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RESEARCH ARTICLE

Synthesis and properties of cyclic acetals of Wallach ketone

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Abstract

Objectives. The work set out to obtain the corresponding cyclohexenyl derivatives of 1,4-dioxaspiro[4.5]decane, 1,5-dioxaspiro[5.5]-undecane, and 1,4-dithiaspiro[4.5]decane by condensation of 2-(cyclohexen-1-yl)cyclohexanone (Wallach ketone) with 1,2-, 1,3-diols, and 1,2-ethanedithiol; to determine reaction duration and process temperature at which the maximum possible yield of the target cyclic derivatives of 2-(cyclohexen-1-yl)cyclohexanone is achieved; to evaluate the anticorrosive properties of the obtained acetals in an acidic medium; to carry out dichlorocarbenation using 1,4-dioxaspiro[4.5]decane as an example, and to establish the structure of the obtained isomers.

Methods. Target compounds including cyclic acetals were obtained by a classical organic synthesis method involving condensation of 2-(cyclohexen-1-yl)cyclohexanone (Wallach ketone) with 1,2-, 1,3-diols, and 1,2-ethanedithiol. The following analysis methods were used to determine the qualitative and quantitative composition of the reaction masses: gas–liquid chromatography (Crystallux-4000M chromatograph with a flame ionization detector, a 25 m × 0.33 mm capillary column containing 100% polydimethylsiloxane as a stationary phase 0.5 μm), nuclear magnetic resonance spectroscopy (BrukerAM-500 device with operating frequencies of 500 and 125 MHz), and elemental microanalysis (rapid gravimetry method). Chlorine and sulfur were determined by the Schöniger method.

Results. Under conditions of thermal heating of Wallach ketone with 1,2-, 1,3-diols, and 1,2-ethanedithiol, 1,4-dioxaspiro[4.5]decane, 1,5-dioxaspiro[5.5]undecane, and 1,4-dithiaspiro[4.5]decane were obtained with a yield of 95%. 5,5-Dimethyldioxane derivative was found to have a moderate inhibitory effect on acid corrosion of carbon steel St20 at a temperature of 60°C. Dichlorocarbenation of 1,4-dioxaspiro[4.5]decane was shown to occur with the formation of a mixture of two diastereomers (ratio is 1 : 2) as evidenced by doubled signals of carbon atoms in the carbon spectrum.

Conclusions. 2-(Cyclohexen-1-yl)cyclohexanone **1** condenses with 1,2-, 1,3-diols, and ethanedithiol to form the corresponding spirocyclic derivatives in high yields. It is shown that 1,4-dioxaspiro[4.5]decane undergoes dichlorocarbenation under Mąkosza reaction conditions to form polycyclic *gem*-dichlorocyclopropane as a mixture of two diastereomers. 7-(Cyclohex-1-en-1-yl)-3,3-dimethyl-1,5-dioxaspiro[5.5]undecane is confirmed to inhibit steel corrosion in acidic media.

Keywords

Wallach ketone, cyclic acetals, diols, cyclocondensation, acid catalysis, dichlorocarbenation, anti-corrosion activity

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НАУЧНАЯ СТАТЬЯ

Синтез и свойства циклических ацеталей кетона Валлаха

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Аннотация

Цели. Конденсацией 2-(циклогексен-1-ил)циклогексанона (кетона Валлаха) с 1,2-, 1,3-диолами и 1,2-этандитиолом получить соответствующие циклогексенильные производные 1,4-диоксаспиро[4.5]декана, 1,5-диоксаспиро[5.5]ундекана и 1,4-дитиаспиро[4.5]декана; определить длительность реакции и температуру проведения процесса, при которых достигается максимально возможный выход целевых циклических производных 2-(циклогексен-1-ил)циклогексанона и оценить антикоррозионные свойства полученных ацеталей в кислой среде; на примере 1,4-диоксаспиро[4.5]декана осуществить дихлоркарбенирование и установить строение полученных изомеров.

Методы. Целевые соединения, такие как циклические ацетали, были получены классическим способом органического синтеза — конденсацией 2-(циклогексен-1-ил)циклогексанона (кетона Валлаха) с 1,2-, 1,3-диолами и 1,2-этандитиолом. Для определения качественного и количественного состава реакционных масс были использованы следующие методы анализа: газожидкостная хроматография (хроматограф Кристаллюкс-4000М с пламенно-ионизационным детектором, капиллярной колонкой 25 м × 0.33 мм, содержащей 100%-й полидиметилсилоксан в качестве неподвижной фазы 0.5 μm), спектроскопия ядерного магнитного резонанса (прибор «BrukerAM-500» с рабочими частотами 500 и 125 МГц) и элементный микроанализ (метод экспресс-гравиметрии; хлор и серу определяли методом Шёнигера).

Результаты. В условиях термического нагрева кетона Валлаха с 1,2-, 1,3-диолами и 1,2-этандитиолом получены 1,4-диоксаспиро[4.5]декан, 1,5-диоксаспиро[5.5]ундекан и 1,4-дитиаспиро[4.5]декан с выходом 95%. Установлено, что 5,5-диметилдиоксановое производное обладает умеренным ингибирующим эффектом по отношению к кислотной коррозии углеродистой стали Ст20 при температуре 60°С. Определено, что дихлоркарбенирование 1,4-диоксаспиро[4.5]декана протекает с образованием смеси двух диастереомеров (соотношение 1 : 2), о чем свидетельствуют удвоенные сигналы атомов углерода в углеродном спектре.

Выводы. 2-(Циклогексен-1-ил)циклогексанон **1** конденсируется с 1,2-, 1,3-диолами и этандитиолом с образованием соответствующих спироциклических производных с высокими выходами. Показано, что 1,4-диоксаспиро[4.5]декан вступает в реакцию дихлоркарбенирования в условиях реакции Макоши с образованием полициклического *гем*-дихлорциклопропана в виде смеси двух диастереомеров. Найдено, что 7-(циклогекс-1-ен-1-ил)-3,3-диметил-1,5-диоксаспиро[5.5]ундекан способен тормозить коррозию стали в кислых средах.

Ключевые слова

кетон Валлаха, циклические ацетали, диолы, циклоконденсация, кислотный катализ, дихлоркарбенирование, антикоррозионная активность

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INTRODUCTION

Linear and cyclic ketals are widely used in organic and medicinal chemistry [1, 2]. Glycerol ketals are effective repellent additives [3], while diacetals of diglycerol and dipentaerythritol have been proposed as components for polymer materials [4, 5]. In recent years, cyclic ketone ketals have attracted increased attention from researchers due to their ability to inhibit acid corrosion, reduce corrected wear spot diameter, and act as additives to fuels and oils [6, 7]. Cyclohexanone is used as an industrial ketone in large-scale synthesis of caprolactam, polyamides, and adipic acid [8]. During these reactions, dimers and oligomers of cyclohexanone are formed as byproducts in an amount of 5–15% [9, 10], among which the main compound is 2-(cyclohexen-1-yl) cyclohexanone referred to as Wallach ketone (**1**) [11]. The literature describes the synthesis of antimalarial [12] and antirheumatic [9] compounds, as well as high-density jet fuel components based on ketone **1** [10]. The combination of the bicyclic fragment of ketone **1** and the cycloacetal group allows for the creation of compounds with cytotoxicity against tumor cell lines [13], herbicides [14], and fuel additives [15, 16]. In this regard, the aim of this study was to develop a method for obtaining polycyclic spiroacetals and spirothioacetals based on 2-(cyclohexen-1-yl)cyclohexanone **1.**

MATERIALS AND METHODS

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ (25°C) using an Avance-III HD spectrometer (*Bruker*, USA) at operating frequencies of 500 and 125 MHz for ^{1}H and ^{13}C nuclei, respectively. The residual solvent signals served as the internal standard: δ_H 7.66, δ_C 77.0 ppm for the ^{1}H and ^{13}C spectra, respectively. Gas chromatographic analysis of reaction mixtures and isolated compounds was performed on a Crystallux-4000M chromatograph (*Meta-Chrom*, Russia) equipped with a flame ionization detector and a capillary column (25 m × 0.33 mm) containing 100% polydimethylsiloxane as the stationary phase (0.5 μm). Elemental microanalysis was performed using the express gravimetric method; chlorine and sulfur were determined using the Schöniger method.

Ketone **1** was obtained according to a known method [17]. Commercially available diols (*Sigma-Aldrich*, USA), solvents, and other reagents were used without further purification.

The physical constants, elemental analysis data, and spectral characteristics of the obtained compounds are presented in Tables 1 and 2, while the yields are given in Table 3.

General method for obtaining 1,4-dioxaspiro[4.5]decanes 3a,c and dithiaspiro[4.5]decane 3b

A mixture of 35.7 g (0.20 mol) of ketone **1**, 0.3 mol of the corresponding diol or ethanedithiol, 0.3 g (1.6 mmol, 0.8 mol %) of TsOH H_2O, and 100 mL of benzene was heated with a Dean–Stark apparatus for the time indicated in Table 3, monitoring the composition of the reaction mixture by gas–liquid chromatography (GLC). The reaction mixture was then cooled and stirred vigorously for 5 min with 50 mL of a saturated $NaHCO_3$ solution. The aqueous part was extracted three times with ether, the combined organic phase was dried over Na_2SO_4, the solvents were evaporated on a rotary evaporator, and the residue was distilled under vacuum.

General method for obtaining 1,4-dithiaspiro[4.5]decanes 3d,e

A mixture of 35.7 g (0.20 mol) of ketone **1**, 0.1 mol of the corresponding diol, 0.3 g of TsOH H_2O, and 100 mL of benzene was heated with a Dean–Stark apparatus for 1 h, then an additional 0.15 mol of the diol was added with continued heating for the total period indicated in Table 3. The composition of the reaction mixture was monitored by GLC. After cooling, the reaction mixture was treated as described above.

Method for obtaining 6-(7,7-dichlorobicyclo[4.1.0]heptan-1-yl)-1,4-dioxaspiro[4.5]decane (mixture of diastereomers 4a,b) [16]

To a solution of 11.1 g (50.0 mmol) of ethylene ketal **3a**, 331 mg (1.47 mmol) of Et_3BnNCl, and 0.5 mL of 96% EtOH in 150 mL (1.85 mol) of $CHCl_3$, cooled in an ice bath and stirred vigorously (overhead stirrer, 1000 rpm), a cooled solution of 50 g (1.25 mol) of NaOH in 50 mL of water was added dropwise. After adding the NaOH solution, the reaction mixture was stirred for another hour, after which point GLC showed complete conversion of the starting compound **3a**. After adding 500 mL of water to the reaction mixture, the organic layer was separated, washed with 5% AcONa, water, and dried over Na_2SO_4. Following evaporation of the solvent, the residue was distilled under vacuum. We thus obtained 28.1 g (92%) of a colorless liquid that gradually darkens during storage.

Table 1. Physical constants, elemental analysis data and ^{1}H NMR spectra of compounds **3a**–**d** and **4a**,**b**

No.	T_{boil}, °C (mm Hg)	Found, %		Gross formula	Calculated, %		^{1}H NMR spectrum (500.00 MHz; δ, ppm; *J*, Hz)
		C	H		C	H	
3a	138–140 (2.0)	75.63	10.18	$C_{14}H_{22}O_2$	75.63	9.97	5.47 (s, 1H), 3.87–3.69 (m, 4H), 2.06–1.88 (m, 5H), 1.67–1.59 (m, 4H), 1.56–1.34 (m, 7H), 1.22–1.12 (m, 1H)
3b[1]	151–152 (0.5)	66.01	9.09	$C_{14}H_{22}S_2$	66.09	8.72	5.72 (s, 1H), 3.24–3.13 (m, 4H), 2.24–2.16 (m, 4H), 2.06–1.93 (m, 3H), 1.77–1.33 (m, 4H), 1.62–1.48 (m, 5H), 1.31–1.20 (m, 1H)
3c	110–122 (0.4)	76.53	10.56	$C_{15}H_{24}O_2$	76.23	10.24	5.44 (s, 1H), 4.04–3.98 (m, 1H), 3.88–3.71 (m, 3H), 2.76–2.70 (m, 1H), 2.25–2.16 (m, 1H), 2.06–1.87 (m, 6H), 1.79–1.50 (m, 6H), 1.43–1.20 (m, 4H), 1.06–0.98 (m, 1H)
3d	153–155 (0.6)	77.30	10.62	$C_{17}H_{28}O_2$	77.22	10.67	5.40 (s, 1H), 3.71–3.66 (m, 2H), 3.57–3.50 (m, 2H), 2.80–2.76 (m, 2H), 2.00–1.91 (m, 4H), 1.68–1.44 (m, 11H), 1.04 (s, 3H), 0.67 (s, 3H)
4[2]	160–161 (0.5)	59.29	7.49	$C_{15}H_{22}Cl_2O_2$	59.02	7.27	4.04–3.91 (m), 2.58–2.49 (m), 1.86–1.01 (m)

[1]Found 25.34% S; calculated 25.20% S.

[2]Found 23.07% Cl; calculated 23.23% Cl.

Table 2. ^{13}C NMR spectra of compounds **3a**–**d** and **4a**,**b**

No.	^{13}C NMR spectrum (125 MHz; δ, ppm)							
	C^1	C^2	C^3	C^4	C^5	C^6	CH_2	R*
3a	64.88, 64.82		110.94	52.89	137.54	124.15	36.94, 29.41, 29.00, 25.71, 25.65, 24.11, 23.62, 22.61	–
3b	45.79, 39.47		73.34	56.44	139.13	125.27	38.12, 32.03, 29.82, 26.49, 25.83, 25.65, 23.59, 22.57	–
3c	58.93, 58.72		99.40	55.36	138.68	123.58	28.61, 28.49, 28.11, 25.99, 25.64, 25.60, 23.50, 22.73, 22.58	–
3d[1]	69.36, 69.09		99.09	54.10	137.93	123.51	29.29, 28.31, 27.75, 26.10, 25.59, 23.54, 22.76, 22.66	23.07, 22.18
4a,**b**[2]	64.77, 63.63, 63.54, 63.49		111.85, 110.90	51.40, 50.33	31.65, 29.89	32.74, 31.65	36.79, 35.23, 28.48, 27.14, 25.98, 25.44, 24.11, 23.82, 21.67, 21.10, 20.30, 20.25, 19.71, 19.65, 19.17, 19.07	–

Note: *R = H (**3a**–**3c**, **3e**, **4a**,**b**); Me (**3d**).

[1]δ ($\underline{C}Me_2$): 30.15 ppm.

[2]δ ($\underline{C}Cl_2$): 74.40, 73.90 ppm.

Table 3. Synthesis of cyclic acetals **3a**,**c**,**d** and thioacetal **3b**

Diol (dithiol)				Reaction time, h	Acetal (thioacetal)	
No.	R	X	*n*		No.	Yield, %
2a	H	O	0	2	**3a**	85
2b	H	S	0	2	**3b**	83
2c	H	O	1	6	**3c**	69
2d	Me	O	1	4	**3d**	74
2e	H	O	2	48	**3e**	0

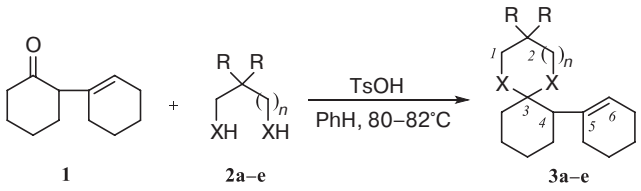
Method for determining the anticorrosion activity of substances in an acidic environment

The inhibitory activity tests of the synthesized compounds were conducted on St20 steel samples (composition, wt %: Ni + Cu < 0.3%, As < 0.08%, Mn 0.35%, Cr < 0.25%, Si 0.17–0.37%, S 0.040%, P < 0.035%) measuring 60 × 20 × 1 mm. Prior to testing, the samples were sequentially treated with PS-11 and PS-12 sandpaper and their surface area was measured using calipers. Next, they were washed with water, ethanol and acetone, then dried in a desiccator. The corrosive environment was a 1 M hydrochloric acid solution. Corrosion rate was measured gravimetrically by the decrease in the mass of the metal sample. The effectiveness of the protective action of inhibitor **3d** was determined as the ratio of the corrosion rates of steel samples in inhibited and uninhibited 1 M HCl solution at a concentration of the compound under study of 4 g/L^{-1}. The inhibitor was evaluated based on the braking coefficient $\gamma = k_0/k_{inh}$, where k_0 and k_{inh} are the corrosion rates in the background solution and in the solution with the studied **3d** inhibitor additive, as well as based on the protection efficiency $Z = (1 - 1/\gamma)\cdot 100$ (%).

RESULTS AND DISCUSSION

The condensation of ketone **1** with ethylene glycol **2a** was carried out under standard conditions (acid catalyst, water removal by Dean–Stark method). The target 1,4-dioxaspiro[4.5]decane **3a** was formed with an 85% yield [18] (Scheme 1, Table 3). The reaction of 1,2-ethanedithiol **2b** with ketone **1** was carried out under the same conditions to yield 1,4-dithiaspiro[4.5]-decane **3b** at 83%.

When transitioning from 1,2-diols **2a**,**b** to 1,3-diols **2c**,**d**, it was necessary to increase the reaction time by 2–3 times to achieve acceptable yields (64–70%) of acetals **3c**,**d**. When 1,4-butanediol was used, the formation of the corresponding seven-membered ring **3e** was not observed.

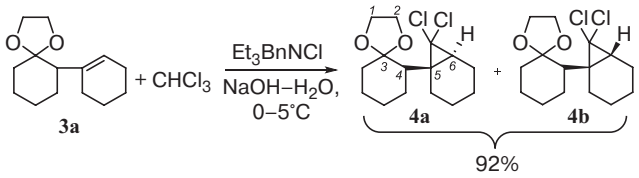


Scheme 1. Interaction of Wallach ketone **1** with reagents **2a**–**e** (the details of substituents, heteroatoms and ring size are given in Table 3)

To confirm the structure of the obtained heterocycles, ^{13}C NMR spectra obtained using the dept-135 technique are the most informative. The spectra of acetals **3a**,**c**,**b** show characteristic signals at δ_C 58–82 ppm that correspond to the α-carbon atoms of the 1,3-dioxocycloalkane fragments ($C^{1,2}$), signals for the nodal atom (C^3) at δ_C 99–113 ppm and the CH group (C^4) at δ_C 51–56 ppm, as well as the carbon atoms of the double bond at δ_C 137–139 (C^5) and δ_C 122–125 (C^5) ppm. In the ^{13}C NMR spectrum of thioacetal **3b**, the signals for the C^1, C^2, and C^3 carbon atoms of the heterocycle are shifted to a higher field as compared to acetals **3a**,**c**,**b** (Table 2). In the ^{1}H NMR spectra of compounds **3a**–**d**, the characteristic proton signal at the double bond (H^6) in the region of δ_H 5.4–5.7 ppm is reliably interpreted. The signals from the remaining protons are in a strong field and represent poorly resolved groups of multiplets (see Materials and Methods section, Table 1).

It was previously shown that the carbon-carbon double bond in ketone **1** [19, 20] and acetal **3a** [21] is sufficiently reactive to form three-membered rings. In this regard, we performed dichlorocarbenation

of acetal **3a** under Makosha reaction conditions to form *gem*-dichlorocyclopropane **4**. As evidenced by the doubled signals of carbon atoms $C^{1,2}$ (δ_C 64.77, 63.63, 63.54, 63.49 ppm), C^3 (δ_C 111.85, 110.90 ppm), C^4 (δ_C 51.40, 50.33 ppm), C^5 (δ_C 51.40, 50.33 ppm), C^6 (δ_C 32.74, 31.65 ppm) in the ^{13}C NMR spectra, dichlorocarbenation occurs with the formation of a mixture of two diastereomers **4a**,**b** (Scheme 2, Table 2). According to the ^1H NMR spectra (based on the intensity of characteristic signals) and the results of gas chromatography, the diastereomer ratio is 1 : 2.



Scheme 2. Carbenation of acetal **3a** under Makosza reaction conditions

Ketone **1** is known to inhibit acid corrosion [22]. We found that ketal **3d** has a slightly lower inhibiting effect (67%) than ketone **1** (85%) under acidic corrosion conditions (1 M HCl) of St20 carbon steel at 60°C. The remaining acetals showed even less protective ability. Thus, the introduction of a cycloacetal fragment into the structure of the Wallach ketone reduces its ability to inhibit the acid corrosion of steel, which is likely due to the decreased polarity of acetals **3** compared to ketone **1**.

CONCLUSIONS

It is established that 2-(cyclohexen-1-yl)cyclohexanone (Wallach ketone) condenses with 1,2-, 1,3-diols, and ethanedithiol to form the corresponding spirocyclic derivatives in high yields. It is shown that the double bond of the cyclohexene fragment of the heterocycle readily adds dichlorocarbene under Mąkosza reaction conditions to form a polycyclic *gem*-dichlorocyclopropane as a mixture of two diastereomers. 7-(Cyclohex-1-en-1-yl)-3,3-dimethyl-1,5-dioxaspiro[5.5]undecane is confirmed to inhibit steel corrosion in acidic environments.

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Authors’ contributions

B.V. Vazhenin—conducting research, literature review.

A.A. Golovanov—collecting and processing the material, statistical processing.

Yu.G. Borisova—collecting and processing the material, writing the text of the article.

G.Z. Raskil’dina—advising on planning, methodology, and implementation of the research.

S.S. Zlotskii—conceptualization of the research paper, critical revision with the introduction of valuable intellectual content.

The authors declare no conflicts of interest.

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