24. N. S. Smirnova, L. I. Markova, K. M. Korshunova, and G. I. Rybina, *Studies in the Synthesis and Catalysis of Organic Compounds* [in Russian], Izd. Saratov Univ., Saratov (1983), p. 208.
25. V. G. Kharchenko, N. S. Smirnova, L. I. Markova, G. I. Rybina, and K. M. Korshunova, USSR Author's Certificate, No. 910,633; *Byull. Izobret.*, No. 9, 86 (1982).
26. V. G. Kharchenko, N. S. Smirnova, L. K. Kulikova, L. V. Vlasova, L. I. Markova, G. I. Rybina, and K. M. Korshunova, *Khim.-farm. Zh.*, No. 6, 688 (1983).
27. N. S. Smirnova, L. M. Yudovich, and G. I. Rybina, *Nucleophilic Reactions of Carbonyl Compounds*, Abstracts of Reports, All-Union Conference, Saratov (1985), p. 37.
28. N. S. Smirnova, L. M. Yudovich, G. I. Rybina, and L. I. Markova, *The Chemistry of Dicarbonyl Compounds*, Abstracts of Reports of the 6th All-Union Conference, Riga (1986), p. 204.
29. V. G. Kharchenko, N. S. Smirnova, L. M. Yudovich, G. I. Rybina, and L. I. Markova, *Zh. Org. Khim.*, **23**, 576 (1987).
30. V. G. Kharchenko, N. S. Smirnova, L. M. Yudovich, G. I. Rybina, and O. V. Bryukhanova, *Zh. Org. Khim.*, **23**, 2333 (1987).
31. N. S. Smirnova, V. G. Kharchenko, L. I. Markova, L. M. Yudovich, and G. I. Rybina, in: 4th All-Union Symposium on Heterogeneous Catalysis and the Chemistry of Heterocyclic Compounds, Abstracts of Reports, Riga (1987), p. 134.
32. V. G. Kharchenko, N. S. Smirnova, and A. P. Kriven'ko, in: 4th All-Union Symposium on Heterogeneous Catalysis and the Chemistry of Heterocyclic Compounds, Abstracts of Reports, Riga (1987), p. 30.

REACTIONS AT SURFACES.

3.* REACTIONS OF 3-METHYL-3-BUTEN-1-OL WITH CARBONYL COMPOUNDS ON METAL SALT SURFACES

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Condensation of 3-methyl-3-buten-1-ol with pentanal or acetone occurs on metal salt surfaces at room temperature to give di- and tetrahydropyrans.

We have reported [1] that the condensation of 3-methyl-3-buten-1-ol (I) with carbonyl compounds on solid carrier surfaces depends to a large extent on physical adsorption. The presence of a developed surface enables the molecules of the reactants to orient themselves appropriately, and to form a transitional complex which is converted into products. It could be that this reaction would occur even in the absence of such surfaces, if coordinating centers such as metal ions are present which are able to form sufficiently reactive intermediate complexes.

We have now examined the condensation of the alcohol (I) with pentanal (IIa) and acetone (IIb) at the surfaces of salts of mono-, di-, and trivalent metals. In addition to the change on the central atom, the anion, reactant, and salt (previously dehydrated) ratios were varied [2]. It is known [3] that water of crystallization is not directly bonded to the metal ion, but occupies free sites in the salt crystal lattice. By dehydrating the salts, access of the reactants to the central ion and complexation therewith were facilitated. All the experiments were carried out at ambient temperatures (Tables 1 and 2).

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*For Communication 2, see [1].

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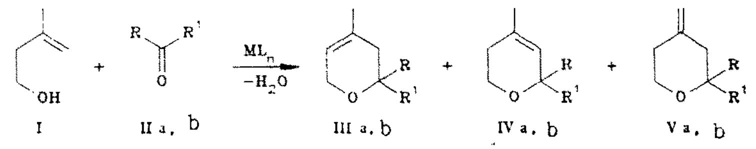
The alcohol (I) was found to react with the carbonyl compounds (II) in the presence of the salts to give the unsaturated cyclic ethers (III-V).



II—V a R=H, $R^1=C_4H_9$; b $R=R^1=CH_3$; M — metal , L_n — ligand

In the presence of acid catalysts, this reaction is usually carried out with removal of water as an azeotropic mixture with hydrocarbons [4]. If this is not so, in addition to dihydropyrans, tetrahydropyranols are formed [5]. Condensation of salt surfaces is selective with respect to ethers (III-V), owing in all probability to binding of the water liberated as hydrates. In addition, water facilitates expulsion of the reaction products from the coordination sphere of the salts. The yields obtained using pentanal were usually greater than with acetone, although this difference was considerably reduced when conversion of the alcohol (I) was allowed for (selectivity). The best results were obtained using the salts of trivalent metals.

As will be seen from the results given here, the yields of products were highly dependent on the nature of the cation which, in turn, determines the stability of the bond. In fact, for a given coordination number the stability of the bond increased with increasing ionic potential of the central atom, i.e., the ratio of the ionic charge on the metal to its radius [3]. Using literature values for the ionic radii (coordination number 6) [6] the ionic potentials were calculated: Al^{3+} 52.63, Fe^{3+} 44.78, Co^{2+} 25.64, Fe^{2+} = Cu^{2+} 25.00, Mn^{2+} 21.98, Na^+ 10.20. This sequence is quite close to that found for the stabilities

TABLE 1. Condensation of the Alcohol (I) with (IIa) and (IIb) at the Surfaces of Metal Salts ML_n [20 h, 20°C, alcohol (I)/ML_n = 1:10, mole]

ML_n	Compound	Conversion of alcohol (I)	Yield of (III-V), %	Selectivity, %	Isomer ratio (III):(IV):(V)
Na_2SO_4	IIa	10	2	20	36:32:32
	IIb	9	—	—	
$MnSO_4$	IIa	61	55	91	35:25:40
	IIb	59	44	75	1:43:56
$FeSO_4$	IIa	72	67	93	44:22:34
	IIb	59	48	85	1:42:57
$CuSO_4$	IIa	60	50	84	36:25:39
	IIb	58	43	75	1:43:56
$CoSO_4$	IIa	69	46	67	39:22:39
	IIb	19	13	69	1:42:57
$Fe_2(SO_4)_3$	IIa	92	81	88	50:24:26
	IIb	65	58	90	1:44:56
$Al_2(SO_4)_3$	IIa	98	96	98	45:24:31
	IIb	58	50	86	1:42:56
CuF_2	IIa	60	45	75	41:21:38
$CuCl_2$	IIa	79	75	95	50:24:26
CuI_2	IIa	52	43	88	33:30:37
$CuMoO_3$	IIa	20	1	5	29:25:46

TABLE 2. Condensation of the Alcohol (I) with Pentanal (IIa) on a $CuSO_4$ Surface (20°C)

Alcohol (I)/$CuSO_4$, mole	t_{react}, h	Conversion of alcohol (I),%	Yield of (IIIa-Va), %*	Selectivity, %
1:0,02	20,0	3	1	32
1:1	20,0	21	13	62
1:5	20,0	59	49	83
1:10	20,0	60	50	83
1:20	0,2	20	15	74
1:20	2,0	34	27	80
1:20	40,0	62	51	83

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*Ratios of isomers (III:IV:V) (34...36):(23...25):(37...39).

of a series of complexes for Irwin–Williams O-donor ligands [3], and the yields of products (III-V) in these reactions correlate in general with the values of the ionic potentials. There are some differences in the case of divalent metals, but this could be due to slight differences in the values of the potentials themselves, or to analytical errors.

The type of ligand also has some effect on the product yields, as will be seen in the case of copper salts. The structure of the salt is known to be determined by the coordination environment of the metal. For example, metal fluorides have a three-dimensional skeletal structure, whereas the remaining halides are linear, layered crystals, and the sulfates have the rhombic structure, etc. [7]. Evidently the shape and dimensions of the crystal hydrate cells, the structure of which is determined by the ligand, influence the course of the reaction.

The salts in this reaction function essentially as catalysts, and their amounts should be catalytic. However, as will be seen from Table 2, in such a case [alcohol (I)/$CuSO_4$ = 1:0.02, mole] conversion of the alcohol (I) is very low, providing further confirmation of the formation of a hydrate with the water liberated. No free coordination sites are present in the hydrate, so that it cannot form a reactive intermediate. Consequently, the salt is a reactant which participates directly in the reaction, and equimolar proportions of (I)/ML_n should be optimal. In practice, however, not every molecule of the reactants is able to coordinate with every salt cation as a result of steric hindrance. The experimental results are best with a (I)/ML_n ratio of $\leq$1:5, and vary little. Evidently, a large proportion of the salt simply does not participate in the reaction.

As the reaction times were increased from 0.2 to 20 h, the conversion of the alcohol (I) and the yields of products (III-V) increased threefold. No changes were, however, seen on increasing the reaction time to 40 h, which usually indicates the attainment of equilibrium.

The mild conditions used to carry out the experiments offered the hope that the yields of products would be quantitative, but only in the case of $Al_2(SO_4)_3$ were the yields close to 100%. Since no products other than cyclic ethers could be detected in the reaction mixtures, it must be assumed that, in addition to the reactive intermediates, other, more complex, secondary complexes are formed which are incapable of undergoing further reactions.

EXPERIMENTAL

The products were identified by their retention times as compared with samples obtained by standard methods [4, 5]. Analyses were carried out by GLC using an internal standard (LKhM-8MD apparatus, FID, 2000 × 3 mm, 15% PEG on Chromosorb P, nitrogen 40 ml/min).*

The salt hydrate crystals were first calcined at 350°C for 5 h. The reactants were dried over molecular sieve NaA (3A).

2-Butyl-4-methyl-3,6-dihydro-2H-pyran (IIIa), 2-Butyl-4-methyl-5,6-dihydro-2H-pyran (IVa), and 2-Butyl-4-methylenetetrahydropyran (Va). In a 50 ml flask fitted with a ground glass stopper were placed successively 34.6 g of $Al_2(SO_4)_3$, 0.86 g (10 mmoles) of the alcohol (I), and 0.86 g (10 mmoles) of the aldehyde (IIa). The flask and its contents were shaken and kept for 20 h at 20°C. The mixture was then washed with acetone (3 × 35 ml), filtered, the standard added [undecane in the case of (IIa), and decane in the case of (IIb)], and GLC analysis carried out. The yield of products (IIIa-Va) was 96%.

The other experiments were carried out similarly.

LITERATURE CITED

1. U. G. Ibatullin, Yu. V. Pavlov, and M. G. Safarov, *Khim. Geterotsikl. Soedin.*, No. 2, 183 (1990).
2. V. P. Nikol'skii (ed.), *Chemist's Manual* [in Russian], Vol. 2, Khimiya, Leningrad (1971), p. 12.
3. Yu. N. Kukushkin, *The Chemistry of Coordination Compounds* [in Russian], Vysshaya Shkola, Moscow (1985).
4. U. G. Ibatullin, T. F. Petrushina, Z. M. Nurtdinova, Yu. N. Popov, and M. G. Safarov, *Khim. Geterotsikl. Soedin.*, No. 7, 883 (1986).
5. A. A. Gevorkyan, A. S. Arakelyan, and P. I. Kazaryan, *Khim. Geterotsikl. Soedin.*, No. 12, 1611 (1982).
6. V. A. Rabinovich and Z. Ya. Khavin, *A Concise Handbook for Chemists* [in Russian], Khimiya, Leningrad (1978), p. 22.
7. A. Wells, *Structural Inorganic Chemistry* [Russian translation], Vol. 2, Mir, Moscow (1987), p. 85.

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*Correction coefficients were calculated as the arithmetic means of a series of experiments with a relative standard error of 3%. The standard error for GLC analyses due to manual miscalculation of chromatograms is 5%.