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Abstract

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DESTRUCTION OF CYCLOPENTADIENYL COMPOUNDS OF METALS BY BROMINE AND POTASSIUM HYPOBROMITE

The aim of the present work is to study the reaction of cleavage of the ring-metal bond in various cyclopentadienylmetal compounds under comparable conditions, with isolation of both the inorganic and the organic part of the molecule. Until now, cleavage of the ring-metal bond in cyclopentadienyl derivatives of metals has not been widely studied. Data are available only for ferrocene and its derivatives ([1]-[4]), and also for cobalticinium ([5]), in the latter case the action of hydrochloric acid completely destroying the organic part of the molecule. See also the work of Grignard and Courtot ([6], [7]) on C_5H_5MgBr. We succeeded, by bromination under mild conditions, in carrying out the cleavage of $(C_5H_5)_2Fe$, pentaethanodiferrocene ([8], [9]), $(C_5H_5)_2Hg$, and C_5H_5Tl with preservation of the organic part of the molecule. Dicyclopentadienylmercury is thermally unstable at temperatures above $-15°$. Therefore the reaction with bromine was carried out at -17 to $-20°$ for all the compounds studied. Under these conditions only $C_5H_5Br_3$ is formed, and the endpoint of the reaction with Br_2 becomes very sharp.

Pentaethanodiferrocene, besides $C_5H_5Br_3$, also forms a bromide corresponding to the central part of the molecule. The latter evolves HBr at room temperature during the course of the experimental work-up. The structure of the bromide obtained will be studied further. Analysis and molecular weight give the gross formula $C_{20}H_{21}Br_7$. In the products of the bromination reaction of ferrocene (I) and pentaethanodiferrocene (II), along with the bromides $C_5H_5Br_3$ and $C_{20}H_{21}Br_7$, salts of the cations I and II, insoluble in the reaction mixture, were also found (cf. the work of Riemschneider ([10])). These salts are not destroyed by bromine under the experimental conditions; by reduction of them I and II were recovered, and the yield of bromide was calculated on the ferrocene or pentaethanodiferrocene that had reacted, respectively. For I, II, and C_5H_5Tl the yield of $C_5H_5Br_3$ is about 50% of theory. In the case of bromination of $(C_5H_5)_2Hg$ the yield of $C_5H_5Br_3$ is close to quantitative.

We were also the first to carry out the destruction of cyclopentadienyl compounds of Fe, Hg, and Tl by a solution of potassium hypobromite. In this case cleavage of the ring-metal bond and bromination of the organic part of the molecule to hexabromocyclopentadiene C_5Br_6 occur. On the action of potassium hypobromite on cyclopentadiene under comparable conditions, see ([11]) and ([12]). The reaction temperature was maintained at about 0°. The yields of C_5Br_6 are close to the yield described for cyclopentadiene.

In the reaction products of $(C_5H_5)_2Fe$, along with C_5Br_6, C_5HBr_5 was also found. Small amounts of this bromide are also formed in the destruction of C_5H_5Tl. In contrast to potassium hypobromite, potassium hypoiodite does not react with ferrocene under analogous conditions. It is known that the ferrocene system is preserved upon oxidation of acyl derivatives of ferrocene with iodine in pyridine on heating ([13]-[15]), and also upon the action of iodine on ferrocene and its derivatives ([16]).

Reaction of $(C_5H_5)_2Hg$ with Br_2. To a solution of 0.33 g of $(C_5H_5)_2Hg$ in 20 ml of *n*-heptane and 3 ml of benzene, cooled to −20°, 4 ml of a heptane solution of bromine containing 0.157 g of bromine per 1 ml of solution was added dropwise, the temperature of the bath being maintained within −17-20°. Absorption of bromine was instantaneous. At the same time, a cream-colored finely crystalline precipitate forms on the walls of the flask (further addition of bromine gives an unchanged [[unclear: continuation cut off at page bottom]]).

disappearing coloration in the solution). The resulting colorless solution was decanted, the precipitate was washed twice with *n*-heptane (10 ml each), which was combined with the main solution. Weight of the air-dry precipitate of $HgBr_2$: 0.35 g. The heptane was evaporated. Weight of the crystalline cream-colored residue: 0.57 g. It rapidly darkens in the light (!). It has the characteristic odor of unsaturated bromides. M.p. 47-55°. After chromatography on SiO_2 ($d = 12$ mm, $h = 300$ mm, from a heptane : benzene mixture 8 : 2, then heptane : benzene 1 : 1), protected from light, 0.41 g of transparent, colorless, strongly light-refracting crystals with m.p. 63-64° was obtained.

Found, %: C 19.83, 19.86; H 1.71, 1.67; Br 78.65, 78.30
$C_5H_5Br_3$. Calculated, %: C 19.69; H 1.65; Br 78.50

The yield of tribromocyclopentene was 93%. At the experimental temperature of −2-5°, 6 ml of bromine solution was absorbed, and after chromatography on SiO_2 ($d = 12$ mm, $h = 300$ mm, from heptane), isomers of pentabromocyclopentane were obtained, m.p. 96-101° and 105-107°; yield 49%.

Reaction of C_5H_5Tl with Br_2. To a suspension of 1.64 g of freshly sublimed H_5C_5Tl in 20 ml of *n*-heptane and 3 ml of benzene, cooled to −20°, with efficient stirring and at a temperature of −17-20°, 6 ml of a heptane solution containing 0.157 g of bromine per 1 ml of solution was slowly added dropwise, at such a rate that the solution became decolorized before addition of the next portion of bromine. After this, absorption of bromine practically ceased. The resulting solution was decanted; the precipitate in the flask was washed with heptane and benzene, which were combined with the main solution. Removal of the solvents protected from light gave 0.4 g of bromide. The precipitate from the flask was washed with ether; evaporation of the ether gave 0.18 g of a brown resinous nonflammable residue containing Tl. The residue after ether treatment weighed 1.75 g. Sublimation returned 0.64 g of C_5H_5Tl. Chromatography of the bromide on SiO_2 ($d = 12$ mm, $h = 300$ mm, from a heptane : benzene mixture 8 : 2, then heptane : benzene 1 : 1), protected from light, gave 0.25 g of $C_5H_5Br_3$ with m.p. 57-59°; yield 35%; on repeated chromatography, a bromide with m.p. 62.5–64° was obtained.

Found, %: C 19.52, 19.82; H 1.62, 1.69; Br 78.16
$C_5H_5Br_3$. Calculated, %: C 19.69; H 1.65; Br 78.50

At a temperature of +20°, pentabromocyclopentane was obtained, m.p. 103-104° (from alcohol), giving no melting-point depression with an authentic sample; yield 51%.

Reaction of $(C_5H_5)_2Fe$ with Br_2. To a solution of 0.49 g of $(C_5H_5)_2Fe$ in 20 ml of *n*-heptane and 3 ml of benzene, cooled to −20°, a heptane solution of bromine containing 0.157 g of bromine per 1 ml was added dropwise at the rate of bromine absorption; immediately, formation of a ferricinium salt precipitate began, at first blue-green, then changing to khaki color. In total, over 1 h at −17-20°, 10.5 ml of solution was added, after which absorption of bromine ceased. The precipitate was filtered off protected from moisture and washed on the filter with abs. benzene until the bromine color disappeared in the wash solution, while the color of the precipitate changed back to the original one and the volume of the precipitate noticeably decreased.

The organic solutions were evaporated to dryness protected from light. Weight of the residue: 0.27 g. Chromatography of the bromide on SiO_2 ($d = 12$ mm, $h = 300$ mm, from a heptane : benzene mixture 8 : 2, then heptane : benzene 1 : 1) gave 0.14 g of $C_5H_5Br_3$ with m.p. 58-61°. A mixed sample with an authentic sample gave no melting-point depression; a mixed sample with $C_5H_5Br_5$ gave a depression (12°). The precipitate obtained from the reaction was dissolved in dilute aqueous methanol, washed with benzene and ether; evaporation of the ether–benzene layer gave 0.02 g of resin containing no iron. The washed aqueous solution was reduced with Na_2SO_3; $(C_5H_5)_2Fe$ was extracted with benzene; the benzene solution was dried with Na_2SO_4 and evaporated. 0.27 g of $(C_5H_5)_2Fe$ was recovered. The yield of bromide based on reacted ferrocene was 43%.

Reaction of pentaethynodiferrocene with bromine. 0.6 g of pentaethynodiferrocene was dissolved in 3 ml of benzene, and then with stir-

20 ml of *n*-heptane was added with stirring. The resulting suspension was cooled to −20° with stirring. At −17-20° over 1 h 15 min, 14 ml of a heptane solution containing 0.157 g of bromine per 1 ml was added. Standing for 20 min does not lead to disappearance of the excess bromine in the solution. The precipitate of salts was filtered off with protection from moisture and washed repeatedly on the filter with heptane, then 3 times with a heptane + benzene mixture 8 : 2 and once with ether. The resulting solutions must be kept on solid CO_2. The residue was completely dissolved in 150 ml of methanol. The resulting dark-

brown solution was rapidly diluted to 1.5 l with water and, after addition of 50 g of Na_2SO_4, extracted 3 times with small portions of benzene and 5 times with ether. Then the blue-green aqueous solution was reduced with sodium sulfite and extracted with benzene and ether; evaporation of the latter after drying gave 0.30 g of the starting pentaethanoferrocene, purified by reprecipitation from ether into methanol. All the remaining organic solutions were combined and the solvents removed without heating, and when room temperature is reached, evolution of HBr is observed. The resulting yellow residue was exhaustively treated with 70% aqueous methanol. The resulting solution was evaporated, and the residue was extracted with ether; after removal of the ether, the weight of crystalline $C_5H_5Br_3$ was 0.22 g. After purification by chromatography (SiO_2, $d = 12$ mm, $h = 300$ mm, from a heptane : benzene mixture 8 : 2, then heptane : benzene 1 : 1), m.p. 60-62°. There is no depression of the melting point with authentic $C_5H_5Br_3$.

The residue after treatment with 70% methanol was treated with abs. methanol. Evaporation of the solution gave 0.24 g of a light-brown powder, which was washed with heptane; after recrystallization from abs. ethanol, m.p. 65-70° (with decomposition). A sample of the bromide solution (heptane : benzene 1 : 1) obtained in this way was checked for absence of pentabromocyclopentane and tribromocyclopentane by thin-layer chromatography (SiO_2, exposure time 10 min, layer thickness 1.5 mm, development with metallic iodine).

Found, %: C 26.67, 26.94; H 2.42, 2.62; Br 69.49, 69.43

Mol. wt. 760, 746 (benzene, cryoscopy). Gross formula $C_{20}H_{21}Br_7$. Yield of $C_5H_5Br_3$ based on pentaethanoferrocene reacted: 61% of theory.

Reaction of $(C_5H_5)_2Hg$ with KOBr. A solution of 0.34 g of $(C_5H_5)_2Hg$ in 20 ml of benzene was added to a reagent cooled to +2°, prepared from 20 ml of H_2O, 4.5 g of KOH, and 0.65 ml of Br_2. At 0-2° the reaction mixture was kept for 2 h with efficient mechanical stirring. 0.2 g of HgO was filtered off. The benzene layer was separated, and the aqueous layer was washed twice with benzene. The combined benzene solution was dried over Na_2SO_4.

Evaporation of the benzene gave 0.68 g of yellow crystals; after chromatography (SiO_2, $d = 12$ mm, $h = 100$ mm, from n-heptane), 0.60 g of bromide with m.p. 70-72° was obtained. Repeated chromatography gave C_5Br_6 with m.p. 86-86.5°.

Found, %: C 11.22, 11.05; Br 88.99, 89.09
C_5Br_6. Calculated, %: C 11.20; Br 88.80

There is no depression of the melting point with authentic C_5Br_6 ([12]). Yield 61%.

Reaction of C_5H_5Tl with KOBr. 18 g of KOH was dissolved in 80 ml of H_2O. The solution was cooled to +2°. With stirring, 2.5 ml of Br_2 was added so that the temperature of the reaction mixture was no higher than +3—+4°. The solution was cooled to +2°. In one portion, a suspension of 1.8 g of C_5H_5Tl in

15 ml of benzene was added. The reaction mixture was kept for 40 min at +2° with efficient stirring, during which a dark-brown powder of Tl oxide formed. The precipitate was filtered off, washed with benzene until the odor of C_5Br_6 disappeared, dried in air, and sublimed at 90-110°/1 mm Hg. On sublimation, C_5H_5Tl was not found. Weight 1.06 g. The benzene solution was separated from the aqueous layer; the latter was washed 3 times with benzene, which was combined with the main solution. The benzene layer was dried over Na_2SO_4 and evaporated. The residue consisted of dark-yellow crystals with a characteristic odor. Weight 1.95 g, m.p. 67-80°. By chromatography (SiO_2, $d = 12$ mm, $h = 300$ mm, from *n*-heptane), 1.32 g of bright-yellow

plates with m.p. 81-83°; repeated chromatography raises the m.p. to 86-87°. There is no depression of the melting point with an authentic sample of C_5Br_6. Yield 55%.

Reaction of $(C_5H_5)_2Fe$ **with KOBr.** To a solution of 18 g of KOH in 80 ml of H_2O at +2—+4° was added 2.5 ml (0.098 M) of Br_2, and then at +2° a solution of 0.32 g of $(C_5H_5)_2Fe$ in 20 ml of benzene was added. The mixture was kept at +2 —+15° with efficient stirring for 1.5 h; during the first 30 min no visible changes occurred; then the mixture darkened and a dark-brown precipitate separated; the increase in precipitate ceased 1 h-1 h 15 min after the beginning of the experiment. The precipitate was filtered off, washed with benzene, and dried in air. It does not burn, dissolves in HCl, and contains Fe^{3+}. The benzene solution was separated from the aqueous layer; the latter was washed three times with benzene, which was combined with the main solution.

The combined benzene solution was dried with Na_2SO_4 and evaporated. The weight of the crystalline yellow-orange residue was 2.70 g.

Chromatography of three portions of 0.9 g each (SiO_2, $d = 12$ mm, $h = 300$ mm, from *n*-heptane) gave 0.05 g of $(C_5H_5)_2Fe$; 0.26 g of C_5Br_6, m.p. 64-75°; and 0.80 g of a mixture of C_5Br_6 and C_5HBr_5. The dark-violet chromatographic columns were washed with benzene, methanol, water, and then with a concentrated aqueous solution of Na_2SO_3 acidified with H_2SO_4. The reduced columns acquired an amber-yellow color. Ferrocene was extracted from the adsorbent with ether. On evaporation of the ether, the weight of $(C_5H_5)_2Fe$ was 0.13 g. The mixture of C_5Br_6 and C_5HBr_5 was separated by chromatography on a two-stage column (SiO_2, $d_1 = 25$ mm, $d_2 = 12$ mm, $h = 600$ mm, from *n*-heptane), giving 0.50 g of C_5Br_6, m.p. 85-86°, and 0.15 g of light-yellow soft crystals, m.p. 100-102°. See ([12]). The depression of the melting point of the mixture with C_5Br_6 is about 50°.

Found, %: Br 87.32
C_5HBr_5. Calculated, %: Br 86.75

Thus, 60% of $(C_5H_5)_2Fe$ was recovered. The total yield of bromides, based on the ferrocene that reacted, was 71%.

Attempted destruction of $(C_5H_5)_2Fe$ **with a solution of KOJ.** To a solution of 18 g of KOH in 80 ml of H_2O at +2–+4° was added 12.5 g (0.098 M) of J_2, the salt formed partly precipitating. Then, at 2°, a solution of 0.32 g of $(C_5H_5)_2Fe$ in 20 ml of benzene was added. The mixture was kept at +2–+15° with efficient stirring for 1.5 h, with no changes occurring. The benzene solution was separated, the aqueous layer was acidified, and iodine was extracted with chloroform. Inorganic iron was not detected. The benzene solution was washed with water, with a dilute solution of $Na_2S_2O_3$, again with water, dried with Na_2SO_4, and evaporated. The Beilstein test for halogen was negative. The weight of recovered ferrocene was 0.32 g. M.p. 170-172°. It gives no depression of the melting point with authentic $(C_5H_5)_2Fe$. After chromatography of 0.25 g of substance (Al_2O_3, $d = 12$ mm, $h = 150$ mm, from *n*-heptane), the weight was 0.22 g. M.p. 171.5-172.5°.

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