(NO_2). UV spectrum, λ_{max} (log ε): 225 (4.31), 257 (4.28), 291 nm (4.06). PMR spectrum: 8.45 (1H, q, 4-H, $J_{4,3}$ = 8.3 Hz, $J_{4,6}$ = 2.2 Hz), 8.30 (1H, d, 6-H, $J_{6,4}$ = 2.2 Hz), 7.96 (1H, d, 3-H, $J_{3,4}$ = 8.3 Hz), 5.73 (1H, s, CH), 3.95 ppm (3H, s, $COOCH_3$). Mass spectrum, m/z (%): 221 (69) M^{+}, 208 (11), 204 (12), 193 (10), 179 (6), 178 (100), 174 (5), 162 (18), 161 (10), 150 (5), 134 (8), 135 (5), 132 (61), 120 (6), 119 (8), 117 (6), 105 (8), 104 (12), 103 (23).

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REACTIONS ON A SURFACE.

1. CONDENSATION OF 3-METHYL-3-BUTEN-1-OL WITH CARBONYL COMPOUNDS ON SiO_2 AND Al_2O_3

U. G. Ibatullin, Yu. V. Pavlov,
and M. G. Safarov

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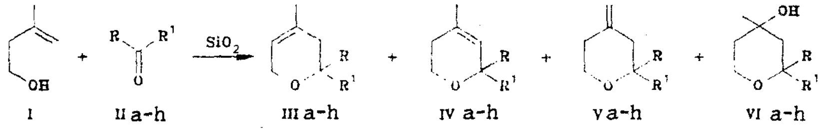
3-Methyl-3-buten-1-ol reacts with various aldehydes and ketones on silica gel and Al_2O_3 surfaces in the absence of solvents and conventional catalysts for this reaction to form derivatives of di- and tetrahydropyrans.

Recently, a series of papers has been published in which silica gel or Al_2O_3 are used in carrying out organic reactions (not in the vapor phase) — for example, for the selective reduction of one of the carbonyl groups in diketones ($LiAlH_4/SiO_2$) [1], with acetalization of ethylene glycol with aldehydes [2], etc. Of particular interest are the nontraditional synthetic methods in which reactions are carried out essentially in the solid phase on a surface of SiO_2 or Al_2O_3. Such a variant was used for the intra- [3] and intermolecular [4] conversion of dicobalthexacarbonyl complexes of enyne derivatives.

Condensation of carbonyl compounds with γ-unsaturated alcohols is a convenient method to obtain six-membered, cyclic ethers. Usually it is carried out by distilling off the forming water as an azeotropic mixture with hydrocarbons [5, 6], on mixing the reactants in an organic solvent [7] or water [8] in the presence of mineral and aromatic sulfonic acids or cation exchange resins. Depending on the conditions, one obtains either isomeric di- and tetrahydropyrans [5, 6] or tetrahydropyranols [8], or a mixture of them [7]. Any information concerning the possibility of carrying out such a condensation on an oxide surface is lacking.

The present work was devoted to studying the reaction of 3-methyl-3-buten-1-ol (I) and carbonyl compounds IIa-h on SiO_2 and Al_2O_3 surfaces in the absence of the catalysts mentioned and of any solvent. It turned out that under these conditions, derivatives of di- (III, IVa-h) and tetrahydropyranones (V, VIa-h) form even at room temperature.



II—VI a $R=H$, $R^1=C_2H_5$; b $R=H$, $R^1=C_4H_9$; c $R=H$, $R^1=i\text{-}C_4H_9$; d $R=H$, $R^1=C_6H_5$; e $R=R^1=CH_3$; f $R=CH_3$, $R^1=i\text{-}C_4H_9$; g $R+R^1=(CH_2)_4$; h $R+R^1=(CH_2)_5$

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TABLE 1. Condensation of Alcohol I with Carbonyl Compounds IIa-h on SiO_2 and Al_2O_3 (20°C, 20 h, oxide:reactants = 10:1 (by mass))

Compound	Yield of products III-V, %	Yield of product VI, %	Ratio of isomers III:IV:V
		SiO_2	
IIa	33,0	—	26 : 36 : 38
IIb	43,8	—	22 : 25 : 53
IIc	10,1	—	21 : 26 : 53
IId	11,9	12,5	41 : 59*
IIe	24,0	1,2	7 : 3 : 90
IIf	1,5	1,0	49 : 51*
IIg	1,7	1,0	45 : 55*
IIh	1,0	—	43 : 57*
		Al_2O_3	
IIa	—	9,6	45 : 55*
IIb	—	13,1	45 : 55*
IIc	—	11,5	45 : 55*
IId	3,0	10,0	45 : 55*
IIe	—	7,5	45 : 55*
IIf	1,1	5,5	45 : 55*
IIg	—	1,0	45 : 55*
IIh	2,1	1,2	47 : 53*

*Ratio of isomers (III + IV)/V.

We carried out the reaction with a series of aldehydes, IIa-d, and ketones, IIe-h, at temperatures from 0 to 100°C, by simply mixing the reactants (in a 1:1 mole ratio) with previously dried carrier (in ratios from 5:1 to 20:1 by mass). The duration of the reaction was from six minutes to 20 h. The experimental conditions and the results obtained are presented in Tables 1 and 2.

As the reaction time and temperature are increased, the yield of compounds III-Vb increases (Table 2), and the change in temperature affects the ratio of isomers. It is known [5, 6] that when the reaction is carried out under ordinary conditions, the principal products are 3,6-dihydro (III) and 5,6-dihydro-2H-pyrans (IV). The latter is practically absent from the reaction mixture when aromatic aldehydes are used [9]. On a SiO_2 surface at 20°C, 4-methylenetetrahydropyrans, V, (50-55% and even 90% with compound IIe) are the preferred product in all cases. At higher temperatures, the content of isomer V decreases, but the amount of isomer III increases (Table 2). When 4-methylenetetrahydropyran is heated on a SiO_2 surface, 4-methyl-5,6-dihydro-2H-pyran (~70%) is formed under the same conditions. This independent experiment shows unambiguously the isomerization of the exocyclic double bond to an endocyclic one.

The effect of the SiO_2/reactants ratio on the results of the reaction is unambiguous: a decrease to 5:1 as well as an increase to 20:1 tells negatively on the yield of products (Table 2).

Comparing the behavior of the different carbonyl compounds (Table 1), one has to take note of the low reactivity of ketones (besides acetone). The inertness of ketones compared to aldehydes was observed also in the acetalization of ethylene glycol with the use of oxides [2], although the reaction conditions differed markedly from ours. Of the aldehydes, aliphatic ones having a normal structure are more active. When benzaldehyde and ketones are condensed, the reaction mixture contains pyranols, VI, in addition to pyrans III-V; when the reaction is carried out on Al_2O_3, these are the major products.

In addition to the factors discussed, it is necessary to mention the important role of the prior dessication of the oxides. Thus, one cannot condense aldehyde IIb with alcohol I at 18°C on SiO_2 containing 3% water. If, however, this is done at 100°C (20 h), products are formed (2.9% compounds III-Vb and 4.5% VIb). In all probability, water is adsorbed on the active centers of the oxide, and organic compounds I-VI cannot displace it, so the reaction does not go. At 100°C, a slow dehydration of the surface begins, and the water immediately takes part in the reaction. This explains the predominant formation of pyranol, which was not on SiO_2 under other conditions. Apparently, it is not possible to remove water from an Al_2O_3 surface under our conditions immediately and to such an extent as from SiO_2. Consequently, the reaction on it goes poorly and leads to pyranols.

TABLE 2. Condensation of Alcohol I with Aldehyde IIb on SiO_2 (20°C, SiO_2:reactants = 10:1 (by mass))

Reaction time	Yield of products III-Vb, %	Ratio of isomers IIIb:IVb:Vb
6 min	10,5	20...22 : 25...28 : 50...55
1 h 30 min	28,1	20...22 : 25...28 : 50...55
3h	32,1	20...22 : 25...28 : 50...55
20 h	43,8	20...22 : 25...28 : 50...55
20 h*	17,8	20...22 : 25...28 : 50...55
20 h**	33,2	20...22 : 25...28 : 50...55
1 h	11,2	22 : 25 : 53
1 h***	25,4	30 : 30 : 40
20 h***	44,0	67 : 22 : 11

*SiO_2:reactants = 5:1.
**SiO_2:reactants = 20:1.
***100°C.

EXPERIMENTAL

Reaction products were identified by comparing retention times with samples obtained by known methods [5-7, 9]. The GLC analyses were done on an LKhM-8MD instrument (flame ionization detector, 2000 × 3 mm, 15% PEGA on Chromosorb P, nitrogen carrier gas, 40 ml/min).

The SiO_2 (for chromatography, LL_{254}) and Al_2O_3 (for chromatography, neutral) were first calcined for five hours in a muffle furnace at 400°C.

2-Butyl-4-methyl-3,6-dihydro-2H-pyran (IIIb), 2-Butyl-4-methyl-5,6-dihydro-2H-pyran (IVb), and 2-Butyl-4-methylenetetrahydropyran (Vb). In a 50 ml flask with a ground stopper place, in order, 17.2 g SiO_2, 0.86 g (10 mmole) alcohol I, and 0.86 g (10 mmole) aldehhyde IIb. Agitate and keep in the closed flask for 20 h at 20°C. The reaction mixture is then washed with methanol (3 × 25 ml), filtered off, and analyzed by GLC after addition of a standard (decane). Yield, 43.8%.

All of the remaining experiments were run in an analogous way.

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