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HETEROORGANIC FURAN DERIVATIVES.

61.* TRIMETHYL(5-METHYL-2-FURYL)SILANE AND TRIMETHYL(5-METHYL-2-FURYL)GERMANE

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The transformations of trimethyl(5-methyl-2-furyl)silane and trimethyl(5-methyl-2-furyl)germane were studied upon vapor-phase oxidation by atmospheric oxygen on a V-Mo-Ag-O catalyst. Under these conditions, trimethyl(5-formyl-2-furyl)silane and trimethyl(5-formyl-2-furyl)germane are formed albeit in only 5-7% yield. This low yield is a consequence of the thermal instability of the starting compounds and the aldehydes formed. The oxidation of 2-methyl-5-tert-butylfuran was studied under comparable conditions. The corresponding aldehyde was obtained in 30% yield. A scheme was proposed for the catalytic oxidation of 5-substituted 2-methylfurans.

The catalytic oxidation of methyl-substituted heterocyclic compounds by oxygen in the vapor phase on oxide catalysts is a means for the preparation of the corresponding heteraryl-aldehydes [2]. Vanadium oxide and molybdenum oxide, characterized by variable valence of the metal and labile oxygen, and their mixtures with various additives are used as catalysts.

This method has been used for the preparation of formyl derivatives of pyridine [3-5], pyrazine [6, 7], pyrimidine [6], thiophene [8], and thiazoline [9]. In the case of furan derivatives, the liquid-phase catalytic oxidation of 5-methylfurfural by atmospheric oxygen gives furan-2,5-dialdehyde in addition to the major reaction product, furan-2,5-dicarboxylic acid [10]. This result indicates the possibility of oxidizing the methyl group of 5-methylfurfural to a formyl group.

Various biologically active compounds have recently been prepared from 5-trimethylgermyl-(Ia) and 5-trimethylsilylfurfural (IIa). Aldehydes Ia and IIa were obtained by a six-step synthesis from furfural in 70-80% yield [11-13]. In light of previous results [2-10], we may assume that another method for the preparation of aldehydes Ia and IIa may be used for the catalytic vapor-phase oxidation of the methyl group attached to the ring in trimethyl(5-methyl-2-furyl)germane (Ib) and trimethyl(5-methyl-2-furyl)silane (IIb).

In the present work, we studied the catalytic vapor-phase oxidation of Ib and IIb and their carbon analog, 2-methyl-5-tert-butylfuran (IIIb), in order to determine the direction of their transformations and elucidate the feasibility of obtaining the corresponding aldehydes by this method.

The catalytic oxidation of Ib-IIIb was carried out by the action of atmospheric oxygen in the presence of a catalyst consisting of V_2O_5 , MoO_3 , and Ag_2O (V:Mo:Ag = 1:1:0.02) in the vapor phase at 300-450°C and contact time from 0.1 to 0.5 sec. The catalyst composition is optimal for the oxidation of 2,5-dimethylfuran to 5-methylfurfural as shown by preliminary experiments. The pulse macrocatalytic method was used which permits the operative determina-

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TABLE 1. Characteristics of Transformations of 5-Substituted 2-Methylfurans under Catalytic Oxidation Conditions on a V_2O_5 - MoO_3 - Ag_2O Catalyst at $430^\circ C$ ($V:Mo:Ag = 1:1:0.2$, $\tau = 0.3$ sec)

Starting compound	M	$C_{furyl}-M$ bond energy, kcal/mole [14]	Conversion, %	Aldehyde formed	Aldehyde yield, %
Ib	Ge	58	100	Ia	5-7
IIb	Si	75	70-80	IIa	5-7
IIIb	C	83	50-60	IIIa	30

tion of the optimal reaction conditions, and a flow system was used for the treatment of the reagents for purposes of their isolation and identification. This catalyst was introduced as a powder in the pulse microreactor, while about 10% active phase was supported on inert corundysium with $0.1 \text{ m}^2/\text{g}$ specific surface.

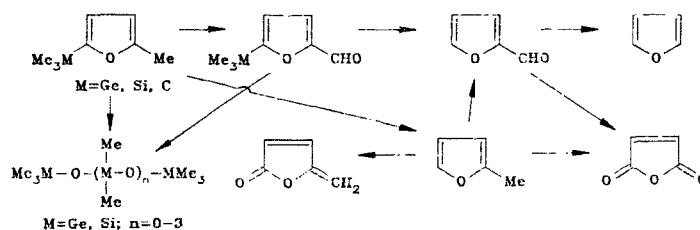
A study of the catalytic oxidation of Ib showed that under the conditions studied, aldehyde Ia is formed but its maximum yield does not exceed 5-7% at $430^\circ C$ (contact time $\tau = 0.3$ sec). In this case, the starting reagent is virtually completely converted to a series of compounds containing a five-membered ring formed in 10-15% yield: furan, sylvan, 5-methyl-2-(5H)-furanone (protoanemonin), furfural, and maleic anhydride. In addition, various germoxanes and products of extensive oxidation (CO , CO_2 , and H_2O) are also formed. Trimethyl-(2-furyl)germane was not found in the oxidation products as a consequence of the markedly greater strength of the $C_{furyl}-C$ bond in comparison with the $C_{furyl}-Ge$ bond [14].

The yield of aldehyde IIa is also 5-7% in the catalytic oxidation of silane IIb with the analogous formation of furan, xylvan, protoanemonin, furfural, maleic anhydride, siloxanes, and complete oxidation products. The conversion of silane IIb is somewhat less than in the case of germane Ib (70-80%) at $430^\circ C$ ($\tau = 0.3$ sec).

The major product of the catalytic oxidation of IIIb is the corresponding aldehyde, 5-tert-butylfurfural (IIIa) obtained in 30% yield under the conditions studied. The reaction products also contained furan, sylvan, protoanemonin, furfural, maleic anhydride, CO , CO_2 , and H_2O . The overall conversion of IIIb under comparable conditions is less than in the oxidation of Ib and IIb (Table 1).

The total conversion of the compounds Ib-IIIb under these catalytic oxidation conditions is largely related to their decomposition at the $C_{furyl}-M$ bond (Table 1), especially in the case of the germanium and silicon derivatives. The yields of aldehydes Ia and IIa are low due to their instability as well as the instability of starting compounds Ib and IIb (low strength of the $C_{furyl}-M$ bond, where $M = Ge, Si$) since the catalytic oxidation is carried out in the vapor phase under vigorous conditions (at high temperatures providing for sufficient lability of the catalyst oxygen). On the other hand, the catalytic oxidation of carbon derivative IIIb proceeds rather smoothly with relatively high yield of aldehyde IIIa and may have preparative value.

Our study has shown that the qualitative composition of the products of all the 5-substituted 2-methylfurans Ib-IIIb under catalytic oxidation conditions is identical and these reactions may be represented by the following scheme.



EXPERIMENTAL

The starting reagents, trimethyl(5-methyl-2-furyl)silane (IIb), trimethyl(5-methyl-2-furyl)germane (Ib) and 2-methyl-5-tert-butylfuran (IIIb) were obtained by reported procedures [15-17].

The procedure for catalyst preparation, study of the catalytic oxidation in the pulse and flow modes and chromatographic analysis were analogous to those described in our previous work [7]. The products of the catalytic oxidation were identified by gas-liquid chromatography and chromato-mass spectrometry on a Kratos MS-50 mass spectrometer at 70 eV relative to correspondence of retention times and mass spectra with those of authentic samples.

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