pyridone (II) was heated under reflux for 2 days. At the end of this period the reaction mixture was filtered, the catalyst washed well with benzene, and the solvent removed on a steam bath under a stream of nitrogen. The residue was distilled *in vacuo* to yield 5.4 g. (52%) fraction of a colorless liquid boiling at 60–64° at less than 0.5 mm. and a 4.2 g. (40%) fraction of colorless liquid that crystallized in the receiver; b.p. 80–88° at less than 0.5 mm. The former fraction was shown, on the basis of its infrared spectrum, to be starting material and the latter fraction was the desired 1,6-dimethyl-2-pyridone (IV).

The solid distillate was purified by recrystallization from dry ether to yield 3.7 g. (94% recovery) of hygroscopic, white crystalline solid; m.p. 54–56° in air or 55–57° in a sealed tube; reported[4], b.p. 110° at 2 mm.

Method B. If the identical reaction were run employing benzene as a solvent, the yield of 1,6-dimethyl-2-pyridone (IV) was only 30%.

1,6-Dimethyl-2-pyridone hydrochloride. A solution of 1.87 g. (0.015 mole) of 1,6-dimethyl-2-pyridone (IV) in 10 ml. of dry ether was saturated with dry hydrogen chloride gas. The precipitate was filtered, washed well with ether, and dried. The yield of white solid was 2.25 g. (97%); m.p. 138–168°. The product was recrystallized from methanol-ether to yield 2.21 g. (96%) of white crystalline solid; m.p. 198–201° in a sealed tube; reported[4] m.p. 202–203°.

1-Phenyl-6-methyl-2-pyridone (V). *Method A.* A well stirred suspension of 1.3 g. of 5% palladium on carbon, 50 ml. of *p*-(*n*-propyl)anisole and 12 g. (0.064 mole) of 1-phenyl-6-methyl-5,6-dihydro-2-pyridone (III) was heated under reflux for 2 days. At the end of this period the reaction mixture was filtered and the catalyst washed well with benzene. The filtrate was then extracted with three 200-ml. portions of 10% hydrochloric acid. The combined acid extracts were washed twice with 100 ml. of chloroform, made basic with 50% sodium hydroxide solution, and the resulting basic solution extracted three times with 200 ml. of ether. The combined ether extracts were dried over anhydrous sodium sulfate, filtered, and the ether solution evaporated to 70 ml. on a steam bath. The solution was cooled to room temperature and filtered to yield 5.8 g. (49%) of white rhombic crystals; m.p. 136–139° in a sealed tube. Two additional recrystallizations from ether netted an analytic sample that exhibited a melting point of 136–139° in a sealed tube.

Anal. Calcd. for $C_{12}H_{11}ON$: C, 77.81; H, 5.99; N, 7.56. Found: C, 78.21; H, 5.59; N, 7.82.

Method B. If an identical reaction were run according to Method A employing xylene as the solvent, the yield of 1-phenyl-6-methyl-2-pyridone (V) was only 28%.

1-Phenyl-6-methyl-2-pyridone hydrochloride. A solution of 1 g. (0.0054 mole) of 1-phenyl-6-methyl-2-pyridone (V) in 1 ml. of dry methanol and 10 ml. of dry ether was saturated with dry hydrogen chloride gas. Twenty milliliters of ether was added to the solution which was then cooled for 2 hr. in an ice bath. The solution was filtered, the precipitate washed with ether, and dried to yield 1.17 g. (98%) of white crystalline solid; m.p. 172–179° in a sealed tube. The product was recrystallized from methanol-ether to give 1.06 g. (90%) of white crystals; m.p. 198–201° in a sealed tube. Three additional recrystallizations from the same solvent combination gave an analytic sample that exhibited a melting point of 201–204° in a sealed tube.

Anal. Calcd. for $C_{12}H_{12}NOCl$: C, 65.01; H, 5.46; N, 6.32; Cl, 15.99. Found: C, 65.37; H, 5.78; N, 6.04; Cl, 15.46.

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Reductive Carbonylation Synthesis of Metal Carbonyls. V. Synthesis of Manganese Carbonyl from π-Methylcyclopentadienylmanganese Tricarbonyl[1]

HAROLD E. PODALL[2] AND ALBERT P. GIRAITIS

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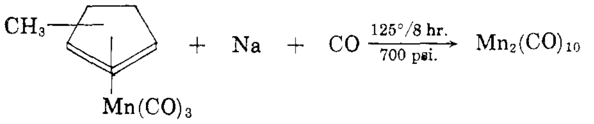
Only two satisfactory methods have thus far been reported for the preparation of manganese carbonyl. One involves the use of the sodium benzophenone ketyl for forming a metastable manganese intermediate for carbonylation,[3] while the other involves the use of an alkylaluminum compound as a selective reducing agent for the manganese salt in the presence of carbon monoxide.[4,5] The latter reaction has been named reductive-carbonylation.[4] This paper deals with a third method which is much more convenient for preparing manganese carbonyl, based on reductive carbonylation with metallic sodium.

We have found that manganese carbonyl can be readily prepared in 45–50% yields by reductively carbonylating π-methylcyclopentadienylmanganese tricarbonyl (I) with sodium in diethylene glycol dimethyl ether (diglyme) solvent at about 125°. Highest yields were obtained when employing three gram-atoms of sodium per mole of I in diglyme. Use of smaller quantities of sodium resulted in decreased yields, while a 50% increase in sodium resulted in an uncontrollable reaction which set in at 122° and ruptured the safety disk of the reactor. The reaction was found to be considerably slower in benzene, requiring a temperature of about 200°, and gave only a 15% yield of manganese carbonyl. In diglyme, on the other hand, under comparable conditions, carbonylation set in at 100° or lower and resulted in a 50% yield. It appears therefore that diglyme plays a very important role in this reaction. One possibility here is that the diglyme serves to stabilize a manganese carbonyl moiety such as $Mn(CO)_3$ for carbonylation.



I

Use of other manganese salts in place of I resulted in decreased yields due to the formation of

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(1) For paper IV, see H. Podall, H. B. Prestridge, and H. Shapiro, *J. Am. Chem. Soc.*, **83**, 2057 (1961).

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metallic manganese. It appears therefore that the methylcyclopentadienyl group serves to moderate the reactivity of the manganese atom toward reduction.[6]

An investigation of the stoichiometry of the reaction indicated that five sodium atoms and three carbon monoxide molecules are consumed per $Mn(CO)_5$ formed regardless of the solvent and temperature up to 200°. The reaction mixture generally contained a brown viscous oil which was insoluble in petroleum ether and did not appear to contain free manganese carbonyl prior to hydrolysis. Unchanged I was generally evident, and methylcyclopentadiene could not be detected before or after hydrolysis. Sodium did not appear to react with carbon monoxide to any significant extent under the conditions employed. Accordingly, it appears that the large excess of sodium required may be due solely to its reaction with the cyclopentadienyl group, and that the sodium methylcyclopentadienide which may be formed reacts further with carbon monoxide. It is suggested that the brown oil contains the sodium salt of manganese carbonyl, probably as a diglyme complex, $(diglyme)_2$ $Na^+ Mn(CO)_5^-$, and that the manganese carbonyl arises by oxidative-hydrolysis of the latter. Further work is required to define the various products of the evidently complex reaction involving I, sodium, and carbon monoxide.

EXPERIMENTAL

To a 1-l. Parr autoclave were added 80 ml. (0.50 mole) of π-methylcyclopentadienylmanganese carbonyl (Ethyl Corp.), 300 ml. of dry diglyme, and 100 ml. of a 40% dispersion (1.48 g.-atoms) of sodium in Nujol (Plough, Inc.). The autoclave was then pressurized with 700 p.s.i. of C.P. carbon monoxide and the mixture was heated with stirring to 125° for 8 hr. with intermittent repressurizing to speed up the reaction. The reaction mixture was then carefully quenched with about 500 ml. of water at 0° (or 25–65° under 500 p.s.i. of carbon monoxide) and steam distilled. The yield of manganese carbonyl was 45.7 g. (48%), m.p. 151–153° (uncorrected).

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[6] The oxidation state of manganese in I can be considered formally as +1.

Acylation, Bromination and Oxidation of 4-Pyrones and Pyronones[1]

L. L. WOODS AND P. A. DIX

Received Nov. 7, 1960

A review of pertinent literature[2-4] on the chemistry of 6-methyl-2-pyronone fails to show that the compound when treated with acetic anhydride or acetyl chloride regenerates dehydroacetic acid. We have found this to be a very easy transformation to accomplish in the presence of trifluoroacetic acid, further the acid does not degrade dehydroacetic acid to any appreciable degree when refluxed in its presence for as long as twenty-four hours.

Since the acetylation proved to be so facile it was decided to prepare a series of pyronone compounds similar to 3-acetyl-6-methyl-2-pyronone (dehydroacetic acid) by changing the acyl group in position 3.

It was found that not only would different acyl halides place different groups in position 3, but when two equivalents of the acyl halide were used, a second acyl radical was placed on the nucleus without destruction of the ring structure, presumably at position 5 since it is very unlikely that a second acyl group could be put on position 3 without rupture of the ring. The pyronones synthesized are listed as the I_{A-F} series in Table I.

Pyronone when treated in the presence of three equivalents of an acyl halide such as *m*-nitrobenzoyl chloride gave 2-(*m*-nitrophenyl)-3,5-di(*m*-nitrobenzoyl)-6-methyl-4-pyrone (II).

A verification of the structure of the compounds in the I_{A-F} series was obtained by using compounds I_A and $_B$ as models. Carbon dioxide was eliminated from them by the usual hydrochloric acid method and the method of Light and Hauser[6] to form the 2-aryl-4-pyrones described in the experimental portion of this report as compounds III and IV respectively.

One of the objectives of our study of the pyrones was to devise methods of oxidizing the various mononuclear 4-pyrones without rupture of the ring. A method to effect this oxidation has been found using chloranil as the oxidant. The product of such an oxidation appears to be a 6,6′-bipyrone as indicated by the figure adjacent to Table II in which the substances formed by the oxidation are listed as compounds V_{A-D}. Infrared spectra run on the substances with a Beckman IR-5 failed to show more than an intensification of the absorption bands of the starting materials; however, ultraviolet absorption spectra do show an unmistakable difference.

The absorption maxima for the two model compounds V_A and V_B are slightly but definitely different from the substances from which they are derived, kojic acid and α-chloro-α-deoxy-kojic acid respectively.

The bromination studies included in this report consists of an inelegant generalized method for

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[1] The investigations reported here were supported by the Robert A. Welch Foundation.

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