

# HETEROCYCLIZATION OF $\beta,\gamma$ -DICHLORO KETONES AS A METHOD FOR THE SYNTHESIS OF FURAN DERIVATIVES

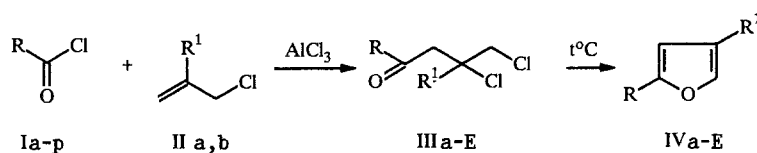
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*Dichloro ketones obtained from acyl chlorides and allyl or  $\beta$ -methylallyl chloride undergo spontaneous cyclization to give 2-alkyl- and 2,4-dialkylfurans when they are heated; the intermediates in the case of 2,3-dichloropropene split out a molecule of hydrogen chloride to give 3,4-dichloro-2-butenones.*

Despite the abundance of methods for the synthesis of furan derivatives [1], most methods for obtaining 2-alkyl- and 2,4-dialkylfurans are multistep processes [2] or include the use of organolithium reagents [3, 4]. This pertains in particular to frequently used alkyl-substituted furans.

It has previously been shown in brief communications [5-7] that the reaction of acyl chlorides with allyl chloride in the presence of aluminum chloride is accompanied by the formation of alkylfurans and can be used for the synthesis of the latter. The present paper correlates the research in this field.

Under the conditions of the Kondakov—Krapivin reaction [8] carboxylic acid chlorides Ia-p react with allyl chloride (IIa) or  $\beta$ -methylallyl chloride (IIb) with the intermediate formation of unstable  $\beta,\gamma$ -dichloro ketones IIIa-E, which form 2-alkyl- and 2-alkyl-4-methylfurans IVa-E in 5-92% yields during fractional distillation in vacuo.



I, III, IV a R=Et, b,q R=Pr; c,r R=i-Pr; d,s R=Bu; e,t R=i-Bu f,u R=C<sub>5</sub>H<sub>11</sub>; g,v R=C<sub>6</sub>H<sub>13</sub>; h,w R=C<sub>7</sub>H<sub>15</sub> i,x R=c C<sub>5</sub>H<sub>9</sub>; j,y R=c C<sub>6</sub>H<sub>11</sub>; k,z R=1-chlorocyclohexyl; l,A R=4-chlorocyclohexyl, m,B R=1-chlorocyclopentyl; n,C R=1,4-dichlorocyclohexyl; o,D R=2-methylcyclohexyl, p,E R=2-methyl-4-chlorocyclohexyl; IIa,IIIb-p, IVb-p R<sup>1</sup>=H; IIb,IIIa, IVa, q-E R<sup>1</sup>=Me

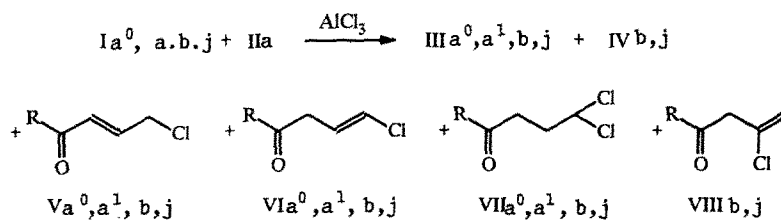
The structure of IVa-E was confirmed by PMR spectral data. The signals of the protons of the furan ring in IVb-p show up in the form of three characteristic multiplets at 5.80-7.40 ppm, while the two singlet signals at 5.60-5.80 and 6.70-6.95 ppm in the case of furans IVa, q-E correspond to two protons of the furan ring. The yields and some characteristics of furans IVa-E are presented in Table 1 and are in good agreement with the literature data [6, 9-18].

Furans cannot be obtained from aromatic acid chlorides by this method. With the exception of furan IVa, which was obtained in 5% yield, attempts to synthesize 2-methyl- and 2-ethylfuran from acetic and propionic acid chlorides were also unsuccessful; the reactions lead to complex mixtures of chloro ketones. Mixtures of six principal types of products — 3,4-dichlorobutanone derivatives IIIa<sup>0</sup>, a<sup>1</sup>, b, j, 4-chloro-2-butenone derivatives Va<sup>0</sup>, a<sup>1</sup>, b, j, 4-chloro-3-butenone derivatives VIa<sup>0</sup>, a<sup>1</sup>, b, j, 4,4-dichlorobutanone derivatives VIIa<sup>0</sup>, a<sup>1</sup>, b, j, 3-chloro-3-butenone derivatives VIIIb, j, and derivatives IVb, j — are formed in the reaction of acid chlorides Ia<sup>0</sup>, a, b, j with IIa in the presence of AlCl<sub>3</sub>.

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TABLE 1. Characteristics of 2-R-4-R<sup>1</sup>-Furans IVa-E

Compound	Empirical formula	bp, °C (mm)	$n_D^{20}$	Yield, %
IVa	C <sub>7</sub> H <sub>10</sub> O	48...50 (50)	1,4400	5
IVb	C <sub>7</sub> H <sub>10</sub> O	45...48 (50)	1,4465	10
IVc	C <sub>7</sub> H <sub>10</sub> O	43...45 (50)	1,4383	15
IVd	C <sub>8</sub> H <sub>12</sub> O	49...52 (40)	1,4495	35
IVe	C <sub>8</sub> H <sub>12</sub> O	45...47 (40)	1,4490	54
IVf	C <sub>9</sub> H <sub>14</sub> O	38...40 (4)	1,4484	68
IVg	C <sub>10</sub> H <sub>16</sub> O	53...54 (5)	1,4503	84
IVh	C <sub>11</sub> H <sub>18</sub> O	67...68 (6)	1,4526	92
IVi	C <sub>9</sub> H <sub>12</sub> O	47...49 (5)	1,4860	86
IVj	C <sub>10</sub> H <sub>14</sub> O	55...58 (5)	1,4870	91
IVk	C <sub>10</sub> H <sub>13</sub> OCl	108...110 (5)	1,5105	64
IVl	C <sub>10</sub> H <sub>13</sub> OCl	112...115 (5)	1,5095	70
IVm	C <sub>9</sub> H <sub>11</sub> OCl	88...90 (10)	1,4970	56
IVn	C <sub>10</sub> H <sub>12</sub> OCl <sub>2</sub>	119...121 (5)	1,5180	55
IVo	C <sub>11</sub> H <sub>16</sub> O	82...85 (5)	1,4895	66
IVp	C <sub>11</sub> H <sub>15</sub> OCl	94...96 (6)	1,4920	61
IVq	C <sub>8</sub> H <sub>12</sub> O	54...56 (50)	1,4458	13
IVr	C <sub>8</sub> H <sub>12</sub> O	49...51 (50)	1,4375	20
IVs	C <sub>9</sub> H <sub>14</sub> O	65...68 (50)	1,4525	48
IVt	C <sub>9</sub> H <sub>14</sub> O	50...52 (50)	1,4490	62
IVu	C <sub>10</sub> H <sub>16</sub> O	46...50 (3)	1,4512	70
IVv	C <sub>11</sub> H <sub>18</sub> O	82...85 (10)	1,4531	86
IVw	C <sub>12</sub> H <sub>20</sub> O	95...96 (3)	1,4554	92
IVx	C <sub>10</sub> H <sub>14</sub> O	63...65 (15)	1,4840	84
IVy	C <sub>11</sub> H <sub>16</sub> O	72...74 (15)	1,4855	92
IVz	C <sub>11</sub> H <sub>15</sub> OCl	125...127 (10)	1,5075	66
IVa	C <sub>11</sub> H <sub>15</sub> OCl	135...137 (25)	1,5060	70
IVB	C <sub>10</sub> H <sub>13</sub> OCl	102...104 (5)	1,4980	62,5
IVC	C <sub>11</sub> H <sub>14</sub> OCl <sub>2</sub>	131...133 (3)	1,5165	59
IVD	C <sub>12</sub> H <sub>18</sub> O	90...92 (5)	1,4815	67
IVE	C <sub>12</sub> H <sub>17</sub> OCl	97...99 (2)	1,4902	61



III-VIII a<sup>0</sup> R=Me; a, a<sup>1</sup> R=Et; b R=Pr; j R=c-C<sub>6</sub>H<sub>11</sub>

Compounds IIIa<sup>0</sup>, a<sup>1</sup> and Va<sup>0</sup>, a<sup>1</sup>-VIIa<sup>0</sup>, a<sup>1</sup> were isolated in the individual state by preparative GLC and were identified from the PMR spectral data. Criteria for the assignment of the signals in the PMR spectra of IIIb, j and Vb, j-VIIIb, j in the reaction mixtures were developed on the basis of the results obtained. Spectral data for chloro ketones IIIa<sup>0</sup>, a<sup>1</sup>, b, j, V-VIIa<sup>0</sup>, a<sup>1</sup>, b, j, and VIIIb, j are presented in Table 2.

The trans configuration of the double bond in compounds of the V type was established on the basis of the spin-spin coupling constants (SSCC), which are 15-16 Hz for the olefinic protons. The olefins of the VI type have a cis configuration of the double bond ( $J = 10-11$  Hz). Compounds V, VI, and VIII are formed in the elimination of one molecule of hydrogen chloride from unstable  $\beta, \gamma$ -dichloro ketones III, while dichlorides VII are formed by the addition of HCl to olefins of the VI type.

We used GLC to analyze the compositions of the reaction mixtures obtained in the reaction of acid chlorides Ia<sup>0</sup>, a, b, j with IIa immediately after decomposition of the reaction mixtures with water and after heating. The results obtained are presented in Table 3. A comparison of the left-hand and right-hand parts of Table 3 shows that  $\beta, \gamma$ -dichloro ketones of the

TABLE 2. PMR Spectra of III, V-VIIa<sup>0</sup>, a<sup>1</sup>, b, j, and VIIIb, j

Compound	$\delta$ , ppm (SSCC, J, Hz), 360 MHz, in CDCl <sub>3</sub>
IIIa <sup>0</sup>	2,2 s (3H, MeCO); 3,05 d (2H, COCH <sub>2</sub> , J = 6); 3,8 d (2H, CH <sub>2</sub> Cl, J = 5,8); 4,5 m (1H, CHCl)
IIIa <sup>1</sup>	1,1 t (3H, Me, J = 7); 2,45 q (2H, CH <sub>2</sub> CO, J = 7); 2,97 d (2H, COCH <sub>2</sub> , J = 6); 3,77 d (2H, CH <sub>2</sub> Cl, J = 5); 4,47 m (1H, CHCl)
IIIb	0,83 t (3H, Me, J = 7); 1,6 m (2H, CH <sub>2</sub> ); 2,53 t (2H, CH <sub>2</sub> CO, J = 7); 2,9d (2H, COCH <sub>2</sub> , J = 8); 3,73 d (2H, CH <sub>2</sub> Cl, J = 7); 4,42 m (1H, CHCl)
III j	0,93...2,2 m (10H, CH <sub>2</sub> ring); 2,55 m (1H, CH, ring); 3,03d (2H, COCH <sub>2</sub> , J = 6,6); 3,77d (2H, CH <sub>2</sub> Cl, J = 7); 4,5 m (1H, CHCl)
Va <sup>0</sup>	2,22s (3H, MeCO); 4,17 d (2H, CH <sub>2</sub> Cl, J = 5,6); 6,05...7,1 m (2H, CH=CH, AB part ABX <sub>2</sub> , $\delta_A = 7,0$ , $\delta_B = 6,23$ , $J_{AB} = 15,6$ , $J_{AX} = 5,6$ , $J_{BX} = 0$ )
Va <sup>1</sup>	1,09 t (3H, Me, J = 7); 2,47 q (2H, CH <sub>2</sub> CO, J = 7); 4,2d (2H, CH <sub>2</sub> Cl, J = 5,5); 6,1...6,9 m (2H, CH=CH, AB part ABX <sub>2</sub> , $\delta_A = 6,33$ , $\delta_B = 6,73$ , $J_{AB} = 15$ , $J_{BX} = 5,5$ , $J_{AX} = 0$ )
Vb	0,87 t (3H, Me, J = 7); 1,6 m (2H, CH <sub>2</sub> ); 2,52 t (2H, CH <sub>2</sub> CO, J = 7); 4,1d (2H, CH <sub>2</sub> Cl, J = 5,5); 6,1...6,8 m (2H, CH=CH, AB part ABX <sub>2</sub> , $\delta_A = 6,2$ , $\delta_B = 6,7$ , $J_{AB} = 16$ , $J_{BX} = 5,5$ , $J_{AX} = 0$ )
V j	1,0...2,2 m (10H, CH <sub>2</sub> ring); 2,5 m (1H, CH ring); 4,15d (2H, CH <sub>2</sub> Cl, J = 6); 6,0...6,9 m (2H, CH=CH, AB part ABX <sub>2</sub> , $\delta_A = 6,3$ , $\delta_B = 6,8$ , $J_{AB} = 16,5$ , $J_{BX} = 5,5$ , $J_{AX} = 0$ )
VIa <sup>0</sup>	2,2 s (3H, MeCO); 3,4 d (2H, COCH <sub>2</sub> , J = 5); 5,8...6,4 m (2H, CH=CH, J = 11)
VIa <sup>1</sup>	1,12 t (3H, Me, J = 7); 2,45 q (2H, CH <sub>2</sub> CO, J = 7); 3,35 d (2H, COCH <sub>2</sub> , J = 5,5); 5,4...6,3 m (2H, CH=CH, AB part ABX <sub>2</sub> , $\delta_A = 5,93$ , $\delta_B = 6,2$ , $J_{AB} = 10$ , $J_{AX} = 5,5$ , $J_{BX} = 0$ )
Vb	0,85 t (3H, Me, J = 7); 1,6 m (2H, CH <sub>2</sub> ); 2,5 t (2H, CH <sub>2</sub> CO, J = 7); 3,23d (2H, COCH <sub>2</sub> , J = 5); 5,5...6,4 m (2H, CH=CH, J = 10)
VI j	0,9...2,1 m (10H, CH <sub>2</sub> ring); 2,5 m (1H, CH ring); 3,36 d (2H, COCH <sub>2</sub> , J = 5); 5,5...6,3 m (2H, CH=CH, J = 10,5)
VIIa <sup>0</sup>	2,15 s (3H, MeCO); 2,47 dF (2H, CH <sub>2</sub> , J = 6 & 5,5); 2,72 t (2H, COCH <sub>2</sub> , J = 6); 6,04 t (1H, CHCl <sub>2</sub> , J = 5,5)
VIIa <sup>1</sup>	1,15 t (3H, Me, J = 7); 2,4 q (2H, CH <sub>2</sub> CO, J = 7); 2,48 m (2H, CH <sub>2</sub> ); 2,68 t (2H, COCH <sub>2</sub> , J = 6); 5,9 t (1H, CHCl <sub>2</sub> , J = 6)
VII b	0,85 t (3H, Me, J = 7); 1,6 m (2H, CH <sub>2</sub> ); 2,5 t (2H, CH <sub>2</sub> CO, J = 7); 2,4 m (2H, CH <sub>2</sub> CCl <sub>2</sub> ); 2,7 m (2H, COCH <sub>2</sub> , J = 7); 6,0 t (1H, CHCl <sub>2</sub> , J = 5)
VII j	0,95...2,1 m (10H, CH <sub>2</sub> ring); 2,4 m (2H, CH <sub>2</sub> CCl <sub>2</sub> ); 2,55 m (1H, CH ring); 5,95 t (1H, CHCl <sub>2</sub> , J = 5,5);
VIII	0,8 t (3H, Me, J = 7); 1,6 m (2H, CH <sub>2</sub> ); 2,8 t (2H, CH <sub>2</sub> CO, J = 7); 3,72 s (2H, COCH <sub>2</sub> ); 5,7...6,2 m (2H, =CH <sub>2</sub> , $\delta_A = 5,9$ , $\delta_B = 5,78$ , J = 3)
VIII	0,93...2,2 m (10H, CH <sub>2</sub> ring); 2,5 m (1H, CH ring); 3,67 s (2H, COCH <sub>2</sub> ); 6,0...6,12 m AB (2H, =CH <sub>2</sub> , J = 1)

III type, the stabilities of which may be the critical factor that affects the yields of furans, are probably the principal source of the furan derivatives. Thus the first step in the reaction of the acyl chlorides with allyl chloride is electrophilic addition in accordance with the Markownikoff rule (compare this with the data in [18]) to give  $\beta$ , $\gamma$ -dichloro ketones, which are then capable of: a) undergoing cyclization to give a furan derivative and b) splitting out of a molecule of HCl to give olefins of the V and VI type, which are not capable of undergoing subsequent cyclization. We studied the possibility of cyclization of Va<sup>0</sup>, a<sup>1</sup> and VIa<sup>0</sup>, a<sup>1</sup> by heating individual samples and established that furan derivatives are not formed in this case.

Compounds of the VIII type, which vanish when the reaction mixtures are heated (see Table 3), may serve as another possible source of the furans.

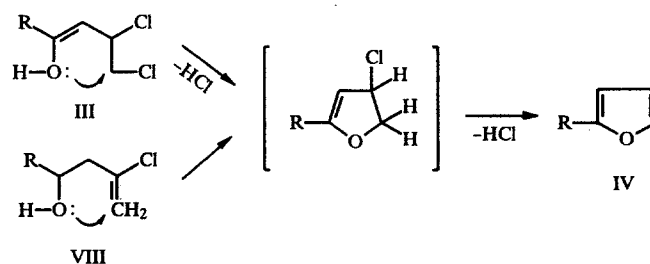


TABLE 3. Compositions of the Reaction Mixtures in the Reaction of Acid Chlorides Ia<sup>0</sup>, a, b, j with Allyl Chloride

Compound	Composition of the reaction mixtures, %								
	before heating					after heating			
	III	V	VI	VII	VIII*	III	V	VI	VII
a <sup>0</sup>	53	22	14	11	—	24	46	5	24
a <sup>1</sup>	62	3	15	20	—	3	33	40	23
b <sup>**</sup>	50	22	3	22	3	10	41	9	25
j <sup>***</sup>	74	6	5	4	11	—	10	6	4

\*Absent after heating.

\*\*The reaction mixture contained 15% furan IVb after heating.

\*\*\*The reaction mixture contained 80% furan IVj after heating.

TABLE 4. Characteristics of Vj-o, z-E and IXi-p

Com- pound	Empirical formula	$n_D^{20}$	bp, °C (mm)	Yield, %
Vj	C <sub>10</sub> H <sub>15</sub> ClO	1,4960	112...115 (3)	56
Vk	C <sub>10</sub> H <sub>14</sub> Cl <sub>2</sub> O	1,5240	139...140 (5)	61
Vl	C <sub>10</sub> H <sub>14</sub> Cl <sub>2</sub> O	1,5215	135...137 (5)	63
Vm	C <sub>9</sub> H <sub>12</sub> Cl <sub>2</sub> O	1,5100	118...121 (10)	65
Vn	C <sub>10</sub> H <sub>13</sub> Cl <sub>3</sub> O	1,5305	150...154 (5)	68
Vo	C <sub>11</sub> H <sub>17</sub> ClO	1,4925	122...125 (3)	62
Vz	C <sub>11</sub> H <sub>16</sub> Cl <sub>2</sub> O	1,5212	152...154 (10)	55
Va	C <sub>11</sub> H <sub>16</sub> Cl <sub>2</sub> O	1,5206	149...151 (10)	53
Vb	C <sub>10</sub> H <sub>14</sub> Cl <sub>2</sub> O	1,5060	126...130 (8)	68
Vc	C <sub>11</sub> H <sub>15</sub> Cl <sub>3</sub> O	1,5295	156...160 (6)	66
Vd	C <sub>12</sub> H <sub>19</sub> ClO	1,4890	128...130 (3)	70
VE	C <sub>12</sub> H <sub>18</sub> Cl <sub>2</sub> O	1,5168	150...153 (5)	83
IX <sup>i</sup>	C <sub>9</sub> H <sub>12</sub> Cl <sub>2</sub> O	1,5100	108...110 (1)	A-80, B 76
IX <sup>j</sup>	C <sub>10</sub> H <sub>14</sub> Cl <sub>2</sub> O	1,5150	132...133 (2)	A-77, B 84
IX <sup>k</sup>	C <sub>10</sub> H <sub>13</sub> Cl <sub>3</sub> O	1,5300	175...177 (4)	A-72, B 82
IX <sup>l</sup>	C <sub>10</sub> H <sub>13</sub> Cl <sub>3</sub> O	1,5280	161...163 (2)	A-82, B 85
IX <sup>m</sup>	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> O	1,5265	149...154 (3)	A-83, B 78
IX <sup>n</sup>	C <sub>10</sub> H <sub>12</sub> Cl <sub>4</sub> O	1,5465	179...182 (3)	A-73, B 69
IX <sup>o</sup>	C <sub>11</sub> H <sub>16</sub> Cl <sub>2</sub> O	1,5132	135...138 (2)	A-83, B 86
IX <sup>p</sup>	C <sub>11</sub> H <sub>15</sub> Cl <sub>3</sub> O	1,5270	170...173 (3)	A-80, B 80

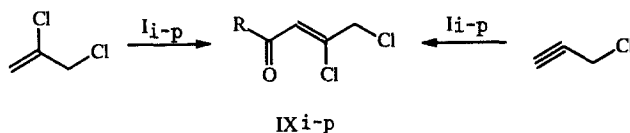
\*A indicates the yield obtained by the reaction of the acyl chloride with 2,3-dichloropropene, while B indicates the yield obtained with propargyl chloride.

Heterocyclization of olefins of the V type does not occur, probably as a consequence of the trans configuration of the double bond, while heterocyclization of compounds of the VI type does not occur because of the reverse (as compared with VIII) orienting effect of the chlorine atom on the pathway of addition to the double bond. The tendency of  $\beta,\gamma$ -dichloro ketones III to eliminate HCl decreases with an increase in the molecular mass and the degree of branching of radical R, which leads to an increase in the yields of the furan derivatives (see Table I). The increase in the yields can also be explained by the increase in the molecular mass, which leads to an increase in the boiling point of the reaction mixture, which facilitates cyclization. Let us note that bulky radicals, particularly branched ones, change the geometry of the molecules with drawing together in space of the electrophilic and nucleophilic centers.

The introduction of an electron-donor methyl substituent into the allyl chloride molecule increases the stabilities of the resulting dichloro ketones IIa, q-E, and, as a consequence, the yields of furan derivatives increase (see Table I). The formation of a small amount of 2-ethyl-4-methylfuran (5%) could be detected even when propionic acid chloride was introduced into the

reaction (compare this with allyl chloride). Thus the reaction of acyl chlorides with  $\beta$ -methylallyl chloride may serve as a convenient preparative method for obtaining 2-alkyl-4-methylfurans IVq-E.

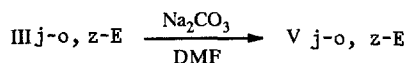
At the same time, the introduction of an electron-acceptor substituent into the allyl chloride structure hinders cyclization, changing the reaction pathway to the elimination of a molecule of hydrogen chloride. Thus substituted 3,4-dichloro-2-butenones IXi-p (the letter designations are the same as for I) are formed in 70-80% yields in the reaction of acyl chlorides Ii-p with 2,3-dichloropropene.



This reaction may serve as a preparative method for the synthesis of dichlorides with this structure.

The structure of IXi-p was confirmed by IR and PMR spectral data: singlets of a chloromethyl group at 4.50-4.75 ppm and of an olefinic proton at 6.3-6.7 ppm are observed. Absorption bands of a C—Cl bond ( $730-740\text{ cm}^{-1}$ ), a carbonyl group ( $1690-1700\text{ cm}^{-1}$ ), and a CH=C bond ( $3050-3080$  and  $1600-1620\text{ cm}^{-1}$ ) are present in the IR spectra of chloro ketones IX. The structure of these compounds is also confirmed by their formation by the addition of acyl chlorides Ii-p to propargyl chloride in the presence of  $\text{AlCl}_3$ .

Let us note that chlorides of the V type are formed in 10-30% yields as a side product in the synthesis of furans IVa-E, whereas they are formed in 56-68% yields (the letter designations are the same as for III) when the reaction mixtures are treated with sodium carbonate in DMF.



The structure of Vj-o, z-E was confirmed by IR and PMR spectral data: signals of protons of a double bond at 6.1-7.2 ppm with SSCC 15-17 Hz, which constitutes evidence for a trans configuration of the double bond, and absorption bands of a carbonyl group ( $1660-1680\text{ cm}^{-1}$ ), a trans-C=C bond ( $1630-1650$  and  $930-990\text{ cm}^{-1}$ ), and a C—Cl bond ( $750-760\text{ cm}^{-1}$ ) are present in the corresponding spectra.

The yields and some characteristics of Vj-o, z-E and IXi-p are presented in Table 4.

Thus the reaction of acyl chlorides with allyl chloride and its derivatives under the conditions of the Kondakov—Krapivin reaction is a convenient one-step method for obtaining higher 2-alkyl- and 2,4-dialkylfurans, as well as substituted 4-chloro-2-butenones.

## EXPERIMENTAL

The IR spectra of thin films of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in  $\text{CCl}_4$  or  $\text{CDCl}_3$  were obtained with Tesla BS-467 (60 MHz) and Bruker AM-360 (360 MHz) spectrometers with tetramethylsilane (TMS) as the internal standard. Analysis by GLC was accomplished with a Khrom-5 chromatograph with a glass column (3000 by 3 mm), a flame-ionization detector, nitrogen as the carrier gas, a gas-flow rate of 60 ml/min, and 5% SE-30 on a Chromaton N-AW-DMCS support at  $130-250^\circ\text{C}$ . Preparative GLC was accomplished with a PAKhV-08 chromatograph with a catharometer as the detector, helium as the carrier gas, a gas-flow rate of 150 ml/min, a steel column (4500 by 5 mm), and 5% SE-30 on a Chromaton N-AW-DMCS support at  $150-250^\circ\text{C}$ . The purity of the reaction products was monitored by TLC on Silufol UV-254 plates.

The results of elementary analysis of Vj-o, z-E and IXi-p for C, H, and Cl were in agreement with the calculated values.

**General Method for Obtaining 2-R-4-R<sup>1</sup>-Furans IVa-E.** Method 1. A 34.7-g (0.26 mole) sample of aluminum chloride and 0.25 mole of acid chloride Ia-p were added successively at  $-20^\circ\text{C}$  to 100 ml of dry dichloroethane. After 10 min, 0.27 mole of allyl chloride (IIa) or  $\beta$ -methylallyl chloride (IIb) was added slowly at the same temperature, and the reaction mixture was stirred for 1 h and then decomposed with 5% HCl. The organic layer was separated, and the aqueous layer was extracted with ether ( $2 \times 100$  ml). The combined organic layers were washed with water and 5%  $\text{NaHCO}_3$  solution and dried

with  $\text{MgSO}_4$ . The solvent was removed by distillation, and the residue was distilled for 0.5 h under low-vacuum conditions (100-150 mm) and then fractionally distilled in vacuo.

**General Method for Obtaining 1-R-4-Chloro-2-butenones Vj-o, z-E.** The reaction mixture prepared by general method 1 from the same amounts of reagents was added dropwise, after evaporation of the solvent, to a suspension of 27.6 g (0.26 mole) of sodium carbonate in 50 ml of DMF at  $80^\circ\text{C}$ , and the mixture was stirred for 20 min and then cooled and treated with 300 ml of water. The aqueous mixture was extracted with ether ( $2 \times 100$  ml), the ether layer was washed successively with water, 0.1 N HCl, and water, and dried with  $\text{Na}_2\text{SO}_4$ . The ether was removed by distillation, and the residue was fractionally distilled in vacuo.

**General Method for Obtaining 1-R-3,4-Dichloro-2-butenones IXi-p. A.** This method is similar to method 1, except that, instead of allyl chloride, 2,3-dichloropropene was added at  $20^\circ\text{C}$  to a mixture of  $\text{AlCl}_3$  and acyl chloride li-p in dichloroethane.

**B.** A 34.7-g (0.26 mole) sample of  $\text{AlCl}_3$  and 0.25 mole of acid chloride li-p were added at  $-20^\circ\text{C}$  to 100 ml of dichloroethane, after which 20.1 g (0.27 mole) of propargyl chloride was added dropwise at  $-15^\circ\text{C}$ , and the reaction mixture was treated as indicated in method 1. The solvent was then removed by distillation, and the residue was fractionally distilled in vacuo.

### LITERATURE CITED

1. N. K. Kochetkov (ed.), *General Organic Chemistry* [in Russian], Vol. 9, Khimiya, Moscow (1985), p. 141.
2. J. A. Elix and M. V. Sargent, *J. Chem. Soc.*, No. 5, 595 (1968).
3. S. M. Kelly and T. Huynh-Bu, *Helv. Chim. Acta*, **66**, 1850 (1983).
4. I. Akimoto and A. Suzuki, *Synthesis*, No. 2, 146 (1979).
5. A. G. Ismailov and É. I. Mamedov, *Zh. Org. Khim.*, **10**, 1129 (1974).
6. I. I. Ibragimov, M. M. Guseinov, R. A. Gadzhily, V. G. Dzhafarov, and S. P. Godzhaev, *Khim. Geterotsikl. Soedin.*, No. 10, 1434 (1973).
7. A. G. Ismailov, *Dokl. Akad. Nauk Azerbaidzhansk. SSR*, **30**, 33 (1974).
8. V. N. Belov and T. A. Rudol'fi, *Reactions and Methods of Investigation of Organic Compounds* [in Russian], Vol. 7, Goskhimizdat, Moscow (1958), p. 255.
9. J. P. Gonesnard and G. J. Martin, *Bull. Soc. Chim. France*, No. 12, 4452 (1969).
10. S. A. Giller and A. É. Berzin', *Khim. Geterotsikl. Soedin.*, No. 4, 487 (1966).
11. N. I. Shuikin, O. A. Korytina, B. L. Lebedev, N. A. Averina, and N. A. Karev, *Khim. Geterotsikl. Soedin.*, No. 3, 291 (1970).
12. Y. Pascal, J. P. Morizur, and J. Wiemann, *Bull. Soc. Chim. France*, No. 8, 2211 (1965).
13. W. E. Neff, E. N. Frankel, E. Selke, and D. Weisleder, *Lipids*, **18**, 1839 (1983).
14. F. J. Jaeggi, M. Tsubuki, T. Y. R. Tsai, and K. Wiesmer, *Heterocycles*, **19**, 1839 (1982).
15. R. A. Comier and M. D. Francis, *Synth. Commun.*, **11**, 365 (1981).
16. T. Morel and P. E. Verkade, *Rec. Trav. Chim.*, **70**, 35 (1981).
17. C. N. Rahn, D. M. Sand, and R. L. Glass, *J. Org. Chem.*, **44**, 3420 (1979).
18. N. N. Mushkalo and L. K. Mushkalo, *Ukr. Khim. Zh.*, **36**, 915 (1970).