



SYNTHESIS OF TRANS-2-BENZYLOXY-3(4-CHLORO(BROMOPHENYL)OXIRANES AND THEIR APPLICATION AS ANTIMICROBIAL ADDITIVES TO OILS AND FUELS

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ABSTRACT

The condensation reaction of chloromethylbenzyl ether with chloro(bromo)-substituted benzaldehydes in the presence of sodium hydroxide under the conditions of interphase catalysis (catalyst – TEBAC) has been studied. The synthesis method for 2-benzyloxy-3-aryloxiranes has been developed. The synthesis of oxiranes takes place stereoselectively with the formation of *trans*-isomers. The obtained compounds have been studied as antimicrobial additives for lubricating oils and fuels.

KEYWORDS

Chloro(bromo)-substituted benzaldehydes;
Chloromethylbenzyl ether;
Trans-isomers;
2,3-disubstituted oxiranes;
Interphase catalysis;
antimicrobial additives.

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Introduction

Bacteria and fungi deteriorate not only the quality of fuels and oils, but also lead to corrosion of reservoirs, lubricating and fuel systems of engines, etc. During microbiological enzymatic oxidation of hydrocarbons with the formation of organic acids that have surface-active properties, fuels are emulsified and thus they become biodamaged [1]. The growth of microorganisms in fuels depends on the presence of water with traces of mineral salts and the optimum temperature. In a fuel that does not contain water, the development and growth of microflora is impossible. Despite the development of modern industry, moisture cannot be avoided during the storage and working of fuels; and traces of water are sufficient for the growth of microorganisms. In the case of lubricating oils [2], if the engine has a closed system of circulating type lubrication, then the presence of bacteria and fungi does not affect the properties of the oils and does not impair the operation of the engines, since in these systems the oil heats up to 120-180 °C in certain areas and this disinfects itself. The development of microorganisms is inevitable in engines and mechanisms with open lubricating systems. Biodeterioration of fuels and oils leads to environmental pollution and economic losses. An effective method of protecting petroleum products from microbiological damage is a chemical method, i.e. introduction of antimicrobial additives – biocides into their composition. Considering the ability of microorganism to easily adapt to environmental conditions, the synthesis and study of new multifunctional additives for oils and fuels is a very urgent task.

Heteroatomic organic compounds are widely applied as antioxidant, anticorrosive, and antimicrobial additives to oils and fuels [3].

Oxiranes are an important class of organic compounds that are actively used in targeted organic synthesis of

various biologically active drugs [4]. Substituted oxiranes containing functional groups are of great interest. Among the most studied of such substituted oxiranes are glycidic esters obtained by the condensation of aromatic aldehydes with chloroacetic acid esters in the presence of bases (the Darzens reaction) [5]. In recent years, we have been studying various condensation reactions occurring in presence of chloromethyl propargyl ether [6–8]. In [6], we first carried out similar condensation of propargylchloromethyl ether with aromatic aldehydes (ketones) and obtained 2-aryl-1-propargyloxiranes.

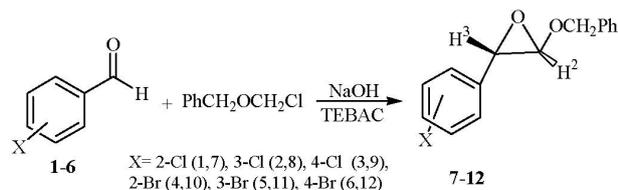
We expanded the range of studying reagents of condensation and improved the experimental technique, and during the interaction of chloro(bromo)-substituted benzaldehydes 1–6 with chloromethylbenzyl ether in an aqueous medium in the presence of a interphase catalyst triethylbenzylammonium chloride (TEBAC), we obtained *trans*-isomers – 3-haloaryl-2-benzyloxyoxiranes 7–12 with a satisfactory yield (62.1–69.7%). The composition and structure of compounds 7–12 have been confirmed by the data of elemental analysis, IR spectra and ¹H, ¹³C NMR spectroscopy. In the ¹H NMR spectra, the existence of two doublet signals of H² and H³ protons of the oxirane ring is characteristic besides the signals of aromatic protons and two doublets in the region of ~4.1 ppm. with J=14.4 Hz (OCH₂ group). The spin-spin coupling constant for these protons is ~3 Hz, which is typical for *trans*-located protons of the oxirane cycle. An analysis of the chemical shifts of the same protons shows that the high-field signal is in the region of ~4.1 ppm. and this signal apparently belongs to H³, while the signal of another H² proton is low-field and is located in the region of 4.2–4.7 ppm. In this case, the introduction of acceptor substituents into the aryl group at C³ significantly reduces the chemical shift of this proton. This result also confirms the *trans*-configuration of the compounds. Indeed, in this case, the H² proton is located in the *cis*-position to the aryl group at the C³ atom, and the presence of acceptor groups in the aryl

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<http://dx.doi.org/10.5510/OGP2022SI100688>

substituent reduces the chemical shift of this proton.

An experimental feature of this work is the use of the



method of the process of interphase alkaline catalysis. In this case, it is possible to avoid the use of organic solvents and strong bases (for example, sodium alcoholate), which prevents the destruction processes of the initial reaction products. The mechanism of condensation is similar to the Darzens reaction [2] and includes the formation of the anion and ether at the aqueous and organic phase boundary. Next, the anion is transferred to the organic phase by the aid of TEBAC catalyst and the anion reacts with the aldehyde forming the reaction product.

The yields of bromo-derivatives (10-12) are higher than yields of the chlorine analogues (7-9).

Compounds 7-12 are light yellow crystalline substances; their composition is confirmed by elemental analysis data.

As is seen from the data in table 1, synthesized compounds (7-12) have antimicrobial activity. Moreover, at a concentration of 1.0%, compounds 7-9 in synthetic and base oils showed high bactericidal properties (2.6-3.0 cm), almost twice the standard. Compounds 10-12 showed a result equal to the standard (1.2-1.6 cm).

Compounds 7-9 in the oil T-22, along with the bactericidal property, also showed fungicidal properties (1.3-1.7 cm), and they acted only on bacteria in the fuel (1.5-2.1 cm).

The obtained compounds have been studied in synthetic oil (diester of succinic acid), base oil T-22, and in fuel (gasoline-95) as antimicrobial additives. The analysis showed that the synthesized compounds effectively inhibit the growth of the abovementioned bacteria and fungi, and the diameter of the suppression zone of the adduct microorganisms is two times more than the control drug. Taking into account the above, trans-2-benzyloxy-3-(4-chloro(bromophenyl)oxiranes can be proposed as antimicrobial additives for oils and fuels.

Experimental part

^1H and ^{13}C NMR spectra have been recorded on Bruker SF-300 device (Germany) at frequencies of 300.15 and 100.31 MHz, respectively, in CDCl_3 solutions (internal standard HMDS). IR spectra of the compounds have been recorded on Specord 75 IR spectrometer within the interval of 4000-400 cm^{-1} in KBr. The purity of the obtained compounds has been controlled by TLC on Silufol UV-254 plates («Chemapol», Czech Republic), and appearing - in iodine vapor. Elemental analysis has been performed on the Perkin-Elmer Series II 2400 device (Perkin-Elmer, USA). We used commercial reagents from «Aldrich» and «Sigma», and the melting point has been determined on the Electrothermal 9100 device (Great Britain).

GLC analysis has been carried out on the «ЛХМ-8 МД» (Russia) chromatograph; steel column (300×3 mm) with 5% PEGS (polyethylene glycol succinate) on dinochrome P, carrier gas – helium (40 cm^3/min), detector-cathorometer, column temperature – 150 °C, evaporator – 230 °C.

General techniques for the preparation of oxiranes (7-12). A suspension formed from the mixture of 50 mmol of halogen-substituted aldehyde (1-6), 7.2 g (5 mmol) of chloromethylbenzyl ether (2), 0.24 g (6 mmol) of NaOH, and 0.1 g of TEBAC and 10 mL of water has been stirred at room temperature for 2-5 h. The crystalline compounds have been filtered off, washed with water and recrystallized from ethanol.

trans-2-Benzyloxy-3-(2-chlorophenyl)oxirane (7) has been obtained based on the result of 2-chlorobenzaldehyde (1) and chloromethylbenzyl ether. Yield 64.1%. T_{melt} 86-88 °C (from ethanol). IR spectrum, ν , cm^{-1} : 1579, 1484, 1446, 1293, 1110, 888, 808, 698. Spectrum of ^{13}C NMR, δ , m.d.: 4.06 (d, ^1H , $J=3.1$ Hz, $^3\text{C-H}$), 4.07 (d, $J=14.4$ Hz, ^1H , OCH_2), 4.11 (d, $J=14.4$ Hz, ^1H , OCH_2), 4.25 (d, $J=3.1$ Hz, ^1H , $^2\text{C-H}$), 7.24-7.26 (m, 2H, ArH) 7.49-7.56 (m, 4H, ArH), 7.66 (t, $J=7.2$ Hz, ^1H , ArH), 8.05 (d, $J=7.2$ Hz, 2H, ArH). Spectrum of ^{13}C NMR, δ , m.d.: 62.8, 74.3, 93.6, 120.5, 123.6, 123.4, 124.5, 125.8, 131.7. It has been found (%): C 69.17; H 5.11; Cl 13.21. $\text{C}_{15}\text{H}_{13}\text{ClO}_2$; and calculated (%): C 69.10; H 5.03; Cl 13.60.

trans-2-Benzyloxy-3-(3-chlorophenyl)oxirane (8) has been obtained from 3-chlorobenzaldehyde (1) and chloromethylbenzyl ether. Yield 63.9%, T_{melt} 84-86 °C (from ethanol). IR spectrum, ν , cm^{-1} : 1578, 1482, 1443, 1294, 1110, 884, 806, 693. Spectrum of ^{13}C NMR, δ , m.d.: 4.04 (d, ^1H , $J=3.1$ Hz, $^3\text{C-H}$), 4.05 (d, $J=14.3$ Hz, ^1H , OCH_2), 4.12 (d, $J=14.3$ Hz, ^1H , OCH_2), 4.24 (d, $J=3.1$ Hz, ^1H , $^2\text{C-H}$), 7.23-7.27 (m, 2H, ArH) 7.45-7.54 (m, 4H, ArH), 7.65 (t, $J=7.1$ Hz, ^1H , ArH), 8.03 (d, $J=7.1$ Hz, 2H, ArH). Spectrum of ^{13}C NMR, δ , m.d.: 62.8, 74.3, 93.6, 120.5, 123.6, 123.4, 124.5, 125.8, 131.7. It has been found (%): C 68.88; H 4.92; Cl 13.32. $\text{C}_{15}\text{H}_{13}\text{ClO}_2$ and calculated (%): C 69.10; H 5.03; Cl 13.60.

trans-2-Benzyloxy-3-(4-chlorophenyl)oxirane (9) has been obtained from 4-chlorobenzaldehyde (1) and chloromethylbenzyl ether. Yield 62.1%. T_{melt} 85-87 °C (from ethanol). IR spectrum, ν , cm^{-1} : 1578, 1483, 1445, 1292, 1111, 884, 805, 697. Spectrum of ^{13}C NMR, δ , m.d.: 4.04 (d, ^1H , $J=3.0$ Hz, $^3\text{C-H}$), 4.07 (d, $J=14.2$ Hz, ^1H , OCH_2), 4.11 (d, $J=14.2$ Hz, ^1H , OCH_2), 4.25 (d, $J=3.0$ Hz, ^1H , $^2\text{C-H}$), 7.24-7.26 (m, 2H, ArH) 7.50-7.57 (m, 4H, ArH), 7.66 (t, $J=7.0$ Hz, ^1H , ArH), 8.05 (d, $J=7.0$ Hz, 2H, ArH). Spectrum of ^{13}C NMR, δ , m.d.: 62.8, 74.3, 93.6, 120.5, 123.6, 123.4, 124.5, 125.8, 131.7. It has been found (%): C 69.14; H 5.13; Cl 13.44. $\text{C}_{15}\text{H}_{13}\text{ClO}_2$ and calculated (%): C 69.10; H 5.03; Cl 13.60.

trans-2-Benzyloxy-3-(2-bromophenyl)oxirane (10) has been obtained from 2-bromobenzaldehyde (1) and chloromethylbenzyl ether. Yield 69.1%. T_{melt} 108-110 °C (from ethanol). IR spectrum, ν , cm^{-1} : 1580, 1482, 1445, 1292, 1110, 887, 806, 698. Spectrum of ^{13}C NMR, δ , m.d.: 4.06 (d, ^1H , $J=3.1$ Hz, $^3\text{C-H}$), 4.06 (d, $J=14.3$ Hz, ^1H , OCH_2), 4.11 (d, $J=14.3$ Hz, ^1H , OCH_2), 4.24 (d, $J=3.1$ Hz, ^1H , $^2\text{C-H}$), 7.23-7.27 (m, 2H, ArH) 7.49-7.57 (m, 4H, ArH), 7.67 (t, $J=7.2$ Hz, ^1H , ArH), 8.04 (d, $J=7.2$ Hz, 2H, ArH). Spectrum of ^{13}C NMR, δ , m.d.: 62.8, 74.3, 93.6, 120.5, 123.6, 123.4, 124.5, 125.8, 131.7. It has been found (%): C 58.83; H 4.11; Br 26.16. $\text{C}_{15}\text{H}_{13}\text{BrO}_2$ and calculated (%): C 59.04; H 4.29; Br 26.18.

trans-2-Benzyloxy-3-(3-bromophenyl)oxirane (11) has been obtained from 3-bromobenzaldehyde (1) and chloromethylbenzyl ether. Yield 69.7%. T_{melt} 101-103 °C (from ethanol). IR spectrum, ν , cm^{-1} : 1578, 1485, 1446, 1292, 1110, 887, 807, 694. Spectrum of ^{13}C NMR, δ , m.d.: 4.05 (d, ^1H , $J=3.1$ Hz, $^3\text{C-H}$), 4.06 (d, $J=14.2$ Hz, ^1H , OCH_2), 4.12 (d, $J=14.2$ Hz, ^1H , OCH_2), 4.25 (d, $J=3.1$ Hz, ^1H , $^2\text{C-H}$), 7.23-7.27

(m, 2H, ArH) 7.50-7.58 (m, 4H, ArH), 7.67 (t, J=7.2 Hz, ¹H, ArH), 8.04 (d, J=7.2 Hz, 2H, ArH). Spectrum of ¹³C NMR, δ , m.d.: 62.8, 74.3, 93.6, 120.5, 123.6, 123.4, 124.5, 125.8, 131.7. It has been found (%): C 59.01; H 4.32; Br 26.14. C₁₅H₁₃BrO₂ and calculated (%): C 59.04; H 4.29; Br 26.18.

trans-2-Benzoyloxy-3-(4-bromophenyl)oxirane (12) has been obtained based on the result of 4-bromobenzaldehyde (1) and chloromethylbenzyl ether. Yield 68.4%. Tmelt 105-107 °C (from ethanol). IR spectrum, ν , cm⁻¹: 1579, 1484, 1446, 1293, 1110, 888, 808, 698. Spectrum of ¹³C NMR, δ , m.d.: 4.04 (d, 1H, J=3.1 Hz, ³C-H), 4.06 (d, J=14.4 Hz, ¹H, OCH₂), 4.11 (d, J=14.4 Hz, ¹H, OCH₂), 4.24 (d, J=3.1 Hz, ¹H, ²C-H), 7.23-7.28 (m, 2H, ArH) 7.49-7.56 (m, 4H, ArH), 7.67 (t, J=7.1 Hz, ¹H, ArH), 8.05 (d, J=7.1 Hz, 2H, ArH). Spectrum of ¹³C NMR, δ , m.d.: 62.8, 74.3, 93.6, 120.5, 123.6, 123.4, 124.5, 125.8, 131.7. It has been found (%): C 58.87; H 4.24; Br 26.11. C₁₅H₁₃BrO₂ and calculated (%): C 59.04; H 4.29; Br 26.18.

The synthesized compounds (7-12) have been studied as antimicrobial additives in synthetic oil – diester of succinic acid, in base oil T-22, and fuel – gasoline-95 at the Institute of Chemistry of Additives named after acad. A.M. Kuliyevev of Azerbaijan National Academy of Sciences. The analysis has been carried out according to the zonal diffusion method based on GOST 9.052-88 and GOST 9.082-77. Bacteria – *Pseudomonas aeruginosa*, *Mycobacterium lacticolum*, fungi – *Aspergillus niger*, *Cladosporium resinae*, *Penicillium chrysogenum*, *Trichoderma viride* have been taken as test cultures. Meat-

peptone agar (MPA) has been chosen as a nutrient medium for the growth of bacteria, and wort agar for growth of fungi. The exposure time for bacteria was two days, and for fungi - 3-4 days. Samples have been taken at three concentrations (%): 0.25, 0.5, and 1.0. The results of the study have been compared with the data of the control drug – sodium pentachlorophenolate.

Antimicrobial properties have been determined by the zonal diffusion method. First, samples have been prepared for research, %: 0.25, 0.5 and 1.0 solutions of the synthesized compounds (7-12) in the investigated oils and fuels. Next, 20-25 ml of nutrient medium has been poured into a Petri dish. After solidification of the medium on the surface, microorganisms have been sown, and using a sterile stick, holes with diameter of 10 mm and deep of 4-5 mm have been opened. 0.3-0.5 ml of the test sample has been added to these wells. Next, Petri dishes have been placed in the thermostat and kept for two days for bacteria and 3-4 days for fungi at 29 ±2°C. For comparison, sodium pentachlorophenolate has been tested as a standard in the same dilutions under similar conditions.

The effectiveness of the antimicrobial activity of the investigated compounds (7-12) has been determined by the diameter size of the inhibition zone of the microorganism growth – the larger the size, the more effective the antimicrobial activity of the compound. The results of the study are presented in the table.

Antimicrobial properties of 7-12 compounds						
Compounds	Concentration %	Suppression zone for the growth of the microorganisms, cm				
		Synthetic oil (diether of succinic acid)	Oil T-22		Fuel (Gasoline-95)	
		Bacteria (<i>Pseudomonas aeruginosa</i> , <i>Mycobacterium phlei</i>)	Bacteria (<i>Pseudomonas aeruginosa</i> , <i>Mycobacterium phlei</i>)	Fungi (<i>Aspergillus niger</i> , <i>Penicillium chrysogenum</i>)	Bacteria (<i>Pseudomonas aeruginosa</i> , <i>Mycobacterium phlei</i>)	Fungi (<i>Cladosporium resinae</i>)
7	1.0	3.0-3.0	2.2-2.5	1.4-1.2	—	—
	0.5	1.8-2.0	2.0-1.8	1.0-1.0	1.8-2.0	1.0-1.2
	0.25	1.0-1.0	1.1-1.0	+++	1.4-1.4	+++
8	1.0	1.2-1.3	1.2-1.4	+++	—	—
	0.5	1.0-1.0	+++	+++	1.5-1.6	+++
	0.25	+++	+++	+++	1.1-1.2	+++
9	1.0	3.0-2.8	2.5-3.0	1.4-1.6	—	—
	0.5	2.5-2.5	2.0-2.0	1.0-1.0	1.3-1.4	+++
	0.25	1.4-1.4	1.2-1.3	+++	1.1-1.1	+++
10	1.0	1.3-1.5	1.4-1.6	+++	—	—
	0.5	1.1-1.2	1.0-1.0	+++	1.5-1.7	+++
	0.25	+++	+++	+++	1.2-1.2	+++
11	1.0	1.3-1.7	1.4-1.6	+++	—	—
	0.5	1.0-1.2	1.0-1.0	+++	1.5-1.7	+++
	0.25	+++	+++	+++	1.2-1.2	+++
12	1.0	1.5-1.5	1.3-1.5	+++	—	—
	0.5	1.0-1.2	1.0-1.0	+++	1.4-1.7	+++
	0.25	+++	+++	+++	1.2-1.2	+++
Standard (sodium pentachlorophenolate)	1.0	1.3-1.4	1.3-1.4	1.3-1.4	—	—
Control	0	+++	+++	+++	+++	+++

Note: (+++) – growth of microorganisms, (–) – not investigated.

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Синтез транс-2-бензилокси-3(4-хлор(бромфенил) оксираны и применение их в качестве антимикробных присадок к маслам и топливам

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Реферат

Исследована конденсация хлорметилбензилового эфира с хлор(бром)замещенными бензальдегидами в присутствии гидроксида натрия в условиях межфазного катализа (катализатор – ТЭБАХ). Разработан метод синтеза 2-бензилокси-3-арилоксиранов. Синтез оксиранов проходит стереоселективно с образованием транс-изомеров. Исследованы полученные соединения в качестве антимикробных присадок к смазочным маслам и топливам.

Ключевые слова: хлор(бром)замещенные бензальдегиды; хлорметилбензиловый эфир; транс-изомеры; 2,3-дизамещенные оксираны; межфазный катализ; антимикробные присадки.

Trans-Benzoloksi-3(4-xlor(bromfenil) oksiranlar və onların yağlara və yanacaqlara antimikrob əlavələr kimi tətbiqi

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Xülasə

Xlorometilbenzil efirinin benzaldehydlərin xlorlu (bromlu) törəmələri ilə natrium hidrogenoksid iştirakında fazalararası kataliz şəraitində kondensləşməsi tədqiq olunmuşdur (katalizator – TEBAH). 2-benziloksi-3-ariloksiranın sintez metodu işlənilib hazırlanmışdır. Oksiranların sintezi trans-izomerlərin əmələ gəlməsi istiqamətində stereoselektiv olaraq gedir. Alınan birləşmələr sürtkü yağlarına və yanacaqlara antimikrob əlavələr kimi öyrənilmişdir.

Açar sözlər: benzaldehydlərin xlorlu (bromlu) törəmələri; xlorometilbenzil efiri; trans-izomerlər; 2,3-diəvəzölünmüş oksiranlar; fazalararası kataliz; antimikrob əlavələr.