

Impact Factor:

ISRA (India) = 3.117	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIHHI (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 8.716	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 5.667	OAJI (USA) = 0.350

SOI: [1.1/TAS](#) DOI: [10.15863/TAS](#)

International Scientific Journal Theoretical & Applied Science

p-ISSN: 2308-4944 (print) e-ISSN: 2409-0085 (online)

Year: 2019 Issue: 04 Volume: 72

Published: 27.04.2019 <http://T-Science.org>

SECTION 9. Chemistry and chemical technology

QR – Issue



QR – Article



Adilya Aliyoldash Mahmudova
PhD in Chemistry, Leading Scientific Researcher
Azerbaijan State Pedagogical University
adila.mahmudova@gmail.com

Gulnar Hajimammad Mammadova
aspirant,
Institute of Chemistry of Additives, Azerbaijan National
Academy of Sciences, Azerbaijan
memmedova1987@gmail.com

Sabir Sahib Babayev
PhD in Chemistry, Leading Scientific Researcher,
Institute of Chemistry of Additives, Azerbaijan National
Academy of Sciences, Azerbaijan
aki05@mail.ru

Sabir Ahmad Mammadov
Doctor in Chemistry, Professor, Head of Laboratory,
Institute of Chemistry of Additives, Azerbaijan National
Academy of Sciences, Azerbaijan
mamedov.39@inbox.ru

Lala Fahraddin Zeynalova
aspirant,
Institute of Chemistry of Additives, Azerbaijan National
Academy of Sciences, Azerbaijan
zlali@inbox.ru

STUDY OF REACTIVITY OF HYDROXYL GROUP IN 1-ARYLOXYNONANOL-2

Abstract: The reactivity of hydroxyl group in 1-aryloxynonanol-2 which was obtained by the interaction of heptyloxirane with substituted phenols in the presence of sodium metal was studied. The content of aromatic radical intensifies protonization of hydroxyl group. As a result in the reaction of 1-aryloxynonanol-2 with α -chloro ethers (chloro methoxyethyl) yields of ethers with dimethylaniline make 75-85%. The reaction of obtaining amides and thioamides with isocyanates and isothiocyanates also goes easily. The position of a substituent in phenol fragment has a little effect on the reactivity of hydroxyl group.

Key words: aryloxynonanol-2, α -chloro ethers, urethane, arylisocyanates, arylisothiocyanates, antimicrobial property.

Language: English

Citation: Mahmudova, A. A., Mammadova, G. H., Babayev, S. S., Mammadov, S. A., & Zeynalova, L. F. (2019). Study of reactivity of hydroxyl group in 1-aryloxynonanol-2. *ISJ Theoretical & Applied Science*, 04 (72), 371-376.

Soi: <http://s-o-i.org/1.1/TAS-04-72-47> **Doi:**  <https://dx.doi.org/10.15863/TAS.2019.04.72.47>

Impact Factor:

ISRA (India) = 3.117	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIHHI (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 8.716	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 5.667	OAJI (USA) = 0.350

1. INTRODUCTION

1,2-dioxyethers alkanes have been widely used in medicine and have high antibacterial and fungicide properties [1,2]. Apart from ethers the content of amino groups gives the compounds antiarrhythmic and analgesic properties [3], but in the presence of pyrrolidine fragment ethers are antagonists of calcium receptors [4]. Considering their valuable properties, the method of obtaining aminocyclohexyl ethers has been developed [5].

2. EXPERIMENTAL

IR-spectra of obtained compounds were registered at spectrometer "Nicolet IS-10, NMR H^1 -spectra were registered at spectrophotometer "Tesla-467" with a frequency of 80 MHz. The purity of the compounds was determined by Gas-Liquid Chromatography analysis using LKhM-8MD chromatograph with a flame ionization detector. Temperature of a column is 200 °C. Temperature of an evaporator is 260 °C. Helium is used as a carrier gas.

Synthesis of 1-phenoxy-2-nonanol (I). 66.9 g (0.3 mol) of 1-bromium-2-nonanol was added drop by drop into the mixture of 28.2 g (0.3 mol) of phenol and 30 g of 40% aqueous solution of NaOH at 80-85 °C and vigorous mixing. During mixing the mixture was heated up to 80-85 °C for 5 hours. Obtained ether was extracted with benzene. Benzene solution was washed out with water till neutral reaction, dried, benzene was distilled, and then the residue was distilled under vacuum. 48.7 g (66 %) of product was obtained.

The compounds II and III were synthesized similarly. Their characteristics are given in the table 1.

Synthesis of 1-(2-methylphenoxy)-2-ethoxymethoxynonane (IV). 10 g (0.04 mol) of 1-(2-methylphenolxy)-nonanol-2 and 6.05 g (0.051 mol) of freshly-distilled dimethylaniline were dissolved in 70 ml of anhydrous benzene. At room temperature and mixing for 30 min 4.7 g (0.5 mol) of freshly-distilled α -chloromethylethyl ether dissolved in 30 ml of anhydrous benzene was added. Reaction mass was mixed at room temperature for an hour, and then at 55-60 °C for 3-4 hours. It was cooled, washed out with 5% solution of HCl and then with water till neutral reaction. Benzene solution was dried Na_2SO_4 , benzene was distilled, and then the residue was distilled under vacuum by collecting fractions boiling at 146-148 °C/3 mmHg. 8.2 g (70%) of product was obtained. Compounds V and VII were synthesized similarly.

Synthesis of 1-(2-methylphenoxy)-2-acetoxynonane (VIII). 10 g (0.04 mol) 1-(2-methylphenoxy)-nonanol-2 (compound I) and 6.1 g (0.05 mol) of dimethylaniline were dissolved 60 ml of anhydrous benzene. During mixing 3.93 g (0.05 mol) of chloro acetyl was added into the solution drop by drop. At 45-50 °C and mixing reaction mass was heated for 3-4 hours. Then it was cooled, washed out with 5% solution of HCl and water till neutral reaction. Benzene solution was dried, benzene was distilled, and then the residue was distilled under vacuum by collecting fractions boiling at 134-136 °C/1 mmHg. 8.2 g (70%) of product was obtained. Compounds IX and X were obtained similarly. Their physical and chemical properties are given in the table 1.

Synthesis of 1-phenoxy-2-N-phenylurethanenonane (X). 10 g (0.04 mol) of 1-phenoxy-2-nonanol was dissolved in 40 mol of anhydrous benzene. At 80-85 °C and mixing 5.95 g (0.05 mol) of phenylisocyanate was added drop by drop into the solution of 20 ml anhydrous benzene. The mixture was mixed at 80-85 °C for 3-4 hours. Then it was cooled till room temperature, 25 ml of anhydrous hexane was added. Precipitated crystals were filtered and then recrystallized from the mixture of hexane-benzene (3:1). 9.7 g (68.1%) of product was obtained. Compounds XI and XIII were synthesized similarly.

In NMR H^1 -spectrum (Fig.1) of 1-phenoxy-2-N-phenylcarbamidenonane (compound XI) protons CH_3 and $(CH_2)_5$ appear in unresolved form at 0.8-1.4 ppm, but protons CH_2-Ar , CH and CH_2-o are observed in the form of doublet at 5,3 ppm.

3. RESULTS AND DISCUSSION

Considering high bioactivity of ethers of carboxylic acids and aromatic phenols containing active functional groups, currently strengthened studies on the development of more rational methods of their obtaining are carried out.

The dynamic kinematic determination of α,α -disubstituted carboxylic ethers catalyzed with N-heterocyclic carbenes was conducted by interesterification reaction of alcohols [7] by using organic compounds of actinide metals as catalysts with asymmetric tandem esterification reaction with proton transfer between aldehydes and alcohols. The developed method of esterification is suitable for a wide range of applications of substrates in the synthesis of different ethers. Reactivity of chlorine atom in alkanols under the impact of hydroxyl group in β -position was studied. It was found [8] that the reaction of m-methylphenol with 1-bromium-2-hydroxyoctan-ol-2 goes with high yield.

Studies on the reaction of 4-chlor-2-butanol or chloropropanol with oxalic acid also showed reactivity of hydroxyl group [9].

Impact Factor:

ISRA (India)	= 3.117	SIS (USA)	= 0.912	ICV (Poland)	= 6.630
ISI (Dubai, UAE)	= 0.829	PIHII (Russia)	= 0.156	PIF (India)	= 1.940
GIF (Australia)	= 0.564	ESJI (KZ)	= 8.716	IBI (India)	= 4.260
JIF	= 1.500	SJIF (Morocco)	= 5.667	OAJI (USA)	= 0.350

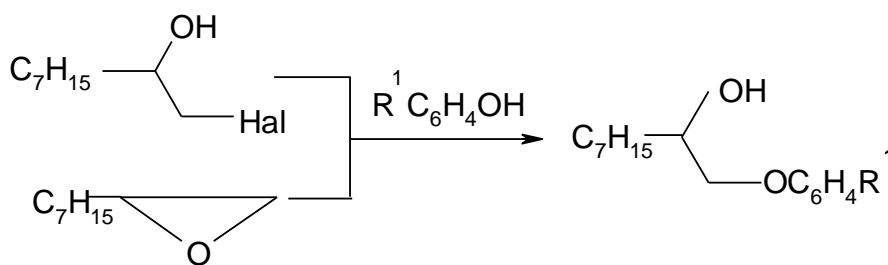
The content of chlorine atom in 1-position and 3-position in propanol propylthiogroups activate hydroxyl group and due to this esterification goes smoothly and the yields are very high. Moreover, 1-aryloxyalkylpropanols easily react with isocyanates or thioisocyanates forming carbamates and thiocarbamates [9,10].

1-(*m*-tolxyloxy)-octanol-2 was synthesized by the reaction of *m*-cresol with 1-bromium-2-octanol. Reactivity of hydroxyl group in the reactions with α -chloromethylpropyl ether, acetylchloride and during condensation with aromatic isocyanates and thioisocyanates was studied. All synthesized

carbamates and thiocarbamates have effective bactericide properties against staphylococcus, candida, typhoid fever and penicillin [11].

It was established [12] that the content of carbamate groups in 1-(*N,N*-diethyldithiocarbamate)-2-propanol does not block the reaction with arylisocyanates and isothiocyanates. On the contrary, yields of carbamates and thiocarbamates increase. Synthesized amides have high bactericide properties.

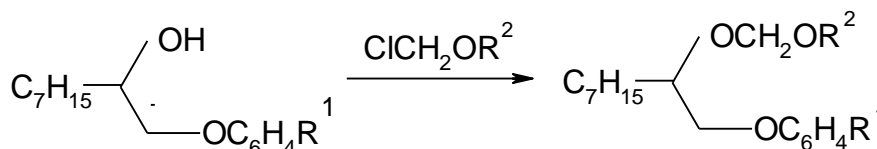
We have proposed the research on the reaction of aryloxynonal-2 with substituted phenols. 1-bromium-nonanol-2 and heptyloxirane were obtained by the known method:



R¹=H(I); *o*-CH₃(II);
m-CH₃(III); *p*-CH₃(IV)

Scheme 1

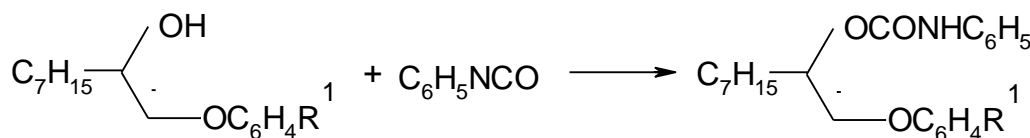
Due to the impact of electron acceptor aryloxy-fragment hydrogen of hydroxyl group is easily substituted with α -chloroethers forming polyethers with high yields:



R¹=*o*-CH₃, R²=C₂H₅ (V); R¹=*m*-CH₃,
R²=C₂H₅(VI); R¹= *p*-CH₃, R²= C₂H₅(VII);
R¹=*o*-CH₃, R²= COCH₃(VIII); R¹=*m*-CH₃,
R²= COCH₃(IX), R¹= *p*-CH₃, R²= COCH₃(X)

Scheme 2

For confirmation of hydroxyl group the synthesis of urethanes was carried out by the reaction of arylisocyanates with aryloxynonal-2:



R¹= H (XI); *o*-CH₃ (XII);
m-CH₃ (XIII); *p*-CH₃ (XIV)

Scheme 3

Impact Factor:

ISRA (India) = 3.117	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIHII (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 8.716	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 5.667	OAJI (USA) = 0.350

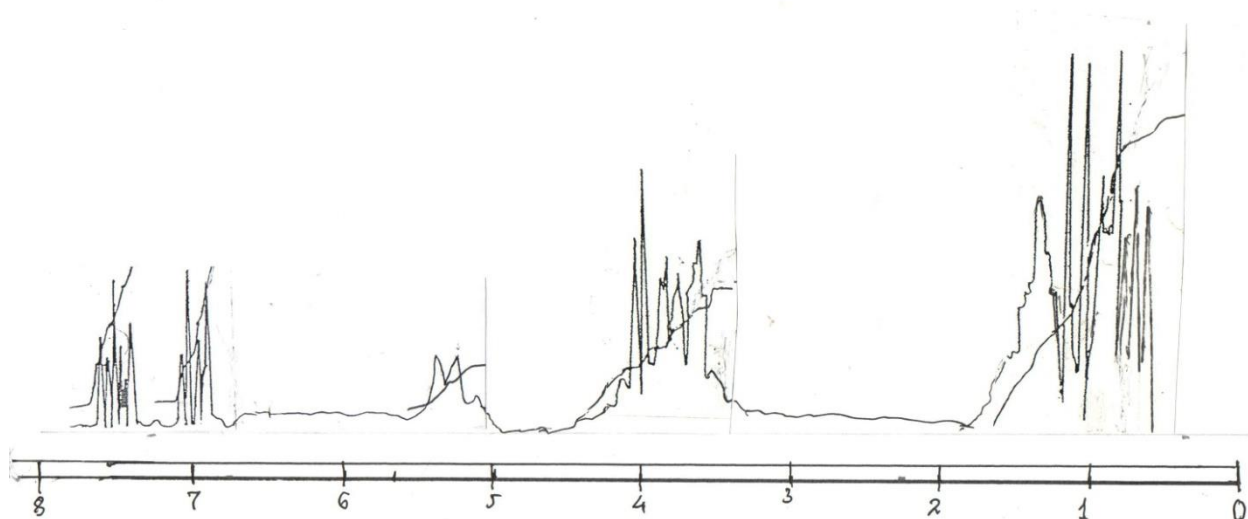


Fig.1. NMR-spectrum of 1-phenoxy-2-N-phenylcarbamidenonane (compound XI)

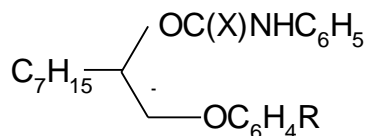
Aromatic ether groups containing urethane are highly effective as additives to lubricating oils. Moreover, representatives of this class of organic compounds are highly effective antimicrobial preparations.

Compounds (X – XIII) were studied as antimicrobial additives to lubricating oils (in the composition of oil M-8). The results are given in the

table 2. As table shows amides (compounds X - XIII) have fungicide properties and their effectiveness does not much depend on the position of a substituent in aromatic nuclear. They are more effective than industrial fungicide.

Amides containing a substituent in p-position are more effective than the substituents in other positions.

Table 2. Antimicrobial properties of 1-oxyphenyl-2-N-phenylureido-or-thioureidononanes (X - XVII):



X	R	Concentration, %	Diameter of depression zone of microorganisms, cm	
			Mixture of bacteria	Mixture of fungi
O	H	0,3	1,8	2,2
		0,5	2,2	2,8
O	o - CH ₃	0,3	2,1	2,8
		0,5	2,6	3,2
O	m - CH ₃	0,3	1,9	2,8
		0,5	2,7	3,4
O	π - CH ₃	0,3	2,3	3,5
		0,5	2,1	3,9
S	H	0,3	2,8	2,1
		0,5	3,2	2,9
S	o - CH ₃	0,3	3,1	2,4
		0,5	3,9	2,6
S	m - CH ₃	0,3	2,9	2,5
		0,5	3,5	2,8
S	π - CH ₃	0,3	3,1	2,1
		0,5	3,6	2,2
Vazin		0,8-1	3,0	2,8

Impact Factor:

ISRA (India) = 3.117	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIHHI (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 8.716	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 5.667	OAJI (USA) = 0.350

Table 1. Physical and chemical properties of synthesized compounds (I-XIV)

№№ Comp.	Yield %	T _{boil} /mm Hg of T _{melt.} , °C	n _D ²⁰	d ₄ ²⁰	MR _D		Chemical formula	Analysis, %		
					Found	Calcul.		C	H	N
								Found /Calculated		
I	66,9	170- 171/1 35-36	-	-	-	-	C ₁₅ H ₂₄ O ₂	<u>78,18</u> 78,27	<u>10,05</u> 10,16	-
II	66,5	173- 174/1	1,4922	0,9532	76,13	76,221	C ₁₆ H ₂₆ O ₂	<u>76,67</u> 76,75	<u>10,29</u> 10,46	-
III	63,7	178- 179/1 39-40	-	-	-	-	C ₁₆ H ₂₆ O ₂	<u>76,70</u> 76,75	<u>10,29</u> 10,46	-
IV	68,8	179- 180/1 49-50	-	-	-	-	C ₁₆ H ₂₆ O ₂	<u>76,91</u> 76,75	<u>10,22</u> 10,46	-
V	70,3	144- 145/3	1,4702	1,9384	91,74	92,12	C ₁₉ H ₃₀ O ₃	<u>73,8</u> 73,98	<u>10,31</u> 10,45	-
VI	70,3	146- 147/3	1,4724	1,9392	92,16	91,9	C ₁₉ H ₃₂ O ₃	<u>73,8</u> 73,98	<u>10,33</u> 10,45	-
VII	70,9	143- 144/3	1,4922	0,9532	76,13	76,221	C ₁₆ H ₂₆ O ₂	<u>73,8</u> 73,98	<u>10,33</u> 10,45	-
VIII	73,5	134- 135/1	1,4758	0,9695	84,94	85,12	C ₁₈ H ₂₈ O ₃	<u>73,7</u> 73,98	<u>10,31</u> 9,63	-
IX	74,6	133- 134/1	1,4750	0,9692	84,96	85,12	C ₁₈ H ₂₈ O ₃	<u>73,60</u> 73,98	<u>9,41</u> 9,63	-
X	77,8	135- 136/1	1,4754	1,9681	84,89	85,12	C ₁₈ H ₂₈ O ₃	<u>74,08</u> 73,98	<u>9,85</u> 9,63	-
XI	71,2	55-56	-	-	-	-	C ₂₂ H ₂₉ O ₃	<u>74,18</u> 74,36	<u>8,01</u> 8,17	<u>8,85</u> 3,94
XII	70,8	45-46	-	-	-	-	C ₂₃ H ₃₁ NO ₃	<u>74,62</u> 74,79	<u>8,31</u> 8,4	<u>3,61</u> 3,79
XIII	71,9	48-49	-	-	-	-	C ₂₃ H ₃₁ NO ₃	<u>74,65</u> 74,79	<u>8,18</u> 8,4	<u>3,67</u> 3,79
XIV	76,1	46-47	-	-	-	-	C ₂₃ H ₃₁ NO ₃	<u>74,65</u> 74,79	<u>8,18</u> 8,4	<u>3,67</u> 3,79

References:

- Kimpe, N. D., Doeleris, M., & Contreras, J. (1996). *Tetrahedron Lett.*, V.37, pp. 3171-3176.
- Thery, O., & Etienne, N. (2007). *Tetrahedron Lett.*, pp. 1546-1550.
- Schenone, S. O. (2000). *Farmaco*, V. 55, №6, pp. 495-498.
- Cavai, A. V., & Mikkilineni, A. B. (2005). *Bioorg.Med.Chem.*, V.15, №24, pp. 5478-5482.
- Bernard, A., Michael, J. A., & Walker, R. A. (n.d.). *Patent 6174879 USA*.
- Chen, X., Feng, J., Xu, J., & Mou, C. (2016). *J..Am. Chem. Soc.*, 138, № 23, pp. 7212-7215.

Impact Factor:

ISRA (India)	= 3.117	SIS (USA)	= 0.912	ICV (Poland)	= 6.630
ISI (Dubai, UAE)	= 0.829	PIHII (Russia)	= 0.156	PIF (India)	= 1.940
GIF (Australia)	= 0.564	ESJI (KZ)	= 8.716	IBI (India)	= 4.260
JIF	= 1.500	SJIF (Morocco)	= 5.667	OAJI (USA)	= 0.350

- Liu, H., & Eisen, M. S. (2017). *Organometallics*, 36, № 8, pp. 1461-1464.
- Hasanov, V. S., Mahmudova, A. A., Babaeva, G. V., & Bakhshieva, I. S. (2013). *AzChemJ. № 4*, pp. 101-105.
- Hasanov, V. S., Mahmudova, A. A., Babaeva, G. V., Rahimov, I. R. (2014). *AzChemJ. № 1*, pp. 104-108.
- Hasanov, V. S., Mahmudova, A. A., Babaeva, G. V., Bakhshieva, U. S., & Akperli, G. N. (2014). *AzChemJ. № 3*, pp. 110-115.
- Hasanov, V. S. (2013). *AzChemJ. № 4*, pp. 101-105.
- Babaeva, G. V., & Zeynalova, L. F. (2013). *AzChemJ, № 3*, pp. 121-124.