PREPARATION OF BISARENE COMPLEXES OF CHROMIUM FROM 1,4-DIPHENYLBUTANE

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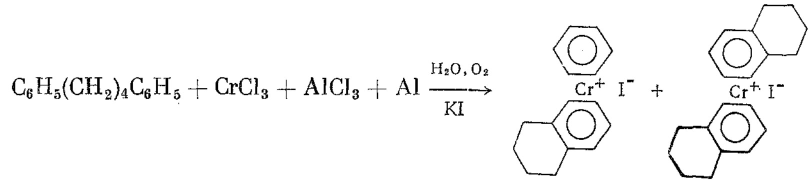
The reaction of aromatic hydrocarbons with $CrCl_3$ in the presence of $AlCl_3$ and Al dust is the most convenient method for the synthesis of the bisarene complexes of chromium (BACC) [1, 2]. In the present paper we studied the behavior of 1,4-diphenylbutane (DPB) under the conditions of the Fischer reaction. Besides the BACC, containing DPB as the ligand, the formation of complexes, containing the products of the isomerization and transalkylation of DPB as ligands, could also be expected, similar to the situation that exists in the synthesis of complexes from the alkylbenzenes [2, 3]. It was found that a complete isomerization of DPB to tetralin occurs under the conditions of forming the BACC.

When a mixture of DPB, $CrCl_3$, $AlCl_3$, and Al is heated in refluxing octane a mixture of the BACC was obtained, which were oxidized to the corresponding cations and isolated as the iodides (total yield equals ~40%). Based on the TLC data, the mixture contains four compounds. Two principal compounds were isolated by preparative TLC, namely the benzoyltetralinchromium (BzTC) and bis(tetralin)chromium (BTC) iodides:



The BzTC and BTC iodides were reduced to the neutral complexes. The structure of the BzTC was proved by mass spectrometry. An intense peak with a mass number of 262 corresponds to the molecular ion, while the peak with m/e 131 corresponds to the doubly charged molecular ion 262. Peaks with m/e 132 and 78 are also present in the mass spectrum, which correspond to the molecular ions of tetralin and benzene. The peaks with m/e 184 and 130 correspond to the ions that are formed as a result of cleaving the benzene and tetralin ligands. The intensity of the first of these peaks is eight times higher than that of the second, which is in agreement with the data given in [4-6] regarding the strengthening of the arene –chromium bond when alkyl groups are inserted in the benzene ring.

The oxidative cleavage of the BzTC and BTC iodides gave benzene and tetralin in the first case, and tetralin in the second case (based on the GLC data):

$$[(C_{10}H_{12})Cr(C_6H_6)]^+ \xrightarrow{HCl,\,H_2O_2} C_{10}H_{12} + C_6H_6$$
$$[(C_{10}H_{12})_2Cr]^+ \xrightarrow{HCl,\,H_2O_2} 2C_{10}H_{12}$$

BTC iodide was obtained by counter synthesis from tetralin. Previously it had been synthesized from benzenebiphenylchromium by the exchange of the ligands in the presence of $AlCl_3$ [7].

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By means of a special experiment it was established that DPB is isomerized completely to tetralin under the reaction conditions. Attempts to avoid the isomerization by running the reaction under milder conditions proved unsuccessful. Thus, the same tetralin complexes are formed, but in lower yields, when the reaction is run in refluxing hexane.

EXPERIMENTAL

The GLC analysis of the cleavage products of the complexes was run on an Aerograph Model 1860-4 chromatograph, the analysis being run in parallel on 2 stainless steel columns (1.5 × 6 mm), which were filled with Varoport (100-120 mesh) containing 3% of SE-30. The detection was based on the heat conductivity. The helium flow rate was 40 ml/min. The first 3 min of the analysis were run at 50°, and then at 50-200° (rate of temperature rise equals 8 deg/min).

The mass spectrum of benzenetetralinchromium (m/e, relative height of peak, %, ion): 52, 100, Cr^+; 78, 15.8; $C_6H_6^+$; 91, 5.5, $C_7H_7^+$; 104, 9.1, $C_6H_4(CH_2)_2^+$; 130, 6.5, $C_6H_6Cr^+$; 131, 6.7, M^{2+}; 132, 5.8, $C_6H_4(CH_2)_4^+$; 184, 51.2, $C_6H_4(CH_2)_4Cr^+$; 262, 26.3, M^+, was obtained on a Varian–MAT CH-8 instrument at an ionizing electron energy of 70 eV, and was recorded by a loop oscillograph with a linear scanning of the magnetic field.

All of the experiments were run in an argon atmosphere.

Preparation of 1,4-Diphenylbutane. To a solution of 22.7 g of phenyllithium (from 62.7 g of bromobenzene [8]) was added in 1 h a solution of 29.2 g of 1,4-dibromobutane in 20 ml of ether. After stirring at ~20° for 10 h the mixture was hydrolyzed with water, and the ether layer was evaporated. After recrystallization from petroleum ether we obtained 20.4 g (57% yield) of DPB, mp 51-52°; cf. [9].

Preparation of Bisarene Complexes of Chromium from DPB. A stirred mixture of 5.3 g of $CrCl_3$, 7.7 g of $AlCl_3$, 0.8 g of Al dust and 7.0 g of DPB in 150 ml of octane was refluxed for 5 h. To the mixture after cooling were added 150 ml of methanol, 32 g of KOH in 150 ml of water, and 10 g of formamidinesulfinic acid. The mixture was stirred vigorously for 1 h. The organic layer was separated, and 50-70 ml of benzene was added to the aqueous solution. After stirring for 1 h the benzene layer was separated and portions of benzene were added until the benzene layer ceased to be colored. Then 50 ml of water was added to the combined organic fractions, and a stream of air was passed through the mixture until the color had been removed completely from the organic layer. The aqueous solution was treated with dry KI until precipitation was complete. The orange precipitate of the iodides of the bisarene complexes of chromium was filtered (2.5 g). Another 2.8 g of mixed iodides was extracted from the mother liquor with chloroform.

Based on the data of TLC on Al_2O_3 in the system: acetone–ethanol (12 : 1) the mixture of reaction products consists mainly of the bis(tetralin)chromium and benzenetetralinchromium iodides (R_f 0.69 and 0.55, respectively). In addition, two other compounds with close R_f values (~0.3) are present in the mixture. The pure compounds were isolated by preparative TLC in the indicated system. The compounds were deposited on the Al_2O_3 in chloroform, and were extracted with ethanol. From 2.5 g of the mixture we isolated 1.2 g (8%) of BTC iodide and 0.95 g (7%) of BzTC iodide as orange crystals, and also 0.1 g of a mixture of the other two products as a brownish oil. The BTC and BzTC iodides were recrystallized from absolute ethanol. Found: C 54.18; H 5.63; Cr 11.87; I 28.85%. $C_{20}H_{24}CrI$. Calculated: C 54.18; H 5.46; Cr 11.72; I 28.64%. Found: C 49.41; H 4.72; Cr 13.49; I 32.52%. $C_{16}H_{18}CrI$. Calculated: C 49.37; H 4.66; Cr 13.36; I 32.61%.

The reduction of 0.25 g of BTC iodide with 0.5 g of formamidinesulfinic acid in aqueous methanol solution, in the presence of 1.9 g of KOH, gave bis(tetralin)chromium as an orange oil in quantitative yield. In a similar manner, from 0.45 g of BzTC iodide was obtained 0.4 g of the neutral complex, which after sublimation at 100° ($9 \cdot 10^{-3}$ mm) represented a bronze solid with mp 56-59° (Ar).

The oxidative cleavage of the iodides was accomplished by shaking 0.05 g of the iodide with 1 ml of 15% HCl solution and 2-3 drops of H_2O_2 under a layer of octane (1 ml). The octane solutions were analyzed by GLC.

In a special experiment a mixture of the bisarene complexes of chromium (from 3.5 g of DPB) was subjected to oxidative cleavage. Based on the GLC data, the cleavage products contained tetralin, benzene, and two unidentified substances as an impurity; DPB was absent. DPB was also not detected in the organic layer that remained after converting the complexes to the cationoid form.

Preparation of Bis(tetralin)chromium Iodide from Tetralin. A stirred mixture of 0.9 g of $CrCl_3$, 1.34 g of $AlCl_3$, 0.14 g of Al and 1.6 g of tetralin in 35 ml of octane was refluxed for 5 h. After the reaction mixture was worked up by the above described procedure we obtained 0.77 g (30%) of BTC iodide, which, based on the TLC data, was identical with that obtained from DPB.

CONCLUSIONS

1,4-Diphenylbutane reacts with chromium chloride in the presence of $AlCl_3$ and Al in refluxing octane to give bis(tetralin)chromium and benzenetetralinchromium.

LITERATURE CITED

1. E. O. Fischer and J. Seeholzer, Z. Anorg. Allgem. Chem., 312, 244 (1961).
2. G. Huttner, E O. Fischer, and C. Elschenbroich, J. Organometal. Chem., 3, 330 (1965).
3. G. G. Devyatykh, V. A. Umilin, and Yu. V. Zverev, Izv. Akad. Nauk SSSR, Ser. Khim., 1689 (1969).
4. G. G. Devyatykh, N. V. Larin, and P. E. Gaivoronskii, Zh. Obshch. Khim., 39, 1823 (1969).
5. G. G. Devyatykh, N. V. Larin, and P. E. Gaivoronskii, Dokl. Akad. Nauk SSSR, 198, 585 (1971).
6. G. E. Herberich and J. Müller, J. Organometal. Chem., 16, 11 (1969).
7. F. Hein and K. Kartte, Z. Anorg. Allgem. Chem., 307, 22 (1960).
8. T. V. Talalaeva and K. A. Kocheshkov, Methods of Heteroorganic Chemistry: Li, Na, K, Rb, and Cs [in Russian], Nauka (1971), p. 152.
9. T. Midgley, A. Henne, and H Leicester, J. Amer. Chem. Soc., 58, 1961 (1936).