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REACTION OF CHLOROANHYDRIDES OF CYCLOALKANECARBOXILIC ACIDS WITH SOME ALLYLIC CHLORIDES

V.A. Guseinova, G.A. Zaidova, E.I. Mammadov

Azerbaijan Technical University,
H. Javid Ave. 25, AZ 1073, Baku, Azerbaijan, e-mail: huseynova.vaqifa@mail.ru

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Abstract: *The reactions of electrophilic addition of cycloalkane carboxylic acid chlorides with allyl chlorides were studied. It was found, that depending on the chloride structures, 2- and 2,4-substituted furans, 1-R-3,4-dichloro-2-butene-1-ones and 1-R-3,4,4-trichloro-1-butanones were obtained.*
Keywords: *chloroanhydrides of cycloalkane carboxylic acids; 3-chloroprene; 2-methyl-3-chloropropen; 2,3-dichloropropene; 3,3-dichloropropene; 2- and 2,4-substituents furans; 1-R-3,4-dichloro-2-butene-1-ones; 1 -R-3,4,4-trichlor-1-butanones.*
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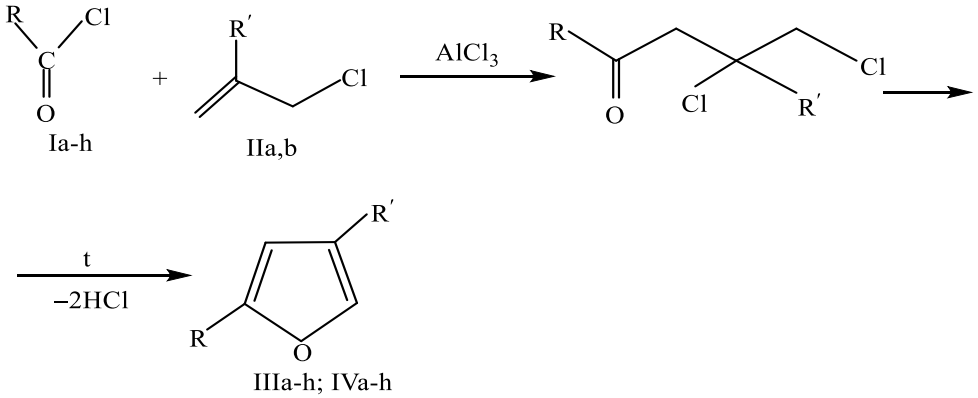
Introductıon

Five-membered heterocyclic compounds with one or two heteroatoms are often found among natural compounds, and therefore, the development of new simple methods for the synthesis of such structures is one of the important problems of modern organic chemistry [1-3]. 1,4-difunctional compounds, most especially, 1,4-haloketones, were successfully used to construct a five-membered heterocycle with one or two heteroatoms [4-10].

As is known, the electrophilic addition of chloroanhydrides of carboxylic acids to 3-chloro- and 2-methyl-3-chloropropenes in the presence of $AlCl_3$ occurs regiospecifically, various products were obtained in keeping with Markovnikov's rule depending on the structure of carboxylic acids. So, when taking chloroacetic-, chloropropionic- and chlorobutyric anhydrides, the mixtures of saturated and unsaturated chloroketones were mainly obtained, but when taking chlorocarboxylic anhydrides which have bulky radicals ($\geq C_4$), the main reaction products were 2- and 2,4-substituted furan derivatives [7,11].



R= *c*-C_5H_9 (a); *c*-C_6H_{11} (b); 1-Cl-*c*-C_5H_8 (c); 1-Cl-*c*-C_6H_{10} (d); 4-Cl-*c*-C_6H_{10} (e); 2-Me-*c*-C_6H_{10} (f); 2-Me-4-Cl-*c*-C_6H_9 (g); 1,4-Cl_2-*c*-C_6H_9 (h).

R′=H (IIa,IIIa-h); CH_3 (IIb, IVa-h).

The structures of furans III and IV have been confirmed by IR and PMR spectroscopic data.

In the Proton MR spectra of compounds III, the signals of the protons of the furan ring appear in the form of three characteristic multiplets in the 5.72-7.17 ppm region; and in the spectra of furans IV, two protons of the furan ring correspond to two singlet signals in the 5.70-5, 82 and 6.93-7.05 ppm regions (table 1).

Table 1. PMR spectra of furans III, IV

Compound	δ, m.d.			
	R (H; KCCB, J, Hz)	R^1	H^3, 1H	H^5, 1H
IIIb	1,08-2,1m (10H, cycle); 2,58m (1H, cycle)	5.98 m (1H)	5,72 m	7,08 m
IIId	1,1-2,0m (10H, cycle)	6.08 m (1H)	5,80 m	7,10 m
IIIf	0,87d (3H, $>CH-CH_3$, J=6); 1,0-2,2m (10H, cycle).	6.12 m (1H)	5,85 m	7,15 m
IIIg	0,9д (3H, $>CH-CH_3$, J=6,2); 1,2-2,2m (9H, cycle); 4,12m (1H, >CHCl).	6.15 m (1H)	5,87 m	7,17 m
IVb	1,1-2,3m (10H, cycle); 2,61m (1H, cycle).	1.94 c (3H, CH_3)	5,74 c	7,04 c
IVe	1,2-2,3m (10H, cycle); 4,08m (1H, >CHCl).	1.98 c (3H, CH_3)	5,70 c	6,93 c
IVf	0,89d (3H, $>CH-CH_3$, J=6); 1,0-2,2m (10H, cycle).	2.0 c (3H, CH_3)	5,78 br.s	7,02 c
IVg	0,85d (3H, $>CH-CH_3$, J=6); 1,2-2,3m (9H, cycle); 4,05m (1H, >CHCl).	1.98 c (3H, CH_3)	5,82 c	7,05 c

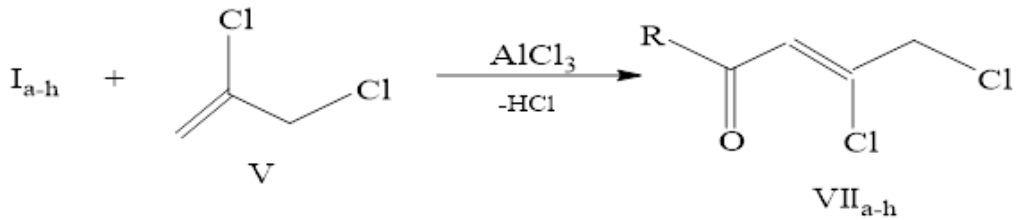
The IR spectra of compounds III, IV have the following absorption bands specific to the furan ring: (cm^{-1}) 3110-3130-ν_{CH}; 1590-1596 and 1508-1510−$\nu_{C=C}$, $\nu_{C=C}$; 870-890-δ_{CH}.

Dichloroethane and methylene chloride were the most suitable solvents.

The highest yields of furans III,IV were achieved in the following ratio of the initial components I:II:$AlCl_3$=1:1.1:1.05.

The reaction temperature significantly depends on the structure of allyl chlorides[9].

We used 2,3-dichloropropene (V) and 3,3-dichloropropene (VI) to determine the possibility of heterocyclization of 1,4-chloroketones in five-membered heterocyclic compounds as allylic chlorides.



R-above-mentioned radicals

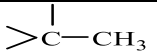
As compared with chloride IIb, there was a chlorine atom with –J-inductive effect instead of the methyl group in 2,3-dichloropropene. In contrast to chlorides IIa and IIb, the addition of ChA CACA to 2,3-dichloropropene (V) in the presence of $AlCl_3$ occurs at a higher temperature (+20÷+25°C), a violent evolution of hydrogen chloride was observed directly during the reaction and 1- R-3,4-dichloro-2-buten-1-ones (VIIa-h) is obtained with 72-83% yield (table 2).

Table 2. Properties of 1-R-3,4-dichloro-2-buten-1-ones (VIIa-h).

Compound	R	$T_{boiling}$, °C (mmHg)	n_D^{20}	d_4^{20}	Yield, %
VIIa	*c*-C_5H_9	108-110(1)	1.5045	1.1986	76
VIIb	*c*-C_6H_{11}	125-127(1)	1.5065	1.1724	78
VIIc	1-Cl-*c*-C_5H_8	149-153(4)	1.5205	1.3030	73
VIId	1-Cl-*c*-C_6H_{10}	170-174(5)	1.5245	1.2877	72
VIIe	4-Cl-*c*-C_6H_{10}	161-163(2)	1.5234	12864	83
VIIf	2-Me-*c*-C_6H_{10}	135-138(2)	1.5045	1.1671	83
VIIg	2-Me-4-Cl-*c*-C_6H_9	170-173(3)	1.5220	1.2805	80
VIIh	1,4-Cl_2-*c*-C_6H_9	175-182(3)	1.5410	1.3886	73

The structure of ketones VII was confirmed by IR and PMR spectroscopy (table 3).

Table 3. IR and PMR spectra of compounds VIIb,d-f

Compound	R	PMR spectrum, δ, m. d. (KCCB, J, Hz)			IR spectrum ($см^{-1}$)
		R	-CH_2-Cl, 2H br.s	-CH= 1H, br.s	
VIIb	*c*-C_6H_{11}	0.9-2.2m (10H, cycle); 2.62m (1H, cycle)	4.72	6.53	3118,3075(ν_{CH});1730,1705,1684 ($\nu_{C=O}$); 1618($\nu_{C=C}$).
VIId	1-Cl-*c*-C_6H_{10}	1.0-2.1m (10H, cycle)	4.74	6.60	3110,3070(ν_{CH});1725,1700,1680 ($\nu_{C=O}$); 1616($\nu_{C=C}$).
VIIe	4-Cl-*c*-C_6H_{10}	1.2-2.1m(8H, cycle); 2.66m (1H, >CHCl cycle); 4.04m (1H, >CHCl cycle).	4.75	6.70	3110,3080(ν_{CH});1734,1702,1691 ($\nu_{C=O}$); 1610($\nu_{C=C}$).
VIIf	2-Me-*c*-C_6H_{10}	0.88d (3H,( , J=6); 1.1-2.4m (10H, cycle)	4.64	6.60	3105,3040(ν_{CH});1710,1694,1680 ($\nu_{C=O}$); 1608($\nu_{C=C}$).

As a continuation of the study, 3,3-dichloropropene (VI) was taken. Chloroanhydrides of Ib,e were added to chloride VI according to Markovnikov's rule at a temperature of -10÷-15oC in the presence of AlCl3 and the resulting compounds 1-R-3,4,4-trichloro-1-butanones (VIIIb,e) turned out to be stable substances: they did not eliminate HCl and do not cyclize to furan derivatives during distillation.

Experimental part

IR and PMR spectra were recorded on a "UR-20" spectrometer in the form of a thin layer and on a Briker AM-360 instrument (360 MHz), respectively, HMDS or TMS was chosen as an internal standard.

1.Obtaining the initial allylic chlorides. 3-Chloropropene (IIa) and 2-methyl-3-chloropropene (IIb) among initial allylic chlorides were in the form of commercial preparations.

2,3-Dichloropropene (V) has been obtained by dehydrochlorination of 1,2,3-trichloropropane with KOH in absolute alcohol [11]. Physicochemical constants of dichloride V: $t_{boiling}$-93-95°C; n_D^{20}-1.4600; d_4^{20} -1.2084, yield 87%.

3,3-dichloropropene(VI) was obtained from acrolein and PCl_5 according to the known method illustrated in [12]: $t_{boiling}$ -83-84°C, n_D^{20}-1.4462; d_4^{20} -1.1689.

2. Synthesis of chloroanhydrides of cycloalkanecarboxylic acids

2.1. Obtaining chloroanhydrides Ia,b,e-g. ***2.2. Obtaining chloroanhydrides Ic,d,h.*** The appropriaste 1-chloro-substituted chloroanhydrides of cycloalkanecarboxylic acids (Ic,d,h) were obtained by chlorination of chloroanhydrides Ia,b,e.

The general technique for obtaining chloroanhydrides Ic,d,h. A weighed portion of the chloroanhydride (Ia,b,e) was placed in a specially prepared chlorinator and heated up to a temperature of 60-70°C. A weak flow of chlorine obtained by the interaction of concentrated hydrochloric acid with $KMnO_4$ was passed through the chlorinator. The flow of chlorine was stopped when the weight of the chlorinator with the content is 5-10% less than theoretical. After repeated distillation, α-chloro-substituted chloroanhydrides Ic, d, h have been obtained (table 4).

Table 4. Some characteristics of chloroanhydrides Ia-h.

Compound	$T_{boiling}$, °C (mmHg)	n_D^{20}	d_4^{20}	Yield, %
Ia	158-160	1.4650	1.1034	92
Ib	181-183	1.4760	1.0945	94
Ic	75-80 (15)	1.4920	1.2931	76
Id	108-112(15)	1.4960	1.2527	80
Ie	105-108(15)	1.4955	1.2498	90
If	78-80(15)	1.4766	1.0969	86
Ig	138-140(15)	1.5164	1.3595	88
Ih	130-135(20)	1.5150	1.3860	78

3. Acylation of 3-chloro– and 2-methyl-3-chloropropenes (IIa,b).

3.1. Synthesis of furans IIIa-h. First 34.7g (0.26mol) of $AlCl_3$ and then 36.6g (0.25mol) of chloroanhydride of cyclohexanecarboxylic acid (Ib) were added to 100 ml of dry dichloroethane at -20°C. After that, 20.7g (0.27mol) of 3-chloropropene were gently added at a temperature of -15÷-20°C. The reaction mixture was stirred until achieving the room temperature and decomposed with 5% HCl, the organic layer was separated, and the aqueous layer was extracted with ether (2×100 mL). The combined organic layers were washed with water, then with 5% $NaHCO_3$ solution and dried over $CaCl_2$. The solvents were removed, and the residue is distilled in the vacuum, as a result of that 2-cyclohexylfuran was obtained (IIIb, table 5). Furans IIIa,c-h were obtained by the analojical method, the characteristics of which are shown in Table 5.

3.2. Synthesis of furans IVa-h. According to the above method, chloroanhydrides Ia-h were condensed with 2-methyl-3-chloropropene (IIb) at a temperature of -20÷-25°C; and 2-cycloalkyl-4-methylfurans obtained (IVa-h, Table 5).

Table 5. Some characteristics of furans IIIa-h, IVa-h.

Compound	$T_{boiling}$, °C (mmHg)	n_D^{20}	d_4^{20}	Yield, %
IIIa	47-49 (5)	1.4860	0.9922	86
IIIb	55-58 (5)	1.4870	0.9908	91
IIIc	88-90 (10)	1.4970	1.1290	56
IIId	108-110(5)	1.5105	1.1328	64
IIIe	102-105(5)	1.5095	1.1261	68
IIIf	82-85(5)	1.4825	0.9666	66
IIIg	110-112(4)	1.4920	1.0507	56
IIIh	119-121(5)	1.5180	1.2355	55
IVa	63-65 (15)	1.4840	0.9812	84
IVb	72-74 (15)	1.4855	0.9626	92
IVc	102-104 (5)	1.4980	1.1078	62
IVd	125-127(10)	1.5075	1.1098	66
IVe	135-137(25)	1.5060	1.1033	70
IVf	90-92 (5)	1.4815	0.9605	67
IVg	97-99(2)	1.4902	1.0582	61
IVh	131-133(3)	1.5165	1.2069	59

4. Synthesis of 1-R-3,4-dichloro-2-buten-1-ones (VIIa-h). 0.1mol of chloroanhydride of cycloalkanecarboxylic acid (Ia-h) was added dropwise with stirring to a suspension consisting of 14.7g (0.11mol) of aluminum chloride and 70 ml of dichloroethane, cooled down to -15°C. Then the temperature was raised up to +20° C and 13.3g (0.12mol) of 2,3-dichloropropene were added dropwise. In this case, a violent evolution of hydrogen chloride occured. The reaction mixture was stirred for another 0.5 hour at a temperature of +20÷+25°C until stopping the evolution of hydrogen chloride and poured onto ice acidified with HCl. The organic layer was separated, the aqueous layer extracted with ether (2×100 ml); the combined organic extracts were washed with water, then with 5% $NaHCO_3$ solution and dried over $CaCl_2$. The solvents were removed, and the residue was distilled to obtain 1-R-3,4-dichloro-2-buten-1-ones (VIIa-h), the

characteristics and yields of compounds are shown in Table 2.

5. Obtaining of 1-R-3,4,4-trichloro-1-butanones (VIIIb,e). The acylation of 3,3-dichloropropene with chloroanhydride of cyclohexane- and 4-chlorocyclohexanecarboxylic acids was carried out according to the 3.1 method at a temperature of -10÷-15°C in the presence of $AlCl_3$ and the trichlorobutanones VIIIb,e were obtained by distillation.

1-Cyclohexyl-3,4.4-trichloro-1-butanone (VIIIb): $t_{boiling.}$102-105°/3mm, n_D^{20}-1,4865, d_4^{20}-1,2028. IR spectra (см$^{-1}$): 1705 ($\nu_{C=O}$); 759,686 (ν_{C-Cl}). PMR spectra (δ,m,d): 0,83-2,0 (11H,m), 2,42 (2H,m, $COCH_2$), 3,67 (1H,t, CHCl), 6.02 (1H,m, $CHCl_2$). Yield is 52%.

1-(4´-Chlorocyclohexyl)-3,4,4-trichloro-1-butanone(VIIIe): $t_{boiling.}$118-120/3mm, n_D^{20} 1,5030, d_4^{20} 1,3164. IR spectra(см$^{-1}$): 1714($\nu_{c=o}$), 751,680(ν_{C-Cl}). PMR spectra: 1,2-2,2(10H,m), 2,4(2H,m, $COCH_2$), 3,59(1H,t, CHCl), 5,97(1H,m, $CHCl_2$). Yield is 56%.

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TSİKLOALKANKARBON TURŞULARI XLORANHİDRİDLƏRİNİN BƏZİ ALLİL TİPLİ XLORİDLƏRLƏ REAKSİYASI

V.Ə. Hüseynova, Z.Ə. Zaidova, E.İ. Məmmədov

Azərbaycan Texniki Universiteti,
AZ 1073 Baki, H.Cavid pr.107; e-mail: huseynova.vaqifa@mail.ru

Tsikloalkankarbon turşuları xloranhidridlərin allil tipli xloridlərlə elektrofil birləşmə reaksiyaları tədqiq edilmişdir. Müəyyən olunmuşdur ki, xloridlərin quruluşundan asılı olaraq 2- və 2,4-əvəzlifuranlar, 1-R-3,4-dixlor-2-buten-1-onlar və 1-R-3,4,4-trixlor -1-butanonlar alınır.

Açar sözlər: *tsikloalkankarbon turşularının xloranhidridləri; 3–xlorpropen; 2-metil-3-xlorpropen; 2,3-dixlorpropen; 3,3-dixlorpropen; 2- və 2,4-əvəzlifuranlar; 1-R-3,4-dixlor-2-buten-1-onlar; 1-R-3,4,4-trixlor-1-butanonlar.*

РЕАКЦИЯ ХЛОРАНГИДРИДОВ ЦИКЛОАЛКАНКАРБОНОВЫХ КИСЛОТ С НЕКОТОРЫМИ ХЛОРИДАМИ АЛЛИЛЬНОГО ТИПА

В.А. Гусейнова, Г.А. Заидова, Э.И. Мамедов

Азербайджанский Технический Университет,
AZ1073 Баку, пр. Г. Джавида, 107; e-mail:huseynova.vaqifa@mail.ru

Исследованы реакции электрофильного присоединения хлорангидридов циклоалканкарбоновых кислот с хлоридами аллильного типа. Установлено, что в зависимости от структуры хлоридов получаются 2- и 2,4-замещенные фураны, 1-R-3,4-дихлор-2-бутен-1-оны и 1-R-3,4.4-трихлор-1-бутаноны.

Ключевые слова: *хлорангидриды циклоалканкарбоновых кислот; 3-хлорпропен; 2-метил-3-хлорпропен; 2,3-дихлорпропен; 3,3-дихлорпропен; 2- и 2,4-замещенные фураны; 1-R-3,4-дихлор-2-бутен-1-оны; 1-R-3,4,4-трихлор-1-бутаноны.*