacetamides were obtained on the basis of substituted chloroacetamides. More extensive studies, including temperature dependence, showed that at high temperatures the reaction cannot be stopped at the stage of formation of

the N-methylol derivative: the N-methylolchloroacetamide molecule condensing with the second molecule, and leads to the formation of N,N'-oxydimethylene bischloroacetamide. As further studies showed, N,N'-methylenebischloroacetamides were also obtained at high temperatures, by the reaction of chloroacetamide and formaldehyde, taken at the ratio of 2:1.



In this case, we can assume that, first, formaldehyde reacts with chloroacetamide and N-methylolchloroacetamide is obtained, the latter in its turn, condensing with the second molecule of chloroacetamide, which leads to the formation of N,N'-methylenebischloroacetamide[6,7,8].

Based on N-substituted chloroacetamides, a number of new compounds have been synthesized, both with thiocarbonate and amide groups in the molecule, by interacting with the salts of xanthogenic acids, including the preparation of N, N'-oxydimethylene and N, N'-methylenebisalkylxanthatoacetamides.



Z=CH₂OCH₂, R=C₂H₅, C₄H₉, C₆H₁₃.
Z=CH₂, R=C₂H₅, C₄H₉, C₆H₁₃.

The reactions were carried out not in water medium, but in a solution of dimethylformamide. This can be explained by the fact that the N,N'-methylene- and N,N'-oxydimethylene bischloroacetamides – are the compounds with high melting temperatures, therefore poorly dissolve in water and during the reaction their concentrations are very small, which in

turn causes too long reaction time, dimethylformamide is more suitable for use because it is a solvent suitable for all reaction components. To expand the synthetic possibilities of obtaining these substances by alternative methods was also of interest[9,10].

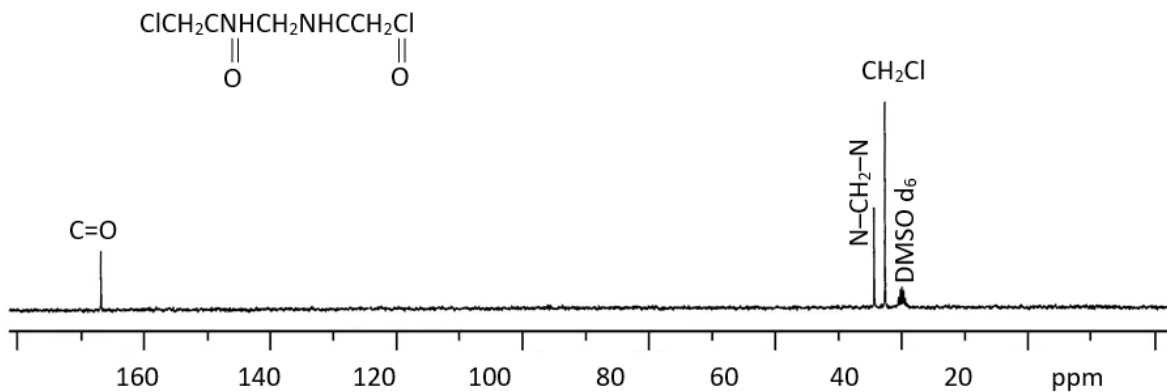
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(a)



(b)

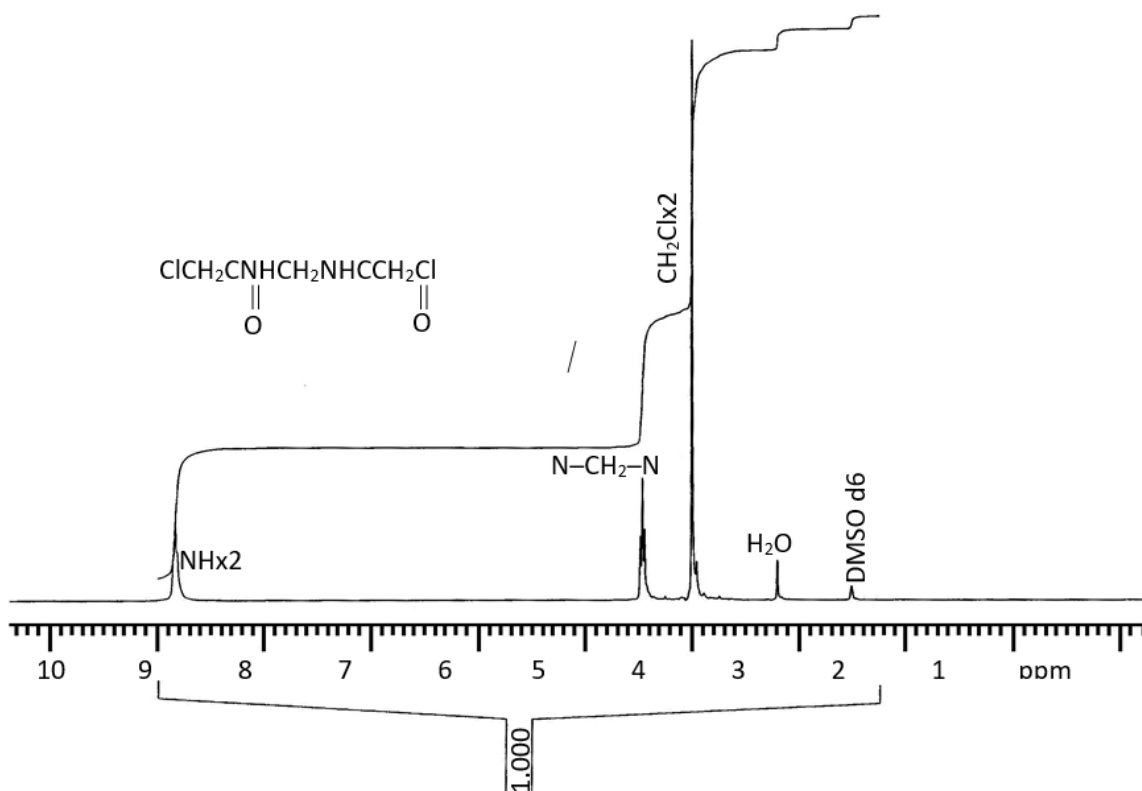


Fig. 1. N, N'- Methylenebischloracetamide in dimethylsulfoxide D₆ solution ¹H (a) and ¹³C (b) NMR spectrs.

NMR spectrum ⁶C in dimethylsulfoxide D¹³ solution of n,n-methylene bischloracetamide has been studied. NMR¹H, δ, m.h. 4c (4H, 2CH₂Cl), 4.44t (2H,

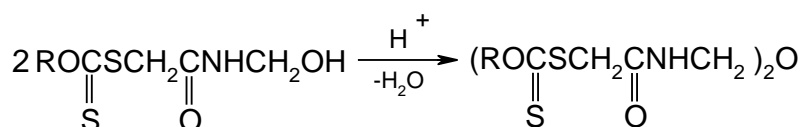
That is, the methods used to prepare N,N'-oxydimethylene and N,N'-methylenebischloroacetamides were also used to prepare N,N'-oxydimethylene and N,N'-methylenebisalkyloxanthanoacetamides.

NCH₂N), 8,82t (2H, 2NH). NMR¹³C, δ_c, m.h.: 42.45 (CH₂Cl), 44.34 (NCH₂N), 166.7 (C=O)

An alternative method for the preparation of N, N'-oxydimethylenebisalkyloxanthogenates was the condensation of two molecules of O-alkyl-S- (N-methyl-carbamoyl) xanthates in a weakly acidic medium (pH = 5-6)

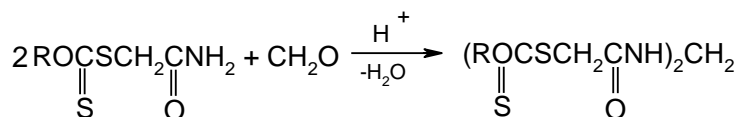
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N, N'-methylenebisalkylxanthanoacetamides were prepared by condensation of O-alkyl-S-carbamoylmethylxanthanoethoamide and

paraformaldehyde in the presence of hydrochloric acid (catalyst).



The IR-spectrums of absorption were taken with the SPECORD-75IR IR spectrophotometer, made by Karl-Zeis (GDR) firm, using prisms KBr in the 4000-400 cm^{-1} region. Absorption bands (most characteristic): stretching vibrations of the C-H bond 2928-2856 cm^{-1} , stretching vibrations of the N-H 3384-3192 cm^{-1} bond, stretching vibrations of the C=O 1648 cm^{-1} carbonyl group, and an intense absorption band of 768 and 556 cm^{-1} C-Cl bonds correspond to functional bonds and groups of synthesized compounds, which confirms their structure.

The structure of the compounds was also confirmed by ^1H NMR and ^{13}C NMR spectra, taken in a solution of dimethyl sulfoxide (DMSO d_6). NMR spectra were recorded on "Bruker AC300" spectrometer with operating frequency of 300.13 MHz and 75.47 MHz.

The main characteristic signals of the peaks corresponding to the chlorinated derivative of acetamide:

NMR ^1H , δ ppm: 4c (4H, 2CH₂Cl), 4.44t (2H, NCH₂N), 8.82t (2H, 2NH). NMR ^{13}C , δ , ppm: 42.45 (CH₂Cl), 44.34 (NCH₂N), 166.7 (C=O).

Characteristic signals of the peaks of N, N'-oxydimethylene and N, N'-dimethylenebisalkylxanthogen tetraacetamides:

NMR ^1H , δ ppm: 0.97t (6H, 2CH₃), 141m 4c (4H, 2CH₂), 177m (4H, 2CH₂), 3.83c (4H, 2SCH₂), 4.4t (2H, NCH₂N), 4.54t (4H, 2CH₂O), 8.88t (2H, 2NH), ^{13}C NMR, δ ppm: 14.2 (CH₃), 19.2 (CH₃-CH₂), 30.0 (C₂H₅-CH₂), 39.0 (SCH₂), 74.2 (CH₂O), 167.0 (C=O), 213.5 (C=S).

Purification of the products was carried out by distillation in vacuum or by recrystallization from alcohol.

Conclusion

New compounds - N, N'-oxydimethylenebisalkylxanthoacetamide and N, N'-methylenebis-alkyloxanthogenacetamide, the structure of which was proved by NMR spectroscopy data. The initial N-methylolchloroacetamide with a yield above 80% is obtained by carrying out the reaction in isopropyl alcohol at a 1: 1: 0,05 component ratio (mole NaOH).

It must be noted that it is impossible to prevent the interaction of chloroacetamide with formaldehyde in the first stage of the reaction, i.e., in the stage of obtaining N- metiloxlorasetamid in the reactions with the participation of the acid catalysts, because, partially condensed it turns into N, N¹ - oksidimetilenbisxlorasetamide. But if the temperature regime (60 - 70° C) and especially the acidity (pH= 5-6) of the condition is exactly controlled, it can be possible to obtain the pure final product. When the acidity of the condition is extended (pH \leq 2), then losing formaldehyde gradually, N, N¹-oksidimetilenbisxlorasetamid turns into the final product N, N¹- metilenbisxlorasetamid, which is more durable both chemically and thermally.

Summing all the above- mentioned, we come into conclusion that studying in complex the interaction of xloracetamide and formaldehyde, it is possible to identify the influence of different factors to the process of reaction, as well as, the components of the obtained products and their conversion. Here, in the reaction of xloracetamide with formaldehyde the main object is to obtain sulphur derivatives, which are able to dissolve in the oil. For that reason, we obtained these products.

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