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INTERACTION OF CHROMIUM VAPOUR WITH BENZONITRILE AND BROMOBENZENE

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Summary

Bis(benzonitrile)chromium was isolated from the reaction of benzonitrile with chromium vapour. The major process was accompanied by cyclotrimerization of benzonitrile to form 2,4,6-triphenyltriazine. Phenyl bromide reacted with chromium to give insignificant amounts of cationic bis(arene)chromium compounds containing bromobenzene, diphenyl and benzene as ligands.

The interaction of arene with chromium vapour on the cooled walls of a reaction vessel under high vacuum is a convenient route to bis(arene)chromium compounds containing various substituents in the arene ligand [1—4]. Electron-withdrawing substituents hinder the arene—chromium complexation and the reaction is, as a rule, accompanied by side processes. In a number of cases, bis(arene)chromium complexes could not be obtained at all. Thus, attempts to synthesize bis(benzonitrile)chromium proved a failure [5]. Neither were organochromium compounds isolated from the reactions of chromium with phenyl bromide and phenyl iodide; these reactions only gave diphenyl and chromium halides [5]. On the other hand, fluoro- and chlorobenzenes form the corresponding complexes in 32 and 24% yields, respectively [5].

In this work we undertook a more detailed study of the reaction of atomic chromium with benzonitrile and bromobenzene. The application of a new separation technique has provided the possibility of isolating bis(arene)chromium compounds.

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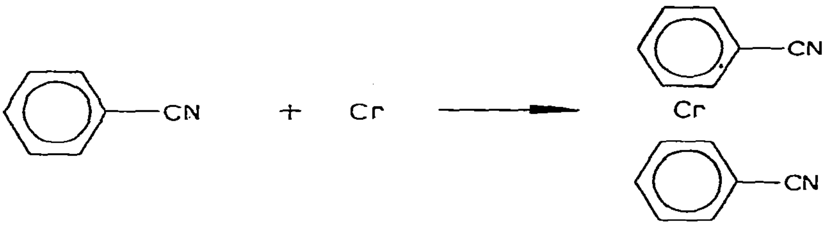
* Deceased.

Results and discussion

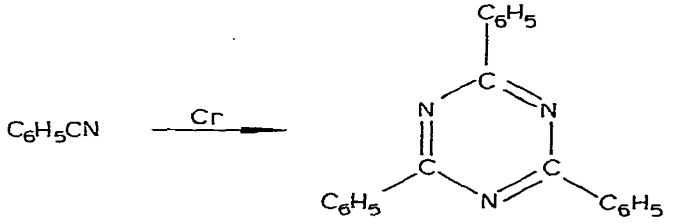
Chromium vapour reacts with benzonitrile to give a mixture of organochromium and organic products. Chromatography of the mixture on Al_2O_3 gave bis(benzonitrile)chromium in a 4% yield based on chromium vapour:



Bis(benzonitrile)chromium was characterized by elemental analysis and physico-chemical measurements. The IR spectrum of the complex contained an absorption band at 2221 cm^{-1} corresponding to the CN group stretching vibrations and the bands characteristic for the metal—ligand bonds in bis(arene)chromium complexes: 464 cm^{-1} (asymmetric tilting vibration) and 501 cm^{-1} (asymmetric stretching vibration). The mass spectrum of bis(benzonitrile)chromium contained a weak feature corresponding to the molecular ion (m/e 258), the ligand and chromium ions, and the fragment ions $(C_6H_5CNCr)^+$ and $(CrCN)^+$. The structure of the complex was also confirmed by the analysis of the products formed by photochemical decomposition of the complex in CH_2Cl_2: according to GLC, the complex only contained benzonitrile as a ligand.

The presence of two electron-withdrawing groups in the bis(benzonitrile)chromium molecule stabilizes the complex towards oxidation. The complex is air-stable for a long period of time. The half-wave potential of the reversible one-electron oxidation of bis(benzonitrile)chromium ($E_{1/2}$ -0.175 V vs SCE) is shifted by 0.625 V to positive values from that of unsubstituted dibenzenechromium.

The formation of the chromium complex is accompanied by cyclotrimerization of benzonitrile in the presence of atomic chromium: a small amount of 2,4,6-triphenyltriazine was isolated from the reaction. The product was identified by comparison of its melting point and TLC on Al_2O_3 with those of a reference specimen.



Cyclotrimerization of the triple carbon—carbon bond promoted by some atomic metals has been described earlier [6,7]. As far as we know this is the first example of C≡N trimerisation under the same conditions.

Thus, the major process in the interaction of benzonitrile with chromium vapour is the formation of the π-complex, although it is hindered by the presence of an electron-withdrawing group in the arene ring. In addition, benzonitrile undergoes cyclotrimerization under these conditions.

Bromobenzene mainly undergoes dehalogenation under the action of atomic chromium to give diphenyl and $CrBr_3$ [5]. The results obtained in this work show that certain amounts of the initial compound (bromobenzene) and the products of its transformation (benzene and diphenyl) react with chromium to give a mixture of bis(arene)chromium complexes in the oxidized form.

Experimental

The reaction of chromium vapour with arenes was run in a stationary stainless steel reactor. The reactor was equipped with a heated ligand inlet system, a resistively heated vaporizer, and a system for siphoning off reaction products. The isolation and purification of neutral bis(arene)chromium complexes were carried out under argon.

The IR spectrum of bis(benzonitrile)chromium in Nujol was registered on a UR-20 instrument. The mass spectrum was obtained on an MS-30 mass spectrometer. The conditions were: ionizing voltage 70 eV, inlet temperature 200° C. GLC analysis of the decomposition products of bis(arene)chromium complexes was performed using silicon OV-101 (5%) as immobile phase on chromosorb W-AW with flame-ionization detection.

Interaction of benzonitrile with chromium vapour

Chromium metal (0.9 g, 0.018 g-at) was introduced into the reactor in small portions in an electrically heated tungsten wire basket (42 A, 10 V). Simultaneously, benzonitrile vapour (ca. 100 g) was introduced into the reactor. The process was run for about 1.5 h. After that the reactor was warmed up and filled with argon. The products were siphoned off into a Schlenk tube. Excess benzonitrile was removed under vacuum, the residue was dissolved in benzene and chromatographed on alumina. A mixture of organic products (0.27 g) was eluted with petroleum ether. A yellow band was eluted with petroleum ether/benzene (1/1) to give, after evaporation, bis(benzonitrile)chromium (0.2 g). The complex crystallizes from benzene as brown needles, decomposing at 205—206° C.

Found: C, 65.47; H, 3.80; Cr, 20.81. $C_{14}H_{10}N_2Cr$ calcd.: C, 65.12; H, 3.88; Cr, 20.16%. Mass-spectrum, *m/e* (rel. int., %) (ion): 258 (1) (P^+), 154 (14) $(C_6H_5CNCr)^+$, 103 (13) $(C_6H_5CN)^+$, 78 (8) $(CrCN)^+$, 52 (100) $(Cr)^+$.

The mixture of organic products was repeatedly chromatographed on Al_2O_3. A small amount of an oily product (not identified) and traces of diphenyl (detected by TLC on Al_2O_3, comparison with authentic sample) were eluted with petroleum ether. Elution with benzene gave 2,4,6-triphenyltriazine, m.p. 233° C (Lit. m.p. 233—235° C [8]).

Interaction of bromobenzene with chromium vapour

Cocondensation of chromium vapour (0.6 g) and bromobenzene (100 g) was carried out as described above. The reaction mixture was filtered. The liquor did not contain any organochromium compounds and was left unstudied. The dark-brown precipitate was dissolved in water, and KI was added to the aqueous solution after extraction with benzene. The solution was evaporated and the residue was treated with chloroform under heating. The chloroform solution contained a mixture of iodides of bis(arene)chromium cations (0.2 g).

Thin-layer chromatography of the solution on Al_2O_3 in acetone/methanol (4/1) gave a yellow band, R_f 0.51 (in the same system, bis(chlorobenzene)chromium iodide has R_f of 0.46).

The oxidative decomposition products (HCl and H_2O_2) of bis(arene)chromium complexes in CH_2Cl_2 were found by GLC to contain benzene, diphenyl and bromobenzene.

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