Electrosynthesis of 1,1,1-Tribromodimethylsulfone (II). A current of 6 A was passed through the electrolyzer described above containing 600 ml of an aqueous solution containing 120 g KBr, 70 g $NaHCO_3$, and 7.8 g DMSO at 20-22°C (27 A·h was introduced). The extraction of (II) was carried out as in the case of (I) to give 11.8 g (36% yield, 28% current yield) (II), mp 235-237°C (from toluene—hexane). PMR spectrum (δ, ppm): 3.47 s (3H). Found, %: C 7.45; H 1.10; Br 71.87. $C_2H_3Br_3O_2S$. Calculated, %: C 7.26; H 0.91; Br 72.46.

Preparation of (II) by the Oxidation of 1,1,1-Tribromomethyl Methyl Sulfide. A sample of 61.7 g (0.21 mole) 1,1,1-tribromomethyl methyl sulfide in 100 ml glacial acetic acid was added dropwise, with rapid stirring and cooling to 18-21°C over 5 h, to 51.8 g fine-crystalline CrO_3 in 300 ml glacial acetic acid. The reaction mixture was stirred at this temperature for an additional 1 h and then poured into 2 liters cold water and neutralized with $NaHCO_3$. The precipitate was filtered off and dried over P_2O_5 to give 37.9 g (55%) (II), mp 235-236°C (from toluene—hexane).

CONCLUSIONS

The electrochemical bromination of DMSO in alkaline media leads to the formation of $(CBr_3)_2SO_2$ (in the presence of Na_2CO_3) or $CBr_3SO_2CH_3$ (in the presence of $NaHCO_3$).

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HYPOPHOSPHOROUS ACID AS A HYDRIDE ION DONOR

O. A. Karpeiskaya, A. A. Belyi, Z. N. Parnes,
and M. E. Vol'pin

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Ionic hydrogenation of hydrogenolysis requires proton and hydride ion donors. Hypophosphorus acid, H_3PO_2 (I), is presumably both a proton donor and hydride ion donor. In order to check this hypothesis, we selected the ionic hydrogenation of 1-methylcyclohexene (II). This compound readily undergoes ionic hydrogenation to give methylcyclohexane by the action of hydride ion donors such as Et_3SiH and strong acids such as CF_3CO_2H [1]. However, 1-methylcyclohexene in the presence of (I) is not converted to methylcyclohexane at 40°C over 4 h with a ten-fold excess of acid. The lack of a reaction between (I) and (II) may be explained either by assuming that H_3PO_2 is a poor proton donor or a poor hydride ion donor. The reaction of (I) with (II) does not proceed in the presence of Et_3SiH which is an active hydride ion donor. Thus, H_3PO_2 is a poor proton donor. However, when CF_3CO_2H is added to a reaction mixture of (I) and (II) in order to increase the acidity of the medium, ~5% methylcyclohexane was found in the reaction products. Hence, the P—H bond may serve as a hydride ion donor.

When a carbocation such as the tropylium cation participates in the reaction, then, despite its low activity as a hydride ion acceptor, the reduction proceeds even by the action of 50% aqueous solution of (I) and cycloheptatriene is formed in ~25% yield. In this case, the reaction of (I) with the tropylium ion proceeds to give the mono- and dicycloheptatrienyl

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A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 473-474, February, 1988. Original article submitted April 10, 1987.

derivatives of (I) in addition to ionic hydrogenation. This is indicated by the ^{31}P NMR spectra of the reaction mass: δ_1 27.5 ppm (doublet, J_{P-H} = 545 Hz) and δ_2 52.5 ppm (singlet) which correspond to alkylphosphorous and dialkylphosphonic acids (81.01 MHz in CH_2Cl_2 with 85% H_3PO_4 as the external standard [2]).

Upon the use of diphenylchloromethane and 1-chloro-1-methylcyclohexane as the carbocation source and $AlCl_3$, the ionic hydrogenation in the presence of (I) proceeds under mild conditions (20°C over 1 h) with the formation of 22% diphenylmethane and 27% methylcyclohexane.

Ionic hydrogenolysis proceeds upon the action of (I) on triphenylcarbinol at 40°C over 4 h with a 93% yield of triphenylmethane. Diphenylcarbinol is converted to diphenylmethane under the same conditions, albeit in only 12% yield. This decrease in yield is apparently related to difficulty in forming the cation due to insufficient acidity of (I). We should note that except for the reactions with $C_7H_7BF_4$, we used (I) with ≤0.2% water. At high water contents in the acid, ionic hydrogenation and hydrogenolysis either do not occur at all or the product yield is low (the yield is only ~50% in the case of Ph_3COH).

EXPERIMENTAL

The products of the ionic hydrogenation were analyzed by gas-liquid chromatography on a Tsvet-129 chromatograph with a flame ionizaton detector and helium gas carrier using a 1500 × 4-mm glass column packed with Elastomer E-301 on Chromosorb W, HP 100/120 mesh (for the products of the conversion of Ph_3COH) and a 2500 × 4-mm glass column packed with 5% GESE-30 silicone on Chromaton-Super 100/120 mesh (for the products of the conversion of Ph_2CHOH, Ph_2CHCl, and $C_7H_7BF_4$). We also used a Chrom-5 chromatograph with a flame ionization detector and nitrogen gas carrier using a 2400 × 3-mm stainless steel column packed with SE-30 silicone on Chromaton N-AW-HMOC (0.16-0.20 mm) [for the products of the conversion of 1-chloro-1-methylcyclohexane and (II)]. The products were identified relative to authentic samples and the internal standard method was used for quantitative analysis.

The sample of hypophosphorous acid was dried as described by Brauer [3]. The moisture content was determined by potentiometric titration.

Ionic Hydrogenation of Ph_3COH by Hypophosphorous Acid. A sample of 0.260 g (0.001 mole) Ph_3COH in 1 ml CH_2Cl_2 was added to a pear-shaped flask equipped with a reflux condenser and magnetic stirrer maintained at 40°C. Then, 0.66 g (0.01 mole) anhydrous hypophosphorous acid was added dropwise and the mixture was stirred for 4 h. The solution was neutralized and extracted thrice with CH_2Cl_2. The organic layer was analyzed by gas-liquid chromatography.

The ionic hydrogenation of Ph_2CHOH and 1-methylcyclohexene by hypophosphorous acid was carried out by the same procedure.

Ionic Hydrogenation of 1-Chloro-1-methylcyclohexane and Ph_2CHOH by Hypophosphorous Acid in the Presence of $AlCl_3$. A sample of 0.001 mole 1-chloro-1-methylcyclohexane or Ph_2CHCl was added to the reaction flask equipped with a reflux flask and a magnetic stirrer and dissolved in 1 ml CH_2Cl_2. Then, 0.01 mole $AlCl_3$ was added upon cooling to 0°C. The mixture was stirred at ~12°C for 15 min. The solution turned orange and then brown after the dropwise addition of 0.005 mole H_3PO_2. The temperature of the cooling bath was gradually raised to room temperature. After 1 h, the mixture was neutralized and extracted thrice with CH_2Cl_2. The mixture was analyzed by gas-liquid chromatograph. The order of the addition of the reagents does not have a significant effect on the product yields. The best result (27% methylcyclohexane) was obtained upon the initial mixing of H_3PO_2 with $AlCl_3$ and the subsequent addition of 1-chloro-1-methylcyclohexane at 0°C.

Ionic Hydrogenation of $C_7H_7BF_4$ by Hypophosphorous Acid. A sample of 0.001 mole $C_7H_7BF_4$ was introduced into a pear-shaped flask equipped with a reflux condenser and magnetic stirrer. Then, 1 ml CH_2Cl_2 and heptane as the internal standard were added. A sample of 1.32 ml 50% aqueous H_3PO_2 was added with stirring. After 4 h, the mixture was thrice extracted with CH_2Cl_2. The organic layer was analyzed by gas-liquid chromatography.

CONCLUSIONS

Hypophosphorous acid is a protonating agent and relatively good hydride ion donor in ionic hydrogenation and hydrogenolysis.

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SYNTHESIS AND MOLECULAR STRUCTURES OF ANTIFERROMAGNETIC $(Cp_2Cr_2SCMe_3)\cdot(\mu_3\text{-}S)_2RhL_2$ CLUSTERS. FIRST OBSERVATION OF Cr—Rh BONDS

A. A. Pasynskii, I. L. Eremenko, V. R. Zalmanovich,
V. V. Kaverin, B. Orazsakhatov, V. M. Novotortsev,
A. I. Yanovskii, and Yu. T. Struchkov

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An increase of the activity of rhodium hydroformylation catalysts has been reported upon the introduction of thiolate bridges [1] and upon the combination of the rhodium complexes with transition elements of the beginning of the periods [2]. In order to obtain catalyst models, we synthesized rhodium complexes, in which binuclear chromium sulfide fragments are used as the ligands. $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2RhL_2$ clusters [$L_2 = \pi\text{-}C_8H_{12}$ (I) and $(CO)_2$ (II)] were formed in the reactions of $(CpCrSCMe_3)_2S$ with $(\pi\text{-}C_8H_{12}RhCl)_2$ or $(Acac)Rh\cdot(CO)_2$ in benzene at 20 and 80°C, respectively. These clusters were isolated by crystallization from benzene—heptane or chromatography on alumina and characterized by x-ray diffraction structural analysis (Table 1, Figs. 1 and 2).

The unit cell parameters for (I) are as follows: a = 9.913(8), b = 13.994(11), c = 18.242(12) Å, α = 91.96(3), β = 95.91(2), γ = 106.24(2)°, Z = 4 (two independent molecules), space group $P\bar{1}$. The unit cell parameters for (II) are as follows: a = 16.966(5), b = 13.190(5), c = 17.885(6) Å, Z = 8, space group Pbca. In both clusters, the diamagnetic rhodium(I) atom is coordinated to two sulfur atoms of the antiferromagnetic $Cp_2Cr_2(SCMe_3)(S)_2$ fragment, which has short Cr—Cr bonds [2.687(1) Å in (I) and 2.708(1) Å in (II)]. These bond lengths are almost the same as in starting $(CpCrSCMe_3)_2S$ (2.689 Å) [3]. We should note the augmentation of the ligand environment of the Rh(I) atoms to typical square planar due to the C=C double bonds [1.395(9) Å] of coordinated 1,5-cyclooctadiene in (I) located perpendicularly to the plane of the RhS_2 group or two CO groups in cluster (II). In addition, extremely elongated Rh—Cr bonds are formed [3.018(1) and 3.010(1) Å in (I) and 3.010(1) and 3.134(1) Å in (II)]. This is apparently a consequence of the electronic features of Rh(I) since the Co(I) atom in the $Cp_2Cr_2(SCMe_3)\cdot(\mu_3\text{-}S)Co(CO)_2$ cluster (III), which is analogous to (II), has a tetrahedral environment and forms short Co—Cr bonds (2.579 and 2.592 Å); the Cr—Cr bond is also short (2.617 Å) [3]. We should note that, despite the relative antibonding nature of the Cr—Cr and Rh—Cr bonds in (II) in comparison with (III), there is a marked enhancement of the antiferromagnetic exchange interactions in (II): μ_{ef} drops from 0.78 to 0.58 B. m. in going from 295 to 80 K, which is described in the framework of the dimeric Heisenberg—Dirac—Van Flack model [4] with exchange parameter $-2J = 592\ cm^{-1}$ (2% monomer impurity, 4% mean-square error) in comparison to 530 cm^{-1} in the case of cluster (III) [3].

EXPERIMENTAL

All the operations in the synthesis of (I) and (II) were carried out in a pure argon atmosphere in absolute solvents. The starting $(\pi\text{-}C_8H_{12}RhCl)_2$ [5], $AcacRh(CO)_2$ [6], and $(CpCrSCMe_3)_2S$ complexes [7] were obtained according to reported procedures. The IR spectra

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N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 474-477, February, 1988. Original article submitted April 10, 1987.