

hexanecarboxylate, 51075-31-1; 2-bromo-2-methylpropanal, 13206-46-7; 2-chloro-3-phenylpropanal, 19261-37-1; 2-bromo-6-cyano-hexanal, 51157-28-9.

### References and Notes

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- (9) Crude product appears to be a 1,2-dichloro-1-siloxy compound which expels trimethylchlorosilane on warming above room temperature.
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- (12) Reaction at room temperature afforded about 80% of **4** and 20%  $\alpha,\alpha$ -dibromopropiophenone.
- (13) In contrast to the report of Hill and Stotter<sup>11</sup> there is no difficulty in obtaining pure **6** from **5**.
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## An Improved Synthesis of Benzenetricarbonylchromium<sup>1</sup>

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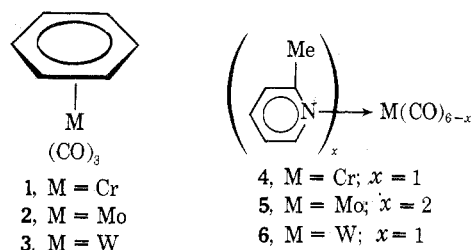
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Since the discoveries of arenetricarbonylmetal complexes in the late 1950's,<sup>2-6</sup> this class of organometallic compounds has been rather extensively investigated.<sup>7</sup> The parent member of this series, benzenetricarbonylchromium (**1**), has been shown to undergo a variety of interesting reactions, including ligand exchange,<sup>8,9</sup> Friedel-Crafts acetylation,<sup>10-12</sup> and reactions with *n*-butyllithium resulting either in metalation<sup>13,14</sup> or nucleophilic addition to a carbonyl ligand to form a carbene-chromium complex.<sup>15</sup> Additional studies concerning the reactivity of **1** in which benzene serves as a  $\pi$ -coordinated ligand in transition metal chemistry would seem highly desirable. Unfortunately, most of the previously reported syntheses of **1** involve high-pressure, autoclave-type carbonylation reactions. The single report by Nicholls and Whiting<sup>3</sup> that **1** can be prepared in 30% yield from a reaction at reflux of benzene and hexacarbonylchromium in diethylene glycol dimethyl ether has proven to be unreliable in our laboratory, and the reaction is furthermore complicated by the

rapid and extensive sublimation of hexacarbonylchromium from the reaction flask.

In this note, we describe a convenient and improved synthesis of **1** which should make this organochromium compound readily available for further study. This procedure has been extensively checked by students in our undergraduate organic chemistry laboratory and has been found to be very reliable. The method is based on a general synthesis of arenetricarbonylmetal complexes originally developed by Pruett, *et al.*,<sup>16,17</sup> and involves the refluxing under nitrogen of equivolume amounts of benzene and 2-picoline containing hexacarbonylchromium. Under these conditions, carbon monoxide is rapidly evolved, and little or no sublimation of hexacarbonylchromium occurs. These results are due presumably to the intermediate formation of (2-picoline)pentacarbonylchromium (**4**)<sup>18</sup> or related complexes which subsequently react with benzene present to form high yields of **1**.



Several attempts to extend this procedure to the synthesis of benzenetricarbonylmolybdenum (**2**) and benzenetricarbonyltungsten (**3**) resulted instead in the formation of the 2-picoline complexes bis(2-picoline)tetracarbonylmolybdenum (**5**) and (2-picoline)pentacarbonyltungsten (**6**), respectively, as the only identifiable products. Complex **6**, a yellow, air-stable solid, was identified by elemental analysis, a molecular weight determination, and its nmr spectrum. Complex **5**, a dark-yellow solid, was found to be moderately sensitive to air, and was best handled and stored under nitrogen. It was only very slightly soluble in organic solvents, and its solutions were very air sensitive. A related complex, bis(pyridine)tetracarbonylmolybdenum, has been previously prepared both by photochemical<sup>19</sup> and thermal<sup>20</sup> reactions between pyridine and hexacarbonylmolybdenum.

Additional studies concerning the chemistry of **1** are in progress and will be reported in subsequent papers.

### Experimental Section

**Reaction of Benzene, 2-Picoline, and Hexacarbonylchromium.** Into a 500-ml, single-necked flask was added 100 ml of 2-picoline, 100 ml of benzene, and 8.80 g (0.04 mol) of hexacarbonylchromium. After addition of several boiling chips, a wide-bore condenser fitted on the top with a three-way stopcock was inserted, and the system was evacuated under reduced pressure until boiling had commenced. Nitrogen was then bled into the system to equalize the pressure. This process was repeated about ten times to ensure an oxygen-free atmosphere. The reaction mixture was then heated to reflux for 96 hr, during which time carbon monoxide was evolved and the color turned to dark red.<sup>21</sup> After this period, the reaction mixture was allowed to cool to room temperature under nitrogen. The flask was transferred to a rotary evaporator and the excess benzene, 2-picoline, and hexacarbonylchromium were removed under water aspirator pressure with gentle heating on a steam bath. The yellow-green residue was extracted repeatedly with hot ethyl ether and the extracts were filtered. This process was repeated until the extracts were virtually colorless. The combined extracts were subsequently evaporated to dryness and the residue was washed with pentane to remove any remaining 2-picoline. After drying, there remained 7.75 g (91%) of yellow crystals of benzenetricarbonylchromium (**1**), mp 160-161° dec (lit.<sup>6</sup> mp 162-163°).

The product can be further purified either by sublimation at 80–85° (ca.  $10^{-3}$  mm) or by recrystallization from ethyl ether to yield yellow crystals of 1, mp 162–163°. A proton nmr spectrum of 1 in  $\text{CDCl}_3$  solution exhibits a single resonance at  $\tau$  4.68.

In similar experiments in which the reflux period was 9, 48, 82, and 162 hr, the yields of 1 were 8, 62, 82, and 94%, respectively. In a reaction in which equimolar amounts of hexacarbonylchromium and 2-picoline were heated to reflux in excess benzene for 68 hr, the yield of 1 was only 6%.

**Reaction of Benzene, 2-Picoline, and Hexacarbonylmolybdenum.** A mixture of 10.56 g (0.04 mol) of hexacarbonylmolybdenum, 100 ml of benzene, and 100 ml of 2-picoline was heated to reflux under nitrogen as described above. When heating was commenced, gas evolution was noted and the reaction mixture turned yellow. After a reflux period of 96 hr, the solution was dark orange and a yellow precipitate had formed. The solid was filtered under nitrogen, washed twice with benzene, and dried overnight at aspirator pressure. There remained 12.2 g (77%) of a powdery yellow solid, tentatively identified as bis(2-picoline)tetracarbonylmolybdenum (5), mp ca. 175° dec ( $\text{N}_2$ ) with darkening from ca. 150°.

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{14}\text{MoN}_2\text{O}_4$ : C, 48.73; H, 3.58; N, 7.10. Found: C, 48.44; H, 3.58; N, 7.35.

An attempted sublimation of 5 *in vacuo* was not successful. No sublimate could be detected at temperatures up to 80°, and heating above this temperature resulted in considerable darkening of the solid, a metallic mirror, and hexacarbonylmolybdenum being formed.

**Reaction of Benzene, 2-Picoline, and Hexacarbonyltungsten.** A mixture of 7.04 g (0.02 mol) of hexacarbonyltungsten, 100 ml of benzene, and 100 ml of 2-picoline was heated to reflux under nitrogen as described above. After 70 hr, the dark red reaction mixture containing a brown solid was allowed to cool to room temperature and the solvents were removed using a rotary evaporator and a water bath maintained at 50–60°. The residue which remained was transferred to a vacuum sublimator. Sublimation at 80–100° ( $10^{-3}$  mm) over a 24-hr period produced 1.00 g (12%) of yellow crystals of (2-picoline)pentacarbonyltungsten (6), mp 85–86° ( $\text{N}_2$ ).

*Anal.* Calcd for  $\text{C}_{11}\text{H}_7\text{NO}_5\text{W}$ : C, 31.68; H, 1.69; N, 3.36; W, 44.09; mol wt, 417. Found: C, 31.45; H, 1.42; N, 2.94; W, 44.4; mol wt, 415, 420 (osmometric in benzene).

Nmr ( $\text{CDCl}_3$ )  $\tau$  7.20 (s,  $\text{CH}_3$ ), 2.67, 2.13, 1.13 (m, ring protons); nmr ( $\text{CDCl}_3$ ) for 2-picoline  $\tau$  7.45 (s,  $\text{CH}_3$ ), 2.93, 2.43, 1.47 (m, ring protons).

An ir spectrum of the material collected in the trap during the sublimation indicated it to be essentially pure hexacarbonyltungsten. The black residue which remained after sublimation of 6 is pyrophoric, and should be decomposed under nitrogen.

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**Registry No.**—1, 12082-08-5; 5, 51270-99-6; 6, 39210-59-8; benzene, 71-43-2; 2-picoline, 109-06-8; hexacarbonylchromium, 13007-92-6; hexacarbonylmolybdenum, 13939-06-5; hexacarbonyltungsten, 14040-11-0.

## References and Notes

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- A very small amount of hexacarbonylchromium occasionally sublimes into the condenser during the early stages of the reaction. This can be scraped back into the reaction vessel, if desired.

## Kinetics of Oxidation of Aldo Sugars by Cerium(IV) in Aqueous Sulfuric Acid

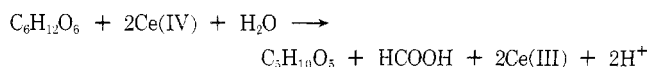
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The metal ion oxidation of aldo sugars, in acid medium, seems to have received very little attention. The oxidation of glucose by chromium(VI)<sup>1</sup> and that of arabinose<sup>2</sup> by cerium(IV) in sulfate medium are reported, however, in the literature. Since this work had been completed there has appeared a report on the oxidation of glucose by cerium(IV) in perchloric acid.<sup>3</sup> Nevertheless, the present study adds a few significant new results besides confirming most of the results of Pottenger and Johnson.<sup>3</sup> The inherent interest in starting this work had been to examine whether the oxidation of these sugars involved exclusively its pyranose structure or also the open-chain structure having a free aldehyde group, because it is well known that glucose reduces Fehling's solution and adds hydrocyanic acid but in contrast to the ordinary aldehydes it does not give the Schiff's test.

**Products and Stoichiometry.** The qualitative analysis of the oxidized reaction mixtures, having excess concentrations of either glucose or mannose, indicated the absence of formaldehyde<sup>4a</sup> and gluconic and glucuronic acid<sup>4b</sup> and the presence of arabinose and formic acid.<sup>4c</sup> The quantitative estimation of formic acid indicated that 2 equiv of cerium(IV) are used per mole of formic acid formed. The stoichiometric equation of the reaction could be written as shown below.



## Experimental Section

The method used to follow the progress of the reaction has been described elsewhere.<sup>5</sup> The reaction has been studied at 25° and it has been followed for more than 2 half-lives. The kinetic runs have been carried out in the presence of a large excess of sugar so that the rate of reduction of cerium(IV) is controlled by the substrate concentration only and not by the concentration of the product which accumulates in the reaction mixture. The first-order rate constant  $k_1$ , with respect to cerium(IV), was calculated as has been described earlier.<sup>5</sup>

**Kinetic Results.** The rate constant  $k_1$  increased proportionately with the increase in substrate concentration. The plots of rate constant  $k_1$  vs. [substrate] were linear and passed through the origin. The second-order rate constant  $k_2$  (Table I) for each substrate was obtained from the slopes of these plots.

The other results, based on the kinetic data (available as supplementary material, see paragraph at end of paper), are only briefly summarized here. The rate constant  $k_1$  decreased with the increase in (a) bisulfate ion concentration at constant hydrogen ion; (b) ionic strength, which was adjusted with sodium perchlorate; (c) deuterium oxide concentration (v/v consideration). How-