

A NEW SYNTHESIS OF THE CHROMIUM HEXACARBONYL

Sir:

We wish to report a new synthesis of chromium hexacarbonyl starting from easily available chromium compounds which appear to have been converted now for the first time, into the hexacarbonyl.

At present the only well described method for this synthesis is the "Grignard method" discovered by Job and Cassal¹ and substantially improved by Owen and co-workers.² Recently Fischer and Hafner³ synthesized the carbonyl starting from chromium bis-cyclopentadienyl (no yield reported). Both these valuable methods suffer from some disadvantages such as the unsatisfactory over-all yields,⁴ or the requirement of a rather involved procedure for preparing the suitable starting material.

We have now observed⁵ that chromic acetylacetonate, chromic and chromous salts of organic acids such as acetic and 2-ethylhexanoic can be reduced easily and converted into the hexacarbonyl under high pressure of carbon monoxide if pyridine or related bases are employed as a reaction medium.

Our method consists in dissolving (or suspending) any one of the above compounds in pyridine, containing catalytic amounts of halogens or halogenated substances. The mixture is then treated at 80–170° with an excess of powdered magnesium or zinc and 100–300 atm. of carbon monoxide. When soluble chromium compounds are employed the yields are as high as 80–90%.

(1) A. Job and A. Cassal, *Compt. rend.*, **183**, 392 (1926).

(2) B. B. Owen, J. English, Jr., H. G. Cassidy and C. Vanderbilt Dundon, *This Journal*, **69**, 1723 (1947).

(3) E. O. Fischer and W. Hafner, *Z. Naturf.*, **10b**, 140 (1955).

(4) W. H. Cumming, J. A. Horn and P. O. Ritchie, *J. Appl. Chem.*, **2**, 624 (1952).

We believe the base to play an essential role in the synthesis because intermediate pyridine-containing complexes are formed in the course of the reaction.

It is also noteworthy that the hexacarbonyl as such is still present in substantial quantities in the end-products of the reaction. This seems not to happen in the synthesis by the Grignard method, the hexacarbonyl, in this case, being produced uniquely after the hydrolysis of the reaction mixtures.⁴

Experimental.—Chromium acetylacetonate (17.5 g.), magnesium (4.5 g.) and 80 g. of a 2% solution of iodine in dry pyridine are charged in a stainless steel oscillating autoclave of 500-ml. capacity. After removal of air, oscillation is started and pure oxygen-free carbon monoxide is compressed into the vessel up to a pressure of 190 atm. The autoclave is then warmed to 160° within one hour and maintained at this temperature ($\pm 2^\circ$) for six hours, while pressure drops from 325 to 285 atm. After cooling and venting, the hexacarbonyl and the other reaction products are quantitatively transferred into a 3-liter two-necked distillation flask with the aid of a large amount of water. On distillation of the mixture, the white hexacarbonyl is drained off. The distillate is filtered, washed with chilled methanol and paper dried. Sublimation of the powder at 70–75° at 15 mm. affords 9.0 g. of pure chromium hexacarbonyl in coarse crystals (yield 82%).

(5) Italian Patent Application No. 671, February 4, 1957 (to Montecatini S.p.A.).

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