UDC 547.279

CYANALKYLATION OF MERCAPTOACETIC ACID ESTERS

K.Z.Guseinov, *M.A.Mirzoyeva, P.A.Aliyev

Baku State University

gasimhuseynov@bsu.edu.az

*A.Guliyev Institute of Chemistry of Additives, NAS of Azerbaijan

mziya-m@rambler.ru

Received 07.06.2021

Accepted 30.07.2021

The addition of mercaptoacetic acid esters (MAAE) to nitriles of acrylic, methacrylic, and crotonic acids easily occurs in the presence of triethylamine as a catalyst to form the corresponding 2-cyanoalkylalkoxycarbonylmethyl sulfides.

Keywords: esters of mercaptoacetic acid, sulfide, nitriles of acrylic-, methacrylic- and crotonic acids.

doi.org/10.32737/0005-2531-2021-4-30-34

Introduction

A number of methods for the synthesis of organosulfur compounds are known, among which synthesis based on thiols is of great importance. Having an active hydrogen atom in their molecule, thiols easily react with unsaturated compounds to form various sulfides [1–3].

Previously, we studied the influence of organosulfur compounds obtained on the basis of various thiols on the anticorrosive properties of motor oils, and for the first time it was found that compounds containing the $-\text{SCH}_2\text{COOR}$ fragment (R – aliphatic radicals) in the molecule are much more effective than other sulfides [4].

Of undoubted interest are the synthesis of MAAE derivatives containing, in addition to sulfide sulfur in the molecule, the $-\text{COOR}$ group, as well as the $-\text{CH}_2\text{CH}_2\text{CN}$ group, and the study of their influence on the quality of lubricating oils. For this purpose, the reactions of various MAAE with nitriles of acrylic, methacrylic and crotonic acids have been studied. It was found that in the presence of triethylamine as a catalyst, the reactions of MAAE with nitriles of these acids proceed contrary to Markovnikov's rule, resulting in the formation of the corresponding 2-cyanoalkylalkoxycarbonylmethyl sulfides:

R = C₂H₅ (I), C₃H₇ (II), *i*-C₃H₇ (III), C₄H₉ (IV), *i*-C₄H₉ (V), C₅H₁₁ (VI), C₆H₁₃ (VII), C₇H₁₅ (VIII), C₈H₁₇ (IX), (CH₂)₅CH (X), C₂H₅ (XI), *i*-C₃H₇ (XII), C₄H₉ (XIII), C₂H₅ (XIV), *i*-C₃H₇ (XV), C₄H₉ (XVI)

Experimental part

To obtain 2-cyanoalkylalkoxycarbonylmethyl sulfides (I–XVI), MAAE were used as starting products, which were synthesized by the reaction of mercaptoacetic acid with the corresponding alcohols in the presence of HCl as a catalyst, according to the method described in [5]. The IR spectra of the substances were recorded on a UR-20 device with a thin layer. The PMR spectra were recorded on a Varian T-60 spectrometer with an operating frequency of 60 MHz in a CCl₄ solution, the internal standard was TMS.

General procedure for the synthesis of compounds (I–XVI). 0.005 mol of triethylamine

is added with stirring to a mixture of 0.1 mol of mercaptoacetic acid ester and 0.1 mol of unsaturated nitrile and incubated for 3 hours at 70–80°C. 2-Cyanoalkylalkoxycarbonylmethyl sulfide is isolated by distillation in vacuum. The synthesized sulfides (I–XVI) are colorless liquids with a characteristic odor. They are highly soluble in organic solvents, but insoluble in water.

The physical-chemical characteristics of the synthesized sulfides are presented in Table 1.

Results and discussion

The procedure for the addition of MAAE to unsaturated acid nitriles was confirmed by an independent synthesis:

The physical constants and spectral characteristics of 2-cyanoethylbutoxycarbonylmethyl sulfide and the product obtained by the reaction of mercaptoacetic acid butyl ester with chloropropionic acid nitrile in the presence of an equimolar amount of triethylamine are identical. IR and NMR spectral data also confirm the structure of the synthesized compounds.

As a specific object of detailed discussion, let us consider the spectra of 2-cyanoethylcyclohexyloxycarbonylmethyl sulfide (X).

Everything that will be said about this product applies equally to other products in this series. The IR spectra of compounds (X) (Figure 1) contain absorption bands in the fields of 2260, 1730, and 1290 cm^{−1}, which indicates the presence of C≡N, C=O, and C–O bonds, respectively [6].

In the case of the interaction of the cyclohexyl ester of mercaptoacetic acid with acrylonitrile, the formation of two isomeric products of the following structures is possible:

The absence of an absorption band at 1380 cm^{−1}, characteristic of the CH₃ group in the IR spectrum, indicates the formation of a product corresponding to structure A.

In the PMR spectrum of compounds (X) (Figure 2), the protons of the methylene groups

of the cyclohexyl ring are observed as a multiplet at δ=1–2.1 ppm. The proton of the methine group of the cyclohexyl ring gives a multiplet at δ=4.4–4.8 ppm. The protons of the SCH₂COOR group appear as a singlet with a chemical shift of δ=3.3 ppm.

Fig. 1. IR spectrum of 2-cyanoethylcyclohexyloxycarbonylmethyl sulfide (X).

Fig. 2. PMR spectrum of 2-cyanoethylcyclohexyloxycarbonylmethyl sulfide (X).

Table 1. The physical-chemical characteristics of cyanoalkylalkoxycarbonylmethyl sulfides

Compounds	Yield, %	B.p. (P mm merc.c.), °C	d_{20}^4	n_{20}^d	MR _D		Found, %				Brutto formula	Calculated, %			
					found	calc.	C	H	N	S		C	H	N	S
I	90	101–102 (0.4)	1.1290	1.4813	43.68	44.00	48.30	6.75	7.90	18.34	C ₇ H ₁₁ NO ₂ S	48.53	6.40	8.08	18.51
II	91	116–117 (0.3)	1.0975	1.4790	48.39	48.62	51.54	7.11	7.30	17.25	C ₈ H ₁₃ NO ₂ S	51.31	6.99	7.48	17.12
III	88	106–107 (0.5)	1.0877	1.4742	48.40	48.62	51.10	7.18	7.22	16.91	C ₈ H ₁₃ NO ₂ S	51.31	6.99	7.48	17.12
IV	90	125–130 (0.4)	1.0744	1.4775	52.98	53.23	53.55	7.77	6.80	16.20	C ₉ H ₁₅ NO ₂ S	53.70	7.51	6.96	15.93
V	93	114–115 (0.2)	1.0679	1.4754	53.10	53.23	53.94	7.72	7.14	15.75	C ₉ H ₁₅ NO ₂ S	53.70	7.51	6.96	15.93
VI	88	136–137 (0.2)	1.0546	1.4758	57.54	57.85	55.54	8.12	6.67	15.11	C ₁₀ H ₁₇ NO ₂ S	55.78	7.96	6.50	14.89
VII	92	142–143 (0.2)	1.0375	1.4751	62.23	62.47	57.42	8.58	6.27	14.18	C ₁₁ H ₁₉ NO ₂ S	57.60	8.35	6.11	13.98
VIII	93	154–156 (0.3)	1.0256	1.4744	66.70	67.09	59.62	8.73	5.65	13.52	C ₁₂ H ₂₁ NO ₂ S	59.22	8.69	5.75	13.17
IX	84	165–166 (0.4)	1.0081	1.4740	71.74	71.70	60.91	9.25	5.28	12.62	C ₁₃ H ₂₃ NO ₂ S	60.66	9.01	5.44	12.46
X	89	150–151 (0.2)	1.1149	1.5014	60.10	60.27	57.83	7.61	6.41	13.67	C ₁₁ H ₁₇ NO ₂ S	58.11	7.53	6.16	14.10
XI	70	161–162 (6)	1.1040	1.4793	48.13	48.62	51.66	7.24	7.65	17.01	C ₈ H ₁₃ NO ₂ S	51.31	6.99	7.48	17.12
XII	84	139–140 (1)	1.0677	1.4722	52.81	53.23	53.24	7.60	7.18	15.62	C ₉ H ₁₅ NO ₂ S	53.70	7.51	6.96	15.93
XIII	87	172–173 (4)	1.0457	1.4730	57.76	57.85	56.14	7.82	6.82	14.95	C ₁₀ H ₁₇ NO ₂ S	55.78	7.96	6.50	14.89
XIV	72	146–147 (2)	1.1175	1.4825	47.82	48.62	51.12	7.18	7.30	17.24	C ₈ H ₁₃ NO ₂ S	51.31	6.99	7.48	17.12
XV	85	145–146 (1.5)	1.0705	1.4764	53.07	53.23	53.42	7.82	6.71	16.18	C ₉ H ₁₅ NO ₂ S	53.70	7.51	6.96	15.93
XVI	92	169–170 (3)	1.0511	1.4758	57.76	57.85	55.32	8.16	6.74	14.76	C ₁₀ H ₁₇ NO ₂ S	55.78	7.96	6.50	14.89

In the PMR spectrum of compounds (X) (Figure 2), the protons of the methylene groups of the cyclohexyl ring are observed as a multiplet at $\delta=1-2.1$ ppm. The proton of the methine group of the cyclohexyl ring gives a multiplet at $\delta=4.4-4.8$ ppm. The protons of the SCH_2COOR group appear as a singlet with a chemical shift of $\delta=3.3$ ppm.

The resonances of the signals of the protons of two methylene groups of the $\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{S}$ fragment appear as triplets with chemical shifts $\delta a=2.75$ and $\delta b=2.9$ ppm. The absence of resonance signals of protons from the methyl and methine groups of the $\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{S}$ fragment, which would have occurred during the formation of a product corresponding to structure B, also confirms the structure of the synthesized compounds [7].

Thus, the MAAE cyanalkylation method has been used to synthesize oxygen-, sulfur- and

nitrogen-containing organic compounds that are of interest as potential additives to lubricating oils.

References

1. Sintez sulfidov, tiofenov i tiolov. Otv. red. Karaulova E.N. M.: Nauka, 1988. 208 s.
2. Khimiya organicheskikh soyedineniy sery. Pod. red. L.I.Belenkogo. M.: Khimiy, 1988. 320 s.
3. Sardarova S.A., Osmanova S.F., Mamedov F.A., Qamidova Sh.Y. Sintez i issledovaniye slojnikh efirov 1,1-bis-(hidroksikarbonilmetiltio)-1-ariletanov. Khimicheskie Problemi 2015. No 3. C. 319–322.
4. Guseinov K.Z. Funktsionalniye proizvodniye tiolov i fenolov v kachestve prisadok k smazochnym maslam i toplivam. Dis....dokt. khim. nauk. Baku: In-t Khimii Prisadok AN Azerb.SSR, 1991. 471 s.
5. Guseinov K.Z., Gambarov D.G., Mirzoeva M.A., Mamedov F.N., Fati-zade R.F. Sintez efirov tioglikolevoy kisloty i primeneniye ikh v analiticheskoy khimii. Azerb. khim. jurn. 1977. № 6. S. 103–107.
6. Nakanisi K. Infraqrasniye spektry i stroyeniye organicheskikh soyedineniy. M.: Mir, 1965. 216 s.
7. Ionin B.I., Yershov B.A., Koltsov A.I. YAMR spektroskopiya v organicheskoy khimii. L.: Khimiya, 1983. 269 s.

MERKAPTOSİRKƏ TURŞUSU EFİRLƏRİNİN SİANALKİLLƏSMƏSİ

Q.Z.Hüseynov, M.Ə.Mirzəyeva, P.Ə.Əliyev

Trietilaminin katalizator kimi iştirakı ilə merkaptosirkə turşusaunun efirləri akril-, metakril- və kroton turşularının nitrilləri ilə asan birləşmə reaksiyasına daxil olurlar. Birləşmə reaksiyası Markovnikov qaydasının əksinə gedir və nəticədə müvafiq 2-sianalkilalkoksikarbonilmetilsulfidlər əmələ gəlir.

Açar sözlər: merkaptosirkə turşusunun efirləri, sulfid, akril-, metakril- və kroton turşularının nitrilləri.

ЦИАНАЛКИЛИРОВАНИЕ ЭФИРОВ МЕРКАПТОУКСУСНОЙ КИСЛОТЫ

К.З.Гусейнов, М.А.Мирзоева, П.А.Алиев

Присоединение эфиров меркаптоуксусной кислоты (ЭМУК) к нитрилам акрил-, метакрил- и кротоновой кислот легко происходит в присутствии триэтиламина в качестве катализатора с образованием соответствующих 2-цианоалкилалкоксихарбонилметилсульфидов.

Ключевые слова: эфиры меркаптоуксусной кислоты, сульфид, нитрилы акрил-, метакрил- и кротоновой кислот.