SYNTHESIS AND REACTIONS OF BIS(BENZYLCHROMIUMTRICARBONYL)MERCURY

G. A. Razuvaev, A. N. Artemov,
T. G. Kasatkina, and E. N. Poselenova

UDC 542.91 : 541.49 : 547.1'13

Presently, much attention is being focused on the study of heteroorganic derivatives of arylchromiumtricarbonyls. Detailed studies [1-5] of synthetic methods and properties of arylchromiumtricarbonyl derivatives of mercury have been reported. In the present investigation the synthesis and the physical and chemical properties of chromiumtricarbonyl complexes of dibenzylmercury (DBM) are studied.

Preliminary studies idicate that the reaction of $Cr(CO)_6$ with $(C_6H_5CH_2)_2Hg$ in a 1 : 1 diglyme–octane mixture takes place with considerable decomposition of the organomercury compound, resulting in a complex mixture of arylchromiumtricarbonyls. Consequently, to achieve our goal the reaction of DBM with triammoniumchromiumtricarbonyl $(NH_3)_3Cr(CO)_3$ at a much lower temperature was carried out. The reaction was carried out in boiling dioxane in a ratio of 1 : 2. Copious ammonia was liberated and the reaction mass assumed an intense yellow coloration. Yellow crystals of bis(benzylchromiumtricarbonyl)mercury (I) were obtained in 65% yield upon cooling the reaction mixture.

$$(PhCH_2)_2Hg + 2(NH_3)_3Cr(CO)_3 \rightarrow \underset{(I)}{[(CO)_3CrPhCH_2]_2Hg} + 6NH_3$$

Compound (I) is a lemon-yellow crystalline solid, stable in air and decomposing at 214°C, readily soluble in acetone, hot dioxane, dimethoxyethane, and diglyme, less soluble in $CHCl_3$, and insoluble in n-alkanes. PMR spectrum in DMSO-d_6 shows a singlet at 2.06 ppm and a poorly resolved multiplet at 5.1-5.9 ppm (relative intensity 2: 5), which is attributed to the methylene protons and the phenylchromiumtricarbonyl groups. Elemental analysis and IR and NMR spectra confirm the structure of (I) as a π-complex in which the aromatic rings of DBM are coordinated with two chromiumtricarbonyl groups. Further confirmation of the structure of (I) was obtained by investigating the reactions of this compound.

It is known that aromatic compounds of mercury readily react with halogen with the formation of aryl halides and salts of mercury [6]. The reaction of (I) with I_2 was carried out in a solution of dimethoxyethane at −45°C. By the dropwise addition of I_2 in dimethoxyethane to a vigorously stirred solution of (I) in dimethoxyethane, rapid decolorization of the iodine occurred and the reaction was completed upon the addition of 2 moles of I_2. By carrying the above reaction at lower temperature no decomposition of the arylchromiumtricarbonyl structure occurred. Practically no CO was liberated in the reaction. An orange arylchromiumtricarbonyl complex (II) was isolated from the mixture in 79% yield.

$$(I) + 2I_2 \rightarrow \underset{(II)}{2(CO)_3CrPhCH_2I} + HgI_2$$

Compound (II) is an orange crystalline compound with mp 79-81°C. Elemental analysis and IR and PMR spectra (singlet at 4.04 ppm and a multiplet with center at 5.21 ppm) correspond to the proposed structure. This method of preparing (II) has advantages since iodine derivatives of arylchromiumtricarbonyls could not be obtained directly from $PhCH_2I$ and $Cr(CO)_6$.

The majority of organomercuric compounds are easily reduced to metallic mercury and the appropriate hydrocarbons. It was shown [1] that $LiAlH_4$ did not decompose the arylchromiumtricarbonyl structure but resulted in the substitution of mercury by hydrogen. The action of excess $LiAlH_4$ on (I) in ether at ~ 20°C resulted in the isolation of metallic mercury from the mixture. After hydrolysis of the filtrate with dilute H_2SO_4 (1 : 4) and removal of the ether, toluenechromiumtricarbonyl was obtained in 69% yield, which was identified by TLC and GLC.

$$(I) + 2LiAlH_4 \rightarrow 2(CO)_3CrPhCH_3 + Hg$$

One of the simplest methods of obtaining organomercuric salts is the double decomposition of fully substituted derivatives of mercury with salts or oxides of mercury.

Institute of Chemistry, Academy of Sciences of the USSR, Gorky. N. I. Lobachevskii Scientific-Research Institute of Chemistry, Gorky State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1131-1134, May, 1982. Original article submitted July 24, 1981.

0568-5230/82/3105-1008$07.50

Benzylchromiumtricarbonylmercury chloride (III) was synthesized by reaction of (I) with $HgCl_2$.

$$\text{(I)} + HgCl_2 \rightarrow 2\ \underset{\text{(III)}}{(CO)_3CrPhCH_2HgCl}$$

The reaction was carried out in n-butanol with an excess of $HgCl_2$ for 8 h at 80°C. From this reaction (III) was isolated in 76% yield. IR spectra, elemental analysis, and results of the reaction with iodine confirm structure (III). Compound (III) is a yellow crystalline substance, decomposing at 140°C and relatively stable in air as a solid. It is soluble in acetone and dimethoxyethane, moderately soluble in benzene, and insoluble in normal alkanes.

Metal halides, in contrast to mercury salts, do not form stable organometallic compounds, but homolytic cleavage occurs at the C−Hg bond followed by substitution at the Hg atom with halogen in the reaction of $CuCl_2$ [7], or with hydrogen in the case of $CoCl_2$ and $FeCl_3$ [8]. It is known that diphenylmercury [7], DBM [9], and bis(phenylchromiumtricarbonyl)mercury [5] react with $CuCl_2$ to give organochlorine compounds. The reaction of (I) with $CuCl_2$ was carried out in dimethoxyethane at −10°C and 80°C, and of (I) and $CuCl_2$ in 1 : 2 and 1 : 4 molar ratios, respectively. At −10°C and a molar ratio of 1 :2 for (I) and $CuCl_2$, CO was not liberated, but a white precipitate of Cu_2Cl_2 was obtained. From the filtrate two yellow compounds were isolated which were characterized by their solubility in n-hexane. The n-hexane-soluble compound was characterized as benzylchromiumtricarbonyl chloride (IV) on the basis of elemental analysis, GLC, IR spectra, and melting point, and synthesized independently by the procedure given in [10]. The n-hexane-insoluble compound was characterized as compound (III) on the basis of its properties. Therefore, the reaction of compound (I) with $CuCl_2$ can be represented by the scheme

$$\text{(I)} + 2CuCl_2 \rightarrow \text{(III)} + \underset{\text{(IV)}}{(CO)_3CrPhCH_2Cl} + Cu_2Cl_2$$

The yields of compounds (III) and (IV) are 84 and 86%, respectively. Increasing the reaction temperature to 80°C did not change the course of the reaction and the molar ratios of the compounds. Increasing the quantity of $CuCl_2$ (1 : 4) led to significant oxidation of the arylchromiumtricarbonyl compounds by the excess $CuCl_2$ with the liberation of CO and the appearance of $PhCH_2HgCl$, $PhCH_2Cl$, and $CrCl_3$ in the reaction mixture.

Therefore, bis(benzylchromiumtricarbonyl)mercury can easily be prepared as a stable intermediate for the preparation of benzylchromiumtricarbonyl derivatives hitherto not easily accessible.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in Nujol. The PMR spectra of compounds (I)-(IV) were taken on a Tesla BS-487C (80 MHz) with a 10-15% solution in CCl_4 or acetone. The PMR spectra of (I) was taken in $(CD_3)_2SO$ with TMS as external standard.

Dibenzylmercury [11] was synthesized by the Grignard reaction. The solvents were dried from moisture and air. All reactions were carried under argon.

Bis(benzylchromiumtricarbonyl)mercury (I). In an apparatus provided with a condenser, magnetic stirrer, and a buret for measurement of gas evolution, 7.6 g (20 mmoles) of dibenzylmercury and 7.4 g (40 mmoles) of triammoniumchromiumtricarbonyl were placed in 60 ml of dioxane. The mixture was heated at 110°C for 5 h and the reaction mixture filtered through a sintered funnel with a layer of Al_2O_3. Upon cooling the filtrate, a yellow product precipitated which was washed with hot hexane and crystallized from dioxane to yield 3.95 g (65%) of (I). Found %: C 36.78; H 2.96; Cr 15.95. $C_{20}H_{14}Cr_2HgO_6$. Calculated %: C 36.64; H 2.11; Cr 15.87%. IR spectrum(ν, cm^{-1}): 1865 and 1950 (CO). PMR spectrum (δ, ppm); $(CD_3)SO)$: 2.06 (s, CH_2), 5.1-5.9 (m, $PhCr(CO)_3$).

Reaction of bis(benzylchromiumtricarbonyl)mercury with Iodine. To a solution of 0.65 g (1 mmole) of (I) in 100 ml dimethoxyethane stirred and cooled to −45°C was added dropwise a solution of 0.54 g (2 mmole) of iodine in 30 ml dimethoxyethane, and the reaction mixture was stirred for 30 min. The mixture was treated with an aqueous solution of $Na_2S_2O_3$ and extracted with 40 ml benzene. The benzene layer was separated and dried with Na_2SO_4; the solvent was evaporated under vacuum and the yellow residue recrystallized from hexane. The yield of (II) was 0.55 g (79%), mp 79-81°C. Found %: C 35.25; H 3.03; Cr 14.36; I 33.06%. $C_{10}H_7CrIO_3$. Calculated %: C 33.89; H 1.98; Cr 14.41; I 35.87%. IR spectrum (ν, cm^{-1}): 1865 and 1965 (CO). PMR spectrum (δ, ppm): (CCl_4): 4.04 (s, CH_2); 5.0-5.3 (m, $C_6H_5(CO)_3$).

Reaction of bis(benzylchromiumtricarbonyl)mercury with $LiAlH_4$. To a stirred solution of 1.31 g (2 mmoles) of (I) in 200 ml of anhydrous ether was added a fivefold excess of $LiAlH_4$ in 200 ml ether. Metallic mercury soon separates out. The mixture was heated for 1 h and filtered; the filtrate was treated with dilute

H_2SO_4. The ether layer was washed with water and dried with $CaCl_2$ and distilled. The yellow crystalline compound was sublimed under vacuum at 70°C. The yield of toluenechromiumtricarbonyl was 0.54 g (59%), mp 79°C (compared with [12]).

Reaction of bis(benzylchromiumtricarbonyl)mercury with $HgCl_2$. A mixture of 0.98 g (1.5 mmoles) of (I), 1 g of $HgCl_2$ (3.5 mmoles), and 120 ml n-butanol was kept in an evacuated glass sealed tube for 8 h at 85°C with periodic shaking. Upon cooling, yellow crystals separated. The product was washed with hexane and dried under vacuum. The yield of (III) was 1.05 g (76%), mp 140°C (with decomposition). Found %: C 26.90; H 2.41; Cl 8.43. $C_{10}H_7ClCrHgO_3$. Calculated %: C 25.01; H 1.51; Cl 7.68. IR spectrum (ν, cm^{-1}): 1875 and 1950 (CO).

Reaction of bis(benzylchromiumtricarbonyl)mercury with $CuCl_2$. a. A mixture of 1.31 g (2 mmoles) of (I) and 0.54 g (4 mmoles) anhydrous $CuCl_2$ in 120 ml dimethoxyethane was stirred for 1 h at −10°C. The white precipitate of Cu_2Cl_2 was filtered; the yield was 0.39 g (98%). The yellow filtrate was evaporated. The oily residue was dissolved in hexane and filtered, and the solvent was removed under vacuum. The yield of (IV) was 0.43 g (86%), mp 63-65°C (compared with [10]). The yellow residue insoluble in hexane was dried. The yield of (III) was 0.76 g (84%), mp 140°C (with decomposition).

b. The above reaction was carried out for 10 min at 80°C. The reaction products were isolated by a similar manner. The yield of (IV) was 0.42 g (81%); of (III), 0.58 g (79%); and of Cu_2Cl_2, 0.37 g (94%).

c. A mixture of 1.31 g (2 mmoles) of (I) and 1.08 g anhydrous $CuCl_2$ in 120 ml dimethoxyethane was stirred for 1 h at −10°C. The yield of (IV) was 0.41 g (39%); of (III), 0.19 g (20%); and of Cu_2Cl_2, 0.80 g (100%).

CONCLUSION

Bis(benzylchromiumtricarbonyl)mercury was synthesized by the reaction of dibenzylmercury with $(NH_3)_3Cr(CO)_3$ in boiling dioxane. Its reaction was studied with iodine, $LiAlH_4$, $HgCl_2$, and $CuCl_2$.

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