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REACTION OF METAL VAPORS WITH gem-DIHALIDES OF THE METHANE
AND CYCLOPROPANE SERIES

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α -Halogenated organometallic compounds (α -HOMC) are usually very unstable due to a tendency toward α -elimination of the metal halide molecule [1]. In addition, organic gem-dihalides, R_2CX_2 do not form α -halide organomagnesium compounds in the reaction with Mg in normal conditions. For example, dimagnesium derivatives, $CH_2(MgX)_2$, are formed from CH_2Br_2 or CH_2I_2 and Mg in an ether medium [2], and the trihalogenated methyl derivatives of Mg of the CX_3MgCl type, prepared by an exchange reaction of the corresponding polyhalogenated methanes with stable Grignard reagents at low temperatures in an ether medium, rapidly decompose according to a carbene or free-radical mechanism [3]. On the contrary, intermediate formation of α -halide organomagnesium compounds has been proposed in conditions of low-temperature cocondensation of Mg vapors with CCl_4 or Cl_2CHCH_3 based on IR spectral data [4].

The reactions of Mg, Al, and Zn vapors with gem-dihalocyclopropanes both in the absence and in the presence of solvating solvents and Ti, Cr, Fe, and Cu vapors with dihalomethanes were investigated by techniques of matrix synthesis to determine the corresponding α -HOMC or the products of their transformation.

All of the metals were evaporated by heating with an electric current. In these conditions, Mg evaporates in the form of atomic particles in the 1S ground (singlet) state [5]. In cocondensation of Mg vapors and an excess of 1,1-dibromo-2,2-dimethylcyclopropane (I) in a vacuum, a characteristic chestnut-colored matrix is formed immediately on cooling the walls of the reactor to 77°K; this indicates the reaction of the Mg vapors with (I) at the time of cocondensation, since a black matrix is formed in cocondensation of Mg vapors with an inert solvent. In the absence of solvating solvents, high-molecular resinous compounds are primarily formed in the reaction of Mg vapors with (I). Small amounts of 1-bromo-2,2-dimethylcyclopropane (II), 1,1-dimethylcyclopropane (III), and the dimer of the 2,2-dimethyl-1-bromocyclopropyl radical (IV) (yield of less than 1%) are found among the low-molecular products of the reaction. We note the absence of the corresponding allenes and acetylenes formed in the reaction of (I) with metallic Na or Mg in an ether or THF medium in the low-molecular products [6]; this could be due to the ease of condensation of the unsaturated compounds under the effect of the metal vapors [7]. In cocondensation of Mg vapors with a mixture of (I) and ether or THF in the ratio of 1:5, compounds (II) and (III) are formed with significantly higher yields (11 and 26%, respectively, in conversion to the evaporated metal). Formation of these compounds could be due to successive dehalogenation of (I) according to a radical mechanism and cleavage of H atoms from the solvent or starting (I) by the radicals formed.

The data obtained indicate that dehalogenation of (I) takes place according to a free-radical mechanism under the effect of Mg vapors. With respect to the possibility of formation of (II) and (III) by hydrolysis of the intermediate organomagnesium compounds formed, it is excluded by the use of solvents and (I) which are totally free of moisture and by the absence of $Mg(OH)Br$ in the products of the reaction. In addition, our attempts to find such an organomagnesium compound in the reaction medium at 20°C and 77°K using chemical interceptors: tri-

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EXPERIMENTAL

The reactions of the metal vapors with the ligands were conducted in a stationary reactor described previously [11]. Mg, Al, and Zn were evaporated from quartz crucibles heated with a tungsten wire coil. Chromium was evaporated from a Ta boat, and Fe, Cu, and Ti were evaporated from a tungsten wire on which foil made of the corresponding metal has been wound.

The starting dihalides were prepared according to [12] and purified by two distillations in an inert atmosphere.

The PMR spectra were made with a Tesla BS-467 (60 MHz) for 10% solutions in CCl_4 (TMS internal standard), and the mass spectra were recorded on a Varian MAT CH-6. The GLC analysis was performed on a LKhM-8MD chromatograph with a katharometer (He carrier gas, 30 ml/min) on 200×0.3 cm steel columns packed with 5% SE-30 silicone on Chromaton N-AW-DMCS (0.16-0.20 mm) (column 1) on Polysorb-1 (column 2).

Reaction of the Mg Vapors with 1,1-Dibromo-2,2-dimethylcyclopropane (I). In this reaction, 200 mg of Mg were evaporated for 30 min and cocondensed with 12 g of (I) at 77°K. The reactor was heated to 80°C, and the volatile products of the reaction were vacuum distilled into a cold trap. GLC (column 1) revealed 10 mg of 1-bromo-2,2-dimethylcyclopropane (II), 5 mg of 1,1-dimethylcyclopropane (III), and 11 mg of the dimer of the 2,2-dimethyl-1-bromocyclopropyl radical (IV) (yields of <1% for the evaporated metal). The residue on the walls of the reactor flask was extracted with 50 ml of hexane, filtered, and evaporated. Then 1.7 g of a brown resin was found. Found: C 73.60; H 9.89; Br 16.39%. $\text{C}_{30}\text{H}_{48}\text{Br}$. Calculated: C 73.77; H 9.84; Br 16.39%. The PMR spectrum contained singlets at 1.86, 1.76, 1.25, and 0.85 ppm, which appeared against a background of wide lines in the 0.5-2.0 ppm region. The wide signal of insignificant intensity in the 5-ppm region indicated the presence of multiple bonds. A group of intense peaks with m/z of 294-298 was present in the mass spectra of the distillate and residue; they corresponded to the molecular ion of the dimer of the 2,2-dimethyl-1-bromocyclopropyl radical (IV). Our experimentally observed splitting of the peaks corresponded to those obtained theoretically for a set of isotopes of Br atoms.

Reaction of Mg Vapors with (I) in a Medium of THF. In this reaction 0.5 g of Mg was evaporated for 1 h and cocondensed with a mixture of 20 g of (I) and 22 g of THF at 77°K. The reactor was heated to 20°C, and the volatile products of the reaction were distilled into a cold trap. GLC (column 1) revealed 0.66 g of (II) and 0.38 g of (II) (yields of 11 and 26% for the evaporated metal, respectively). The residue on the walls of the reaction flask (2.3 g) contained 0.25 g of unreacted Mg, 1.85 g (99% for the reacted metal) of MgBr_2 , and 0.2 g of resinous products.

Reactions of Highly Dispersed Zn Powder with 1,1-Dibromo-2-phenylcyclopropane (VI) in the Presence of MeOH. In this reaction, 0.6 g of Zn was evaporated for 40 min and cocondensed with a mixture of 3 g of (VI) and 30 g of hexane at 77°K. The reactor was heated to 20°C, filled with N_2 , and 10 ml of MeOH were added and mixed for 30 min. According to the GLC data (column 1), 0.21 g (19% for the evaporated metal) of 1-bromo-2-phenylcyclopropane containing a 3:2 ratio of cis- and trans-isomers was obtained. (According to the data in [13], the ratio of cis- and trans-isomers in the products of the reaction of (VI) with Zn powder in a THF medium is 5:1.)

Reaction of Cr Vapors with CH_2Cl_2 . In this reaction, 0.5 g of Cr was evaporated for 1 h and cocondensed with 30 g of CH_2Cl_2 at 77°K. The reactor was heated to 20°C, filled with N_2 , and the volatile products of the reaction were distilled into a cold trap. GLC (column 1) revealed 0.48 g (yield of ~59% for the evaporated metal) of 1,2-dichloroethane. The solid residue on the walls of the reactor flask was transferred to a Schlenck tube, evacuated, MeOH was added, and the products separated were analyzed by GLC (column 2). Traces of CH_3Cl and 30 mg of CH_2Cl_2 were found.

The reactions of Ti, Fe, and Cu vapors with CH_2Cl_2 and CH_2Br_2 were conducted in a similar manner. In all cases, 1,2-dihalogenated ethanes were the basic products of the reaction.

CONCLUSIONS

1. In the reaction of Mg vapors with 1,1-dibromo-2,2-dimethylcyclopropane at 77°K in a medium of solvating solvents, debromination of the starting gem-magnesium dibromide by a radical mechanism with subsequent cleavage of hydrogen atoms from the solvent by the radicals formed is the basic direction of the reaction.

2. The capacity of metal vapors to debrominate gem-dibromocyclopropanes decreased in the order of Mg, Al, Zn.

3. In the reaction of Cr, Ti, Fe, and Cu vapors with CH_2Cl_2 and CH_2Br_2 at 77°K, cleavage of one halogen atom and recombination of the $\cdot\text{CH}_2\text{X}$ radicals generated occurred with formation of 1,2-dihalogenated ethanes.

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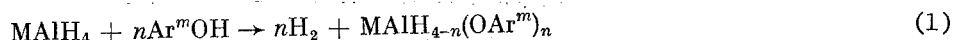
^{27}Al NMR STUDY OF DISPROPORTIONATION OF ARYLOXY DERIVATIVES OF ALKALI-METAL ALUMINUM HYDRIDES IN TETRAHYDROFURAN

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The disproportionation tendency of alkali-metal aluminum hydride derivatives of the type of $\text{MAlH}_4\text{-nR}_n$ has been demonstrated previously by ^{27}Al NMR, where M = Li, Na, or K; R = alkyl, alkynyl, amide, OR' in electron-donor solvents [1-4]. It was shown that their stability is affected by the state of ionic pairs in solution [2, 5, 6]. The suggestion was made that the disproportionation process occurs in intermediate ionic T-structures such as $[\text{M}^+\text{Al}^-\text{H}_4\text{-nR}_n\text{M}^+]^+$ and $[\text{AlR}_n\text{-H}_4\text{-nM}^+\text{AlH}_4\text{-n-R}_n]^-$ [2]. The objective of this paper is to study the effect of steric hindrance on the stability of the complexes by investigating the disproportionation reaction of aryloxy derivatives of Li and Na aluminum hydrides in tetrahydrofuran (THF). The lithium derivatives, which contain sterically hindered phenols, are used as mild selective reducing agents in organic synthesis [7].

We prepared aryloxy derivative complexes of aluminum from the following phenols: $\text{C}_6\text{H}_5\text{OH}$, 4-Me $\text{C}_6\text{H}_4\text{OH}$, 2-Me $\text{C}_6\text{H}_4\text{OH}$, 2,6-Me $_2\text{C}_6\text{H}_3\text{OH}$, and 4-Me-2,6-(t-Bu) $_2\text{C}_6\text{H}_2\text{OH}$ by the following reaction:



where M = Li, Na; n = 1 to 4; $\text{Ar}^1 = \text{Ph}$; $\text{Ar}^2 = 4\text{-MeC}_6\text{H}_4$; $\text{Ar}^3 = 2\text{-MeC}_6\text{H}_4$; $\text{Ar}^4 = 2,6\text{-Me}_2\text{C}_6\text{H}_3$; $\text{Ar}^5 = 4\text{-Me-2,6-(t-Bu)}_2\text{C}_6\text{H}_2$. All the $\text{MAlH}_4\text{-n(OAr}^m)_n$ are highly soluble in THF. The reaction was monitored by the evolution of hydrogen. The composition of the products was determined by ^{27}Al NMR. Table 1 shows our results.

When n = 3, reaction (1) results in the formation of multihydride complexes that are independent of M^+ and the phenol, and are stable in THF. However, the spectra of these complexes contain two signals: singlets in which δ is 41 to 54 and δ is 71 to 86 ppm. The

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