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THE REACTIONS OF BIS-ARENE-CHROMIUM(O) WITH ALKYL HALIDES*

G. A. Razuvaev and G. A. Domrachev
Akademiya Nauk SSSR, Bolshaya Kaluzhskaga 14, Moscow, U.S.S.R.

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Abstract—The reaction of bis-arene-chromium(O), Arene$_2$Cr^0, with alkyl halides, RX, has been investigated; RX was found to be an electrophilic reagent in respect to Arene$_2$Cr^0. Principally the reaction is the oxidation of Arene$_2$Cr^0 by RX with the formation of Arene$_2$CrX and hydrocarbons. The structures of the hydrocarbons formed are determined by the nature of the alkyl radical in RX. In the case of saturated alkyls disproportionation products are formed, and with conjugated alkenyls and aralkyls products of dimerization of radicals are formed. The secondary paths of these reactions are (1) the decomposition of the sandwich molecule with the formation of the salts of chromium and arene, and (2) the evolution of elementary hydrogen. It has been shown by the deuterium label that at least 16·5% of the hydrogen evolved is derived from the Arene$_2$Cr^0. Probably the reaction of Arene$_2$Cr^0 with RX consists of two competing reactions (1) the reversible oxidation of Arene$_2$Cr^0 by alkyl halide, forming Arene$_2$CrX and R·, which gives the radical products, and (2) the alkylation of Arene$_2$Cr^0 by RX with the evolution of H_2.

When a mixture of Arene$_2$Cr^0 and an alkyl halide (RX) is heated, exposed to light or allowed to remain at room temperature (in some cases), yellow-red-brown precipitates or oils are produced. On exposure to air or during hydrolysis the product is partially decomposed, Arene$_2$CrX and chromium being formed. The rate of the reaction depends on the halogen and the alkyl radical in RX and as an example the reaction of bis-ethylbenzene-chromium with n-butyl halides was investigated. With n-butyl iodine the reaction is complete in half an hour, with n-butyl bromide the reaction requires several hours and in the case of n-butyl chloride under the same conditions no reaction takes place. Similar results were obtained with other alkyl halides (ethyl, phenyl) and in the case of the halomethanes, CH_2I_2 reacts rapidly and with evolution of heat at room temperature, but CH_2Cl_2 reacts only slowly and $CHCl_3$ and CCl_4 react with (EtPh)$_2$Cr^0 with violence.

Depending on the alkyl radical the rate of the reaction is decreased in the following order: $CH_3 > C_2H_5 > n\text{-}C_3H_7 > n\text{-}C_4H_9 \geqslant iso\text{-}C_5H_{11}$. Iodobenzene reacts as well as the n-alkyl iodides, benzyl chloride reacts with (EtPh)$_2$Cr^0 quickly on mild heating or on standing and triphenylmethyl chloride reacts readily in a solution of benzene or nitromethane. The reaction of allyl bromide with (EtPh)$_2$Cr^0 proceeds violently at room temperature. In all experiments, the volatile organic products were investigated by vapour-phase chromatography.

During the reaction, the Arene$_2$Cr^0 is oxidized by the RX, the chief products being bis-arene-chromium (I)-halide (in yields up to 95%) and hydrocarbons, the structures of which depend on the nature of the alkyl radical (R). The alkyl radicals from the halides undergo either disproportionation or dimerization.

In the reaction of (EtPh)$_2$Cr^0 with ethyl iodide at 70° without a solvent, the gases evolved consisted of ethane (48%) and ethylene (37%), the total yield of gases (based on ethyl iodide) being 70–84%. No butane was detected in this reaction. In similar

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reactions with n-C_4H_9I only n-butane was found, and with iso-$C_5H_{11}I$ only iso-pentane was observed. The products of dimerization of alkyls (R_2) were not observed in the yields of $\geqslant 1\%$, nor were olefins found, but the formation of small amounts of a white organic material, which could be a polymer, was observed.

The reaction of iodobenzene with $(EtPh)_2Cr^0$ (100°, 15 min) produced benzene, ethylbenzene and a small amount of biphenyl.

The dimerization of radicals was observed in the case of the reactions with allyl, benzyl and triphenylmethyl halides.

The reaction of allyl bromide with $(EtPh)_2Cr^0$ is complete in a few seconds at $\sim 20°$, and $(EtPh)_2CrBr$ and biallyl are formed in yields of ~ 100 and $\sim 80\%$, respectively, propylene was not found.

The reaction with benzyl chloride proceeded according to the general equation (1).

$$3\,(EtPh)_2Cr^0 + 4\,PhCH_2Cl \rightarrow \underset{(73\%)}{2\,(EtPh)_2CrCl} + \underset{(73\%)}{CrCl_2} + \underset{(75\%)}{2\,EtPh} + \underset{(48\%)}{2\,(CH_2Ph)_2} \quad (1)$$

The reaction of triphenylmethyl chloride with $Arene_2Cr^0$ in benzene gives triphenylmethyl radicals (proved by electron spin resonance).

It can be seen from the data presented that the reactions of $Arene_2Cr^0$ with saturated alkyl and aryl halides give the ordinary radical products, in which RH is predominant, but conjugated alkenyl and aralkyl halides produce the dimerization products R_2. Secondary reactions are:

(1) The decomposition of the sandwich molecule with the formation of arene and salts of chromium (observed in some cases), and

(2) The evolution of elementary hydrogen (from traces up to 10–15% in the case of ethyl iodide) and observed in all cases.

The formation of chromium salts can be explained by the disproportionation reaction of the $Arene_2Cr^1X$ formed[1] or by further oxidation of this salt by RX as well as by HCl[2].

The presence of hydrogen as a product of the reaction may be readily explained by the formation of HX[2]. However, it was of interest to investigate the origin of the hydrogen and for this purpose the reaction of ethyl iodide with $(EtPh)_2Cr^0$, labelled by deuterium (containing 5·400 atomic per cent D) in the phenyl groups, was undertaken. The hydrogen evolved after the reaction contained 0·884 atomic per cent of deuterium corresponding to $\sim 16{\cdot}5\%$ of D in the hydrogen envolved.

Consequently, it may be concluded that RX behaves as an electrophilic reagent in respect to $Arene_2Cr^0$. In this connection, it was of interest to investigate the system from the point of view of standard redox potentials E^0.

Taking into account the reversibility of the process (2):

$$Arene_2Cr^+ + e \rightleftarrows Arene_2Cr^0, \quad (2)$$

it can be said that the half-wave polarographic reduction potentials $E_{\frac{1}{2}}$ of $Arene_2Cr^+$[3,4]

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and E^0 of this system are equal. It therefore follows, depending on the arene, that the value of $E^0 \cong -0{\cdot}7\text{–}0{\cdot}8$ v (NHE).

For the reaction (3) under similar conditions

$$CH_3X + e \leftrightarrows CH_3{\cdot} + X^-, \qquad (3)$$

there are the measured values[5] of $E^0 = -0{\cdot}74\text{–}0{\cdot}77$ v (NHE).

If (2) is subtracted from (3), the system in general terms becomes:

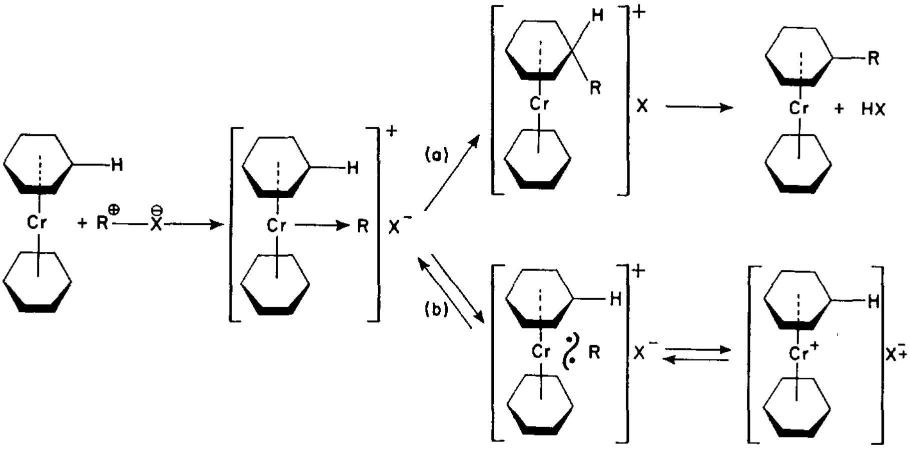
$$Arene_2Cr^0 + RX \rightleftarrows Arene_2Cr^+ + X^- + R{\cdot} \qquad (4)$$

The proximity of the values of E^0 for (2) and (3) supposes the reversibility of the oxidation of $Arene_2Cr^0$ by RX, the equilibrium position being defined by the difference of the values of E^0 for both (2) and (3).

The sequence of the increasing values of $-E_{\frac{1}{2}}$ of RBr:[6] $CH_3(-1{\cdot}59v)$, $C_2H_5(-2{\cdot}04v)$, $n\text{-}C_4H_9(-2{\cdot}23v)$, $n\text{-}C_8H_{17}(-2{\cdot}34v)$ corresponds to the observed rate of the reactions with $Arene_2Cr^0$.

Similarly, the values of $-E_{\frac{1}{2}}$ are decreased in RCl > RBr > RJ > and the ease of the course of the reactions is increased in RCl < RBr < RJ. The most readily reacting compounds are those, in which $|E^0|$ is equal to and, more especially, lower than $|E^0|$ of the sandwich compound (CH_2I_2, allyl bromide and iodide and others).

All these considerations support the conclusion that in the reactions with bis-arene-chromium (0) the alkyl halide behaves as an electrophilic reagent. Further the reactions investigated support the proposed scheme of the action of the electrophilic reagent (RX) on the sandwich[7] (5).



(5)

The formation of ordinary radical products (RH, R_2) and of $Arene_2Cr^+X^-$ confirms (5b), and the presence of H_2 in gases and the tests with the sandwich labelled by deuterium suppose the possibility of the course of the reaction (5a), that is the alkylation of bis-arene-chromium(O). However, the latter reaction proceeds to insignificant extent (~1–5 %). We consider that the extent of the reaction (5a) is determined and depends in the first place on the relation of the values of E^0 in the processes (2) and (3).

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