Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

A convenient synthesis of dimanganese decacarbonyl from inexpensive starting materials at atmospheric pressure

Dimanganese decacarbonyl is a key intermediate for the preparation of many organomanganese compounds. Up to now the detailed study of many aspects of manganese carbonyl chemistry has been hampered by lack of a satisfactory source of dimanganese decarbonyl in large quantities. Numerous preparative methods for dimanganese decacarbonyl have been published[1-7]. All of these preparative methods require high-pressure equipment and, therefore, are limited in scale to available autoclaves. Furthermore, the yields in nearly all of the published methods are either low or variable. The more promising procedures[5,6] present severe fire hazards due to excessive quantities of sodium metal or aluminum alkyls.

One of the published methods[6] for the preparation of $Mn_2(CO)_{10}$ utilizes the reaction of (methylcyclopentadienyl)tricarbonylmanganese, $CH_3C_5H_4Mn(CO)_3$, with sodium metal in diglyme (dimethyl ether of diethylene glycol) solution under carbon monoxide pressure followed by hydrolysis. Following a one-sentence hint in a paper by Booth and Haszeldine[8] that related reactions may be possible at atmospheric pressure of carbon monoxide, we have developed a modification of the reaction between $CH_3C_5H_4Mn(CO)_3$, sodium, and carbon monoxide which can be carried out in conventional three-necked flasks at atmospheric pressure of carbon monoxide. The attractiveness of this method is enhanced by the present inexpensive availability of the $CH_3C_5H_4Mn(CO)_3$ in 20 kg drums owing to its commercial application as a combustion improver for fuel oils. Although the yields by this new method are only in the range 16–20%, the simplicity of this method, the use of conventional laboratory equipment, and the low cost of the starting materials make it possible to carry out this new synthesis on a large scale. Using a 2-liter 3-necked flask 50 g of pure sublimed $Mn_2(CO)_{10}$ can easily be obtained in one run.

Experimental

Materials. Pure dry diglyme must be used for this procedure. Commercial diglyme purchased from Ansul Chemicals, Inc., Marinette, Wisconsin, was purified by distillation over sodium metal at atmospheric pressure (b.p. 161°) preferably under nitrogen. At this temperature the sodium is molten making contact with the diglyme more efficient. Since the sodium is molten at the reaction temperature, any form of sodium metal should be satisfactory. For convenience, sodium spheres (Matheson Coleman and Bell, Norwood, Ohio) were used. The $CH_3C_5H_4Mn(CO)_3$ was purchased from the Ethyl Corporation, New York.

Procedure. The reaction was carried out in the hood in a 2-liter 3-necked flask. One of the side necks of the flask was equipped with an adapter containing two gas inlets: (*a*) A nitrogen inlet terminating far above the level of the liquid, (*b*) A carbon monoxide inlet terminating below the level of the liquid for more efficient contact. The other side neck of the flask was equipped with an adapter containing a pressureequalized dropping funnel and an air-cooled reflux condenser*. A mineral oil bubbler was attached to the outlet of the system at the top of the condenser. The center neck of the flask was equipped with a stirrer driven by an air-operated motor.

After flushing the system with nitrogen, the flask was charged with 100 g (4.35 moles) of sodium spheres and 500 ml of dry purified diglyme. The mixture was heated to the boiling point of the diglyme and the sodium dispersed with good stirring. While maintaining the refluxing and stirring the nitrogen atmosphere was shut off and the carbon monoxide introduced. After allowing about 5 min. for the system to be filled with carbon monoxide, a total of 212 ml (300 g, 1.38 moles) of $CH_3C_5H_4Mn(CO)_3$ was added dropwise from the dropping funnel over a period of about 4 h. A rate of carbon monoxide flow thru the system was maintained sufficient for slow bubbling thru the mineral oil bubbler at the outlet. During the reaction period the solution was kept at the boiling point of the diglyme (about 50 volts on a standard heating mantle). After all of the $CH_3C_5H_4Mn(CO)_3$ had been added the mixture was boiled under reflux with stirring for an additional hour and then allowed to cool to room temperature. The reaction mixture was decomposed by addition of 400 ml of 2-propanol over a period of 2 h while maintaining the carbon monoxide atmosphere. The resulting brown mixture was then acidified with 350 ml of 85% phosphoric acid. The acidification was very exothermic and was moderated by placing the flask in a dry-ice bath. The mixture was kept cold enough to prevent the yellow fumes from escaping from the flask.

After the acid had been added, a large quantity of crystals had separated. These contained most of the $Mn_2(CO)_{10}$ mixed with a large excess of sodium phosphates. These crystals (~500 g) were filtered and washed with many portions of hot water to dissolve all of the sodium phosphates. The washings were discontinued when they were no longer colored and the volume of solid in the filter funnel no longer decreased. The yellow-orange residue, mostly $Mn_2(CO)_{10}$, weighed around 50 g.

The filtrate from the removal of the sodium phosphate mixed with some of the $Mn_2(CO)_{10}$ was allowed to stand for two days at room temperature. The yellow precipitate of $Mn_2(CO)_{10}$ which formed during this time was filtered.

The crude samples of dimanganese decacarbonyl were purified by dissolving in about seven times their weight of boiling toluene, filtering the deep yellow solution, and cooling the filtrate overnight in a freezer at −10°. The purified crystals which separated were sublimed at 70–80° (0.1 mm) to give pure $Mn_2(CO)_{10}$, m.p. 153–154° (lit.[7] 153–154°). The yield ranged from 44 to 53 g [16% to 20% based on $CH_3C_5H_4Mn(CO)_3$].

In repeat experiments conducted on the same scale and in the same manner but at 120° rather than the boiling point of the diglyme (160°), the yield of pure sublimed $Mn_2(CO)_{10}$ was somewhat lower (~34 g, 13%). Reaction between $CH_3C_5H_4Mn(CO)_3$ and sodium metal in diglyme solution in the same manner but using a nitrogen atmosphere rather than a carbon monoxide atmosphere gave only 4.7 g (1.7% yield) of sublimed $Mn_2(CO)_{10}$, m.p. 152–153°. This demonstrates the value of the carbon monoxide atmosphere for introduction of the extra carbonyl groups.

---

* The use of an air-cooled condenser minimizes the hazard associated with the use of such large quantities of sodium. An air-cooled reflux condenser is sufficient to prevent escape of the high-boiling diglyme.

Acknowledgements

We are indebted to the U.S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1211-67. We would like to acknowledge the helpful discussions of Prof. G. R. DOBSON of the University of South Dakota who also prepared large quantities of $Mn_2(CO)_{10}$ by this new method.

Department of Chemistry,
University of Georgia,
Athens, Georgia 30601 (U.S.A.)

R. B. KING*
J. C. STOKES
T. F. KORENOWSKI**

1 E. O. BRIMM, M. A. LYNCH, JR., AND W. J. SESNY, *J. Amer. Chem. Soc.*, 76 (1954) 3831.
2 V. HNIZDA, *U.S. Patent* 2,822,247 (1958).
3 R. D. CLOSSON, L. R. BUZBEE AND G. C. ECKE, *J. Amer. Chem. Soc.*, 80 (1958) 6167.
4 J. F. CORDES AND D. NEUBAUER, *Z. Naturforsch.*, 17b (1962) 791.
5 H. E. PODALL, J. H. DUNN AND H. SHAPIRO, *J. Amer. Chem. Soc.*, 82 (1960) 1325; F. CALDERAZZO, *Inorg. Chem.*, 4 (1965) 293.
6 H. PODALL AND A. P. GIRAITIS, *J. Org. Chem.*, 26 (1961) 2587.
7 R. B. KING, *Organometal. Syn.*, 1 (1965) 89.
8 B. L. BOOTH AND R. N. HASZELDINE, *J. Chem. Soc.*, *A*, (1966) 157.

Received August 15th, 1967

---

* Fellow of the Alfred P. Sloan Foundation, 1967–1969.

** NDEA Predoctoral Fellow.