acetic acid gave 2.35 g. (71%) of fine white crystals, m.p. 175–176°.

Anal. Calcd. for $C_{16}H_{13}O_3Br$: C, 57.67; H, 3.94; Br, 23.98. Found: C, 57.91; H, 3.83; Br, 23.82.

3-(5-Chloro-2-hydroxyphenyl)phthalide. One and one-half grams (0.01 mole) of phthalaldehydic acid was dissolved in 18 ml. of 3:1 concd. sulfuric acid–water. This solution was cooled in an ice-water bath, and 1.28 g. (0.01 mole) of *p*-chlorophenol was added. After mechanically stirring the mixture for 2 hr. the cooling bath was removed and stirring was continued for an additional 2 hr. At this point the thick, milky emulsion was brought into a large volume of cold water, with vigorous stirring. A voluminous white solid separated and gradually settled out. The crude product was removed, washed thoroughly with cold water, and permitted to dry overnight. This gave a white powdery solid weighing 2.3 g. (88%). Recrystallization from ethanol yielded 1.83 g. (70%) of soft, glistening needles. An analytical sample melted at 163.5–164°.

Anal. Calcd. for $C_{14}H_9O_3Cl$; C, 64.51; H, 3.48; Cl, 13.60. Found: C, 64.64; H, 3.29; Cl, 13.73.

3-(5-Methyl-2-methoxyphenyl)phthalide. A solution of 1.5 g. (0.01 mole) of phthalaldehydic acid in 24 ml. of 3:1 concd. sulfuric acid–water was prepared. This was cooled by immersion in an ice-water bath, and 1.22 g. (0.01 mole) of *p*-methylanisole was then added. The mixture was mechanically stirred; after 3 hr. testing showed that the brown oil which had separated as a top layer would solidify in water. The entire reaction mixture was poured with stirring into a large volume of cold water. The gum which separated soon hardened to a yellow solid; when firm it was removed and thoroughly washed with cold water. Drying gave as crude product 2.55 g. (100%) of light yellow solid. Recrystallization from ethanol yielded 2.03 g. (80%) of white crystals, m.p. 120.5–121.5°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.34; H, 5.71.

3-(5-Methyl-2-ethoxyphenyl)phthalide. This phthalide was synthesized by using 1.5 g. (0.01 mole) of phthalaldehydic acid and 1.34 g. (0.01 mole) of *p*-methylphenetole with 24 ml. of 3:1 concd. sulfuric acid–water as the condensing agent. The procedure followed was essentially the same as outlined for 3-(5-methyl-2-methoxyphenyl)phthalide. The crude reaction product weighed 2.42 g. (91%). Recrystallization from ethanol gave 1.98 g. (74%) of white needles. An analytical sample melted at 151–151.5°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.01. Found: C, 76.21; H, 5.92.

3-(2,4,6-Trichloro-3-hydroxyphenyl)phthalide. One and one-half grams (0.01 mole) of phthalaldehydic acid was dissolved in 20 ml. of 1:1 concd. sulfuric acid–20% fuming sulfuric acid. To this solution at room temperature was added 1.98 g. (0.01 mole) of 2,4,6-trichlorophenol, and the mixture mechanically stirred. The dispersed phenol reacted over a period of 3 hr. to give a yellow solution. The reaction vessel was then immersed in a water bath maintained at 60–70°, and stirring was continued for an additional 2 hr. The reaction mixture was poured into a large volume of cold water. The gum which separated hardened very slowly, but became brittle after standing overnight. The crude product, nearly white in color, weighed 3.0 g. (90%). Recrystallization from glacial acetic acid gave 2.6 g. (80%) of nearly white cubic crystals, m.p. 164.5–165°.

Anal. Calcd. for $C_{14}H_7O_3Cl_3$: C, 51.02; H, 2.14; Cl, 32.27. Found: C, 51.10; H, 1.98; Cl, 32.41.

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Unsaturated Lactams. II.[1] The Catalytic Dehydrogenation of α,β-Unsaturated Valerolactams to Pyridones[2]

Maurice Shamma and Paul D. Rosenstock

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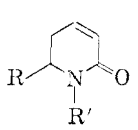
The fact that α,β-unsaturated lactams of type (I) are now readily available[1] induced us to extend the method used by Spath and Galinovsky for the synthesis of pyridones. These two workers found that six-membered saturated lactams could be smoothly dehydrogenated to the corresponding pyridones by treatment with palladium. In the present work, the unsaturated lactams (II) and (III) were dehydrogenated to the pyridones (IV) and (V), respectively.



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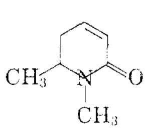

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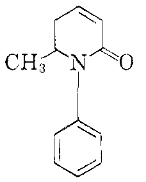

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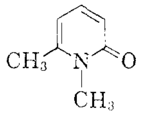

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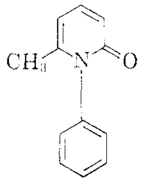

V

As indicated in Table I, the dehydrogenation reactions were found to be temperature dependent.

TABLE I

Dehydrogenation of α,β-Unsaturated Valerolactams to Pyridones with 5% Palladium on Carbon

Solvent	B.P.	% Yield of IV	% Yield of V
Benzene	80°	30	—
Xylene	140°	40	28
p-(*n*-Propyl)anisole	247°	—	49

Catalytic dehydrogenation of α,β-unsaturated lactams can provide a route, therefore, to a variety of substituted pyridones which would be difficult to prepare by other routes.

EXPERIMENTAL[3]

1,6-Dimethyl-2-pyridone (IV). *Method A.* A well stirred suspension of 2 g. of 5% palladium on carbon, 50 ml. of xylene, and 10 g. (0.08 mole) of 1,6-dimethyl-5,6-dihydro-2-

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[1] For paper I see Maurice Shamma and Paul D. Rosenstock, *J. Org. Chem.*, **26**, 718 (1961).

[2] This research was supported in part by grant NSF-G10032 from the National Science Foundation.

[3] Elemental analyses were carried out by A. Bernhardt, Mulheim, Germany.

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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[4] S. Susawa and M. Kirisawa, *Pharm. Bull.* (*Japan*), **3**, 187 (1955).

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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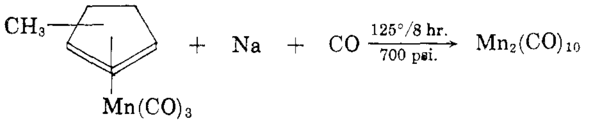
Only two satisfactory methods have thus far been reported for the preparation of manganese carbonyl. One involves the use of the sodium benzophenone ketyl for forming a metastable manganese intermediate for carbonylation,[3] while the other involves the use of an alkylaluminum compound as a selective 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).

[2] Present address: Melpar, Inc., Physical Sciences Laboratory, Falls Church, Va. To whom all inquiries should be addressed.

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[5] H. Podall, J. H. Dunn, and H. Shapiro, *J. Am. Chem. Soc.*, **82**, 1325 (1960).