67. V. A. Anisimova, N. I. Avdyunina, A. M. Simonov, G. V. Kovalev, and Yu. N. Simkina, Khim.-farm. Zh., No. 12, 40 (1978).
68. I. I. Popov, A. A. Zubenko, and A. M. Simonov, Khim. Geterotsikl. Soedin., No. 11, 1535 (1978).
69. I. I. Popov, A. M. Simonov, and A. A. Zubenko, Zh. Org. Khim., No. 5, 1139 (1975).
70. A. A. Zubenko, I. I. Popov, and A. M. Simonov, Khim. Geterotsikl. Soedin., No. 11, 1539 (1978).
71. P. V. Tkachenko, I. I. Popov, A. M. Simonov, and Yu. V. Medvedev, Khim. Geterotsikl. Soedin., No. 7, 972 (1976).
72. P. V. Tkachenko, A. M. Simonov, and I. I. Popov, Khim. Geterotsikl. Soedin., No. 1, 90 (1978).
73. B. A. Tertov and S. E. Panchenko, Zh. Obshch. Khim., 33, 3671 (1963).
74. B. A.Tertov, V. V. Burykin, and I. D. Sadekov, Khim. Geterotsikl. Soedin., No. 3, 560 (1969).
75. B. A. Tertov and V. V. Burykin, Khim. Geterotsikl. Soedin., No. 11, 1554 (1970).
76. B. A. Tertov and P. P. Onishchenko, Zh. Obshch. Khim., 41, 1594 (1971).
77. B. A. Tertov, A. V. Koblik, and N. I. Avdyunina, Khim. Geterotsikl. Soedin., No. 9, 1238 (1971).
78. B. A. Tertov, A. V. Koblik, and Y. V. Kolodyazhnyi (Kolodyazhny), Tetrahedron Lett., No. 12, 4445 (1968).
79. B. A. Tertov and A. S. Morkovnik, Khim. Geterotsikl. Soedin., No. 3, 392 (1975).
80. B. A. Tertov, P. P. Onishchenko, and V. V. Bessonov, Khim. Geterotsikl. Soedin., No. 10, 1410 (1974).
81. B. A. Tertov and Yu. G. Bogachev, Khim. Geterotsikl. Soedin., No. 1, 119 (1981).
82. B. A. Tertov, P. P. Onishchenko, Yu. V. Koshchienko, G. M. Suvorova, and E. N. Malysheva, Khim. Geterotsikl. Soedin., No. 8, 1078 (1982).
83. B. A. Tertov, V. V. Burykin, P. P. Onishchenko, A. S. Morkovnik, and V. V. Bessonov, Khim. Geterotsikl. Soedin., No. 8, 1109 (1973).
84. B. A. Tertov, V. V. Burykin, and A. V. Koblik, Khim. Geterotsikl. Soedin., No. 11, 1552 (1972).
85. B. K. Martsokha and A. M. Simonov, Khim. Geterotsikl. Soedin., No. 5, 779, 784 (1965).
86. A. M. Simonov and Yu. P. Andreichikov, Zh. Org. Khim., No. 4, 781 (1969).

CHEMISTRY OF sym-TETRACYANOETHANE.

2.* CONDENSATION WITH CARBONYL COMPOUNDS

O. E. Nasakin, V. V. Alekseev, P. B. Terent'ev, A. Kh. Bulai, and V. A. Shmorgunov

UDC 543.722.3.6.07:543.422.51

The reaction of tetracyanoethane with carbonyl compounds proceeds via the scheme of aldol addition with subsequent cyclization of the resulting adducts to give 5-amino-2,3-dihydrofuran derivatives, the structures of which were confirmed by the ^{13}C NMR and mass spectra.

We have recently developed convenient methods for the preparation of sym-tetracyanoethane (TCE) (I) [2, 3] and have subsequently reported [4, 5] that it reacts readily with some carbonyl compounds to give derivatives of the 2,3-dihydrofuran series. In order to ascertain the limits of applicability of this reaction, and to definitively establish the structures of the resulting compounds, we investigated the reaction of TCE with a series of aliphatic, aromatic, and heterocyclic carbonyl compounds IIa-o and thoroughly analyzed their PMR, ^{13}C NMR, and mass-spectrometric behavior.

*See [1] for Communication 1.

I. N. Ul'yanov Chuvash State University, Cheboksary 428015. M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1605-1610, December, 1982. Original article submitted April 2, 1982.

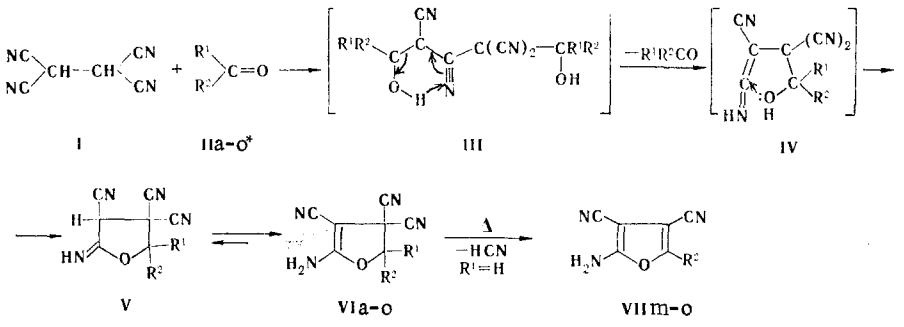
0009-3122/82/1812-1235$07.50

TABLE 1. Properties of VI and VII

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
VIa	167—169	52,6	2,7	34,7	$C_7H_4N_4O$	52,5	2,5	35,0	55
VIc	156—157	54,0	—	31,3	$C_8H_2D_4N_4O$	54,0	—	31,5	65
VIf	126—128	57,4	4,3	29,7	$C_9H_8N_4O$	57,4	4,3	29,8	72
VIg	124—125	59,4	5,1	27,7	$C_{10}H_{10}N_4O$	59,4	5,0	27,7	78
VIh	182—184	59,5	5,1	27,7	$C_{10}H_{10}N_4O$	59,4	5,0	27,7	72
VIi	127—129	61,1	5,6	26,0	$C_{11}H_{12}N_4O$	61,1	5,6	25,9	68
VIm	197—198	66,2	3,5	23,4	$C_{13}H_8N_4O$	66,1	3,4	23,7	78
VIo	>200 (dec.)	60,6	3,0	29,7	$C_{12}H_7N_5O$	60,8	3,0	29,5	76
VIIm	>200 (dec.)	69,2	3,2	20,0	$C_{12}H_7N_3O$	68,9	3,4	20,1	88
VIIn	285—287	56,6	2,3	22,1	$C_{12}H_6N_4O_3$	56,7	2,4	22,0	80
VIIo	>210 (dec.)	63,0	3,0	26,6	$C_{11}H_6N_4O$	62,8	2,9	26,7	80

A study of the reaction conditions showed that in aqueous—organic media cyanide I reacts with carbonyl compounds only when a twofold excess of the latter is present. This makes it possible to assume that the initial product is double aldol condensation product III (Scheme 1), which due to intramolecular proton transfer with splitting out of one molecule of carbonyl compound II gives keteneimine IV, which then undergoes cyclization to the furan derivative (V, VI).

Scheme 1



I IIa-o* III IV

V VIa-o VIIm-o

*The expansion of the a-o groupings is presented in Table 2.

The introduction of cyanide I into the reaction in the presence of pyridinium salts such as pyridinium formate, which probably promotes the formation of keteneimine IV, makes it possible to avoid the necessity for the use of excess carbonyl compound, and the yields of dihydrofurans VIa-o reach 78% (see Table 1). Let us note that when aryl-substituted VIm-o are heated, they lose a molecule of hydrocyanic acid and are converted smoothly to furans VIIm-o, whereas VIa-i, which contain aliphatic groupings, are thermally unstable and upon heating form mixtures of difficult-to-separate reaction products along with condensation products.

Two singlets at 1.74 ($2CH_3$) and 8.3 ppm (NH_2) with an integral intensity ratio of 3:1 are observed in the PMR spectrum of dihydrofuran VId; the chemical shift of the latter signal decreases as the temperature is raised. This constitutes evidence that VId exists in solutions primarily (within the limits of the sensitivity of the method) in the amino form.

The ^{13}C NMR spectra of all of the synthesized compounds (see Table 2) also confirm the existence of the amino form of VI, since, for example, in the case of VId, signals of six carbon atoms that are not coupled with the protons are observed in the spectrum; the $C_{(6)}$ signal is not split under off-resonance conditions. A comparison of the chemical shifts of the carbon atoms of VIa-o (Table 2) shows that they all have identical structures of the amino form. The assignment of the signals in the carbon spectra was made on the basis of structural literature analogies [6, 7]. Let us note that the chemical shifts of the carbon atoms of the nitrile groups in the 3 position are identical when $R^1 = R^2$ but differ when $R^1 \neq R^2$ ($\Delta\delta$ = 0.9-1.8 ppm).

An analysis of the mass spectra of VIa-o (see Table 3) also confirms their structures as 2,3-dihydrofurans. Thus, in the mass spectrum of Ib one of the most intense peaks is the

TABLE 2. ^{13}C NMR Spectra of VI

Compound	R^1	R^2	^{13}C chemical shifts, δ, ppm										
			$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	$C_{(12)}$
VIa	H	H	77,81	42,0—42,5[a]	53,24	170,72	115,35	114,87	—	—	—	—	—
VIb	H	CH_3	82,96	44,58	50.33	168,76	115,65	114,49	113,12	17,77	—	—	—
VIc	D	$^9CD_3$	82,96	44,45	50,33	168,78	115,62	114,49	113,14	17,77 b	—	—	—
VId[c]	$^9CH_3$	$^{10}CH_3$	90,84	50,11	53,02	168,84	115,27	114,09	114,09	25,78	25,78	—	—
VIf	H	$^9CH_2—^{10}CH_3$	87,25	43,61	50,52	168,86	115,62	114,13	112,14	25,59	9,63	—	—
VIg	H	$^9CH_2—^{10}CH_2—^{11}CH_3$	87,76	44,85	53,16	169,89	115,0	114,90	113,57	34,93	19,57	14,08	—
VIh	H	$^9CH(^{10}CH_3)(^{11}CH_3)$	92,75	43,72	53,48	169,78	114,90	114,68	113,63	32,53	19,07	18,68	—
VIi	H	$^9CH_2—^{10}CH(^{11}CH_3)(^{12}CH_3)$	86,55	45,18	53,19	169,89	114,98	114,81	113,57	41,40	26,08	22,76	22,44
VIj	H	$^3CCl_3$	89,70	42,37	51,54	167,84	114,25	113,52	111,74	93,29	—	—	—
VIk	$^9CH_3$	$^{10}CH_2—^{11}CO—^{12}CH_3$	89,41	48,52	50,52	166,79	115,70	114,41	113,47	23,49	50,52	202,1	30,64
VIl	H	2-Furyl	80,26	44,39	50,03	168,78	115,27	114,38	112,55	furyl ring $C_9—C_{12}$ 111.5—113.7 (α); 142.2—146.0 (β)			
VIm	H	Phenyl	88,68	47,68	53,08	170,21	114,87	114,79	113,33	C_6H_5 group $C_9—C_{14}$ 127-134			
VIn	H	3-Nitrophenyl	75,30	46,31	49,98	168,94	115,06	114,14	112,66	3-nitrophenyl group $C_9—C_{14}$ 121.8-148.4			
VIo	H	3-Pyridyl	85,47	47,12	51,16	169,81	115,38	114,57	113,25	pyridyl ring $C_9—C_{13}$ 124.9-152.7			

[a]The signal is lost in the noise. [b]The intensities of these peaks are decreased markedly as compared with the peaks of VIb. [c]For IVe ($R^1 = R^2 = CD_3$).

43 ion peak* (CH_3CO^+, F_5), whereas the 59 ion peak [$(CH_3)_2CO^+H$, F_6] is one of the most intense peaks in the spectrum of Id. Ions of this type are characteristic for furan derivatives [8, 9]. These ions have mass numbers 46 and 66, respectively, in the mass spectra of deuterated VIc, e.

The stabilities of the molecular ions of all of the investigated compounds are relatively low (no more than 5%), and the primary process in their fragmentation is the loss of a molecule of hydrocyanic acid (to give the F_1 and F_1' ions). The intensity of the molecular-ion peak depends to a considerable extent on the temperature in the ion source. Thus in an MKh-1303 spectrometer, the temperature of the ionization chamber of which reaches 200-250°C, the intensities of the molecular-ion peaks of VI do not exceed 0.1-0.5% (relative), whereas the molecular-ion peaks of the compounds are quite intense when the mass spectra are recorded with an MAT-212 spectrometer with a cooled ionization chamber (T ⩽ 100-120°C), although the temperature of vaporization of the samples was close or even exceeded the temperature of their thermal decomposition (150-200°C).

It might be assumed that a tautomeric equilibrium of the VI—V type (Scheme 2) exists in the molecular ion and that both forms of the molecular ion are present in the gas phase. The loss of a molecule of HCN by them leads to F_1 and F_1' fragments, which have different structures and, consequently, undergo fragmentation via different pathways. The F_1' ion, which has the furan structure, undergoes fragmentation, like alkylfurans [8], at the benzyl C—C bond, which leads to the F_3 ion, which is virtually not formed in the fragmentation of the molecular ions of the 2,2-disubstituted derivatives. Characteristic for the latter is the loss of the 2-substituent by the F_1 ion, which is typical for the fragmentation of ethers and tetrahydrofuran derivatives [9]. The subsequent pathways of fragmentation of the primary fragments are shown in Scheme 2, while the intensities of the characteristic ions are presented in Table 4. It should be emphasized that the 130, 129, 103, 77, and 76 ions are characteristic for all of the heterocyclic compounds obtained on the basis of sym-tetracyanoethane (see Scheme 2).

The mass-spectral fragmentation of IZ, which contains a furan residue in the 2 position, is characterized by, in addition to the loss of a molecule of hydrocyanic acid, primary splitting out of isocyanic acid [Scheme 3, ion 183 ($C_{10}H_5N_3O$)], which is probably explained by the presence in the gas phase of the majority of the molecules in the tautomeric V form.

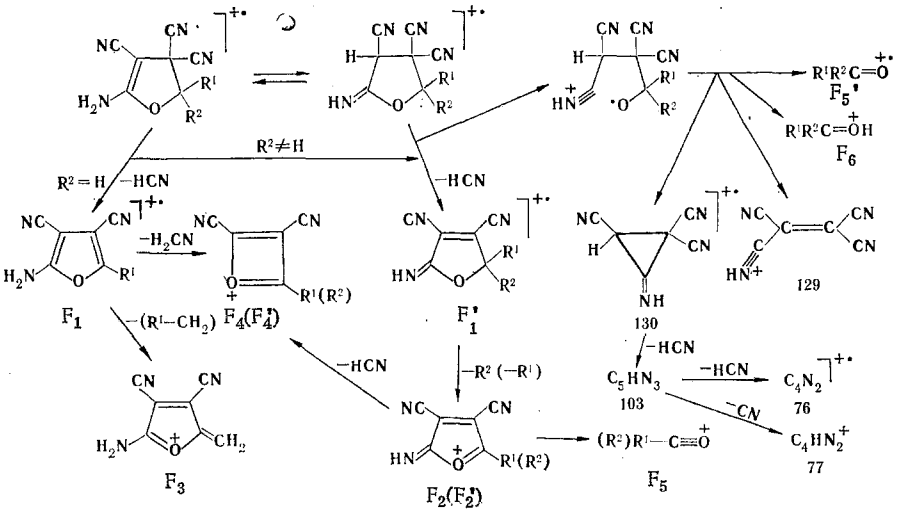
*Here and subsequently, the m/z values of the ions are presented.

TABLE 3. Mass Spectra of VI and VII

Compound	m/z (relative intensities, %)[a]
VIa	160 (71), 134 (100), 133 (75), 130 (35), 105 (29), 104 (23), 103 (29), 79 (24), 78 (78), 77 (96), 76 (34)
VIb	174 (31), 147 (52), 146 (38), 132 (21), 130 (38), 105 (23), 100 (27), 77 (23), 45 (42), 44 (58), 43 (100)
VId	188 (6), 161 (14), 146 (53), 119 (36), 104 (21), 77 (25), 76 (21), 59 (100), 44 (21), 43 (85), 41 (21)
VIf	188 (36), 161 (29), 147 (31), 146 (100), 132 (33), 130 (42), 105 (51), 77 (63), 76 (30), 59 (91), 57 (25)
VIg	202 (11), 175 (17), 148 (22), 147 (11), 146 (66), 130 (8), 106 (24), 84 (9), 77 (11), 55 (100), 43 (26)
VIh	202 (16), 175 (20), 160 (92), 147 (27), 133 (77), 119 (42), 84 (13), 78 (17), 77 (21), 56 (100), 43 (80)
VIi	216 (4), 189 (8), 148 (52), 147 (38), 146 (55), 133 (42), 131 (23), 105 (31), 84 (91), 69 (100), 43 (52)
VIj	276[b] (15), 241[b] (13), 213[b] (14), 199[b] (18), 159 (74), 130[b] (100), 103 (19), 95 (18), 78 (26), 77 (22), 44 (27)
VIk	230 (34), 203 (16), 161 (82), 160 (24), 146 (100), 105 (17), 77 (17), 76 (19), 58 (30), 44 (26), 43 (100)
VIl	226 (10), 199 (67), 183 (88), 156 (31), 144 (20), 143 (27), 128 (52), 116 (20), 101 (24), 44 (51), 43 (89)
VIm	236 (4), 209 (71), 193 (100), 166 (46), 165 (50), 140 (37), 139 (54), 107 (36), 105 (62), 79 (54), 77 (96)
VIn	281 (6), 254 (100), 208 (23), 180 (12), 165 (25), 153 (25), 152 (18), 138 (13), 126 (13), 77 (13), 76 (12)
VIo	237 (4), 210 (100), 194 (15), 155 (25), 118 (21), 108 (16), 106 (19), 79 (35), 78 (34), 63 (15), 57 (34)
VIIm	209 (100), 193 (21), 180 (26), 165 (10), 154 (16), 139 (12), 127 (13), 105 (23), 77 (40), 51 (23), 50 (11)
VIIn	254 (100), 208 (35), 181 (10), 180 (19), 165 (20), 153 (33), 138 (15), 126 (15), 77 (13), 76 (23), 50 (15)

[a]The molecular-ion peak and the 10 most intense peaks are presented. [b]These are the mass numbers of the ions that contain only the ^{35}Cl isotope.

Scheme 2

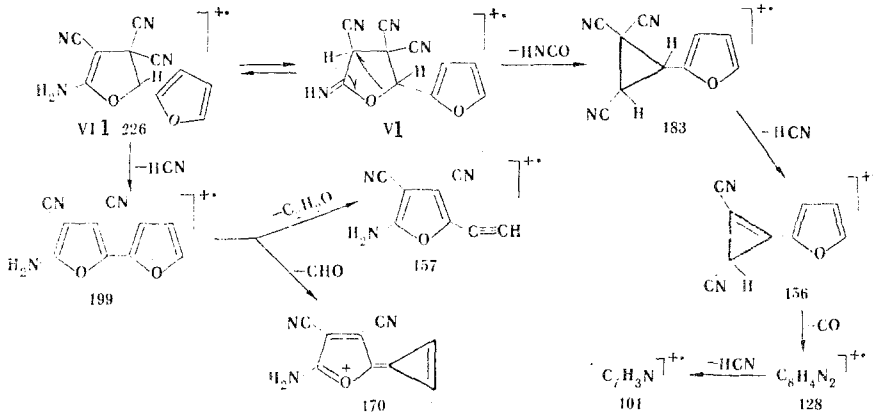


The mass-spectral fragmentation of furan derivatives VIIm-o corresponds completely to the character of the fragmentation of the F_1 ions in the mass spectra of VIm-o, which once more confirms the structures of these fragments. Thus the reaction of cyanide I with carbonyl compounds is a preparative method for the synthesis of cyano-substituted derivatives of furan.

TABLE 4. Intensities of the Peaks of the Principal Characteristic Ions in the Mass Spectra of VI and VII ($\%\Sigma_{39}$)

Compound	M	F_1	F_2	F_2'	F_3	F_4	F_4' (F_4)	F_5	F_5' (F_6)	m/z 130	m/z 129	m/z 103	m/z 77	m/z 76
VIa	9,1	8,2	—	—	—	0,5	0,5	—	—	3,8	0,3	3,5	10,5	3,7
VIb	5,5	8,1	3,2	5,8 (F_3)	5,8	—	—	15,6	9,1	5,8	9,2	2,4	3,5	2,9
VId	1,1	2,2	8,8	8,3 (= F_2)	—	5,5	5,5	13,4	0,4 (15,8)	1,1	—	1,9	4,0	3,4
VIf	4,4	2,9	3,2	0,5	9,9	5,0	1,9	2,5	0,3 (9,0)	4,1	0,3	1,8	6,2	3,0
VIg	2,4	3,6	1,0	—	14,2	2,4	—	0,4	—	1,8		0,5	2,5	1,2
VIh	2,3	2,2	0,7	—	10,1	2,9	—	—	—	0,4		0,6	2,3	0,8
VIi	0,5	0,9	1,3	—	6,2	—	—	—	—	1,4	0,5	1,1	1,6	0,4
VIj	4,3	—	—	—	—	0,5	—	—	—	—	—	2,4	2,8	0,3
VIk	4,7	1,8	11,3	0,6	2,7		9,3	0,5	0,5	0,3	0,3	1,9	1,9	2,2
VIl	0,8	17,5	—	—	—	0,9	—	2,8	1,2 (2,5)	0,2	0,5	1,1	2,7	1,8
VIm	0,3	6,5	—	—	—	0,4	—	5,7	0,4	0,3	0,2	1,4	8,7	0,7
VIn	1,5	21,2	—	1,4	—	—	—	1,7	0,7	1,4	—	1,1	2,8	2,5
VIIm	25,6	—	—	—	—	—	—	4,6	0,3	0,3	0,1	0,9	8,1	1,5
VIIn	19,7	—	—	—	—	—	—	1,3	0,4	0,8	0,3	0,7	2,2	4,0

Scheme 3



EXPERIMENTAL

The course of the reaction and the purity of the compounds obtained were monitored on plates of the Silufol-254 type. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The ^1H and ^{13}C NMR spectra of 15-20% solutions of the compounds of d_6-DMSO were obtained with a Brucker WH-90 spectrometer. The mass spectra were obtained with a Varian MAT-212 spectrometer at an ionization energy of 70 eV. The mass spectra of VIa, f were recorded with an MKh-1303 spectrometer at 50 eV, while the mass spectra of VIk, l were recorded with an AEI MS-30 spectrometer at an ionization energy of 70 eV. In all cases the samples were introduced directly into the ion source and vaporized at 100-170°C.

The synthesis of VIb, d, j-l, n was described in [5].

General Method for the Preparation of VI. A solution of 6.5 g (50 mmole) of tetracyanoethane, 1 g of pyridinium formate, and 50 mmole of the corresponding carbonyl compound in 10 ml of acetonitrile was added to a mixture of 60 ml of acetonitrile, and the mixture was stirred at room temperature for 2 h in a nitrogen atmosphere. Water (100 ml) was added, and the precipitate that formed after 30 min was removed by filtration, washed with water, dried, and recrystallized from benzene. The yields and properties are presented in Table 1. For the isolation of VIa the reaction mixture was evaporated *in vacuo*, and the residue was extracted with ethyl acetate. The extract was washed with water, dried with anhydrous calcium chloride, and treated with hexane. The resulting precipitate was recrystallized from benzene–ethyl acetate.

The synthesis of deutero compounds VIc, e was realized in D_2O with the use of, respectively, CD_3CDO and $(CD_3)_2CO$. For the preparation of VIIm-o dihydrofurans VIm-o were melted and maintained at their melting points for 5-8 min.

LITERATURE CITED

1. O. E. Nasakin, V. V. Alekseev, V. K. Promonenkov, A. Kh. Busai, and S. Yu. Sil'vestrova, Khim. Geterotsikl. Soedin., No. 6, 744 (1981).
2. V. V. Alekseev, O. E. Nasakin, V. A. Kukhtin, A. Ya. Chernikhov, M. N. Yakovlev, and G. N. Petrov, USSR Inventor's Certificate No. 657019; Byull. Izobret., No. 14, 198 (1979).
3. G. N. Petrov, O. E. Nasakin, V. A. Kukhtin, and V. V. Alekseev, USSR Inventor's Certificate No. 672194; Byull. Izobret., No. 25, 106 (1979).
4. V. V. Alekseev, O. E. Nasakin, A. Kh. Bulai, and S. Yu. Sil'vestrova, Khim. Geterotsikl. Soedin., No. 8, 1137 (1980).
5. O. E. Nasakin, V. V. Alekseev, V. K. Promonenkov, A. Kh. Bulai, and Yu. S. Sil'vestrova, Khim. Geterotsikl. Soedin., No. 11, 1565 (1980).
6. J. R. E. Johnson and Fan Kowski, Carbon-13 NMR Spectra, Wiley-Interscience, New York (1972).
7. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley, New York (1972).
8. P. B. Terent'ev, Mass Spectrometry in Organic Chemistry, Vysshaya Shkola, Moscow (1979), p. 125.
9. H. Budzikiewicz, C. Djerassi, and D. H. Williams, Mass Spectrometry of Organic Compounds, Holden-Day, San Francisco (1967), p. 256.

MECHANISM OF CYCLOALKYLATION OF ALLYLCARBINOLS WITH ALDEHYDES AND KETONES

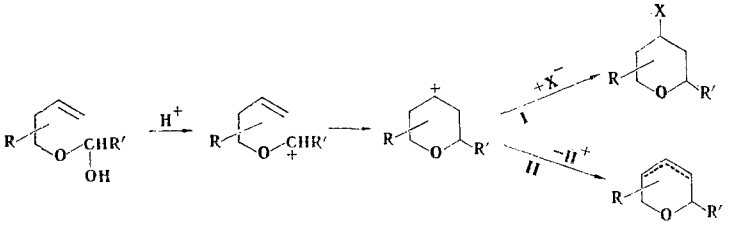
A. A. Gevorkyan, A. S. Arakelyan, and P. I. Kazaryan

UDC 547.811:542.953

The reaction of methallylcarbinols with aldehydes and ketones in the presence of acidic catalysts, which leads to mixtures of dihydropyrans and tetrahydropyranols, was studied. It is shown that the formation of tetrahydropyranols occurs as a result of intramolecular bonding of the hydroxy group in the intermediate hemiacetal formed under the influence of the catalyst.

The reaction of allylcarbinols with aldehydes and ketones in the presence of acidic catalysts is a general method for the preparation of di- and tetrahydropyrans [1-5]. A number of new perfumes that are of practical interest have been found among them [6-8]. In this connection it has become necessary to improve the known methods for the synthesis of pyran derivatives and, in particular, to increase the yields and decrease the amount of waste waters.

According to the generally accepted opinion, the reaction of allylcarbinols with aldehydes and ketones as an intramolecular Prins reaction proceeds through an intermediate tetrahydropyranyl carbonium ion, which is stabilized either by deprotonation or by the addition of anions [9].



In conformity with these concepts, the reaction was carried out experimentally either in the presence of a large excess of anions (pathway I) or, on the other hand, in the absence of anions or in the presence of insufficient anions (pathway II). We obtained data that indi-

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375094.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1611-1613, December, 1982. Original article submitted June 8, 1982.

 0009-3122/82/1812-1240$07.50